

**SYSTEMATIC INVESTIGATION OF ROCK/FLUID INTERACTIONS IN
RESERVOIRS AT NANO –TO – MILLIMETER SCALE:
IMPLICATIONS FOR ENHANCED OIL RECOVERY AND CO₂
STORAGE**

BY

ABUBAKAR ISAH

A Dissertation Presented to the
FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY
In

PETROLEUM ENGINEERING

May 2024

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

This thesis, written by Abubakar ISAH under the direction of his thesis advisors and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR PHILOSOPHY IN PETROLEUM ENGINEERING.**



Dr. Mohamed Ahmed Nasr Eldin
Mahmoud
(Advisor)



Dr. Murtada Saleh Aljawad
(Co-Advisor)



Dr. Dhafer Abdullah Al Shehri
Department Chairman

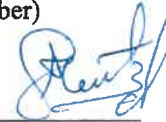
16/07/2024



Dr. Abdullah Sultan
(Member)



Dr. Suliman Saleh Al-Homidan
Dean of Graduate Studies



Dr. Muhammad Shahzad Kamal
(Member)



Dr. Muhammad Arif
(External Member)

Date



© Abubakar ISAH

2024

DEDICATION

I dedicate this work to my caring and dedicated parents Alhaji Isah Sulaiman and late Aisha Umar Sulaiman.

ACKNOWLEDGEMENTS

I would like to warmly acknowledge my advisor Dr. Mohamed Ahmed Nasr ELDin Mahmoud and my co-advisor Dr. Murtada Aljawad for their invaluable assistance and feedback during the experimental part of this work and the writing process.

Special thanks also go to my research committee members, Dr. Abdullah Sultan, Dr. Muhammad Shahzad Kamal and Dr. Muhammad Arif for their support and kind assistance throughout the research.

I am also grateful to King Fahad University of Petroleum & Minerals (KFUPM) for the research support, I am also thankful to the Centre for Integrated Petroleum Research (CIPR) and the College of Petroleum Engineering and Geosciences (CPG) of King Fahad University of Petroleum and Minerals for the research opportunity.

I would like to thank the Chairman of the Department of Petroleum Engineering of KFUPM Dr. Dhafer A. Al Shehri.

Finally, I would like to thank my family and all my friends that made my stay in KFUPM a memorable experience.

Abubakar ISAH

KFUPM, May 2024

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	v
LIST OF TABLES	xi
LIST OF FIGURES	xii
ABSTRACT	xvii
نبدأ مختصرة	xviii
CHAPTER 1	4
INTRODUCTION.....	4
CHAPTER 2	9
LITERATURE REVIEW	9
2.1 Fluid/Rock Interaction in Conventional Rocks.....	9
2.1.1 Surfactant Adsorption/Retention.....	10
2.1.2 Polymer Adsorption/Retention	10
2.1.3 Alkaline – Surfactant – Polymer (ASP) Adsorption/Retention.....	11
2.1.4 Ions Adsorption (from water, oil, carboxylate)	12
2.1.5 Rock Dissolution.....	13
2.1.6 Clay Swelling and Fines Migration.....	14
2.1.7 Wetting and IFT Characteristics	15
2.2 Implications of Rock/Fluid Interactions on EOR.....	16
2.2.1 Wettability Modification.....	16
2.2.2 Change in Surface Charge.....	17
2.2.3 Surface Roughness Modification	18
2.2.4 Formation damage	18
2.3 Rock/Fluid Interaction Quantification Methods and Equipment.....	19
2.3.1 Core-flooding (Tracers, pressure drop, permeability).....	19
2.3.1.2 Effluent analysis.....	20
2.3.2 Contact angle and IFT	21
2.3.3 SEM/Thin section / FE-SEM.....	23
2.3.4 Nuclear Magnetic Resonance (NMR).....	25
2.3.5 Computed Tomography (CT)	26
2.3.6 Atomic Force Microscopy (AFM)	28
2.3.7 Zeta potential	29

2.4	Anhydrite-Rich Reservoirs	34
2.5	EOR Applications in Anhydrite-rich carbonate: Prospects and Challenges	34
2.6	Significance of the Research Study/Contributions	35
2.7	Research Hypothesis	38
2.8	Research Questions	41
2.9	Research Objectives	41
CHAPTER 3		43
GENERAL METHODS		43
3.1	Phase I: Carbonate and tight sandstone samples characterization	43
3.1.1	Task 1: Nano – to – Microstructural characterization	43
3.1.2	Task 2: Surface charge investigation of calcite and anhydrite, dolomite and anhydrite combination.....	44
3.2	Phase II: Wettability characterization across nano-to-millimeter scale.....	48
3.2.1	Task 1: Surface roughness.....	51
3.2.2	Task 2: Nanomechanical tests (nanoindentation).....	51
3.2.3	Task 3: Contact angle measurement	51
3.3	Phase III: Macroscale structural studies.....	52
3.3.1	Task 1: Amott-Harvey wettability Index	52
3.3.2	Task 2: Core-flooding	52
CHAPTER 4.....		54
MULTI-SCALE WETTABILITY CHARACTERIZATION OF ANHYDRITE-RICH CARBONATE ROCKS: INSIGHTS INTO ZETA POTENTIAL, FLOTATION, AND CONTACT ANGLE MEASUREMENTS		54
Summary.....		54
4.1	Background	56
4.2	Materials and Methods	60
4.3	Materials	60
4.3.1	Methods.....	65
4.4	Results and Discussions.....	69
4.4.1	Rock Dissolution.....	70
4.4.2	Surface Charge via Zeta Potential.....	76
4.4.3	Flotation wettability	87
4.4.4	Contact angle.	90
4.4.5	Synthetic rocks composition and minerals distribution	92

4.5	Summary and Conclusions	97
CHAPTER 5		99
EXPLORING THE IMPACT OF MINERALOGY ON PORE STRUCTURE AND FLUID DYNAMICS IN TIGHT RESERVOIR ROCKS: INSIGHTS FOR ENHANCED OIL RECOVERY AND GAS STORAGE		99
Summary.....		99
5.1	Background	101
5.2	Fractal Dimension	105
5.3	Samples and Methods.....	108
5.3.1	Samples.....	108
5.3.2	Experiments	111
5.4	Results.....	112
5.4.1	Physical properties and Mineralogy	112
5.4.2	Pore types and morphology	114
5.4.3	Petrophysical properties	119
5.4.4	Relationships between mineralogy and the physical properties	120
5.4.5	NMR T ₂ Relaxation time Distribution.....	122
5.5	Discussions.....	125
5.5.1	Fractal dimension characteristics using NMR.	125
5.5.2	Relationships between fractal dimensions and physical properties.....	131
5.5.3	Relationship between fractal dimensions and mineralogy	135
5.6	Evaluation of oil recovery Performance	137
5.6.1	Oil recovery by spontaneous imbibition of formation brine.	137
5.6.2	Impact of minerals composition on coreflooding EOR.....	138
5.6.3	Effluent ions analysis	141
5.6.4	Implications for EOR and CO ₂ storage	142
5.7	Conclusions	146
CHAPTER 6		149
ENFORCED CO₂ MINERALIZATION IN ANHYDRITE-RICH ROCKS: SrCl₂		149
Summary.....		149
6.1	Background	150
6.2	Experimental Methodology	156
6.2.1	Fluids	156
6.2.2	Rock sample preparation.....	157

6.2.3	Micro-CT Scan and EDX spectroscopy	160
6.2.4	Acoustic measurements and rock strength tests.....	160
6.2.5	IC, TIC and pH measurements.....	162
6.3	Result and Discussion.....	164
6.3.1	XRD mineralogical analysis	165
6.3.2	EDX analysis.....	171
6.3.3	EDS analysis.....	172
6.3.4	XRF analysis.....	173
6.3.5	XRF elemental analysis.....	173
6.3.6	IC, TIC and pH analyses	175
6.3.7	Micro-CT Analysis	181
6.4	Geomechanical properties analysis	182
6.5	Implications for Carbon Storage.....	188
6.6	Conclusions	191
CHAPTER 7		194
ENFORCED CO ₂ MINERALIZATION IN ANHYDRITE-RICH ROCKS: BaCl ₂		194
Summary.....		194
7.1	Background	195
7.2	Methods	199
7.2.1	Fluids: Brine and CO ₂	199
7.2.2	Experimental Procedure.....	199
7.2.3	Geochemical analysis	202
7.3	Results and Discussions.....	203
7.3.1	Assessment of Minerals Modification via XRD	204
7.3.2	Elemental Composition by XRF	208
7.3.3	SEM Morphology	209
7.3.4	SEM-EDS Analysis.....	212
7.3.5	FTIR Analysis.....	216
7.3.6	Geochemical Analysis	220
7.3.7	Micro-CT Analysis	225
7.3.8	Analysis of the Total Carbon Content.....	233
7.4	Conclusions	234
CHAPTER 8.....		236

EFFECT OF SULFATE-BASED SCALES ON CALCITE MINERAL SURFACE CHARGE AND ITS IMPLICATIONS ON WETTABILITY: INSIGHTS FROM ZETA-POTENTIAL MEASUREMENTS	236
Summary.....	236
8.1 Background.....	237
8.1.1 Wettability alteration and zeta (ζ) potential	242
8.1.2 Smart and low salinity water.....	246
8.2 Materials and Methods	249
8.2.1 Materials	249
8.2.2 Sample Preparation for Zeta potential Measurement.	249
8.2.3 Zeta potential measurement and pH measurement	250
8.3 Results and Discussions.....	250
8.3.1 Calcite in DI, FW, and SW	251
8.3.2 Effect of anhydrite scale on calcite mineral surface charge	253
8.3.3 Effect of oilfield operations.....	256
8.3.4 Scale Control.....	260
8.3.5 Slug injection.	262
8.3.6 Continuous injection	265
8.4 Wettability alteration	268
8.5 Conclusions	269
CHAPTER 9.....	271
EFFECT OF SURFACE ROUGHNESS AND INTERFACIAL TENSION (IFT) OF ROCK WETTABILITY.....	271
Summary.....	271
9.1 Experiments	273
9.2 Results and Discussion	273
9.2.1 Iceland spar contact angle results.....	278
9.2.2 Indiana limestone contact angle results.....	281
9.3 Conclusions	288
References.....	290
Vitae	336

LIST OF TABLES

Table 1.1. Conceptual illustration of measurement types, equipment, and the scale of investigation.....	6
Table 2.1. Summary of the measurement range and principles of measurement of fluid-rock interaction quantification techniques	31
Table 2.2. A summary of the prospects and challenges of EOR applications in anhydrite-bearing reservoirs.....	Error! Bookmark not defined.
Table 3.1. Ionic Compositions of formation brine and Arabian Gulf Seawater	46
Table 3.2. Composition of synthetic rock samples	49
Table 4.1. Composition of synthetic rock samples	63
Table 4.2. Crude oil properties	64
Table 4.3. Ionic composition of Arabian gulf formation water (FW) and seawater (SW)	65
Table 4.4. Anhydrite-calcite samples minerals composition acquired via QEMSCAN	92
Table 4.5. Anhydrite-dolomite samples minerals composition acquired via QEMSCAN	93
Table 5.1. Dimension and basic properties of the samples.	113
Table 5.2. Fractal dimensions of the micropores, mesopores and macropores for the rock samples with their corresponding correlation coefficient.	129
Table 5.3. Summary of the cumulative oil recovery for different production processes	139
Table 6.1. Previous studies on CO ₂ /brine/anhydrite-gypsum mineralization under various conditions and reaction duration.	154
Table 6.2. Ionic composition of Arabian gulf seawater.	157
Table 6.3. Rock properties prior to CO ₂ -brine treatment.	158
Table 6.4. XRD of the rock sample pre- and post-CO ₂ -brine treatments.....	168
Table 6.5. XRF elemental composition (wt.%) of the rock sample pre- and post- supercritical CO ₂ -brine treatments.....	174
Table 7.1. Ionic composition of Arabian gulf seawater.	199
Table 7.2. Dimensions and mass of the samples before and after CO ₂ -brine interactions.....	226
Table 7.3. Volume fractions of the segmented labels with computed amount of grain precipitation and dissolution.	231
Table 8.1: Ionic composition of Arabian gulf formation water (FW) and seawater (SW).(Abdel-Azeim et al., 2021).....	249
Table 9.1. Roughness and sandpaper size for the Indiana limestone (ILS) and the nonporous-nonpermeable calcite.	277

LIST OF FIGURES

Figure 2.1. Determination of contact angle and dimensions of droplet on dolomite sample using SEM; (a) droplet on dolomite; (b) zoom-in of the dolomite surface to estimate left and right contact angles, and droplet dimensions; the right and left contact angles are 69° and 69°, respectively, while the droplet height and width are 17.1 µm and 48.4 µm, respectively (adapted from Deglint et al., (2017) with permission from Springer).	25
Figure 2.2. Determination of wettability alteration of an oil-wet sandstone surface by AFM; (a) clean sandstone surface;(b) aged sandstone surface (oil-wet); (c) aged sandstone surface treated with TX-100; (d) aged sandstone surface treated with TX-100 (adapted from Hou et al., (2018) with permission from Elsevier).	29
Figure 3.1. Research timeline and experimental schedules.	53
Figure 4.1 Middle Eastern carbonate reservoirs rock mineral composition showing a sizeable amount of anhydrite (M. Mahmoud et al., 2021a).	57
Figure 4.2. Effect of anhydrite concentration on the ionic composition and pH of anhydrite-calcite effluent: a) sulfate ion concentration; b) carbonate ion concentration; c) solution pH after 24 hrs.	75
Figure 4.3. Effect of anhydrite concentration on the ionic composition and pH of anhydrite-dolomite effluent: a) sulfate ion concentration; b) carbonate ion concentration; and c) solution pH after 24 hrs.....	76
Figure 4.4. Pure anhydrite, calcite and dolomite mineral surface charge in DI, SW, and FW at 8 pH.	78
Figure 4.5. Effect of anhydrite (1 wt. % to 25 wt. %) On calcite surface charge: zeta potential values of anhydrite-calcite mixture in DI, SW and FW.....	79
Figure 4.6. Effect of anhydrite (1 wt. % to 25 wt. %) on dolomite surface charge: zeta potential values of anhydrite-dolomite mixture in DI, SW and FW.	80
Figure 4.7. –Zeta potential of anhydrite-calcite mixtures in DI, SW and FW: the effect of pH and anhydrite on calcite mineral surface charge at 1, 5, 10, 15, 20, and 25 wt.% anhydrite/calcite sample mixture, respectively.	84
Figure 4.8. Zeta potential of anhydrite-dolomite mixtures in DI, SW and FW: the effect of pH and anhydrite on dolomite mineral surface charge at 1, 5, 10, 15, 20, and 25 wt.% anhydrite/dolomite sample mixture, respectively.	85
Figure 4.9. Flotation wettability of pure rock minerals (anhydrite, calcite, and dolomite).	88
Figure 4.10. Effect of anhydrite (1 wt.% to 25 wt.%) on calcite flotation wettability.	89
Figure 4.11. Effect of anhydrite (1 wt.% to 25 wt.%) on dolomite flotation wettability.....	90
Figure 4.12. Contact angle of pure anhydrite, calcite and dolomite rocks in de-ionized water, seawater and formation water.	91
Figure 4.13. Anhydrite-calcite-dolomite samples compositional analysis by QEMSCAN.....	94
Figure 4.14. Effect of anhydrite (1 wt.% to 25 wt.%) on calcite contact angle.....	96
Figure 4.15. Effect of anhydrite (1 wt.% to 25 wt.%) on dolomite contact angle.	96
Figure 5.1. Illustrated stratigraphic section of the Marrat Formation in central Saudi Arabia (Adapted from (Farouk et al., 2018). This figure presents the lithology and stratigraphic details of the Marrat	

Formation, highlighting the Upper Marrat Member. Note the location from which the six samples were collected for this study, specifically from the lowest cycle of the three identified cycles of dolostone-evaporite interbedding.....	110
Figure 5.2. XRD spectra shows the mineralogy of the samples (S-1 to S-6) composed mainly of anhydrite and dolomite.	114
Figure 5.3. Thin-section photomicrograph of the studied samples. (A) PPL thin-section photomicrograph of sample (S-1) showing the anhydrite blocky crystals with no obvious porosity. (B) XPL of (A). PPL thin-section photomicrograph of anhydrite precipitation within large vug of the dolomite unit (S-4). (D) XPL thin-section photomicrograph showing the anhydrite cement within bivalve skeletal mold (arrow) of sample S-5. (E) PPL thin-section photomicrograph showing gastropod skeletal grain (dotted line) with microporosity within grain chambers of sample S-1. (F) PPL thin-section photomicrograph showing the presence of moldic pores within the skeletal oncoidal grainstone unit (arrow) of sample S-1.....	116
Figure 5.4. Scanning electron microscope-electron dispersive X-ray spectroscopy (left column) showing the corresponding elemental compositions of the six anhydrite/dolomite samples obtained from the Marrat formation.....	118
Figure 5.5. The relationship between the rocks' porosity, anhydrite and dolomite composition, resistivity, average pore size and the log mean of the transverse relaxation time.	120
Figure 5.6. Relationship between the rocks' permeability, anhydrite and dolomite composition, porosity, resistivity, average pore size and the log mean of the transverse relaxation time.	122
Figure 5.7. T2 relaxation measurements for the six rock samples at fully brine saturation and after centrifuge displacement test: S1, S2, S3, S4, S5, and S6, where incremental porosity at fully brine saturation (blue line), cumulative porosity at fully brine saturation (blue continues line), cumulative porosity post drainage with air (red continues line), and incremental porosity post drainage with air (red dashed line).....	125
Figure 5.8. Total NMR fractal dimension (Dt) for the six rock samples at fully brine saturation obtained using NMR method.....	127
Figure 5.9. Multi-scale fractal dimensions: micropore (D1), mesopore (D2), and macropore (D3) obtained using NMR T2 relaxation measurements for the six rock samples at fully brine saturation.	131
Figure 5.10. Relationship between the multi-scale fractal dimensions: micropore (D1), mesopore (D2), and macropore (D3) with anhydrite and dolomite compositions, porosity, permeability, resistivity, and average pore size.....	133
Figure 5.11. Correlation between the multi-scale fractal dimensions: micropore (D1), mesopore (D2), and macropore (D3) with anhydrite and dolomite compositions, porosity, permeability, resistivity, and average pore size.....	136
Figure 5.12. Cumulative oil recovery and pressure gradient profile for sample S-5; 6 pore volumes (PV) of sea water was flooded followed by 4 PV surfactant solution and 8 PV CO ₂	140
Figure 5.13. Cumulative oil recovery and pressure gradient profile for sample S-6; 6 pore volumes (PV) of sea water was flooded followed by 4 PV surfactant solution and 8 PV CO ₂	140
Figure 5.14. Ionis composition of the effluent sample for seawater and surfactant flooding obtained at predetermined pore volumes injected.	142
Figure 5.15. Wettability using contact angle for the rock samples; the top of the section (S-1 to S-3), the dolomite content increases, with decrease in anhydrite content, increasing the oil-wetness, The lower dolomite section (S-4 to S-6) shows oil-wet behavior.....	144
Figure 6.1. The steps followed and the laboratory experiments that were executed for the rock-CO ₂ -brine interactions.....	159
Figure 6.2. Schematic of the static reactor system used in this study for rock-CO ₂ -brine interactions.....	164

Figure 6.3. Rock sample before and after supercritical CO ₂ -brine interactions; (a) before treatment, (b) after CO ₂ -brine treatment, (c) after CO ₂ -brine+SrCl ₂ treatment.....	165
Figure 6.4. XRD mineralogy showing mineralogical compositions before and after supercritical CO ₂ -brine treatments.....	171
Figure 6.5. EDX spectroscopy of the elemental composition before and after supercritical CO ₂ -brine treatments; the colored marks indicate the spectrum points (A); and the corresponding elemental compositions of the points (B) for the untreated, CO ₂ -brine treatment and CO ₂ -brine + SrCl ₂ treatment.	173
Figure 6.6. The ionic composition of the effluent of the rock-CO ₂ -brine interaction.	177
Figure 6.7. The ionic composition of the effluent of the rock-CO ₂ -brine interaction in the presence of SrCl ₂	180
Figure 6.8. Micro-CT scan of the anhydrite-rich rock sample pre- and post-CO ₂ -brine interactions (the scale of the images is 5000 µm).....	182
Figure 6.9. Young's modulus and bulk modulus of anhydrite rock sample pre- and post CO ₂ -brine interactions.....	184
Figure 6.10. Hardness and poisson's ratio of anhydrite rock sample pre- and post CO ₂ -brine interactions.	185
Figure 6.11. Changes in mechanical and petrophysical properties of the sample after supercritical CO ₂ -brine interactions.....	188
Figure 6.12. The total carbon (TC, mg/Kg of rock) results in the solid phase before and after supercritical CO ₂ -brine treatments.	190
Figure 6.13. Conceptual schematic of carbon mineralization in anhydrite-rich formation in the presence of aqueous SrCl ₂	191
Figure 7.1. Rock-CO ₂ -brine interactions experimental flowchart with and without BaCl ₂	202
Figure 7.2. Bulk XRD mineralogy for untreated and CO ₂ -brine treated rock.	205
Figure 7.3. Maps of the dominant elements from X-ray fluorescence (XRF) spectrograph for the untreated, CO ₂ -brine treated, and CO ₂ -brine+BaCl ₂ treated rock.	209
Figure 7.4. SEM morphology of the rock untreated, and post-CO ₂ -brine treatments.....	211
Figure 7.5. SEM-EDX spectroscopic elemental composition of the untreated rock: (A) EDS layered image, (B) elemental composition of the layered map; (C) point-based SEM-EDS showing the spectrum points, (D) elemental composition of the spectra.....	213
Figure 7.6. SEM-EDX spectroscopic elemental composition of the CO ₂ -brine treated rock: (A) EDS layered image, (B) elemental composition of the layered map; (C) point-based SEM-EDS showing the spectrum points, (D) elemental composition of the spectra.....	214
Figure 7.7. SEM-EDX spectroscopic elemental composition of the CO ₂ -brine+BaCl ₂ treated rock: (A) EDS layered image, (B) elemental composition of the layered map; (C) point-based SEM-EDS showing the spectrum points, (D) elemental composition of the spectra.....	216
Figure 7.8. FTIR composition of the untreated rock, and post-CO ₂ -brine interactions. The zoomed-out spectral domains indicate the changes that occur in the dolomite, aragonite, molecular CO ₂ , and the scapolite group for the different CO ₂ -brine treatments.	218
Figure 7.9. The ionic compositions of the key ions in the effluent of the rock-CO ₂ -brine interactions.	222
Figure 7.10. The ionic composition of the effluent of the rock-CO ₂ -brine interaction in the presence of BaCl ₂	223
Figure 7.11. pH of the effluent of the rock-CO ₂ -brine interactions over 360 hours interaction time.	225
Figure 7.12. 2D slices from micro-CT images of sample before and after exposure to CO ₂ -brine. a) pre-exposure 2D µ-CT slice, b) post-exposure 2D µ-CT slice, c) blended image: Grayscale: pre-,	

Yellow: post- CO ₂ -brine. The red boxes show dissolved regions (decrease in intensity) while the green boxes indicate the precipitated regions (increase in intensity of the high-density objects).	228
Figure 7.13. 2D slices from micro-CT images of sample before and after exposure to CO ₂ -brine+BaCl ₂ . a) pre-exposure 2D μ -CT slice, b) post-exposure 2D μ -CT slice, c) blended image: Grayscale: pre-, Yellow: post- CO ₂ -brine+BaCl ₂ . The red boxes show dissolved regions (decrease in intensity) while the green boxes indicate the precipitated regions (increase in intensity of the high density objects).	229
Figure 7.14. Two perspectives of the 3D image obtained from micro-CT scans comparing the surface pre- (a) and post- (b) CO ₂ -brine exposure: Mapping together the high-density material; (c) pre-treated sample's region shown in blue color and post-treated samples in red color; (d) shows the same image but with the blue color's opacity reduced to 0.5.	232
Figure 7.15. Two perspectives of the 3D image obtained from micro-CT scans comparing the surface pre- (a and c) and post- (b and d) CO ₂ -brine exposure: Mapping together the high-density material; (c) pre-treated sample's region shown in blue color and post-treated sample's in red color; (d) shows the same image but with the blue color's opacity reduced to 0.5.	232
Figure 7.16. Total carbon content of the untreated, and post-CO ₂ -brine treated rocks.	234
Figure 8.1. Calcite Mineral surface charge in DI, SW, and FW.	253
Figure 8.2. Effect of anhydrite scale on calcite mineral surface charge. (A) zeta potential values of calcite/anhydrite mixtures in varying fluids. (B) pH value of the mixtures after 24hr. conditioning. The X-axis represents fluids (DI, SW, and FW) in which the mineral was conditioned.	255
Figure 8.3. Effect of Oilfield induced pH and anhydrite scale on calcite mineral surface charge. A-F represents 1, 5, 10, 15, 20, and 25 wt.% anhydrite/calcite sample mixture, respectively.	259
Figure 8.4. Ion concentration analysis.	262
Figure 8.5: Mode of chelating agent injection. (A) slug injection. (B) Continuous injection.	264
Figure 8.6. Effect of slug injection on scale control. A and B: zeta potential values for anhydrite/calcite case scenario in FW and SW, respectively.	265
Figure 8.7. Effect of continuous EDTA chelating agent injection on the calcite/scale surface charge. (A – C) and (D – F) represent 1, 5, and 10 wt.% anhydrite/calcite system in FW and SW environments, respectively.	267
Figure 9.1. Nonporous-nonpermeable calcite: a) optical images, b) and c) are surface topographic images in 2D and 3D, respectively. Polished with 55 μ m (1), 15 μ m (2), 9 μ m (3), 2 μ m (4), and 0.5 μ m sandpapers (5).	274
Figure 9.2. Indiana limestone: roughness of the grain surface; a) optical images, b) and c) are surface topographic images in 2D and 3D, respectively. Polished with 55 μ m (1), 15 μ m (2), 9 μ m (3), 2 μ m (4), and 0.5 μ m sandpapers (5).	275
Figure 9.3. Indiana limestone: roughness around the pore spaces; a) optical images, b) and c) are surface topographic images in 2D and 3D, respectively. Polished with 55 μ m (1), 15 μ m (2), 9 μ m (3), 2 μ m (4), and 0.5 μ m sandpapers.	276
Figure 9.4. Root mean square (RMS) roughness against sandpaper size for the Indiana limestone (ILS) and the nonporous-nonpermeable calcite.	278
Figure 9.5. Peak to Valley (P-T) roughness against sandpaper size for the Indiana limestone (ILS) and the nonporous-nonpermeable calcite.	278
Figure 9.6 Contact angle values at 3 different IFT levels for 5 Iceland spar samples of different roughness.	280
Figure 9.7 Contact angle values of 5 Iceland spar samples of different roughness at 3 different IFT levels.	280

Figure 9.8. Contact angle values at 3 different IFT levels for 5 Indiana limestone samples of different roughness.	282
Figure 9.9. Contact angle values of 5 Indiana limestone samples of different roughness at 3 different IFT levels.	283

ABSTRACT

Full Name : Abubakar Isah

Thesis Title : Systematic Investigation of Rock/Fluid Interactions in Reservoirs at Nano –To – Millimeter Scale: Implications for Enhanced Oil Recovery and CO₂ Storage

Major Field : Petroleum Engineering

Date of Degree : May, 2024

Enhanced oil recovery (EOR) is crucial in oil and gas production operations, it entails injecting fluids into the reservoir to enhance productivity. When fluids are injected, interactions occur between the injected fluids and the reservoir rock/fluids; and the outcomes of rock/fluid interactions critically affect the fluid flow in porous media and the associated hydrocarbon recovery. The associated changes in reservoir properties (porosity, permeability etc.) and flow behavior (i.e. wettability alteration and relative permeability changes) demonstrate variability at a range of scales. Thus, it is of great importance to understand these interactions at multiple scales and their ensuing implications on EOR. In this research, we will utilize different measurement techniques such as scanning probe microscopy (SPM), nuclear magnetic resonance (NMR), micro computed tomography (CT) scan, scanning electron microscopy (SEM), zeta potential, nanoindentation, coreflooding and contact angle measurements having various scales of resolutions ranging from nano –, micro –, and core-scale to probe fluid/rock interactions and wettability of rocks. Carbonate and pure rock minerals from the Saudi Arabian reservoirs will be investigated. The research aimed at probing the validity of the current wettability quantification methodology for porous and permeable rocks compared to those having almost zero porosity and zero permeability. The effect of mineralogical heterogeneity (presence of anhydrite minerals) on carbonate wettability will also be investigated across a range of scales. Further, the wetting behavior as a function of nanomechanical properties on rough and on the flat rock surfaces will be studied. The relationship between rock mineralogy, surface roughness, nanomechanical properties and wettability will be established, and the resulting implications on EOR before and after oil/CO₂/CO₂-foam/brine exposure will be analyzed. The results showed that pure anhydrite is water-wet while calcite and dolomite are intermediate to oil-wet. In addition, anhydrite influences the surface charge at the rock/fluid interface and increases the water wetness in carbonates. For the oil recovery potential, CO₂ injection proves more effective than surfactant flooding in anhydrite-bearing carbonates. Anhydrite undergoes mineral transformation when exposed to CO₂-saturated brine. Therefore, anhydrite-rich rocks can serve as potential CO₂ sink. Thus, findings from this research will provide answers to the questions of how the carbonates wetting behavior changes with mineralogical heterogeneity, and whether anhydrite mineral in carbonate reservoirs be harnessed or avoided. This research therefore provides a systematic investigation of rock/fluid interactions and its implications on EOR and CO₂ storage at various range scales.

نبذة مختصرة

الاسم الكامل: أبو بكر عيسى

عنوان الرسالة: دراسة منهجية لتفاعلات الصخور/السوائل في الخزانات بمقياس النانو إلى المليمتر: الآثار المترتبة على تحسين استخلاص النفط وتخزين ثاني أكسيد الكربون

التخصص الرئيسي: هندسة البترول

تاريخ الدرجة: مايو 2024

يعد الاستخلاص المعزز للنفط أمراً بالغ الأهمية في عمليات إنتاج النفط والغاز، فهو يستلزم حقن السوائل في الخزان لتعزيز الإنتاجية. عند حقن السوائل، تحدث تفاعلات بين السوائل المحقونة وصخور/سوائل الخزان؛ وتؤثر نتائج تفاعلات الصخور/السوائل بشكل حاسم على تدفق السوائل في الوسائط المسامية واستعادة الهيدروكربونات المرتبطة بها. تُظهر التغييرات المرتبطة في خصائص الخزان (المسامية والنفاذية وما إلى ذلك) (وسلوك التدفق) أي تغيير قابلية التبلل وتغيرات النفاذية النسبية (التباين في مجموعة من المقاييس. وبالتالي، من الأهمية بمكان فهم هذه التفاعلات على مستويات متعددة وتأثيراتها على الاستخلاص المعزز للنفط. في هذا البحث، سوف نستخدم تقنيات قياس مختلفة مثل والتصوير المقطعي المحوسب الدقيق، (NMR) والرنين المغناطيسي النووي، (SPM) الفحص المجهرى الماسح وإمكانات زيتا، والحفر النانوي، والغمر المركزي، وزاوية الاتصال، (SEM) والمجهر الإلكتروني الماسح، (CT) قياسات ذات مقاييس مختلفة من الدقة تتراوح بين المقياس النانوي والجزئي والمقياس الأساسي لاستكشاف تفاعلات السوائل /الصخور وقابلية بلل الصخور. سيتم دراسة معادن الكربونات والصخور النقية من المكامن السعودية. يهدف البحث إلى التحقق من صحة المنهجية الحالية لتقدير قابلية التبلل للصخور المسامية والنفاذية مقارنة بتلك التي تحتوي على مسامية ونفاذية صفر تقريباً. سيتم أيضاً دراسة تأثير عدم التجانس المعدني (وجود معادن الأنهيدريت (على قابلية بلل الكربونات عبر مجموعة من المقاييس. علاوة على ذلك، سيتم دراسة سلوك الترطيب كدالة للخصائص الميكانيكية النانوية على الأسطح الصخرية الخشنة والمسطحة. سيتم تحديد العلاقة بين علم المعادن الصخرية وخشونة السطح والخصائص الميكانيكية النانوية وقابلية التبلل، وسيتم تحليل الآثار المترتبة على الاستخلاص المعزز للنفط قبل وبعد التعرض للنفط/ثاني أكسيد الكربون/رغوة ثاني أكسيد الكربون/المحلول الملحي. أظهرت النتائج أن الأنهيدريت النقي رطب بالماء بينما الكالسيت والدولوميت متوسطان إلى رطبان بالزيت. بالإضافة إلى ذلك، يؤثر الأنهيدريت على الشحنة السطحية عند واجهة الصخور/السوائل ويزيد من رطوبة الماء في الكربونات. بالنسبة لإمكانية استخلاص النفط، أثبت حقن ثاني أكسيد الكربون أنه أكثر فعالية من غمر المواد الخافضة للتوتر السطحي في الكربونات الحاملة للأنهيدريت. يخضع الأنهيدريت للتحول المعدني عند تعرضه لمحلول ملحي مشبع بثاني أكسيد الكربون. ولذلك، يمكن للصخور الغنية بالأنهيدريت أن تكون بمثابة بالوعة محتملة لثاني أكسيد الكربون. وبالتالي، فإن نتائج هذا البحث ستوفر إجابات على الأسئلة المتعلقة بكيفية تغيير سلوك ترطيب الكربونات مع عدم التجانس المعدني، وما إذا كان يمكن تسخير معدن الأنهيدريت في خزانات الكربونات أو تجنبه. ولذلك يوفر هذا البحث دراسة منهجية لتفاعلات الصخور/السوائل وآثارها على تخزين النفط المعزز للنفط وثنائي أكسيد الكربون على نطاقات مختلفة.

CHAPTER 1

INTRODUCTION

A precise characterization of rock/fluid interactions is essential for a broad range of subsurface applications e.g. understanding fluid flow in porous medium (Bakhshian et al., 2020; Wei et al., 2017), well stimulation (K. Z. Abdelgawad et al., 2019; Shafiq et al., 2018), enhanced oil recovery predictions (Arif et al., 2020a; Kumar & Mandal, 2018; Olayiwola & Dejam, 2019), and CO₂ and hydrogen geo-storage (Ali et al., 2021; Cui et al., 2018; Zivar et al., 2021). The rock/fluid interactions are strongly dependent on the type of rock and fluids being considered and the associated physicochemical features of the interfaces - thus the theme of ‘rock/fluid interactions’ covers a broad scientific domain. For instance, in enhanced oil recovery, the interaction among the injected fluid, reservoir fluid and the rock surfaces will be a function of type of injected fluid (e.g., surfactant, nanoparticle, carbonated brine, low salinity brine, polymer, CO₂ etc.), and type of rock in question as well as prevailing thermophysical conditions (pressure, temperature and salinity).

Typically, upon injection of a fluid (surfactant, polymer, CO₂, brine) in a porous medium, the possible interactions that may occur include: (i) reactions among the injected and reservoir fluid and reactions among the injected fluid and rock fabric; (ii) adsorption/desorption of certain components/chemicals onto/from the rock surfaces; (iii) precipitation, and (iv) clay swelling and fines migration. The resulting impact of these

interactions is one or more of the followings: a) a change in petrophysical properties, b) a shift in wettability towards oil-wet or water-wet, c) a change in the fluid-fluid interfacial tension, d) a change in relative permeability and capillary pressure characteristics of the system, e) a change in reservoir mechanical properties, and f) adsorption / precipitation. Interestingly, under a given set of conditions, one or more of these mechanisms may occur – thus suggesting the complex nature of these interactions.

Rock/fluid interactions for several rock/fluid systems have been extensively investigated during the last three decades in various context. For instance, the wettability alteration potential of cationic, anionic and nonionic surfactant as a function of their concentration is widely debated recently (Das et al., 2020; Dehaghani et al., 2020; Eslahati et al., 2020; Karimi et al., 2016b; Moradi et al., 2019; Souayeh et al., 2021). While it is generally agreed that surfactants tend to alter wettability towards water-wet and this potential increases with increase in surfactant concentration, still the interactions of surfactant with reservoir rock and fluids are complex to characterize. Furthermore, such interactions may show discrepancy at multiple scales ranging from core-scale down to nano-meter scale. Moreover, CO₂-foam flooding, typically leads to improved oil recovery due to improve sweep efficiency and wettability alteration, and the underlying mechanisms are complex and require a rigorous experimental approach at multiple scales (Al Maskari et al., 2019).

Nevertheless, the outcomes of rock/fluid interactions critically impact the fluid flow in porous medium and the associated oil recovery. Thus, it is crucial to understand these interactions at multiple scale using a range of correlative experimental approaches. For a given rock/fluid system, a range of laboratory experimental tools have been utilized. These include core flooding setup for steady-state and unsteady-state displacement experiments

at the core-scale to determine a) hydrocarbon recovery profiles vs. volume of injected fluid, b) capillary pressure and relative permeability characteristics, and c) quantification of wettability via Amott-indices.

Atomic force microscopy (AFM) allows measurement of a root mean square (RMS) surface roughness which can thus be related to observed wetting behavior. Moreover, scanning electron microscopy (SEM) and field-emission (FE)-SEM allows imaging of the pore space at micro-meter to nano-meter scale to resolve the pore spaces and visualize any changes upon interaction with an injected fluid while NMR relaxation measurements can also confirm the pore structure changes. Furthermore, the advancement in imaging technology and faster computing now has made it possible to measure geometric contact angles within the pore-spaces following the injection (of a certain fluid) using three-dimensional (3D) in-situ micro-CT imaging. Moreover, the electrostatic potential at the rock/fluid or fluid/fluid interface can be characterized via zeta potential measurements which is then correlated to contact angles to obtain a better understanding of the wetting dynamics of the rocks surfaces. Thus, it is clear from above discussion that rock/fluid interactions are complex and require a range of experimental techniques at multiple scales. **Table 1.1** shows a schematic of key experimental techniques for rock/fluid interactions measurement and their associated scale of investigation.

Table 1.1. Conceptual illustration of measurement types, equipment, and the scale of investigation.

		Scale of investigation
--	--	------------------------

Measurement type	Technique/Equipment	Nanoscale	Sub-micron scale	Macroscale	Core-scale
		1 to 100 nm	100 nm to 10 μ m	10 μ m to 1 mm	1mm to 100 mm
Minerology & Heterogeneity	XRD/XRF				
	QEMSCAN				
Pore structure	SEM/Thin Section				
	FIB-SEM/FE-SEM				
	MICP				
Surface Roughness & Intrinsic Wettability	AFM				
	Optical Microscopy				
Dynamic Wettability and Flow Characterization	NMR/MRI				
	Micro-CT imaging				
	Medical-CT				
	Sessile-drop contact angle/Captive bubble method				
	SCAL (Pc, RI-Sw & Kr-Sw)				

This research therefore, aimed at developing a new approach to characterize wettability of carbonate/oil/CO₂-foam/brine systems at multiple scales by capturing the fluid flow dynamics at nano to millimetre scale. The associated impact of anhydrite, calcite and dolomite contents will also be evaluated. The carbonate and sandstone samples from Saudi

Arabian oil fields will be used. Notably, since this project attempts to work on new and pertinent research questions that are to be addressed using a new approach (i.e. multiscale wettability, rock geomechanical properties and mineralogical heterogeneity and its impact on fluid flow in porous medium. The research therefore provides a systematic investigation of the important rock/fluid interactions among the reservoir rock, fluid and key injected fluid (CO₂-foam). To this end, the validity of the current wettability quantification methodology for porous and permeable rocks compared to those having almost zero porosity and zero permeability will be examined. Importantly, the wetting behavior upon interaction with brine and CO₂-foam, and its relationship to the nanomechanical properties (elastic modulus and rock surface hardness) and rock surface topography will also be investigated. The findings of this research will, therefore, enhance the knowledge and understanding of the implications of multiscale wettability and fluid/rock interactions and thereby reduce the uncertainties associated with laboratory-scale predictions and EOR planning.

CHAPTER 2

LITERATURE REVIEW

2.1 Fluid/Rock Interaction in Conventional Rocks

Interaction of reservoir fluids (such as oil, gas, and formation water), injected fluids (surfactant, polymer, CO₂, foam, among others) and the reservoir rock occur over the life of petroleum reservoir. The injected fluids such as CO₂, CO₂-foam, seawater, low salinity water, surfactant, among others, may interact with the reservoir fluids and rock. When these fluids/chemicals are transported in a porous medium, all or some of the following interactions may occur; (i) the injected fluids/chemicals may react with one another and/or with the fabric of the porous media; (ii) some components/chemicals may get adsorbed onto or get desorbed from the surfaces of the rock matrix; (iii) some components may precipitate from the flowing phase onto the rock surface; (iv) the rock minerals may dissolve or get detached from the rock and go into the flowing phase (fines migration). These interactions often affect the overall productivity of the reservoir either negatively or in a favorable manner. Thus, this section provides a literature review of possible fluids-rock interaction in conventional and unconventional rocks during improved oil recovery (IOR) applications.

2.1.1 Surfactant Adsorption/Retention

Rock/fluid interactions, in general, may lead to the entrapment of the injected fluid in porous medium. Surfactant flooding is widely used, for EOR, however, the key challenge (both technically and economically) is the surfactant retention/adsorption in the porous media (Curbelo et al., 2007). Surfactant retention can be referred to as all the mechanisms that remove or reduce surfactant concentration from a flowing solution. During surfactant flooding, surfactant adsorption is only one component of surfactant retention (Hirasaki et al., 2011), others are phase trapping (mechanical entrapment i.e. when large molecules are trapped in narrow flow channel or pores), and hydrodynamic retention (some molecules may be trapped in stagnant flow region), and precipitation. Different mechanisms/driving force in which adsorption of surfactant on the rock surface take place include; electrostatic interactions, hydrophobic solid interactions (hydrocarbon chain–hydrophobic solid site interaction), interactions of van der Waals forces between the non-polar tail – surfactant chains (hydrocarbon chain–chain interaction), chemisorption, hydrogen bonding, covalent bond, and adsorption via ion exchange (Jian et al., 2016; Zhang & Somasundaran, 2006). The adsorption loss and the nature of the adsorption isotherm depends on the co-surfactant and co-solvents (alcohols) used, salinity, Eh, pH, microemulsion viscosity, crude oil type and other variables (Curbelo et al., 2007; Zhang et al., 2016).

2.1.2 Polymer Adsorption/Retention

Polymer molecules adsorbs on surface of rock due to the affinity between them. Polymer adsorption should be less than 1 mg/g of rock for optimal efficiency (Han et al., 2014). Adsorption of polymer can cause severe damage to the formation (Kakati et al., 2020).

Ferreira & Moreno, (2020) reported that polymer adsorbs in multiple sites on rock surface because of its large molecular size, and it is difficult to desorb the entire molecules from the rock surface – suggesting irreversible adsorption (Kakati et al., 2020; Zhang & Seright, 2014). In summary, polymer interactions with carbonate and sandstone rocks have been actively investigated, still the influence of some rock minerals such as anhydrite on polymer adsorption and the predominant adsorption mechanism require further studies. Furthermore, polymers are often combined with surfactants and/or alkalis, and the subsequent subsections describe the interactions in these systems.

2.1.3 Alkaline – Surfactant – Polymer (ASP) Adsorption/Retention

Alkaline/surfactant flooding was proposed by (Nelson et al., 1984), which involves the injection of solution containing both surfactant and alkali for EOR. If polymer and/or alkali is added to surfactant solution, it may partition into the oil, brine and the surfactant films in a different way from the surfactant partition (Hirasaki et al., 2011). When both surfactant and polymer are mixed, competitive adsorption occurs and adsorption decreases because the polymer prevents second layer adsorption of surfactant. It was shown by Cao et al., (2015) and Wang et al., (2015) that using amphoteric surfactant flooding in carbonate cores, the surfactant adsorption is reduced when mixed with polymer in an SP flooding. The main aim of adding alkali in surfactant flooding is to reduce the adsorption of surfactant by sequestering divalent ions in the rock/fluid interface. The role of alkali is to serve as potential-determining ion, to reverse the charge of positively charged mineral site. Alkali also forms foam/soap when it reacts with naphthenic acid in the crude oil which serves as IFT reducing agent, thus alkali can alter the wetting state of rock surface to either

more oil-wet or water wet (Hirasaki et al., 2011) depending on surface/fluid characteristics. Zhang et al., (2016) investigated the adsorption of anionic, nonionic and blended surfactants adsorption in tight rock (0.004 to 0.008 mD) at room temperature using core flooding and UV-spectrometry. They showed that the addition of alkali to anionic surfactant reduces its adsorption. ASP applications in anhydrite-bearing reservoirs has been actively investigated, yet there is no generally acceptable workflow to minimize ASP consumption/degradation by anhydrite during flooding, thus, this area need further investigations.

2.1.4 Ions Adsorption (from water, oil, carboxylate)

To understand the fundamental physico-chemical interactions governing adsorption of ionic species during seawater flooding and smart water EOR in petroleum reservoirs, cations and anions interaction must be understood. Due to partial dissociation of carboxylic group, the oil-water interface becomes negatively charged, while the charge of the rock-water interface is determined by the potential determining ions present in the formation water and the prevailing pH (Strand et al., 2006). In seawater flooding, the major potential determining ions are Ca^{2+} , SO_4^{2-} and Mg^{2+} , with the concentration of SO_4^{2-} about twice Ca^{2+} in seawater, Mg^{2+} has the highest concentration, about twice the concentration of SO_4^{2-} , while the concentration of Ca^{2+} is high in formation water and low concentration of SO_4^{2-} (Pierre et al., 1990; Strand et al., 2006). Calcium ions (Ca^{2+}) can also adsorb on silica and make the silica surface less negative.

It can be summarized from these studies that the adsorption of ionic species such as Ca^{2+} , SO_4^{2-} and Mg^{2+} during seawater flooding trigger wettability reversal. Wettability modification is triggered by SO_4^{2-} due to its ability to either directly displace the adsorbed carboxylate species (Gomari et al., 2006) or by shifting the surface potential toward more negative values thereby weakening the affinity of the carboxylates of the surface (Strand et al., 2006; Zhang et al., 2007). Recently, Song et al. (2020) reported that Na^+ is responsible for oil wetness on calcite surface. This finding is similar to the quantum molecular dynamics (MD) simulation by Liu et al. (2018), and Kolehini et al. (2018) reported that Na^+ resides close to the calcite surface compared to divalent ions (Ca^{2+} , Mg^{2+}), thus reducing the overall calcite/water adhesion energy and consequently, more oil-wet surface. Therefore, reducing the NaCl concentration during low salinity water flooding implies altering the wettability of the calcite surface to more water wetting (Song et al., 2020). The visualization study by Ricci et al., (2013) and Guo & Kovscek, (2019) using atomic force microscopy (AFM) showed that Na^+ exists in the Stern layer closer to the surface than the divalent ions. Similar conclusions were drawn in the work of (Sakuma et al., 2014) based on density function theory (DFT).

2.1.5 Rock Dissolution

Fluid injection into the reservoir system will induce different levels of rock dissolution depending on the type of the injected fluids and the reservoir mineralogy. For example, carbonate rocks are more reactant compared to sandstone, hence, more rock dissolution will be expected in carbonate reservoirs. The fluid type can significantly affect the level of surface dissolution; acids have shown the highest impact due to their fastest reaction rate.

Typically, rock dissolution is associated with chemical EOR which is extensively applied to improve reservoir productivity (e.g., by wettability alteration) and increase oil recovery (Mahmoud & Abdelgawad, 2015; Mahmoud et al., 2017).

2.1.6 Clay Swelling and Fines Migration

Reservoir rocks consist of numerous minerals e.g. sandstone is rich in quartz and also contains clays (illite, kaolinite, chlorite, and smectite) while carbonates are rich in calcite, dolomite, and may also contain clay (Muecke, 1979). These minerals interact with the injected fluids (e.g. brine etc.) leading to alteration of the reservoir properties at various levels. The alteration of reservoir properties includes rock dissolution, clay swelling, and fine migration.

Clay swelling can be induced during the water injection leading to a reduction in the pore space, and hence permeability impairment. The main mechanism for clay swelling is the hydration phenomena that lead to expanding the clay layers (Fink & Thomas, 1964; Foster et al., 1954; Karpiński et al., 2015; Li et al., 2019; Zhang & Low, 1989).

The common factors that influence fines migration process are carrier fluid properties, reservoir type, and operation parameters (Miri et al., 2021). Fluid properties such as salinity, pH, and composition significantly impact fines migration process. Operation parameters such as temperature or pressure can affect the fines migration process. While fine migration can lead to several types of formation damages, it is also reported to be one of the main factors for achieving higher oil recovery (Katende & Sagala, 2019). Fine migration can change the rock surface properties such as wettability, thereby creating favorable flow conditions, and more oil can be produced.

2.1.7 Wetting and IFT Characteristics

There is a consensus that wettability alteration and interfacial tension (IFT) reduction are the mechanisms for oil recovery improvement due to surfactant flooding (Yang et al., 2021). In a water-wet rock, the residual oil is trapped due to capillary forces (Jun Lu & Pope, 2017). Thus, a reduction in IFT following surfactant injection mobilizes the trapped oil and improves oil recovery. The influence of surfactant on wettability alteration is rather more complex where a surfactant arguably turns the rock more water-wet and thus increases the spontaneous imbibition of water.

It is widely agreed that wettability alteration is one of the dominant mechanisms that leads to enhanced oil recovery due to low salinity waterflooding (LSW) (Alotaibi et al., 2011; Kafili Kasmaei & Rao, 2015). While it is generally believed that wettability alteration towards water-wet results in improved oil recovery (due to associated greater water imbibition and oil removal), still a few investigations reported weakly water-wet or mixed-wet as optimal wettability for EOR due to LSW (Ding & Rahman, 2017; Liu & Wang, 2020). Mechanistically, wetting behavior of a rock/oil/brine system is governed by interplay of the interfacial interactions among the thin water film at the rock and oil interface. These interactions and thus the wettability alteration due to LSW are influenced by: a) electric double layer (EDL) expansion, b) multicomponent ion exchange, c) change of interfacial tension, d) pH change, e) fine migration, f) mineral dissolution, and g) micro dispersion formation (Liu & Wang, 2020; Mahani et al., 2017; Morrow et al., 2011; Rezaeidoust et al., 2009; Sadeqi-Moqadam et al., 2016). Specifically, during LSW, the EDL expands due to low ionic concentration leading to an increase in repulsive forces –

thereby shifting the wettability towards more water-wet (Liu & Wang, 2020). While these interactions at the EDL can be determined through zeta potential measurements, the precise quantification of zeta potential of intact reservoir core samples is still a challenge. Furthermore, in terms of multicomponent ion exchange, the high valence ions which act as a bridge between rock and oil, a reduction in their concentration (during LSW) leads to a wettability shift towards water-wet since the bridge gets broken (Liu & Wang, 2020).

2.2 Implications of Rock/Fluid Interactions on EOR

Complex mineralogy in hydrocarbon reservoirs can affect the performance of several EOR operations due to the nature of the minerals present. This section discusses the impact of anhydrite/fluid interaction on rock wettability, formation damage, and rock surface characteristics.

2.2.1 Wettability Modification

The rock wettability depends significantly on the mineralogical composition, changing the surface minerals content can lead to altering the surface wettability. During the EOR process, several interactions will take place due to the physical and chemical reactions between the injected fluids and reservoir matrix. In carbonate reservoirs, different rock minerals will interact differently compared to other minerals due to their variable reaction rates. For instance, anhydrite minerals consist mainly of calcium and sulfate ions which are soluble in different fluids. The dissolution of calcium and sulfate ions is usually associated with magnesium adsorption on the rock surface, due to multi-ion-exchange

phenomena. Consequently, the mineral content on the rock surface will be changed considerably as well as the surface wettability (Mogensen & Masalmeh, 2020). This process can help in designing the EOR applications for anhydrite-rich carbonate reservoirs as well as other heterogeneous reservoir formations.

2.2.2 Change in Surface Charge

Fluid injection into the reservoir system has the potential of changing rock surface charges due to ions dissolution or adsorption on the rock surface (Bonto et al., 2019). Electrokinetic measurements are usually conducted to evaluate the rock surface changes before and after EOR treatments (Kim et al., 2020; Li, 2004). The rock surface charges can be indicated by determining the zeta potential and the double layer thickness (Arif et al., 2017). The degree of surface charge changes depends on the rock mineralogy, injected fluid type, chemical concentration, and reservoir conditions. For example, chemical injection would lead to more changes in the rock surface charges compared to water injection, due to the high rock dissolution by the injected chemicals and enhanced adsorption. For carbonate rocks, the common adsorbed ion is the magnesium due to the multi-ion exchange (MIE) process (Bai et al., 2021; Karoussi & Hamouda, 2007). This phenomenon will lead also to an increase in the negative surface charges for carbonate rocks and improve the rock wettability towards water-wet. However, for carbonate reservoirs with high anhydrite content, the MIE phenomenon could be more complex due to the low anhydrite solubility. There are limited studies in this area, and further research should be conducted to elaborate on the changes in rock surface charges due to mineralogical heterogeneity and fluid/rock interactions.

2.2.3 Surface Roughness Modification

Surface roughness is a key parameter that tends to influence wettability of rock surfaces (Arif et al., 2020). Due to roughness, a rock surface demonstrates a range of peaks and valley; and the associated root mean square (RMS) roughness of rock surfaces ranges from micrometers to nanometers (Arif et al., 2020). The roughness of the rock surface gets modified due to the interaction between the rock matrix and injected fluids. The primary factor for changing the rock surface roughness is rock dissolution. The injected fluids can dissolve part of the rock matrix, leading to more peaks or valleys in the rock surface (AlRatrout et al., 2018).

2.2.4 Formation damage

Fluid injection into the reservoir system can induce some formation damage due to incompatibility between the reservoir fluids/rocks and the injected fluids (Civan, 2015). The common types of formation damages are fine migration, pore throat plugging, and clay swelling (C. Xu et al., 2016). In anhydrite-rich reservoirs, the dissolution of anhydrite and calcite minerals, due to the fluid injection, can lead to fine migration or solid precipitation, and consequently, the reservoir productivity will decrease (AlSada & Mackay, 2017).

During fluid-rock interactions, a complex interplay between mineral detachment, mineral replacement and mineral dissolution processes will control the porosity and permeability of the reservoir rock (Pudlo et al., 2014; Putnis, 2002). Several factors, such as fluid residence time, brine composition, rock mineral composition as well as its location and distribution might play important roles in reservoir quality assessment (Huq et al., 2015).

2.3 Rock/Fluid Interaction Quantification Methods and Equipment

Rock/fluid interactions (discussed above) can occur at multiple scales ranging from nanoscale to core-scale. For instance, fluid adsorption, rock dissolution can be evaluated using several techniques e.g. ion chromatography and inductively coupled plasma (ICP) analysis. The ions concentration in the injected and produced fluids during waterflooding can be analyzed, increasing the concentration of any certain ions (such as calcium or iron) will indicate rock dissolution. On the other hand, a reduction in ions concentration suggests that the ions are adsorbed on the rock surface due to the multi-ion exchange phenomena. Other advanced techniques such as nuclear magnetic resonance (NMR), scanning electron microscope (SEM), X-ray fluorescence (XRF), and X-ray diffraction (XRD) can be used to characterize the rock surface and help in investigating rock surface modification (Abbasi & Khamsehchi, 2021; Nasralla et al., 2018). Furthermore, pH measurements can be used to assess rock dissolution; mineral dissolution can lead to an increase in the pH of the produced effluent by around 10 – 30% depending on the degree of rock dissolution (Abbaszadeh et al., 2016; Mohammadi et al., 2021a). Therefore, this section describes the equipment, measurement methods and principles for examining rock/fluid interactions at various scales.

2.3.1 Core-flooding (Tracers, pressure drop, permeability)

Core flood experiment is conducted for a realistic representation of fluid-rock interaction in porous media. The technique is typically performed on a cylindrical rock plug obtained during coring or from consolidated outcrops or a quarried rock. The usual core flooding procedure is to inject the EOR fluid (i.e. displacing fluid such as surfactant, polymer, smartwater, etc.) at a required and known flowrate into the brine/oil-saturated (displaced

fluid) core. Core flooding experiments can thus be conducted / interpreted in three ways as described below:

Pressure profile during core flooding.

Fluid-rock interaction can be quantified based on the pressure profile during core flooding. An increase in pressure drop across the core can suggest pore plugging by precipitation while a decrease in pressure drop signifies an increase in flow path which may be due to rock minerals dissolution. These can as well be quantified through changes in permeability (Mishra et al., 2014) a high and low pressure drops imply reduction and increase in permeability respectively. This allows for additional evaluation of whether the measured species (surfactant/polymer or ions) loss; was adsorption or a combination of adsorption and precipitation (Mannhardt et al., 1994). Core flooding technique can be used to evaluate fluid-rock interaction using actual reservoir rock and fluid, as well as under reservoir conditions of pressure and temperature for conventional rocks.

Effluent analysis

The effluent is collected, and the corresponding concentrations of individual components can then be determined using various methods such as titration (Gogoi, 2011; Wang et al., 2015), chromatography (Austad et al., 2015; Sharma & Mohanty, 2018), ultra-violet (UV) spectrophotometry (Curbelo et al., 2007; Ferreira & Moreno, 2020; Kakati et al., 2020; Lv et al., 2011; Saxena et al., 2019), total organic content (TOC) measurement (Alhassawi & Romero-Zerón, 2015; Lv et al., 2011; Zhang & Seright, 2015), and total nitrogen (TN) content analysis (Han et al., 2014; Rodriguez et al., 2014). The concentrations of the components are then compared with the injected values to determine

adsorption/precipitation (decrease in concentration), dissolution (increase in the concentration of the dissolved mineral species in the effluent), or migrated fines.

Tracer measurements

Another way to quantify retention using core flooding is to employ a non-reactive tracer (or non-adsorbing, in case of adsorption measurement) which can be injected with the test solution (for example surfactant or polymer) to serve as a check on the material balance (e.g. (Amirmoshiri et al., 2020; Dang et al., 2014; Ghosh & Mohanty, 2019; Romero-Flores et al., 2018)). The relative positions of the tracer and the test solution profiles give a direct visual indication of adsorption. A shift of the surfactant/polymer concentration profile to the right with respect to the tracer profile, indicates adsorption. While if the tracer and surfactant/polymer concentration curves (or normalized concentration curves) vs pore volume (PV) injected (throughput) coincides, it indicates that there is insignificant adsorption (Dang et al., 2014; Mannhardt et al., 1994). The area between the effluent curves for the two components (tracer) and (adsorbate) is directly proportional to the affinity of component, and can be calculated using the trapezoidal method (Strand et al., 2006).

2.3.2 Contact angle and IFT

Wettability refers to the tendency of a solid to be wet by a particular fluid in the presence of another fluid. A range of experimental techniques are available for characterizing the wetting behaviour of a given rock/fluids system. In this context, the Wilhelmy balance, capillary rise contact angle and spontaneous imbibition methods are the classical methods for wettability measurements (Washburn, 1921) while Amott, Amott-Harvey index, and USBM (U.S. Bureau of Mines) require forced imbibition tests via core flooding setup to

quantify wettability (Anderson, 1986). Furthermore, the relative permeability and capillary pressure curves provide an indirect (qualitative) assessment of wetting behaviour.

Specifically, the contact angle method is a direct method for quantifying wettability, and it allows a sensitivity analysis of the influence of pressure, temperature, and salinity (Arif et al., 2019; Iglaue, 2017). Measuring the contact angle at the rock/oil/brine interface can effectively indicate the wettability condition. In general, the contact angle $< 90^\circ$ indicates water-wet condition, while oil-wet status is indicated by a contact angle $> 90^\circ$. The higher the contact angle (through the denser phase), the higher the oil wetness. Three common configurations of contact angle measurements are: a) sessile drop method, b) captive bubble method, and c) tilted plate method (Al-Yaseri et al., 2016; Lander et al., 2002). The tilted plate method allows a simultaneous measurement of advancing and receding contact angles at the leading and trailing edges of brine (or water) droplets in the presence of crude oil or CO₂ (Broseta et al., 2012). Note that the advancing angle mimics the displacement during imbibition mechanism while the receding contact angle is pertinent to drainage behavior (Broseta et al., 2012).

During contact angle measurements, the lighter phase (CO₂, crude oil, decane) is injected into the pressure cell at a predetermined pressure and a fixed cell temperature. This is followed by brine (or water) injection at a low flow rate (typically $\sim 4 \mu\text{l}/\text{min}$) to allow creation of a droplet which is eventually dispensed onto the rock surface (Arif et al., 2019). Finally, the contact angle is measured at the three-phase contact line (TPCL). Note that, in a captive bubble method, the cell configuration is reversed, and the denser phase (brine) is injected first followed by a bubble of lighter phase (Arif et al., 2019). For a detailed illustration of contact angle methods, the reader is referred to a recent review (Arif et al.,

2019). Furthermore, such an arrangement also allows for the measurement of IFT of fluid/fluid system while the droplet is hanging at the edge of the needle (Arif et al., 2017). Contact angle method is arguably more suitable when pure fluids and clean minerals with smooth surfaces are used (Arif et al., 2019; Kaveh et al., 2014). The RMS (route mean square) surface roughness of a given sample can have a notable impact on contact angle where an increase in roughness of a hydrophilic sample tends to decrease the contact angle while increasing roughness of hydrophobic surfaces leads to an increase in contact angle (Al-Yaseri et al., 2016). On the porous surfaces, contact angles are influenced by the organic polish on the rock surface (Kaveh et al., 2014) – which leads to an apparent contact angle. Recent advancements can now allow contact angle measurements from the 3D in-situ micro-CT imaging (Alhammadi et al., 2017), as well as FESEM (Deglinc et al., 2017b) or cryo-BIB-SEM imaging (Schmatz et al., 2015).

2.3.3 SEM/Thin section / FE-SEM

Scanning Electron Microscopy (SEM) is an imaging technique that creates images of a sample through beam rastering or scanning. It uses a focused beam of electrons to generate a visualization of sample surface topographic details. As the electron beam is accelerated on the sample surface, electrons interact with the sample, and as a result, secondary, back-scattered electrons as well as X-rays are emitted. The X-rays and electrons emitted are then captured by detectors and analyzed to obtain information about surface topography, sample density, or chemical composition. The other modified versions of SEM are Field Emission Scanning Electron (FE-SEM) and Focused-Ion-Beam Scanning Electron Microscopy FIB-SEM. It is evident from the literature that, these imaging techniques are crucial for

understanding fluid-rock interaction in various contexts. Thin section images can be used to create two-dimensional microfluidic devices (micromodels) with pore scale geometry that is identical to real rocks to allow for the direct visualization of flow behavior through a porous medium (e.g., (Buchgraber et al., 2012; Song & Kovscek, 2015)). Recent advances in imaging technologies for characterization of fluid – rock interaction such as FIB-SEM can reveal nanometric pore structure (Curtis et al., 2012; Long et al., 2013). 2D-SEM and 3D FIB-SEM imaging are employed to characterize nano-to micro-scale pore structure and connectivity before and after fluid exposure, SEM is also used to assess the fluid distribution and micro-wettability (Clarkson et al., 2016). In addition, SEM imaging allows the visualization of variation in pore surface structure and pore morphology. Alhassawi & Romero-Zerón, (2015) and Hou et al., (2018) performed SEM to determine the change in surface morphology (size and shape) of rocks due to surfactants adsorption. Moreover, SEM imaging is also applied in the study of modification of mineral phases, Prakash et al. (2019) used microscopy (FE-SEM) to evaluate the alteration in mineral phases as a consequence of fluid-rock (CO₂-rich brine -shale) interaction during CO₂ -EOR and CO₂ storage in unconventional reservoirs. Real-time pore-scale imaging of the interactions between reservoir fluids, injected fluids, rock grains, and other rock minerals (clays) particles is needed to develop a fundamental understanding of the mechanisms that govern the recovery efficiency of hydrocarbons reservoirs (Song & Kovscek, 2015). Recently, a real-time FE-SEM imaging of fluids on rock surfaces to enabled quantification of sessile and dynamic micro-droplet contact angles and droplet dimensions was presented by (Deglint et al., 2017a) (see **Figure 2.1**). However, real-time whole-core scans can take long time (up to 40 minutes), making these imaging techniques opaque to the dynamics of

microscale rock minerals (for instance, clay) detachment studies in the time frame that is required (Song & Kavscek, 2015). FIB-SEM allows for high 3D spatial resolution; however, the nanometric scale FIB-SEM is destructive and small sample size is typically used (only a few millimeters in diameter). Thus, large area 2D maps maybe needed using an SEM for in-depth visualization of heterogeneities (Clarkson et al., 2016).

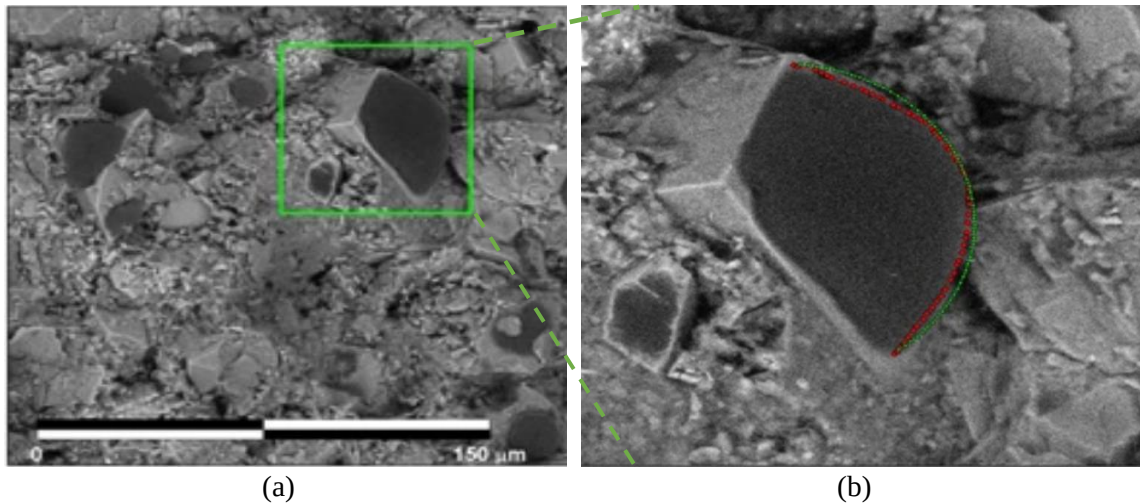


Figure 2.1. Determination of contact angle and dimensions of droplet on dolomite sample using SEM; (a) droplet on dolomite; (b) zoom-in of the dolomite surface to estimate left and right contact angles, and droplet dimensions; the right and left contact angles are 69° and 69° , respectively, while the droplet height and width are $17.1\ \mu\text{m}$ and $48.4\ \mu\text{m}$, respectively (adapted from Deglint et al., (2017) with permission from Springer).

2.3.4 Nuclear Magnetic Resonance (NMR)

There are two types of NMR relaxation times: the longitudinal or spin-lattice relaxation time (T_1) and the transverse or spin-spin relaxation time (T_2). Transverse relaxation T_2 occurs in the xy-plane, whereas the T_1 refers to the decay time of magnetization in the z direction. The transverse relaxation time (T_2) and the longitudinal relaxation time (T_1) usually in milliseconds (ms), are both caused by the magnetic interactions between the hydrogen protons. Both the T_1 and T_2 relaxation times are a function of fluid type and its interaction with the pore structure of the porous media. It is one of the most effective

techniques of characterization of rocks, NMR imaging and quantification can be used to evaluate the pore connectivity (Fleury et al., 2007), wettability alteration (Al-Mahrooqi et al., 2003; Totland et al., 2011; Zhang et al., 2000) where water-wet rocks were found to have lower relaxation times than oil-wet sandstones, because water interacts more strongly with pore walls, such stronger interactions increase surface relaxation and shorten relaxation time (Abbasi et al., 2021). The NMR T_2 relaxation time is faster to acquire than the T_1 relaxation, this account for the more frequent use of T_2 relaxation measurements over the T_1 , and usually gives similar results (Al-Mahrooqi et al., 2006; Ausbrooks et al., 1999). Compared to other imaging techniques, NMR measures fluid, not the rock matrix. The relaxation time is proportional to the pore size, that is, small pores have smaller values of T_2 , and large pores have large T_2 values. It can also be used to obtain pore structure at all length scale with high precision. Meanwhile, NMR measurement is sensitive to environmental conditions (temperature and pressure), it cannot distinguish microfractures from pores (Tang et al., 2021), additionally, differentiating between the pore throats and micropores using NMR is a challenge.

2.3.5 Computed Tomography (CT)

Conventional core experiments failed to capture the pore-scale events that dictate fluid – rock interaction effect (Prakash et al., 2019). Advanced visualization (imaging) techniques such as X-ray computed tomography (X-ray CT) (Vega et al., 2014) and micro X-ray computed tomography (micro X-ray CT) (Nguyen et al., 2013) are able to obtain pore-scale visualization either ex-situ or in-situ . Micro-computed tomography (micro-CT) can be used for analyzing the spatial distribution and textural alteration of constituents of tight

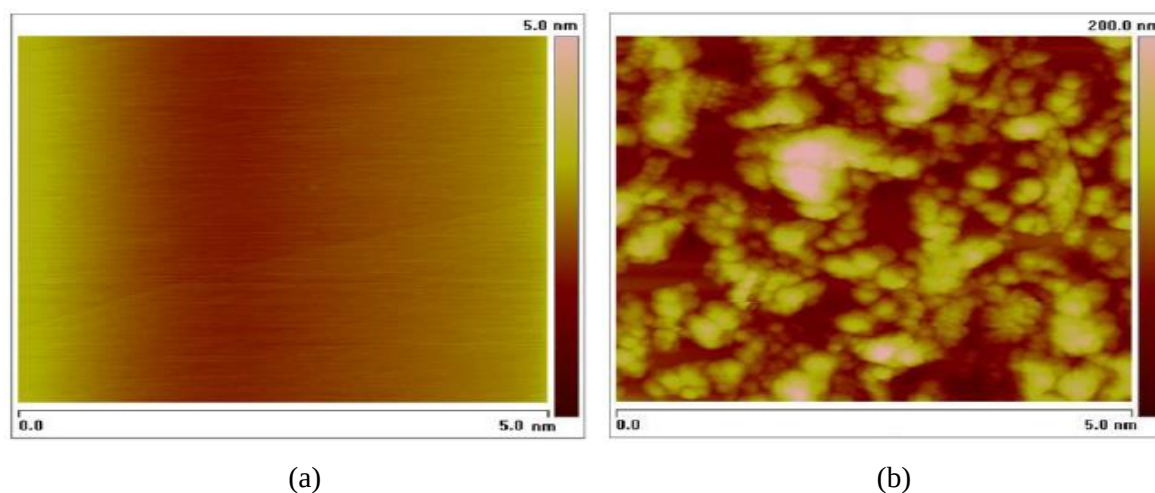
rocks after reaction. Micro-CT imaging, can as well, be carried out before and after fluid-rock interaction to identification dissolution and precipitation in the fluid-rock system and spatial distribution of different minerals in the altered regions based on microstructure changes after exposure. Micro-CT is also employed in pore network modelling to develop an understanding of petrophysical transport behavior in heterogeneous rocks (Bauer et al., 2012; Bultreys et al., 2015, 2016; Peng et al., 2014) and to assess pore geometry on electrical behavior of rock during fluid interaction (Youssef et al., 2008). In order to establish a comprehensive understanding of CO₂-fluid-rock interaction, Prakash et al., (2019) studied the microstructural evolution and chemo-mechanical interaction of shales with CO₂-rich brine using micro-CT. Microstructural evolution such as rock dissolution and precipitation can be observed using CT imaging via porosity change (dissolution implies an increase in porosity while a decrease in porosity of the rock after exposure to reactive fluid, (CO₂-rich brine) corresponds to precipitation and consequent pore blockage). Another advantage of CT imaging technique is the ability to perform in-situ quantification of fluid-rock interaction (Brattekkås & Fernø, 2016).

Meanwhile, the X-ray attenuation coefficient of quartz and clay are similar, the intensity of both minerals is very similar in the micro-CT images, which makes it difficult to differentiate them from the image. Also, since shales and tight rocks have the majority of their pores at nanometer scale and the dimension of a voxel of the scans is typically around 5 μm , not all pores' sizes can be captured in micro-CT images. Hence, it may leave some non-identified pores (Prakash et al., 2019). While CT-scan imaging has the advantage of capturing micron- and large-scale pores for conventional formations, it failed to resolve the required pores and pore connectivity necessary for the extraction of a pore network from

shales and other tight rocks with sub-micron scale pore structure. Another disadvantage of this technique is the difficulty in up-scaling the result to core-scale to estimate flow characteristics (e.g., permeability) (Clarkson et al., 2016).

2.3.6 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a high-resolution microscopic technique invented in 1986 by Binnig (Binnig et al., 1986). Geomaterials, among others, can be imaged at nanoscale using AFM. While SEM typically requires vacuum in the sample chamber, AFM can still work in liquid or air environments. The typical imaging scale of AFM varies from 0.1 nm to 0.01 nm – thereby resolving the atomic scale features (Wang et al., 2021). Some of the key applications of AFM in rock-fluid interactions, include but not limited to, measurement of surface roughness, pore structure, crystalline structure which collectively are known as surface topography. Furthermore, AFM can also measure rock mechanical properties such as elastic modulus and adhesion forces. It can also be employed to determine the change in wettability of rock surfaces (**Figure 2.2**).



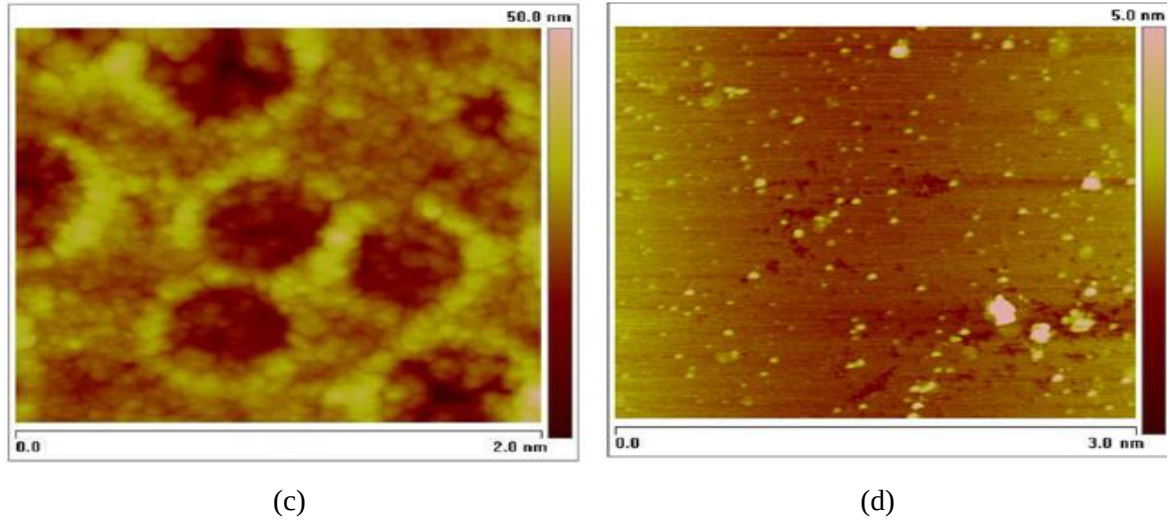


Figure 2.2. Determination of wettability alteration of an oil-wet sandstone surface by AFM; (a) clean sandstone surface; (b) aged sandstone surface (oil-wet); (c) aged sandstone surface treated with TX-100; (d) aged sandstone surface treated with TX-100 (adapted from Hou et al., (2018) with permission from Elsevier).

2.3.7 Zeta potential

To discuss zeta potential, first, we need to define the electric double layer (EDL) model. It is referred as a physical model that describes the ionic charge in the vicinity of a charged particle in a colloidal solution. The EDL consist of a central (layer) fixed charged particle, a surface/titratable charge that is firmly bound to the particle/solid surface, and a slipping charged layer within the solution in contact with the surface. The later contains an excess of ions opposite in sign to the fixed charged (counterions) and has a deficit of ions of the same sign as the fixed charge particle (co-ions). In a colloidal system, the zeta potential measures the difference in the electrical charge between the dense layer of ions surrounding the particle and the charge of the bulk of the suspended fluid surrounding the particles (Strand et al., 2006). Thus, the potential at the slipping plane (where slip with respect to the bulk solution is postulated to occur) is the electrokinetic or zeta potential, ζ (Clogston & Patri, 2011; Delgado et al., 2007). Various methods and techniques used to obtain the

zeta potential of colloidal interfaces are electrophoresis (centered on charged colloidal particles movement with respect to stationary liquid due to applied electric field), electro-osmosis (based on liquid flow caused by an applied electric field to charged porous plug, membrane or capillaries), and streaming current and streaming potential (established on charge displacement in the EDL due to pressure induced liquid movement in pores and capillaries, and can be used to study interfaces of different shapes and geometries).

Based on electrophoretic technique, Helmholtz – Smoluchowski (HS) equation (Eqn. 3) is commonly employed to obtain the zeta potential, for uniform and moderate electric fields:

$$v_e = u_e E \quad (2)$$

where v_e (m s^{-1}), is the particle velocity with respect to a stagnant medium (electrophoretic velocity), E (V m^{-1}) is the applied electric field, u_e ($\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$), is the electrophoretic mobility of the particle and is given by;

$$u_e = \frac{\varepsilon_{eq} \varepsilon_o}{\mu} \zeta \quad (3)$$

where ε_{eq} is the relative permittivity of the electrolyte solution, ε_o is the electric permittivity of vacuum, and μ is the dynamic viscosity of the liquid.

Zeta potential is governed by the nature of the surface, surface charge (which is determined by pH), the concentration and nature of the electrolyte and solvent in the solution. Under given conditions (those parameters fixed), ζ -potentials are unique characteristics for the charge state of interfaces, it is independent of the technique used, therefore, whether different techniques and interpretations are used, identical ζ -potentials values are obtained. It is noteworthy that, researchers often reported different zeta potential values for

supposedly identical interfaces. This is attributed to the fact that zeta potential is not directly measurable property, thus the disparity might be due to an inappropriate model used to convert the electrokinetic signal into a ζ -potential, presence of impurities, or the surfaces are not in fact identical (Delgado et al., 2007).

The principle of zeta potential measurement can be employed to investigate fluid-rock interactions such as adsorption, rock dissolution, measurement of particle size (H. Ding & Rahman, 2018), characterization of wettability modification of rock minerals and surfaces (Jiang et al., 2010), and effect of chemicals and fluid ionic composition on rock minerals (Orozco et al., 2021). Electrokinetic (zeta potential) measurements provide useful information such as identification of the isoelectric point (point of zero charges) in titrations with a potential determining ion (for instance, pH titration) or using ionic reagents such as surfactants, and in the identification of adsorption plateau of ionic species (Delgado et al., 2007). Nevertheless, zeta potential measurements only consider the average of surface charge and fail to provide information about particular charged species on rock surface. Also, difficulties are often encountered when interpreting experimental results obtained for non-ideal surfaces/particles/interfaces such as non-rigid, porous, and rough surfaces or particles (Delgado et al., 2007). An overall summary of fluid-rock interaction quantification methods is provided in **Table 2.1**.

Table 2.1. Summary of the measurement range and principles of measurement of fluid-rock interaction quantification techniques

Method/Technique	Range of measurement	Advantages	Disadvantages	References

Core flooding	≥ 10 mm	1. Fluid-rock interaction can be evaluated on actual reservoir rock and fluid, as well as under reservoir conditions of pressure and temperature. 2. It can as well, be incorporated with other measurement techniques such as X-ray, resistivity, and CT scan for in-depth analysis.	1. Difficult to conduct, and the in-situ behavior of fluid-rock interaction directly from core flood is impossible. 2. It is not effective or impossible to apply for analysis of unconventional rocks (e.g., tight rocks and shale). 3. It is time consuming.	(Sharma & Mohanty, 2018a) (Wang et al., 2015) (Yang et al., 2020)
Contact angle	Sessile drop and captive bubble methods = millimeter scale	1. Allows robust quantification of wettability. 2. Measurements can be done for a broad range of influencing factors (e.g. pressure, temperature, salinity etc.).	1. Surface contamination and cleaning methods may introduce a bias in reported contact angles. 2. It is not a bulk measurement.	(Arif et al., 2019; Iglauer, 2017)
SEM/ FE-SEM/ FIB-SEM	0.8 nm – 1 mm	1. High resolution images can be obtained; FIB-SEM allows for high 3D spatial resolution, it can reveal nanometric pore structure. 2. Applied to both conventional and unconventional rocks (nano-to micro-scale).	1. Nanometric scale FIB-SEM is destructive and small sample size is typically used (only a few millimeters in diameter). 2. Thus, large area 2D maps maybe needed for in-depth visualization of heterogeneities	(Lim et al., 2018)(Clarkson et al., 2016)
Thin Section	1 μ m – 2 mm	1. It is fast and the experimental preparation is easy. 2. It captures mineral and	1. Low resolution compared to SEM and CT. 2. Sample size limitation.	(Reedy et al., 2014)(Tang et al., 2021)

		cementation types, 2D pore types and pore connectivity.		
NMR/MRI	0.1 nm – 10 mm	1. High resolution and non-destructive. 2. It can also be used to obtain pore structure at all length scale with high precision.	1. It is affected by test environmental conditions (temperature and pressure). 2. It is unable to distinguish between the pore throats and micropores, and pores and microfractures.	(Khather et al., 2019) (Gao & Li, 2015)
CT	10 nm – 10 mm	1. Captures 3D distribution of microstructure at high resolution in non-destructive manner. 2. In-situ CT images allow pore-scale visualization of fluid distribution. 3. The spatial distribution and textural alteration of tight rocks after reaction can be obtained.	1. High test cost and long time to acquire. 2. Difficulty in up-scaling the result to core-scale to estimate flow characteristics (e.g., permeability).	(Maire & Withers, 2014) (Gou et al., 2019) (Falat et al., 2020)(Clarkson et al., 2016)
AFM	nanometer scale	1. Provides 3D surface profile as opposed to 2D SEM image. 2. Samples do not require coating thereby preventing any damage to sample. 3. Provides higher	1. Maximum height on the order 10-20 microns can be imaged in the single scan. 2. AFM has low scanning speed compared to SEM (several minutes required for a scan).	(Wang et al., 2021)

		resolution than SEM.		
Zeta potential	nanoscale	1. Easy and fast to acquire. 2. Can be applied to all rock types.	1. Zeta potential is not directly measurable property, thus, for supposedly identical interfaces, disparity in values might occur due to inappropriate model used to convert the electrokinetic signal into ζ - potential. 2. Zeta potential measurement is very sensitive to impurities. 3. Assessment of wettability is qualitative	(Delgado et al., 2007)(Clogston & Patri, 2011).

2.4 Anhydrite-Rich Reservoirs

Anhydrite is a common chemically reactive sulfate rock/mineral found in both sandstones and carbonates. The presence of anhydrite, its distribution and the associated anhydrite–fluid–interactions are thus important to precisely evaluate the effectiveness of oil recovery techniques. While anhydrite dissolution is the key interaction mechanism in anhydrite-rich rocks, its presence may also lead to a complex rock wetting behavior. Therefore, this research also explores the effect of anhydrite mineral on EOR such as and CO_2 and CO_2 – brine/ CO_2 -foam will be investigated.

2.5 EOR Applications in Anhydrite-rich carbonate: Prospects and Challenges

Some fluid/rock interactions represent adverse effects while others are favorable to the overall effectiveness of the EOR process. For instance, during low salinity waterflooding, the brine displaces the formation water that initially established equilibria with the rock. Consequently,

anhydrite dissolution occurs. The dissolution of anhydrite results in an increased concentration of the released (into aqueous solution) SO_4^{2-} and Ca^{2+} ions in the low salinity brine (effluent). Furthermore, CO_2 injection and CO_2 -foam injection are known to be the two most suitable methods for EOR in carbonates. This is attributed to their excellent sweep and interfacial properties. Moffitt et al. (2015) also reported that CO_2 -foam flooding can lead to rock dissolution and result in permeability increase. However, additional oil recovery after injection of these fluids can be dramatically lower than expected due to the complex wettability and mineralogical heterogeneity of the carbonate rocks. A summary of the prospects and challenges of EOR applications in anhydrite-containing reservoirs.

2.6 Significance of the Research Study/Contributions

There has been consensus that wettability alteration towards water-wetting is a main mechanism of EOR, however, the understanding of the interplay of various mechanisms causing this wettability shift and the experimental characterization of the effect require a rigorous experimental approach at multiple scales. The current state-of-the-art research on carbonates often ignored the mixed-wet nature of carbonate rocks. There are, however, recent investigations which experimentally evaluated the mixed-wet carbonate wettability. For instance, Alhammadi et al., (2017) explored mixed-wet carbonate behavior via direct observation of contact angles at the curvature of oil-water interface using 3D micro-CT imaging. Moreover, the measurement of advancing and receding contact angles (at the leading and trailing edges of rock/oil/water interface) is regarded as a reliable way of wetting characterization as opposed to static or pseudo-equilibrium contact angles (Arif et al., 2019; Marmur et al., 2017). Recently, Blunt et al. (2019) used micro-CT imaging and the interface energy balance approach to characterize wettability of sandstone rocks in a

thermodynamically consistent manner. It was shown that the contact angles obtained via energy balance at the local capillary equilibrium states are more sensitive than the geometric contact angles measured at the interface of the three-phase contact line (i.e. the rock, oil, and brine interface). Rücker et al. (2020) proposed a wettability upscaling approach by taking into account the wettability changes at the nanoscale to core-scale. In addition, mixed-wet rock wettability state was also related to the nano-scale surface roughness of the rock surface, where it was argued that rougher surfaces leads to lower contact angles arguably due to water occupying the grooves of the rough rock surface (AlRatrout et al., 2018). However, it may be argued that carbonates due to their widespread mineralogical heterogeneity (Oliveira et al., 2019) may exhibit different behavior on a range of length-scales, and this discrepancy maybe even more pronounced for Arabian carbonates with complex mineralogy. Indeed, research have shown a sizeable quantity of anhydrite in Arabian carbonates. This anhydrite may play a vital role in fluid flow through porous media. It is so far not known how the presence of anhydrite and multiscale heterogeneity in carbonates influence wettability, pore connectivity, fluid distribution and fluid flow.

Since rock/fluid interactions are complex and require a range of experimental techniques at multiple scales, and all the fluid-rock interactions quantification techniques have some limitations either in their applicability or measurement range, and uncertainty level. For instance, it is challenging to apply core flooding in unconventional tight rocks. Micromodels are easy to observe and record fluid-solid interaction data, yet, they cannot represent the actual rock situations due to pressure limitations. Imaging technique such as AFM provides high resolution but takes long time. NMR can indicate the pore structure

with high precision, but it is affected by test environmental conditions. Overall, the incorporation of various imaging and characterization tools would be required for better understanding of wettability and rock/fluids interactions at different scales.

Thus, in summary, the state-of-the-art indicates a clear gap in terms of our understanding of the wetting behavior of the Middle Eastern carbonates (Ivanova et al., 2019), and due to massive heterogeneous conditions in carbonates and shales, the expected hydrocarbon recovery may be dramatically lower than the expected. This research will develop a new approach to characterize wettability of carbonate/oil/CO₂-foam/brine systems at multiple scales by capturing the fluid flow dynamics at nano- to millimetre scale. As established earlier, CO₂ EOR and CO₂-foam EOR in Arabian carbonate rocks have demonstrated significant potential as evident from Saudi Aramco's recent project (AlOtaibi et al., 2017). The associated impact of anhydrite in calcite and dolomite will also be evaluated. The rock samples (carbonates and tight sandstone) from Saudi Arabian oil and gas fields will be investigated. Notably, since this research attempts to work on new and pertinent research questions that are to be addressed using a new approach (i.e. multiscale wettability and mineralogical heterogeneity and its impact on fluid flow in porous medium). It is thus expected that the project will lead to better understanding of fluid/rock interaction and associated hydrocarbon recovery. Furthermore, the multiscale characterization of carbonate wettability is a new innovative approach. Thus, the accomplishment of this approach will be a significant milestone for the technological advancement at the institute and at the industry level.

The findings from this research are expected to significantly enhance our knowledge of the fluid/rock interactions and thereby reduce the uncertainties associated with laboratory-scale predictions and EOR planning.

2.7 Research Hypothesis

Based on the reviewed literature, we identified and highlighted some research hypothesis in the domain of rock wetting behavior and fluid-rock interactions, as follows:

1. A crucial, though poorly understood aspect in the context of wettability and fluid/rock interactions, is the presence of anhydrite on wettability and improved productivity. One key example is the giant carbonate oil fields in the Middle East (e.g. Arab-D oil reservoir) which demonstrate appreciable anhydrite content (Clerke et al., 2008) – as high as 20% anhydrite is observed (Mahmoud et al., 2020) – indicating notable mineralogical heterogeneity. Understanding the rock/fluid interaction is key to the success of any enhanced oil recovery (EOR) method. However, EOR methods are significantly affected when the reservoir formation contains calcium sulfate minerals such as anhydrite. Thus, we hypothesize that the presence of anhydrite and its distribution in reservoirs is important to precisely evaluate the impact of any IOR method on oil recovery. We also hypothesize that the presence of anhydrite may be a factor that is responsible for the complex wetting behavior of carbonates at a range of scales. The underpinning logic is that the pure anhydrite is strongly oil-wet (Esfandiyari et al., 2020), while pure calcite is somewhat weakly water-wet (Arif et al., 2017; Lopez-Salinas et al., 2011) – and thus the question remains unclear what would be the wettability of calcite and anhydrite, and dolomite – anhydrite combination.

2. Surface roughness of rocks is known to cause discrepancies in contact angle measurements, meanwhile, the effect of rock surface roughness coupled with the rock nanomechanical properties such as the Young's modulus and surface hardness on the wetting behavior is poorly investigated. We believe that evaluating the rock surface roughness and changes in rock mechanical properties at nano-scale can provide important information about rock wetting behavior. Moreover, imaging techniques can help in quantifying the rock surface topography as well as the rock surface wettability. However, limited studies are available in this area, and more work will be done to investigate the impact of chemical injections (CO_2 and CO_2 -foam) on the combined effects of rock surface roughness, rock elastic modulus, surface hardness and wettability. Thus, nanoindentation and contact angle measurements will be conducted before and after exposure to CO_2 -foam to assess how changes in rock surface roughness and rock mechanical properties affect the wetting characteristics of the rock.
3. Contact angle measurements on clean and flat surfaces is widely applied for characterization of wetting behavior before and after exposure to a certain injected fluid. Contact angle method is arguably more suitable when pure fluids and clean minerals with smooth surfaces are used (Arif et al., 2019; Kaveh et al., 2014). Thus, since the higher the porosity and pore sizes the higher the minimum rock surface roughness attainable, we therefore hypothesis that wettability measurement for permeable and porous rock may not be the actual and valid wettability of the medium, thus, wettability measurements for smooth, zero permeability and zero porosity rock surface should be the base line for measurement of this important petrophysical

parameter. Therefore, since porous rock surfaces have some degree of roughness, without a set standard RMS surface roughness, the validity of wettability measurement results might be contentious. Changes in rock surface roughness will significantly affect the rock surface charges and the wettability conditions (Sari et al., 2020). Therefore, these factors (roughness, surface charges, and wettability) will be studied together to ensure that any change in one of them will not induce a negative impact on the other parameters.

4. Various oil well operations such as drilling, stimulation, CO₂ injection, etc. can induce different formation damages to the reservoir formation which affects the reservoir productivity. Moreover, the severity of the formation damage induced by anhydrite minerals can be estimated based on the reservoir parameters. (Foroutan & Moghadasi, 2013) used neural network techniques to assess the formation damage due to anhydrite precipitation. The effect of several parameters (such as flow rate, temperature, and pressure) on permeability impairment was investigated. However, more studies are required to predict anhydrite formation damage under a broad range of influencing conditions. For example, the reservoir mineralogy, anhydrite content, surface charge, treatment type, and injected fluid type and properties will be considered. Such studies will be helpful for designing the EOR in anhydrite-rich hydrocarbon reservoirs. Additionally, simulation studies will be conducted to examine the fluid/anhydrite interactions at reservoir and molecular scales. Such studies would help in understanding the pore- to molecular-scale processes responsible for improved the oil recovery from anhydrite-rich carbonates with minimum formation damage.

2.8 Research Questions

- What will be the changes in carbonate wetting behavior with mineralogical heterogeneity? Specifically, what would be the wettability of calcite and anhydrite, and dolomite and anhydrite combination?
- Besides, should anhydrite mineral in carbonate reservoirs be harnessed or avoided?
- How does rock surface roughness coupled with mineralogy, rocks' elastic modulus and hardness affect the wetting characteristics of carbonate and tight sandstone pre- and post CO₂- treatments?
- Does the wetting behavior of heterogeneous rocks changes at various length scales (e.g. at the nanoscale, pore-scale (sub-micron scale), and core-scale)?
- Does contact angle measurement for a “flat”, permeable and porous medium represents its actual wettability?

2.9 Research Objectives

The objectives of this research are as follows:

1. To investigate the impact of mineralogical heterogeneity (i.e. anhydrite, dolomite and calcite) on wettability of oil/brine/rock system at various length scales.
2. To investigate fluid-rock interactions and the wettability of oil/brine/rock system for EOR and CO₂ storage applications from nano- to macro-scale.
3. To establish a relationship between rock surface roughness, mineralogy, rocks' nanomechanical properties with wetting characteristics of carbonate, pre- and post CO₂- treatments.

CHAPTER 3

GENERAL METHODS

This section describes the methodology adopted for the research; it is subdivided based on the different objectives. The methodology includes procedures adopted for microstructural analysis/characterization of the rock samples via NMR and imaging techniques (CT scan, QEMSCAN, XRD/XRF, SEM and thin section) and zeta potential measurements. Additionally, nanomechanical and rock surface properties relationship with wettability will be studied using nanoindentation equipment and contact angle measurements. Finally, the macro structural studies will be performed using micro-CT set-up. The different phases of the methodology are explained in the following sections.

3.1 Phase I: Carbonate and tight sandstone samples characterization

3.1.1 Task 1: Nano – to – Microstructural characterization

Rock samples microstructural analysis/characterization via NMR, imaging techniques (CT scan, QEMSCAN, XRD/XRF, SEM, Thin section) and zeta potential measurements will be performed:

Nuclear magnetic resonance (NMR)

State-of-the-art nuclear magnetic resonance relaxation time (NMR T_2) spectroscopy will be used for pore network characterization, this is, to estimate the rocks' pore throat from NMR and pores sizes distribution.

Micro X-ray computed tomography (CT)

Micro-computed tomography (micro-CT) will be used to obtain 3D pore-scale visualization of the pore network. The micro-CT is adopted for analyzing the spatial distribution and textural alteration of constituents of the tight rocks (tight sandstone), identification of dissolution and precipitation in the fluid-rock system and spatial distribution of different minerals in the altered regions based on microstructure changes after exposure to CO₂-foam.

Micro-CT is also employed in pore network modelling to develop an understanding of petrophysical transport behavior in heterogeneous rocks. Here, the ultimate goal is to create a neural network function that can map 2D QEMSCAN to 3D micro-CT data.

Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN)

This measurement provides information on the elemental composition and distribution at each measurement point, it helps to confirm the rocks' bulk mineralogy and its chemical assays.

X-ray diffraction (XRD) and X-ray fluorescence (XRF)

X-ray diffraction of the powdered samples was conducted using the Rigaku Ultima IV which is a state-of-the-art multipurpose x-ray diffraction system (Cu-source). X-ray fluorescence, a non-destructive analytical technique was used to determine the elemental composition of the powdered rock samples.

3.1.2 Task 2: Surface charge investigation of calcite and anhydrite, dolomite and anhydrite combination.

Improved oil recovery processes such as CO₂ foam, low salinity water injection, etc. induce different pH environments in the reservoir due to dissolution or buffering effect of injected

fluids. This will likely lead to adsorption of ionic species that may alter the wetting state of the formation. Thus, this task aimed at understanding the surface charge of rock minerals at different pH environments and to identify conditions that would induce or promote wettability alteration. This will be achieved via zeta potential measurement. Therefore, the research work seeks to (1) provide insight into the surface charge of rock minerals in a wide range of pH environments, (2) identify environments and mineralogical composition that would induce wetting alteration of carbonates (3) evaluate the effect of anhydrite mineral concentrations in rock surface charge.

Materials and Methods

Materials

Anhydrite, calcite, dolomite, and quartz samples were pulverized to a fine powder with their particle sizes measured by dynamic light scattering with backscatter detection. Five different salts: sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), sodium bicarbonate (NaHCO₃), and sodium sulfate (Na₂SO₄) purchased from Sigma-Aldrich were used to prepare the experimental brine, while 0.1 M sodium hydroxide (NaOH) and 1 M and nitric acid (HNO₃) solutions were used for buffer solution preparation.

Sample preparation.

Various proportions (1%, 5%, 10%, 15%, 20% and 25%) of powdered anhydrite minerals in 10 mg calcite mineral samples were conditioned in a 10 ml solutions of deionized (DI) water at various pH values (2 – 12) and left for 24 hours for possible dissolution and to

attain equilibrium before zeta potential measurements were performed. The same time frame (24 hours equilibration time) was adopted throughout the study of the effect of anhydrite mineral concentration on the calcite – anhydrite surface charge. The samples mixtures were sonicated for 3 minutes to ensure the complete interaction of dissociated ions with the surfaces and allowed to attain equilibrium before measurements were conducted. The same procedure carried out for DI water was repeated for sea water and formation water to investigate salinity effect. The Ionic Compositions of formation brine and Arabian Gulf seawater adopted in this research (in accordance with the Arabian gulf brines composition) is shown in **Table 3.1**.

Table 3.1. Ionic Compositions of formation brine and Arabian Gulf Seawater

Ions	Formation water	Seawater ions (ppm)
	ions (ppm)	
Na ⁺	59,491	18,300
Ca ²⁺	19,040	650
Mg ²⁺	2,439	2,110
SO ₄ ²⁻	350	4,290
Cl ⁻	132,060	32,200
HCO ₃ ⁻	354	120
TDS	213,734	57,670

X-ray diffraction

X-ray powder diffraction of the samples was conducted using the Rigaku Ultima IV which is a state-of-the-art multipurpose x-ray diffraction system (Cu-source).

Zeta potential measurements

Zeta potential measurement of powder samples in electrolytic solution was measured using a Malvern Zetasizer Nano ZS instrument. Laser doppler electrophoresis was used to measure the zeta potential of the colloidal suspensions, the cell and instrument were calibrated before measurement. The electrophoretic mobility and conductivity of each sample were measured, and zeta potential is computed.

Based on electrophoretic technique, Helmholtz – Smoluchowski (HS) equation (Eqn. 3) is commonly employed to obtain the zeta potential, for uniform and moderate electric fields:

$$v_e = u_e E \quad (2)$$

where v_e (m s^{-1}), is the particle velocity with respect to a stagnant medium (electrophoretic velocity), E (V m^{-1}) is the applied electric field, u_e ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$), is the electrophoretic mobility of the particle and is given by;

$$u_e = \frac{\varepsilon_{eq} \varepsilon_o}{\mu} \zeta \quad (3)$$

where ε_{eq} is the relative permittivity of the electrolyte solution, ε_o is the electric permittivity of vacuum, and μ is the dynamic viscosity of the liquid.

The measurements were performed at 25 °C and ambient pressure, with each measurement repeated 2 times, and the means value with the standard deviation recorded. Disposable pipettes were used for all zeta potential measurements to avoid contamination.

Task 3: To probe the validity of the current wettability quantification methodology for the conventional rocks (porous and permeable) compared to the zero porosity and zero

permeability rocks. Here, rock samples having almost zero porosities and permeability will be utilized to quantify wetting characteristics. This will then be compared to the wetting behavior of conventional rocks (porous and permeable). Contact angle measurements will be carried out under this task.

3.2 Phase II: Wettability characterization across nano-to-millimeter scale

Nanoindentation and contact angle measurements.

Experiments under this research phase are aimed at establishing the relationship between rock mineralogy, surface roughness, nanomechanical properties and wettability. Thus, nanoindentation, AFM/SPM and contact angle measurements will be conducted before and after exposure to CO₂-foam. Based on their XRD analysis, carbonate, tight sandstone rock samples having almost zero porosity and zero permeability will be obtained or casted to compare the wetting characteristics of the two class of samples. This is aimed at probing the validity of the current wettability quantification methodology for the conventional rocks (porous and permeable rock) compared to the zero porosity and zero permeability rocks. Thus, findings from this research phase will provide answers to the questions of how the rock surface roughness, elastic modulus and surface hardness affect the wetting characteristics of carbonate, tight sandstone pre- and post CO₂-foam treatments. The validity of contact angle measurements for rough, permeable, and porous surfaces will also be assessed under this research theme.

Materials

Anhydrite-rich carbonate, tight sandstone will be used. The fluid, CO₂ foam will be prepared using forming surfactant (Triton X-100, a nonionic surfactant that has a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon hydrophobic group). Rock samples having almost zero porosity and zero permeability were obtained/casted using the molding method.

Sample preparation.

Casting artificial rock samples

Rock samples are often casted to have similar lithology, mechanical, and petrophysical properties to natural rock. Synthetic rock samples are made for the purpose of understanding the influence of mineral content and physical properties of pore spaces. Since one of our aims is to investigate the influence of mineralogy and distribution on carbonate wettability, various rock samples will be synthesized with different anhydrite composition (**Table 3.2**) using cylindrical mold with Portland cement as the artificial binding material. The following compositions will be considered:

Table 3.2. Composition of synthetic rock samples

Sample #	Compositions			Cement slurry
		Set A	Set B	
	Anhydrite (wt%)	Calcite (wt%)	Dolomite (wt%)	
1	1.0	99.0	99.0	5%
2	5.0	95.0	95.0	5%
3	10.0	90.0	90.0	5%
4	20.0	80.0	80.0	5%
5	25.0	75.0	75.0	5%

Core casting procedure:

Step I: The rock minerals are sieved based on the required grain sizes. The petrophysical properties of the sample are controlled by varying the mineralogy, grain size, grain size distribution, grain shape, and cement content (Rice-Birchall et al., 2021). Grain size distribution was controlled by sieving the rock aggregates into different grain size fractions and then mixing these size fractions together to obtain a known grain size distribution.

Step II: The rock minerals, the cement and water are weighed according to the required fractions. Note that the quantity of the cement slurry (mixture of cement and water) influences the petrophysical properties of the casted sample. That is, the higher the cementing fluid, the lower the porosity and permeability (Fedrizzi et al., 2018).

Step III: The rock minerals aggregate and the cementing fluid are then blended to obtain a homogeneous mixture.

Step IV: The cast (molding piece) is cleaned and the inside is lubricated with grease to allow easily removal once samples has been made. Then the mixture is carefully placed in stainless steel mold of required shape (in this case, a cylindrical mold) and mechanical compression was applied for compaction. The porosity and permeability of the simulant rock is set to a required target values since the higher the compressional stress applied during molding, the lower the porosity and permeability.

Step V: The molded sample is then placed in an oven for curing at elevated temperature to develop the required compressive strength. Finally, the finished synthetic rock samples were obtained after curing.

Procedures

The ability to conduct nanoindentation studies with nanometer depth, and sub-nanonewton force resolution is possible using a standard AFM/SPM setup. The AFM/SPM allows for

nanomechanical studies to be conducted alongside topographic analyses. The samples were first flattened using end face grinding equipment and polished to the minimum acceptable indenter RMS roughness, then the advancing and receding contact angles are measured using the tilted plate sessile drop method to assess the wettability. The samples' mechanical properties (elastic modulus and hardness) are computed at nano-scale using the nanoindentation equipment.

3.2.1 Task 1: Surface roughness

The surface roughness of the rocks samples before and after CO₂ foam exposure as well as after every nanomechanical test is analyzed and recorded using AFM and Optical Microscopy at the nano- and micro-scale respectively.

3.2.2 Task 2: Nanomechanical tests (nanoindentation)

Bruker Hysitron TI 980 TriboIndenter system is utilized for nanomechanical testing, based on our application, the Berkovich probe is used for the indenter. The Berkovich probe is trihedral pyramidal indenter, it is a standard nanoindentation probe. It has a total included angle, the angle from one edge to the opposite side, of 142.35°. The half-angle of the probe is 65.35°. The aspect ratio of the probe is 1:8. The radius of curvature for the standard Berkovich probe is approximately 150 nm. This probe work best for most bulk samples compared to other types of probes unless the roughness is more than approximately 50 nm RMS. All TriboIndenter measurements were performed at room temperature with the help of diamond indenter of Berkovich's triangular pyramid probe.

3.2.3 Task 3: Contact angle measurement

The wettability variations at multiple length scales are investigated by measurements of advancing and receding contact angles using the tilted plate contact angle technique.

3.3 Phase III: Macroscale structural studies

The implications of nano- scale to macroscale characterization on EOR

Oil recovery and wettability at macro- to core-scale were assessed under this research phase. Core flooding to monitor changes in porosity, permeability, fluid recovery, and in-situ fluid displacement will be performed. This macro structural studies is performed using micro-CT-and/or NMR-incorporated coreflooding set-up.

3.3.1 Task 1: Amott-Harvey wettability Index

Amott-Harvey wettability index is adopted to quantify the samples core-scale wetting behavior and compared with the contact angle measurements conducted in the previous research phases.

3.3.2 Task 2: Core-flooding

The samples are saturated with brine and then displace using crude oil to attain the irreducible water saturation (S_{wi}) to mimic initial oil migration into reservoir, this is then followed by primary recovery via spontaneous imbibition of 5 wt% NaCl brine. Secondary forced imbibition through injection of brine will be conducted until no oil is produced. CO_2 foam will be injected in the tertiary recovery stage.

Research Timeline

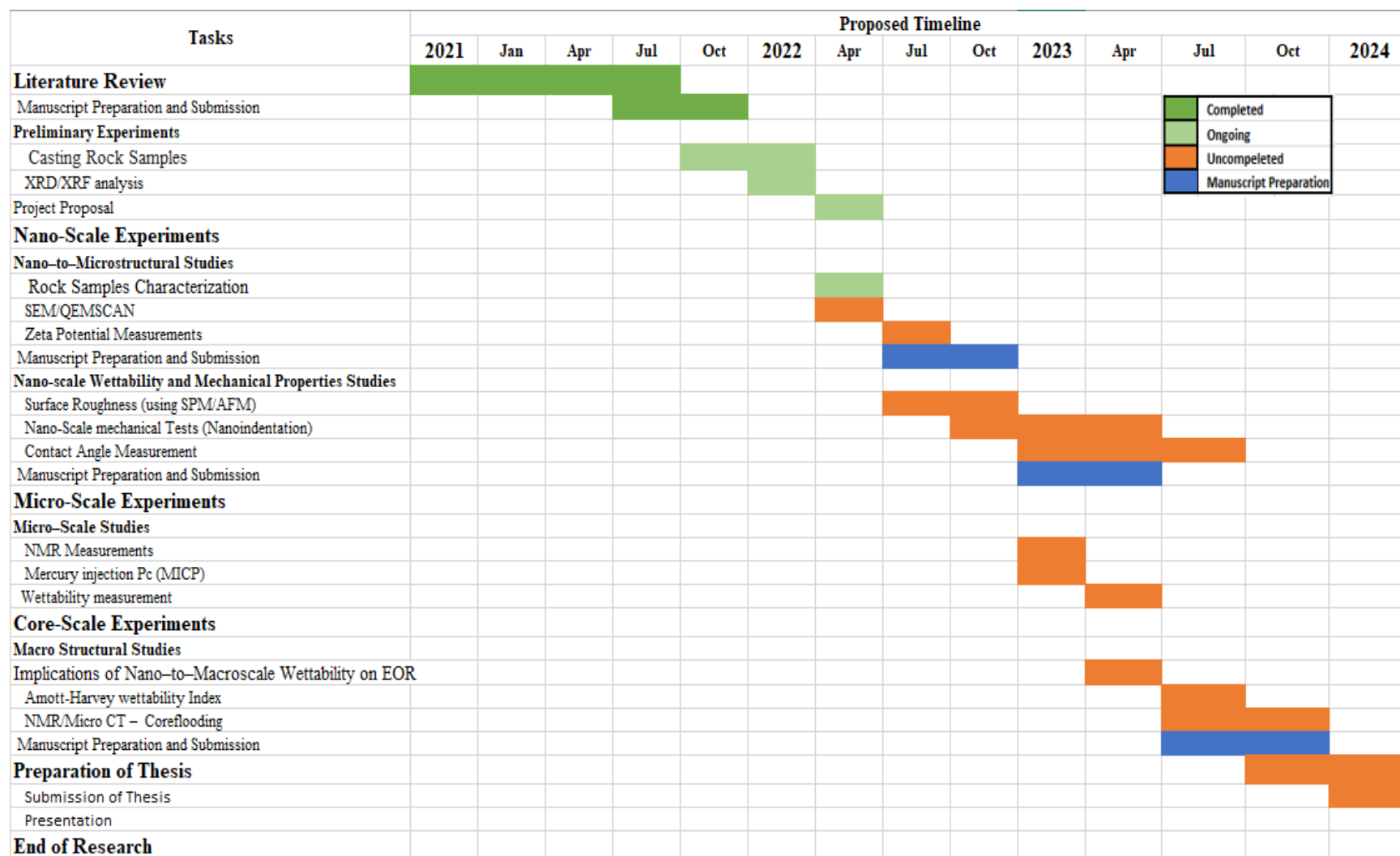


Figure 3.1. Research timeline and experimental schedules.

CHAPTER 4

MULTI-SCALE WETTABILITY CHARACTERIZATION OF ANHYDRITE-RICH CARBONATE ROCKS: INSIGHTS INTO ZETA POTENTIAL, FLOTATION, AND CONTACT ANGLE MEASUREMENTS

Summary

Anhydrite is a chemically reactive rock/mineral with chemical formula CaSO_4 found predominantly in carbonates. The main constituents of anhydrite are calcium and sulfate ions. The presence of anhydrite, its distribution, and the associated anhydrite–fluid–interactions are thus important to precisely evaluate the effectiveness of oil recovery techniques. While anhydrite dissolution is the key interaction mechanism in anhydrite-rich rocks, its presence may also lead to a complex rock wetting behavior. The underpinning logic is that pure anhydrite is strongly water-wet, while pure calcite and dolomite are somewhat intermediate to weakly oil-wet – and thus the question remains unclear what would be the wettability of anhydrite and calcite, and anhydrite and dolomite combination. Moreover, since anhydrite is negatively charged while dolomite and calcite in formation water are positively charged, depending on the mixture composition, pH and the brine type, it is not immediately clear what a combination of anhydrite-calcite, and anhydrite-dolomite charge would be, consequently, the wetting behavior of calcite and dolomite due to anhydrite presence. Therefore, this research explores the effect of anhydrite mineral on carbonates wetting characteristics. The effect of mineralogical heterogeneity, specifically,

the presence of anhydrite minerals in calcite and dolomite wettability is investigated across a range of scales.

The results show that anhydrite dissolution occurs in DI, SW and FW as evident from the general increase in sulfate ions concentration with increased anhydrite content in the anhydrite-carbonate system. We also found that zeta potential demonstrates an instable colloidal system which is indicated by a near-zero and low zeta potential values (less than ± 10) of the anhydrite-carbonate-brine systems. It also shows a non-monotonic behavior of wetting behavior with brine salinity and pH variations. Accordingly, the zeta potential is not a general and valid candidate to justify the wettability behavior of heterogeneous carbonates. However, based on flotation and contact angle techniques of wettability estimation, anhydrite presence has the tendency to alter the wetting state of anhydrite-carbonate-brine-oil systems to more water wet. Thus, findings from this research will provide answers to the question of how the mineralogy affect the wetting characteristics of carbonate. What will be the changes in carbonate wetting behavior with mineralogical heterogeneity? Specifically, what would be the wettability of calcite and anhydrite, and dolomite and anhydrite combination? This research therefore provides a systematic investigation of rock/fluid interactions and its implications on wettability and ultimate recovery of oil at different range scales. The findings from this study will significantly enhance our knowledge of the fluid/rock interactions, in particular, anhydrite-rich carbonate wetting behavior and thereby reduce the uncertainties associated with laboratory-scale predictions and oil recovery planning.

Keywords: Multi-scale wettability, Wettability alteration, Calcite mineral, Dolomite mineral, Anhydrite mineral

4.1 Background

A crucial, though poorly understood aspect in the context of wettability and fluid/rock interactions, is the presence of anhydrite on wettability and improved productivity. One key example is the giant carbonate oil fields in the Middle East (e.g. Arab-D oil reservoir) which demonstrate appreciable anhydrite content (Clerke et al., 2008) – as high as 24% anhydrite is observed (Mahmoud et al., 2020) – indicating notable mineralogical heterogeneity (Figure 4.1). During improve oil recovery processes, physical and chemical reactions between the reservoir matrix and the injected water occurs, consequently, several interactions will take place leading to alteration in reservoir properties. In particular, anhydrite minerals consist mainly of sulfate and calcite ions when dissociated in different fluids. During water injection, rock minerals dissolution occurs, for instance, anhydrite dissolution leads to an increase in concentration of sulfate and calcite ions (Isah et al., 2022a). The release of these ion is sometime accompanied by magnesium adsorption onto rocks surface, as a consequence, the rock surface mineralogy will change significantly, as well as surface wetting behavior (Mogensen & Masalmeh, 2020).

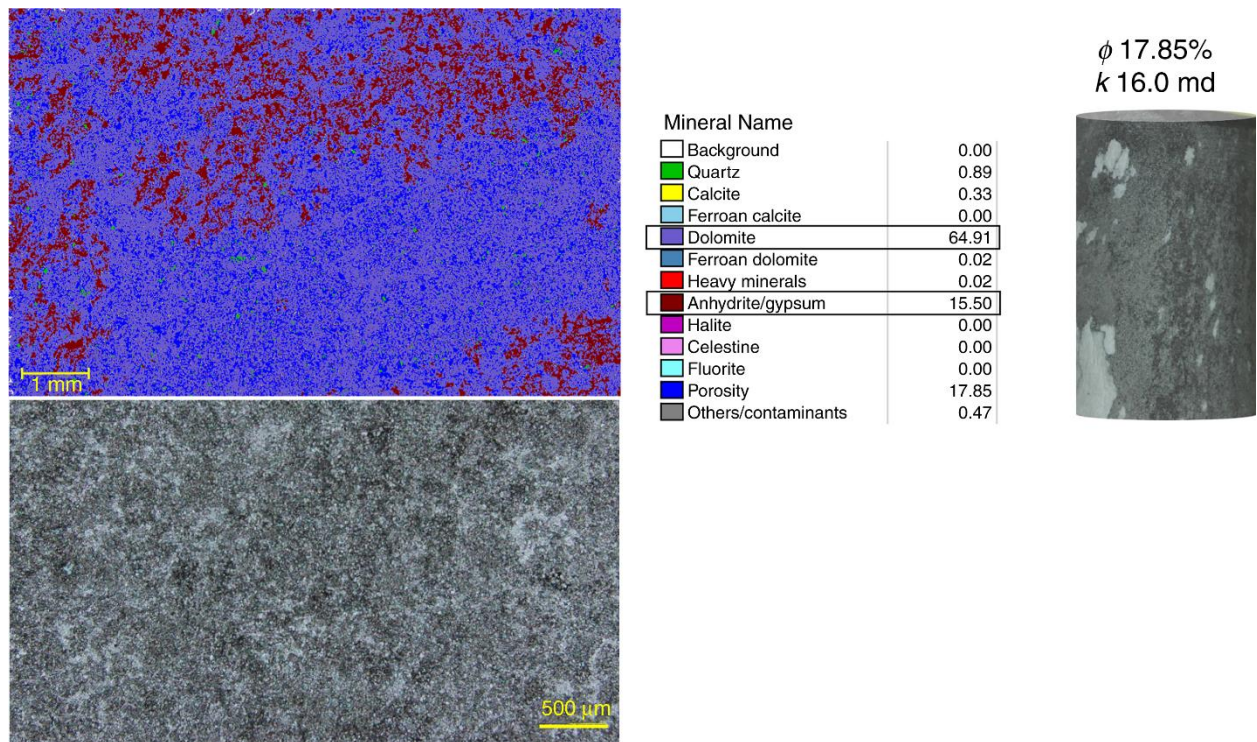


Figure 4.1 Middle Eastern carbonate reservoirs rock mineral composition showing a sizeable amount of anhydrite (M. Mahmoud et al., 2021a).

It is well established that wettability alteration towards water-wetting is one of the governing mechanisms of enhanced oil recovery (EOR), yet, the understanding of the interplay of various mechanisms causing this wettability shift and the experimental characterization of the effect require a rigorous experimental approach at multiple scales (Isah et al., 2022b). The current state-of-the-art research on carbonates often ignores the mixed-wet nature of carbonate rocks. There are, however, recent investigations which experimentally evaluated the mixed-wet carbonate wettability. For instance, Alhammadi et al., (2017) explored mixed-wet carbonate behavior via direct observation of contact angles at the curvature of oil-water interface using 3D micro-CT imaging. Moreover, the measurement of contact angle is regarded as a reliable way of wetting characterization (Arif et al., 2019; Marmur et al., 2017). Rücker et al. (2020) proposed a wettability upscaling

approach by taking into account the wettability changes at the nanoscale to core-scale. In addition, mixed-wet rock wettability state was also related to the nano-scale surface roughness of the rock surface, where it was argued that rougher surfaces leads to lower contact angles arguably due to water occupying the grooves of the rough rock surface (AlRatrout et al., 2018). However, it may be argued that carbonates due to their widespread mineralogical heterogeneity (Oliveira et al., 2019) may exhibit different behavior on a range of length-scales, and this discrepancy maybe even be more pronounced for Arabian carbonates with complex mineralogy.

One of the main complexity of carbonates is the presence of mineral heterogeneity such as anhydrite (Mogharab et al., 2022). Indeed, research have shown a sizeable quantity of anhydrite in Arabian carbonates (M. Mahmoud et al., 2021a). This anhydrite may play a vital role in fluid flow through porous media. It is so far not known how the presence of anhydrite and multiscale heterogeneity in carbonates influence wettability, pore connectivity, fluid distribution and fluid flow. Additionally, visual evidence to support the dissolution of anhydrite and calcite in carbonates and how they contribute to the overall oil recovery is lacking (Tetteh et al., 2020). Hence, one of the purposes of this work is to study the impact of anhydrite mineral on wetting characteristics of carbonates.

Mineralogical composition of rocks has strong influence on its wettability, surface minerals alteration may likely results in altering the wetting state of the rock. In heterogeneous carbonate reservoirs, rock minerals react differently due to their variable solubility and reaction rates. This can be a controlling factor for the design of EOR applications in anhydrite-rich carbonate reservoirs. Understanding the rock/fluid interaction is key to the success of any EOR method. However, EOR methods are significantly affected when the

reservoir formation contains calcium sulfate minerals such as anhydrite (Esfandyari et al., 2020; Mogharrab et al., 2022). Thus, we hypothesize that the presence of anhydrite and its distribution in reservoirs is important to precisely evaluate the impact of any IOR method on oil recovery. We also hypothesize that the presence of anhydrite may be a factor that is responsible for the complex wetting behavior of carbonates at a range of scales. Moreover, anhydrite has more dissolution (2 orders) than calcite and dolomite (Mogharrab et al., 2022), thus the solubility effects of these rock minerals may also play a vital role. The underpinning logic is that the pure anhydrite is strongly water-wet (Mogharrab et al., 2022), while pure calcite and dolomite are somewhat weakly oil-wet (Arif et al., 2017; Lopez-Salinas et al., 2011) – and thus the question remains unclear what would be the wettability of calcite and anhydrite, and dolomite – anhydrite combination.

The presence of anhydrite and in-situ supply of sulfate ions via anhydrite dissolution were emphasized as the main justifications of wettability improvements in anhydrite-rich carbonates (AlQuraishi et al., 2015; Austad et al., 2015; Mogharrab et al., 2022; Yousef et al., 2012). Conversely, other investigators argued that anhydrite-supplied sulfate ion is not capable of changing the wettability of carbonate reservoirs, and does not have influence on low salinity or sea water flooding (Chandrasekhar & Mohanty, 2013; Chen et al., 2018; Mohammadi et al., 2021; Uetani et al., 2019). This shows an insufficient understanding of the actual mechanism and effect of anhydrite minerals on low salinity and sea water flooding, as well as the influence of anhydrite on the wetting characteristics of carbonates. These inconsistent and contradictory results in improved oil recovery efficiencies in carbonate rocks could be sought in the rock chemistry and mineral heterogeneity (Isah et al., 2022a; Mogharrab et al., 2022).

Thus, in summary, the state-of-the-art indicates a clear gap in terms of understanding of the wetting behavior of carbonates, specifically, the Middle Eastern reservoirs (Ivanova et al., 2019) and due to massive heterogeneous conditions in carbonates, the expected hydrocarbon recovery may be dramatically lower than the expected. Thus, the goal of the current study is to develop a systematic approach to characterize wettability of anhydrite/carbonate/oil/brine systems at multiple scales by capturing the interactions at nano- to millimeter scale. Notably, since this research attempts to investigate new and pertinent research questions that are to be addressed using a new approach (i.e. multiscale wettability and mineralogical heterogeneity and its impact on fluid flow in porous medium). Thus, the research will lead to better understanding of fluid/rock interaction and associated hydrocarbon recovery. The findings from this research will significantly enhance our knowledge of the fluid/rock interactions, in particular, anhydrite-rich carbonate wetting behavior and thereby reduce the uncertainties associated with laboratory-scale predictions and oil recovery planning.

1.1 Materials and Methods

4.3.1 Materials

4.3.1.1 Rock properties

Calcite, dolomite and anhydrite rocks were collected from the outcrop of one of the carbonate oil fields in the Middle East. The rock minerals used in this study include calcite, dolomite, and anhydrite samples with average particle sizes of 19.01 μm for calcite, dolomite, and anhydrite for zeta potential measurements. Rock minerals average particle sizes is 50 μm for all flotation measurements, this is to avoid using small particles sizes

that may overestimate oil wetness and also over estimating water wetness which may results from large particle sizes (Sadeghi et al., 2022). Rocks samples used for contact angle measurements are synthesized using sintering technique. All chemicals used in this study were of the American Chemical Society (ACS) reagent grade.

4.3.1.2 Fabrication of Artificial Rock Samples

Some experiments are destructive in nature; therefore, the natural samples cannot be tested repeatedly. Often, natural rock has a high degree of heterogeneity, it is thus difficult to generate the same results from different samples even if the plugs are taken from the same rock body. It is also difficult to analyze the effect of mineralogy and grain size, shape and distribution on the physical and mechanical properties whilst controlling other variables (Rice-Birchall et al., 2021; Shahsavari & Shakiba, 2022). Another important issue is that when several experiments are to be conducted on different samples, some degrees of uncertainty is introduced since the samples may not be identical due to natural events (Kong et al., 2019). Rock samples are often constructed to have similar lithology, mechanical, acoustic and petrophysical properties to natural rock. Synthetic rock samples are made for the purpose of understanding the influence of mineral content and physical properties of pore spaces (Fedrizzi et al., 2018). Artificial rock fabrication has the advantage of overcoming the issue of sample reproducibility, especially when it becomes necessary to reproduce representative mineralogical and petrophysical characteristics of natural rocks. Thus, artificial rock samples allow the repeatability of investigations and makes it possible to study independent property (Gell et al., 2019).

Synthetic rocks are made by either 3D printing or casting using a mold. However, based on the fabrication process and the binding materials employed, different methods have been utilized in the construction of artificial rock samples including (i) sintering natural sand grains or artificial beads (Carbillet et al., 2021); (ii) the use of artificial binding materials such as cement and resins (Galindo et al., 2021; Yan et al., 2021), and; (iii) three-dimensional (3D) printing (Gomez et al., 2019; Kong et al., 2019; Osinga et al., 2015). However, some of these methods may have some drawbacks, for example, the high temperature applied during sintering may lead to microstructural deterioration of rock properties (Shen et al., 2018); some artificial cements such as resins are not chemically similar to those found in natural rocks, and 3D printing of artificial rocks is expensive (Perras & Vogler, 2019). Thus, in this research, artificial rocks samples are made in order to have a well-controlled study of carbonate heterogeneity and a broad range of mineralogical composition. Therefore, for the first time, we use glass powder (coesite) as binding material to replicate quartz in the synthetic rocks.

Synthetic sample using sintering

Customized rocks are made in order to have the required percentage and distribution of different minerals in the rock. We thus used the sintering technique for the creation of synthetic rock samples of a broad range of anhydrite content in both calcite and dolomite. Since our aim is to investigate the influence of anhydrite content and distribution on carbonate wettability and fluid-rock interactions, various rock samples were synthesized with different anhydrite compositions shown in **Table 4.1**. The procedure for the construction of the synthetic rock is given in the following steps:

Step I: The rock minerals (anhydrite + calcite for set A and anhydrite + dolomite for set B) and glass beads (coesite) were grinded and sieved to the required grain sizes (average of 75 μm) and then weighed according to the required fractions (see Table 3). Note that the quantity of the binding/cementing material (coesite) may influence the petrophysical properties of the sintered sample. Thus, the binder was kept constant for all the samples prepared. The rock minerals aggregate and the binder were then mix to obtain a homogeneous mixture.

Step II: The molding piece is cleaned to avoid contaminant and to allow easily removal once samples has been made. Then the mixture is carefully placed in stainless steel mold of cylindrical shape and 10,000 psi mechanical compression was applied for compaction. The porosity and permeability of the simulant rock can be set to a required target values since the higher the compressional stress applied during molding, the lower the porosity and permeability. The high compression pressure was applied to minimize the effects of porosity and permeability on contact angle.

Step III: The molded sample is then placed in a muffle furnace for sintering at 680 $^{\circ}\text{C}$ for 15-minute hold time to develop the required compressive strength (Khan et al., 2019). Finally, the finished synthetic samples are obtained after heating.

Table 4.1. Composition of synthetic rock samples.

Sample #	Compositions		
	Set A		Set B
	Anhydrite (wt%)	Calcite + Coesite (wt%)	Dolomite + Coesite (wt%)
1	1.0	99.0	99.0

2	5.0	95.0	95.0
3	10.0	90.0	90.0
4	15.0	85.0	85.0
5	20.0	80.0	80.0
6	25.0	75.0	75.0

QEMSCAN

QEMSCAN (quantitative evaluation of minerals by scanning electron microscopy) was conducted on the artificial rock samples to confirm the compositions and distribution of the anhydrite-calcite and the anhydrite-dolomite minerals in the synthetic rocks.

4.3.1.3 Fluids

Crude oil

Arab light crude oil was used for all the experiments in this study, **Table 4.2** shows the properties of the crude oil.

Table 4.2. Crude oil properties.

Kinematic viscosity		Dynamic viscosity		Asphaltene
Density at 25 °C (g/ml)	at 25 °C (m ² s ⁻¹)	at 25 °C (MPa.s)	API gravity (°)	
0.8	8.4	7.1	34.6	6.8

Brine

Five different salts: sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), sodium bicarbonate (NaHCO₃), and sodium sulfate (Na₂SO₄) purchased from Sigma-Aldrich were used to prepare the experimental brines, while 0.01 M sodium hydroxide (NaOH) and nitric acid (HNO₃) solutions were used for buffer solution preparation for pH adjustment. The synthetic brine solutions used are with compositions mimicking the Arabian Gulf seawater (SW) and formation water (FW) (**Table 4.3**).

Table 3: Ionic composition of Arabian gulf formation water (FW) and seawater (SW) (Abdel-Azeim et al., 2021).

Table 4.3. Ionic composition of Arabian gulf formation water (FW) and seawater (SW).

Ions	FW (ppm)	SW (ppm)
Na ⁺	59,491	18,300
Ca ²⁺	19,040	650
Mg ²⁺	2,439	2,110
SO ₄ ²⁻	350	4,290
Cl ⁻	132,060	32,200
HCO ₃ ⁻	354	120
TDS	213,734	57,670

4.3.2 Methods

4.3.2.1 Zeta potential measurement

Pure calcite and dolomite powder were used to mimic carbonate rocks considering the fact that these minerals are the main constituent of carbonate rocks. Pure anhydrite powder was added to calcite (anhydrite-calcite) and dolomite (anhydrite-dolomite) in 1 wt.%, 5 wt.%,

10 wt.%, 15 wt.%, 20 wt.% and 25 wt.% to replicate the presence of anhydrite mineral in carbonates. The mixtures were then conditioned in deionized water (DI), seawater (SW), and formation water (FW) as well as in mixtures whose pH was modified to different values (2, 4, 6, 8, 10 and 12) to cover a wide range of possible reservoir pH conditions. The pH adjustment of the DI, SW and FW was achieved using 0.01 M NaOH and HNO₃. For all samples, the total dissolved solids (TDS) particles were 1g, with the compositions of anhydrite, calcite and dolomite as shown in Table 3, however, without coesite except for contact angle measurements. This was followed by the addition of 10 mL of liquid (DI, SW or FW) to the sample mixtures and shaken using the VWR automatic reciprocating shaking bath at 25 °C for 1 hour to allow possible dissolution. The sample mixture is then kept undisturbed for 24hrs. Before zeta potential measurement, the sample mixtures were centrifuged at 25 °C for 2 min at 3000 rpm using a Benchtop Hermle Z326K centrifuge system, sample to be analyzed is taken from the clear supernatant. The zeta potential measurements were conducted using Anton Paar Litesizer 500 at 25 °C and ambient pressure. To avoid contamination, disposable pipettes were used for all zeta potential measurements, and for repeatability, each measurement was repeated 2 times, and the means value and the standard deviation recorded.

4.3.2.2 ICP-OES, TIC and *pH* measurements

The pH of the freshly prepared brines and all samples in this study was measured using the Thermo Scientific™ Orion Star™ A215 pH/conductivity benchtop multi-parameter meter, with an accuracy of ± 0.002 . Various proportions (1 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.% and 25 wt.%) of powdered anhydrite minerals in 1 g calcite/dolomite mineral samples

were conditioned in a 10 ml solutions of deionized (DI) water at average pH of 8.0 and left for 24 hours for possible dissolution and to attain equilibrium before zeta potential, pH and inductively coupled plasma - optical emission spectrometry (*ICP-OES*), and total inorganic carbon (*TIC*) measurements were performed. The *ICP-OES* technique was conducted to analyze the ionic composition (sulfate ions) of the supernatant using the Metrohm's 930 Compact IC Flex–Compact ion chromatography equipment, while the carbonate and hydrogen carbonate ions (the total inorganic carbon (*TIC*)) were determine using the Analytikjena's multi N/C 3100 Flow injection TOC analyzer with an accuracy of ± 1.0 ppm and detection limit up to 0.2 ppm.

The ion chromatography was carried out to determine the change in sulfate and carbonate ions concentrations in the various fluids under different anhydrite compositions. Carbonates (calcite and dolomite) and anhydrite dissolve in solution resulting in change of pH and ionic (Ca^{2+} , Mg^{2+} , CO_3^{2-} , and SO_4^{2-}) concentrations (X. Hao et al., 2021).

The same time frame (24 hours equilibration time) was adopted throughout the study of the effect of anhydrite mineral concentration on the anhydrite-calcite and anhydrite-dolomite surface charge. The samples mixtures were sonicated for 3 minutes to ensure the complete interaction of dissociated ions with the surfaces and allowed to attain equilibrium before measurements were conducted. The same procedure carried out for DI was repeated for SW and FW.

4.3.2.3 Wettability measurement

Different wettability measurement techniques such as the flotation and contact angle were employed to estimate the wetting characteristics of the anhydrite-calcite and anhydrite-dolomite synthetic rocks.

4.3.2.4 Flotation

The rocks minerals (calcite, dolomite and anhydrite) were grinded using the Retsch Mixer Ball mill MM 400 and then sieved. Rock minerals average particle sizes of 75 μm was used for all flotation measurements, this is to avoid using small particles sizes that may overestimate oil wetness and/or overestimate water wetness which may results from large particle sizes (Mwangi et al., 2018a; Sadeghi et al., 2022). 2g of total rock powder for the anhydrite-calcite ($\text{CaSO}_4 + \text{CaCO}_3$) and for the anhydrite-dolomite ($\text{CaSO}_4 + \text{CaMg}(\text{CO}_3)_2$) based on the required compositions (Table 3) was placed in a test tube. The composition was varied for different anhydrite contents (1 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.%) in 2g of total solids. 15 ml each of oil and DI water is poured into the test tube containing the rocks powder mixture and then shaken for 1 hour at 25°C. The mixture is allowed to settle overnight to separate the oil-water emulsion and obtain two phases for oil and water. The oil-wet particles will be suspended in the oil phase while the water-wet particles are settled at the bottom of the test tube in the water phase. The water-wet particles are collected and cleaned with toluene to remove any adsorbed oil and then cleaned with methanol to remove adsorbed salts (in the case of SW and FW). The cleaned sample is then oven dried and weighted. The percentage oil-wet and water-wet particles was calculated and reported. This experimental procedure was repeated for seawater and formation water. Since flotation result may be affected by the test time, test

temperature, particle size and powder quantity, and oil/water volume. We maintain the same measurement procedure and parameters throughout the flotation experiments.

4.3.2.5 Contact angle

To measure the contact angle of anhydrite-calcite and anhydrite-dolomite combination having different mineral composition, synthetic rocks were made using sintering method (see above). The composition and distribution of the anhydrite minerals in the synthetic samples was confirmed using *QEMSCAN* analysis. Since the rocks were made using the same rock particle sizes and under the same conditions, no rock surface polishing was performed. However, prior to contact angle measurement, the rocks surface topography (surface roughness) was analyzed using the Kruss surface roughness analyzer – SRA, the average surface roughness of the rocks samples is 25 μm . Rocks surface wettability is estimated via captive bubble technique of measuring contact angle using the Theta Attension Tensiometer from Biolin Scientific, the contact angle (θ) is computed through the denser phase, all contact angle measurements were carried out at ambient condition. The wettability of the rock samples as estimated by contact angle techniques was conducted in DI, SW and in FW.

4.4 Results and Discussions

Relating electrostatic interactions at the rock/fluid interface to rock wettability.

The effect of anhydrite mineral on calcite and dolomite surface charge and its tendency to alter the wetting state of these rocks minerals is investigated at nanometric scale using the

zeta potential. Different anhydrite compositions (1 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.%) in 1g of total solids was investigated.

4.4.1 Rock Dissolution

Rock dissolution was investigated via ICP-OES, TIC, and pH measurements of anhydrite-calcite and anhydrite-dolomite mixtures in 10 ml each of deionized water (DI), Arabian Gulf seawater (SW) and formation water (FW). Inductively coupled plasma – optical emission spectrometry (*ICP-OES*) technique was conducted to analyze the relative change in ionic composition of the supernatant which is an indication of rock dissolution. The ion chromatography was carried out to determine the change in sulfate and carbonate ions concentrations in the various fluids under different anhydrite compositions. During water flooding in anhydrite-rich reservoirs, the brine displaces the initial water in the formation that initially established equilibrium with the rock matrix. Consequently, anhydrite dissolution occurs. Ruiz-Agudo et al. (2015) showed experimentally that during the interaction of calcite (CaCO_3) surfaces with sulfate-bearing solutions, calcium ion (Ca^{2+}) from the dissolved calcite surface react with sulfate ions (SO_4^{2-}) in the aqueous phase. Ultimately, depending on the reaction conditions of temperature and pressure, calcite is replaced by anhydrite (CaSO_4).

Fig. 2 shows the effect of anhydrite concentration on the ionic composition of anhydrite-calcite effluent. The sulfate ion concentration obtained by subtracting the sulfate content in the base fluid from the sulfate concentration in the effluent is shown in Fig. 2a. Since the initial concentration of SO_4^{2-} in DI (base fluid, i.e., fluid without any rock mineral) and at zero anhydrite concentration is zero, the sulfate concentration indicates how much

anhydrite was dissolved. As the anhydrite composition in the anhydrite-calcite mixture increases from 5 wt.% up to 100 wt.%, sulfate ion concentration increases. The increase in SO_4^{2-} concentration is attributed to dissolution of anhydrite mineral, this is consistent with previous findings (Sharma & Mohanty, 2018b). Brady & Thyne (2016) documented that, in anhydrite-bearing formation, the dissolution of anhydrite during water injection results in an increased concentration of SO_4^{2-} and Ca^{2+} ions in the injected brine. Sulfate ions introduced by anhydrite dissolution can improve surface wettability (Austad et al., 2015b; Karimi et al., 2016; Qiao et al., 2016; Sharma & Mohanty, 2022). Similarly, in both seawater and formation water, sulfate ions concentration increases with increased anhydrite content in the anhydrite-calcite mixture. In anhydrite-containing rocks, the anhydrite serves as a source of dissolved sulfate, thus, the presence of anhydrite in carbonate reservoirs can be favorable to water injection processes (Al-Shalabi et al., 2015; AlQuraishi et al., 2015; Pu et al., 2010). It is further observed that the lower the SO_4^{2-} concentration in the initial fluid (base fluid) the higher the SO_4^{2-} concentration. Largest SO_4^{2-} concentration is seen in DI, followed by FW, while least concentration in sulfate ions in SW is noticeable. The dissolution of anhydrite increases as the concentration of sulfate and calcium ions in the injected fluid decrease because of common ions effect (Al-Shalabi et al., 2015; Isah et al., 2022a). Sulfate is the most important potential determining ion which can be added to smart water flooding or can be generated in-situ by anhydrite minerals dissolution to create low salinity EOR effect (Isah et al., 2022b). An increase in sulfate ions concentration in the aqueous phase is evidence of anhydrite dissolution. Based on equation (1), calcium ion is fed into the brine in an equal mole with sulfate ions during anhydrite dissolution

(Mogharrab et al., 2022). However, reacting high-sulfate brine with carbonate may result in anhydrite precipitation (Ku et al., 2009; Rosenbauer et al., 2005).

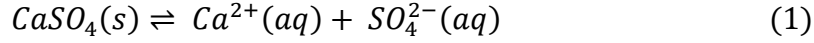
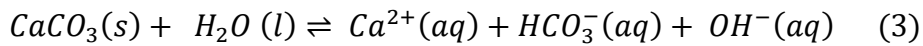
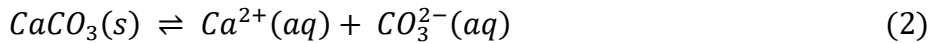
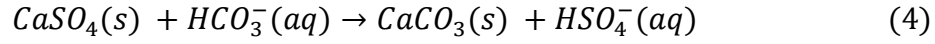


Fig. 2b shows the total inorganic carbon (TIC) concentration, this comprises the carbonate and hydrogen carbonate ions (CO_3^{2-} and HCO_3^-), and it infers carbonate dissolution. A slight increase in TIC is observed in DI, while the TIC concentration decreases in FW, and a non-monotonic behavior in SW. In anhydrite-calcite mixture, increase of the TIC is due to increase in CO_3^{2-} and/or HCO_3^- as a result of calcite dissociation or dissolution, respectively (see the equations 2 and 3) depending on the interaction conditions (E. Ruiz-Agudo et al., 2015). Recently, Mohammadi et al. (2021) documented that diluting sea water intensify dissolution in carbonate. Increased dilution reduces Ca^{2+} ions, thus, shifts the reaction equilibrium to the right and more rock will be dissolved with resulting increase in pH due to additional OH^- ions, this is shown in Fig. 2c. Moreover, it has been reported that partial dissolution of calcite or dolomite in DI increases the solution pH. The dissolution reaction of calcite or dolomite leads to increase in HCO_3^- and OH^- concentrations in DI which will likely increase pH of the solution (Al-Shirawi et al., 2021). It's worth noting that the reverse (mineral precipitation) is also possible (Chandrasekhar et al., 2018).

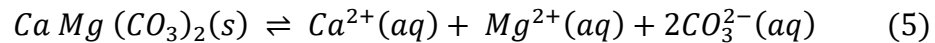


However, a decrease in the TIC content is either due to the consumption of CO_3^{2-} by Ca^{2+} released as a result of anhydrite dissolution or the removal of HCO_3^- via equation 4 to form acidic $\text{HSO}_4^-(\text{aq})$ with corresponding decrease in pH.

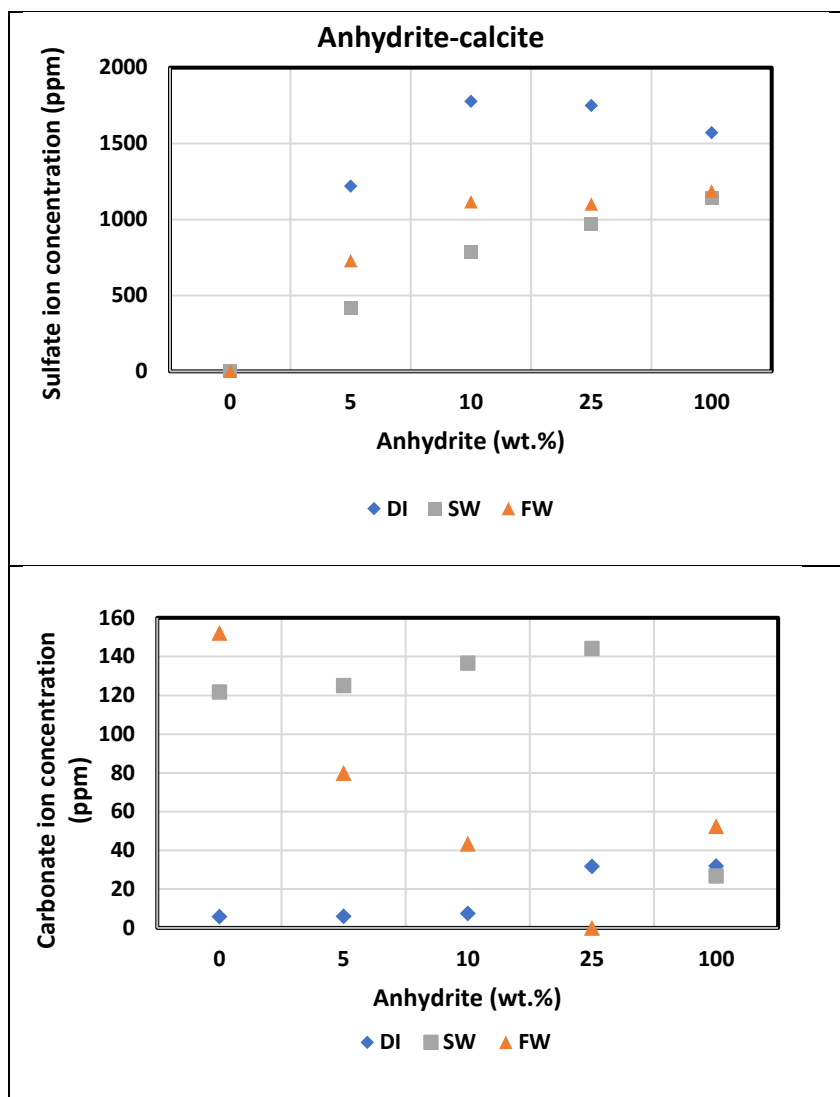


The effect of anhydrite concentration on the ionic composition of anhydrite-dolomite effluent is shown in **Figure 4.2**. Figure 4.2a shows the sulfate ion concentration, the base concentration of SO_4^{2-} in DI and at zero anhydrite concentration is zero. The trends in ionic concentrations in anhydrite-dolomite are similar to those of anhydrite-calcite combination, however, highest SO_4^{2-} concentration is seen in DI, followed by SW, while lowest concentration of sulfate ions is observed in SW.

Moreover, slightly higher carbonate ion concentrations with increase in anhydrite content are observed for anhydrite-dolomite in all the ‘waters’ (Figure 4.2b) which is attributed to the higher carbonate content of the dolomite rock compared to calcite.



Moreover, there is little pH changes with an increase in the anhydrite concentration in the anhydrite-dolomite mixture effluent (Figure 4.2c). However, Chandrasekhar et al. (2018) noted that changes in pH (increase up to pH 8–9) and brine composition can still impact oil recovery at the field scale. The presence of anhydrite in dolomite and calcite affects the pH and solution composition due to their dissolution and consequently, it could affect the interaction between the brine, crude oil and carbonate (Mogharab et al., 2022).



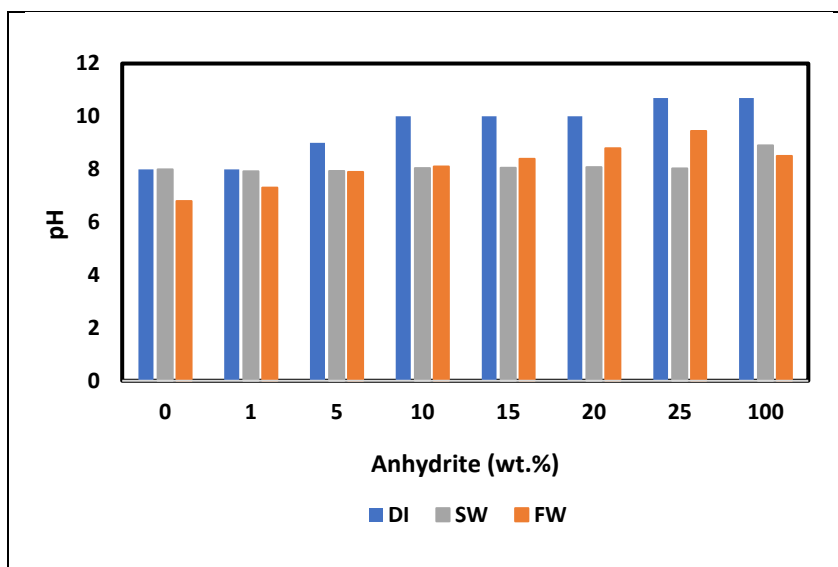
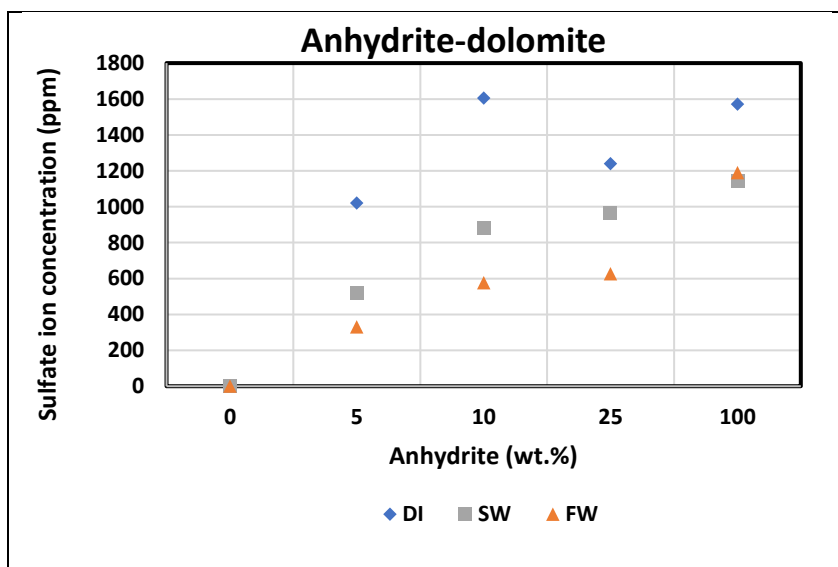


Figure 54.2. Effect of anhydrite concentration on the ionic composition and pH of anhydrite-calcite effluent: a) sulfate ion concentration; b) carbonate ion concentration; c) solution pH after 24 hrs.



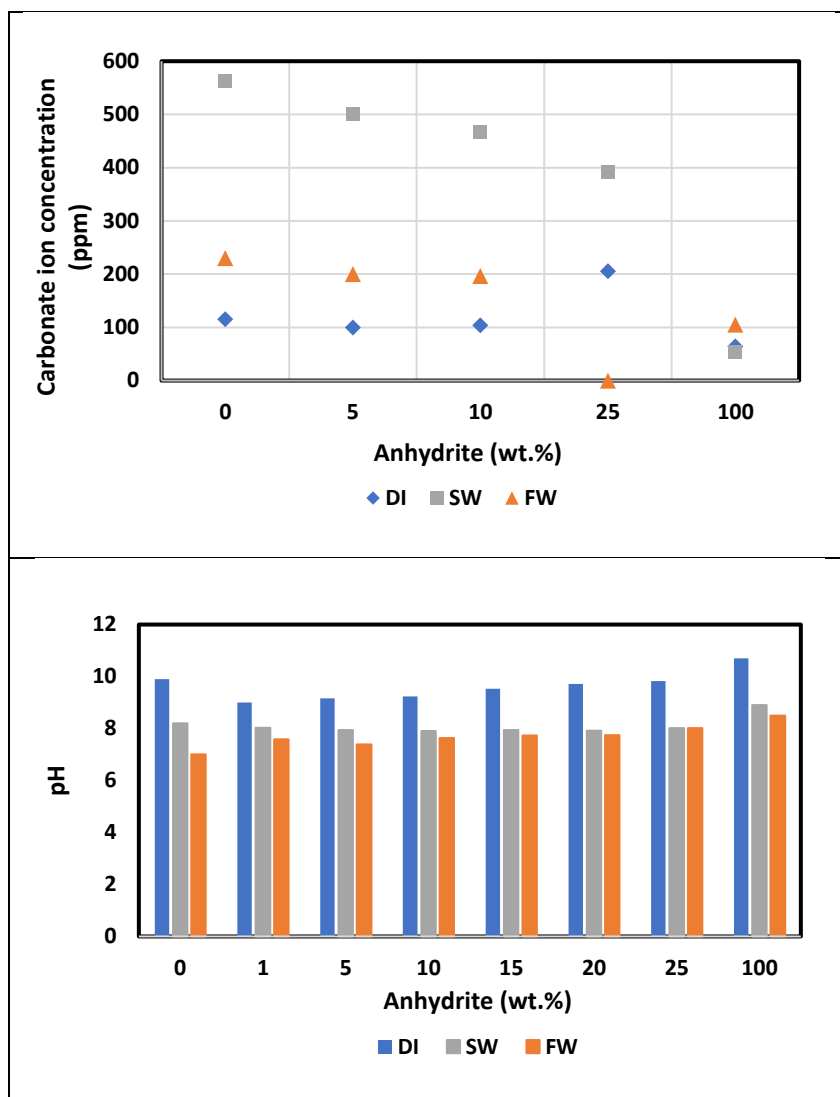


Figure 6.1. Effect of anhydrite concentration on the ionic composition and pH of anhydrite-dolomite effluent: a) sulfate ion concentration; b) carbonate ion concentration; and c) solution pH after 24 hrs.

4.4.2 Surface Charge via Zeta Potential

Zeta Potential of anhydrite, calcite and dolomite in DI, FW, and SW

The surface charge of pure anhydrite, calcite and dolomite minerals is first studied to serve as a benchmark in which the effect of different anhydrite composition would be compared.

The zeta potential of anhydrite, calcite and dolomite minerals in DI, SW, and FW having

an average pH of 8 is shown in **Figure 7**. Anhydrite shows negative surface charge in DI, SW and in FW, this is due to the presence of the sulfate ions (SO_4^{2-}) in the aqueous solution. Anhydrite shows the highest negative charge in seawater which is attributed to the higher contribution of SO_4^{2-} from the seawater than in DI and FW, as well as the SO_4^{2-} supplied due to anhydrite dissolution. Although DI has the lowest SO_4^{2-} content, least magnitude of the negative charge for anhydrite is observed in FW owing to lower mineral dissolution compared to DI water. Similarly, calcite mineral in DI and SW is negatively charged while it shows a positive charge in FW. Al-Balushi et al. (2020) studied the wettability alteration of calcite surfaces under different base and acid numbers, it was shown that the zeta potential of fresh calcite changed from positive to negative over a pH range of 6 – 10 in a 0.001 M potassium chloride (KCl) solution. The zeta potential of fresh calcite at pH 8 was reported as +5 mV, while at pH of 10, 2.7 mV zeta potential value was reported. This is similar the conclusions draw by other researchers (Mohammed, et al., 2022). However, based on the zeta potential analyses, dolomite exhibit positive charge in all the three waters, this is likely due to the presence divalent cations (Mg^{2+} and Ca^{2+}) in this rock mineral. Accordingly, the mineralogical study by (Arif et al., 2020) showed that surface chemistry of carbonate rocks suggest that calcite-based samples are relatively more hydrophilic compared to dolomitic carbonate.

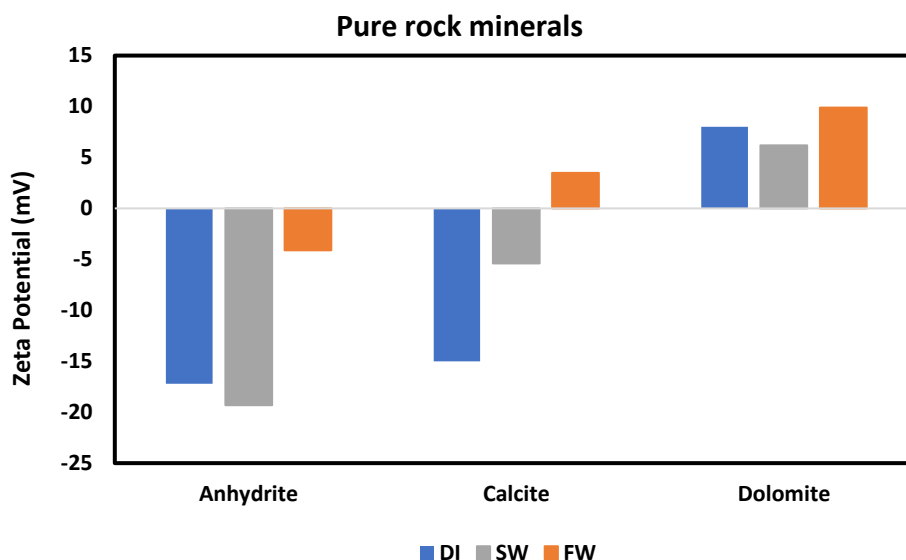


Figure 7.1. Pure anhydrite, calcite and dolomite mineral surface charge in DI, SW, and FW at 8 pH.

Effect of anhydrite on calcite and dolomite minerals surface charge.

The effect of anhydrite concentration (1 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.%) on the surface charge of calcite minerals is shown in **Figure 8**. For DI water, the calcite mineral is observed to remain negatively charged as in the case of pure calcite mineral (see Figure 7 above), however, the magnitude of the surface charge is reduced due to the presence of the anhydrite. The lowest magnitude of the surface charge is observed at 1 wt. % anhydrite concentration. However, above this anhydrite concentration, the surface charge magnitude increases with increased anhydrite content to approximately -3.3 mV at 25 wt. %. The surface charge at 1 wt.% can be attributed to the dominance of the Ca^{2+} at low anhydrite concentration, however, as the anhydrite composition increases above 1 wt. %, the SO_4^{2-} due to dissolution of anhydrite in the DI water dominate the interactions thus the increase the negative surface charge.

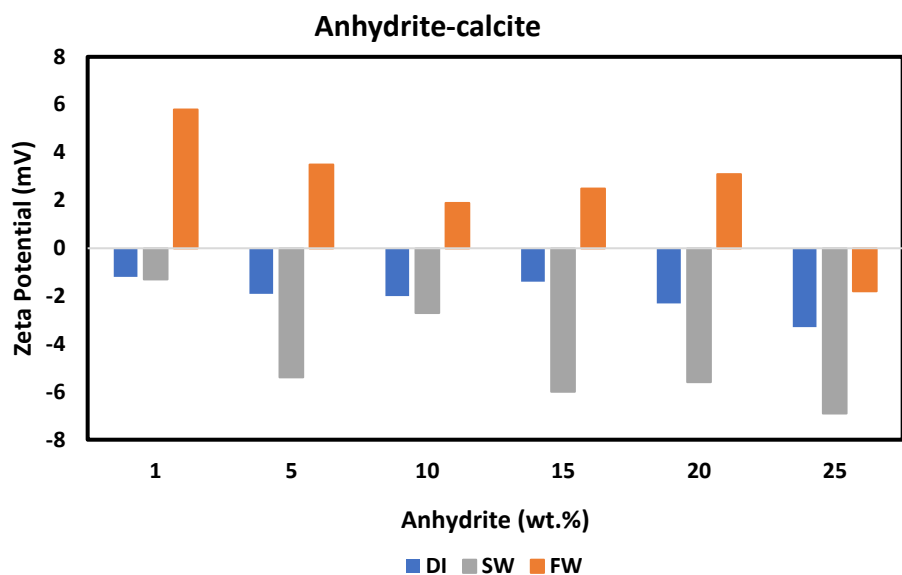


Figure 8.1. Effect of anhydrite (1 wt. % to 25 wt. %) On calcite surface charge: zeta potential values of anhydrite-calcite mixture in DI, SW and FW.

Similarly, the calcite surface charge remains negatively charged in SW for all anhydrite composition, the magnitude of the charge increases from -1.3 mV to -6.9 mV with increased anhydrite concentration. While in the case of FW, the surface charge of the anhydrite-calcite mineral mixture is observed to remain positively charged as in the case of pure calcite mineral (Fig. 4), except for 25 wt.% anhydrite concentration that shows negative charge (-1.8 mV), this due to the higher SO_4^{2-} concentration as the anhydrite concentration increases. The magnitude of the surface charge is reduced due to the presence of the anhydrite, thus, the presence of anhydrite reduces the net positive charge of calcite in formation water.

Figure 9 shows the effect of anhydrite presence (1 – 25 wt. %) in dolomite surface charge via zeta potential. Positive surface charge was observed for pure dolomite minerals in DI, SW and FW (Figure 7), accordingly, an anhydrite-dolomite mixture in DI water exhibit a

positive charge of 2.1 mV at 1 wt. % anhydrite concentration which is lower than the observed surface charge for pure dolomite (8 mV), this is as a result of the negative sulfate ions introduced into the solution by anhydrite dissolution. As the concentration of anhydrite in dolomite rock increases, the magnitude of the surface charge decreases. Anhydrite-dolomite surface charges of 2.1 mV, 1.1 mV, -0.4 mV, -1.1 mV, -2.5 mV and -2.8 mV were observed at anhydrite concentrations of 1 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.% and 25 wt.%, respectively. As the anhydrite concentration increased, more sulfate ions are supplied into the aqueous phase, hence dominating the cationic magnesium and calcium ions in the solution, this thus, results in the observed increase in the anhydrite-dolomite negative surface charge in DI water.

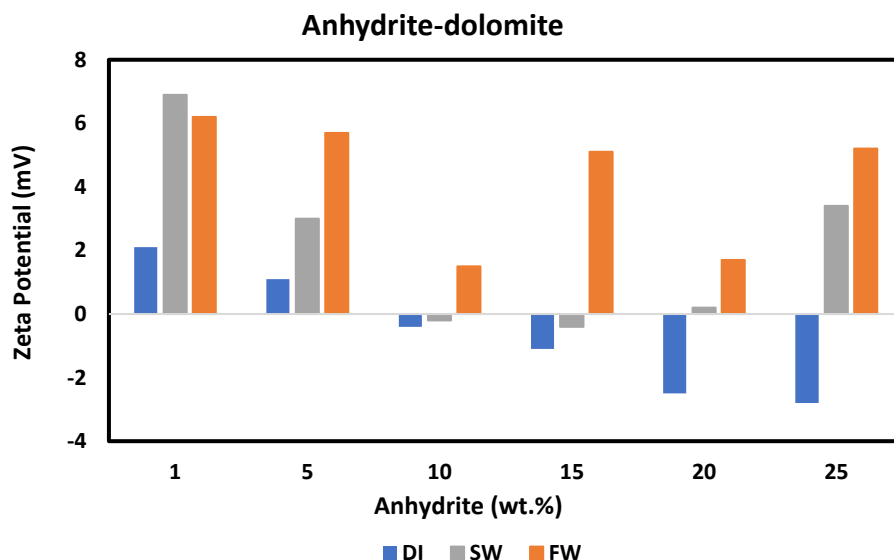


Figure 9.1. Effect of anhydrite (1 wt. % to 25 wt. %) on dolomite surface charge: zeta potential values of anhydrite-dolomite mixture in DI, SW and FW.

Accordingly, Mogharrab et al. (2022) also showed that the presence of anhydrite leads to SO_4^{2-} release in the aqueous phase. Consequently, high negatively charged surface sites will be formed compared to pure calcite or dolomite.

On the other hand, anhydrite-dolomite shows predominantly positive charge in SW and FW, this demonstrate the dominant effect of the divalent Ca^{2+} and Mg^{2+} over SO_4^{2-} in the aqueous solution of the anhydrite-dolomite mixtures. The presence of magnesium ions (Mg^{2+}) in water reduces CaSO_4 precipitation. Thus, the interaction of seawater (which contains Mg^{2+}) can greatly increase the solubility of anhydrite and increase recovery (Strand et al., 2006; Peimao Zhang et al., 2007). Yet, the presence of anhydrite in FW for anhydrite-dolomite shows higher positive charge relative to the surface charge in SW which is explained by the higher concentration of SO_4^{2-} in the SW. In another study, it was shown that the maximum wettability alteration for anhydrite-carbonate mixture was at lower salinity than that of pure calcite. This was attributed to the adsorption of sulfate ions: the anhydrite-carbonate mixture experiences a small decrease in SO_4^{2-} adsorption with salinity reduction in contrast to the large decrease in the case of pure calcite (Mogharrab et al., 2022). In the anhydrite-carbonate mixture there is in-situ supply of SO_4^{2-} in lower salinity by anhydrite dissolution which is not the case for pure carbonate (calcite or dolomite).

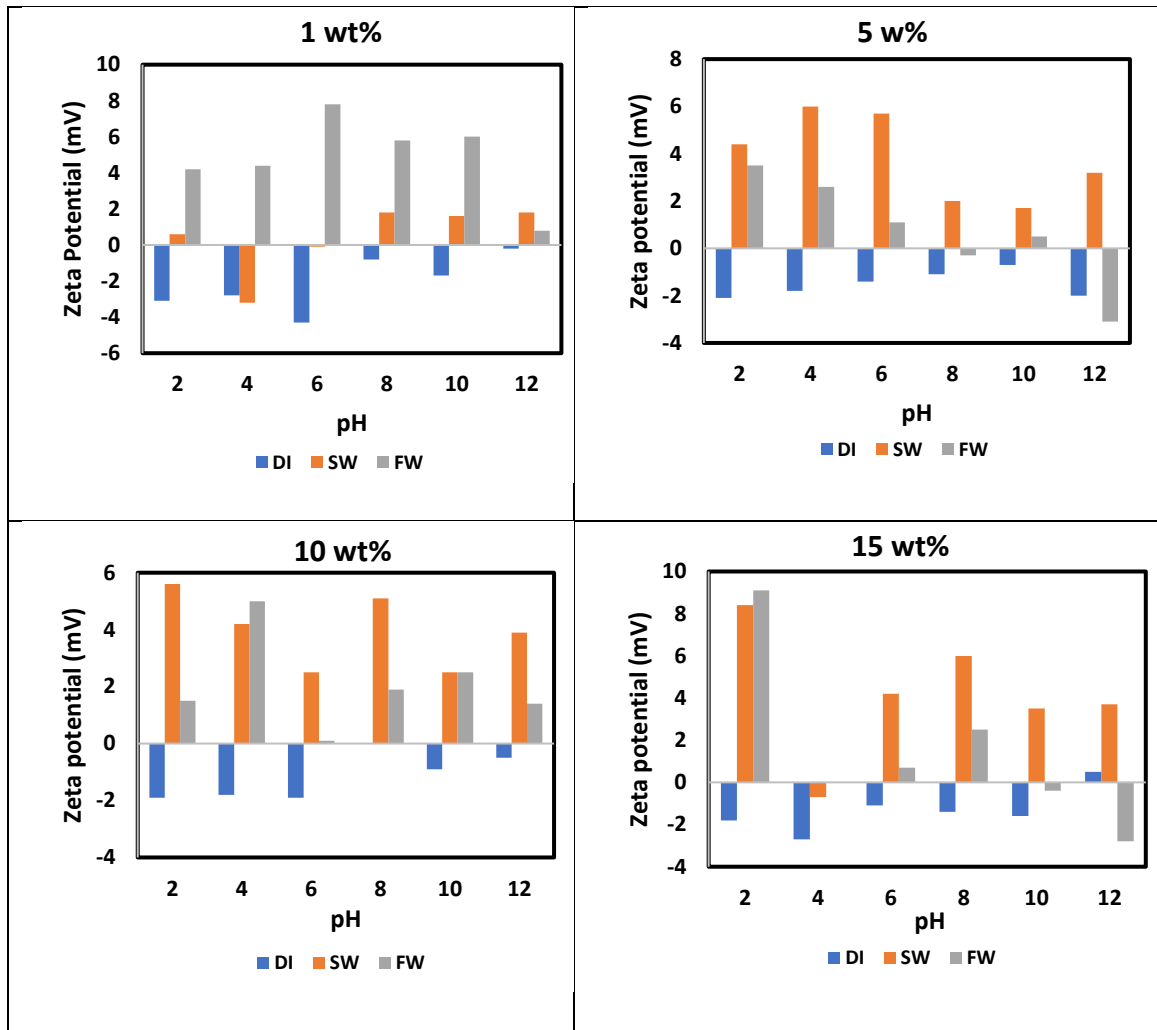
Surface Charge of Anhydrite-Calcite and Anhydrite-Dolomite at Different pH

Changes in pH have significant influence on fluid interactions at the mineral/fluid interfaces. Improved oil recovery processes such as smart water, low salinity water injection, etc. induce different pH environments in the reservoir due to dissolution or

buffering effect of injected fluids (Mohammed, et al., 2022). This will likely lead to adsorption of ionic species that may alter the wetting state of the formation. Correspondingly, Mogharrab et al. (2022) developed an experimental and diffuse double layer (DDL) based surface complexation model (SCM) approach to investigate wettability behavior of carbonates due to anhydrite composition. The presence of 10 wt.% anhydrite over a wide range of brine salinity/composition and the non-monotonic behavior of zeta potential with change in salinity was investigated. The authors showed that the DDL based SCM using PHREEQC suggested an anhydrite dominant window exist in which the presence of anhydrite, its dissolution, and in-situ supply of sulfate ions, lead to altering the wettability to more water wetness. Thus, it is necessary to understand the surface charge of rock minerals at different pH environments and to identify conditions that would induce or promote wettability alteration via zeta potential measurement. Therefore, in this section, we seek to provide insight into the surface charge of rock over a wide range of pH (2 to 12), and to identify pH condition and anhydrite mineralogical composition that would induce wetting alteration in carbonates.

Anhydrite dissolution by low salinity brine can provides additional SO_4^{2-} ions to rock/brine/oil system, thus decreasing the zeta potential and increase water wetting of calcite surface (Al-Shalabi et al., 2014; Austad et al., 2012; Yousef et al., 2012b). **Figure 4.7** shows the zeta potential of anhydrite-calcite mixture in DI, SW and FW at various pH, the effect of pH and anhydrite on calcite mineral surface charge for 1, 5, 10, 15, 20, and 25 wt.% anhydrite in anhydrite-calcite sample mixture demonstrate the non-monotonic behavior of zeta potential with change in solution pH. The zeta potential of the anhydrite-calcite mixture is negative in DI, positive in FW, while the charge sign flipped from

positive to negative as the anhydrite concentration increases in the case of SW. Although there is consistency in the charge signs, the zeta potential values are low; and near-zero (less than ± 10), thus cannot be relied on, with certainty to make conclusions about the propensity of anhydrite to alter the wetting state in anhydrite-calcite surfaces.



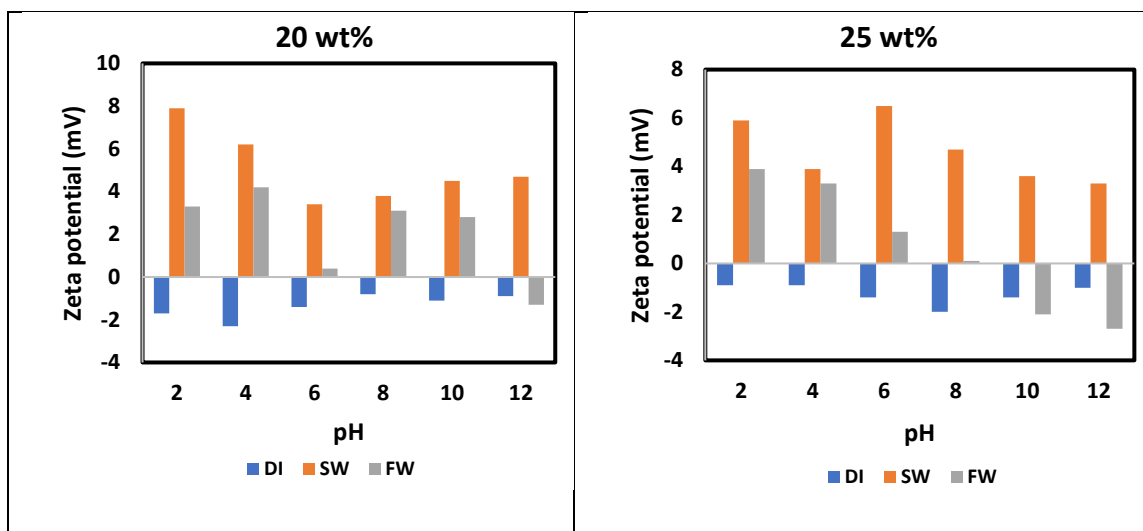


Figure 10. –Zeta potential of anhydrite-calcite mixtures in DI, SW and FW: the effect of pH and anhydrite on calcite mineral surface charge at 1, 5, 10, 15, 20, and 25 wt.% anhydrite/calcite sample mixture, respectively.

Similarly, the zeta potential of anhydrite-dolomite mixture in DI, SW and FW at pH of 2, 4, 6, 8, 10, and 12 is shown in **Figure 4.8**. It is observed that for 1, 5, 10, 15, 20, and 25 wt.% anhydrite in anhydrite-dolomite mixtures the zeta potential behavior is also non-monotonic as the solution pH changes. Based on these observations, one can conclude that even at wide range of pH values and at different anhydrite compositions, the surface charge (via zeta potential measurements) cannot be used to justify the wetting states of neither anhydrite-calcite nor anhydrite-dolomite mixtures.

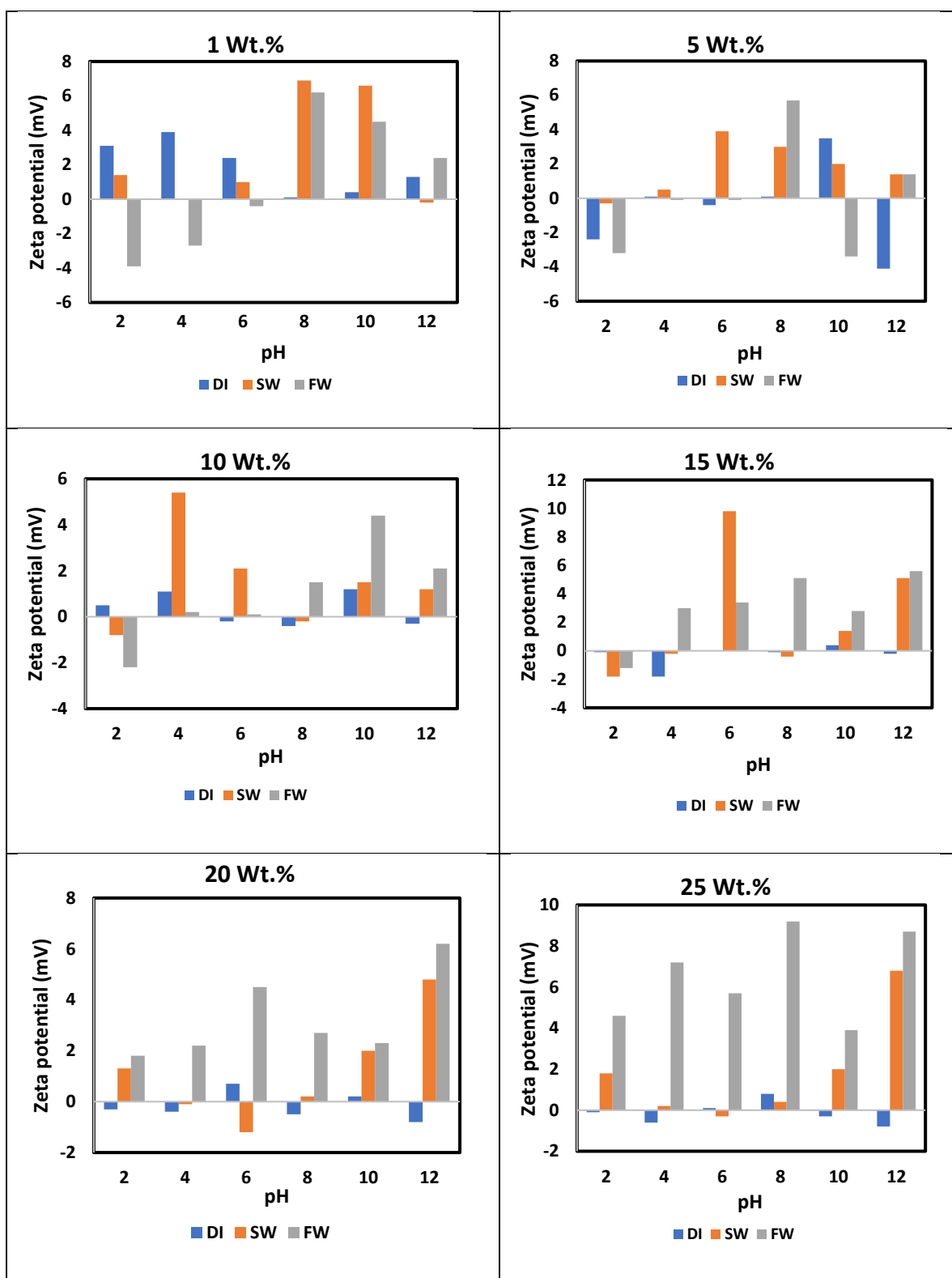


Figure 11. Zeta potential of anhydrite-dolomite mixtures in DI, SW and FW: the effect of pH and anhydrite on dolomite mineral surface charge at 1, 5, 10, 15, 20, and 25 wt.% anhydrite/dolomite sample mixture, respectively.

A similar finding was presented by (Mogharab et al., 2022), the authors showed that and zeta potential measurement and mineral dissolution analyses showed no comprehensive correlation with the wettability state of carbonate particles obtained via flotation technique. The authors noted that zeta potential was not able to justify the wettability states of pure calcite and the mixture of calcite and anhydrite particles in all over ranges of brine salinity and composition studied. However, the equilibrium of anhydrite reversed the surface potential of carbonate from positive to negative and resulted in repulsive (positive disjoining pressure) force (X. Hao et al., 2021). Moreover, the calcite surface charge is influenced by the presence of anhydrite; yet, the magnitude of the surface charge via ζ -potential measurement is insignificant to cause wettability alteration in carbonate (Mohammed, et al., 2022).

In response to a question that states why the maximum anhydrite dissolution cannot make the rock surface at its most negatively charged state, Mogharab et al. (2022) suggested that the non-monotonic behavior of zeta potential with brine properties (salinity/composition) is due to the contribution of other component (e.g., oil components and sulfate ions introduced by anhydrite dissolution) in adjusting the pH of the system. Accordingly, the zeta potential is not a general and valid candidate to justify the wettability behavior of carbonates. Thus, neither the mineral dissolution, nor the zeta potential (electrical surface charge) could justify the non-monotonic behavior of wettability alteration with brine salinity, composition and pH variations.

4.4.3 Flotation wettability

The wettability of the powdered anhydrite, calcite and dolomite pure minerals is first investigated to serve as a reference in which the effect of different anhydrite compositions in calcite and dolomite would be compared. The wettability of pure anhydrite, calcite and dolomite minerals in DI, SW, and FW with an average pH of 8 using flotation technique is shown in **Figure 4.9**. Pure anhydrite particles show percentage water wetness of 59.65 %, 48.85 %, and 51.75 % in DI, SW and in FW, respectively. This shows that the hydrophilicity is highest in DI and lowest in SW. Based on flotation measurement, the presence of sulfate has the tendency to increase oil-wetting of carbonate surfaces (Sohal et al., 2017). In the case of calcite particles, a percentage water wet particles of 24.6 %, 22.35 %, and 17.3 % are observed in DI, SW and FW, respectively. This implies that pure calcite in its powdered form is predominantly oil-wet, and the hydrophobicity increases as the salinity increases. Correspondingly, dolomite in its pure form shows mainly oil-wet since the percentage water-wet particles in DI, SW and FW are 40.95 %, 28.9 % and 29.85 %, respectively. Pure anhydrite particles show the highest percentage water wetness in DI, SW

and FW compared to pure calcite and dolomite particles. However, based on the flotation wettability test, calcite appears less hydrophilic than dolomite particles.

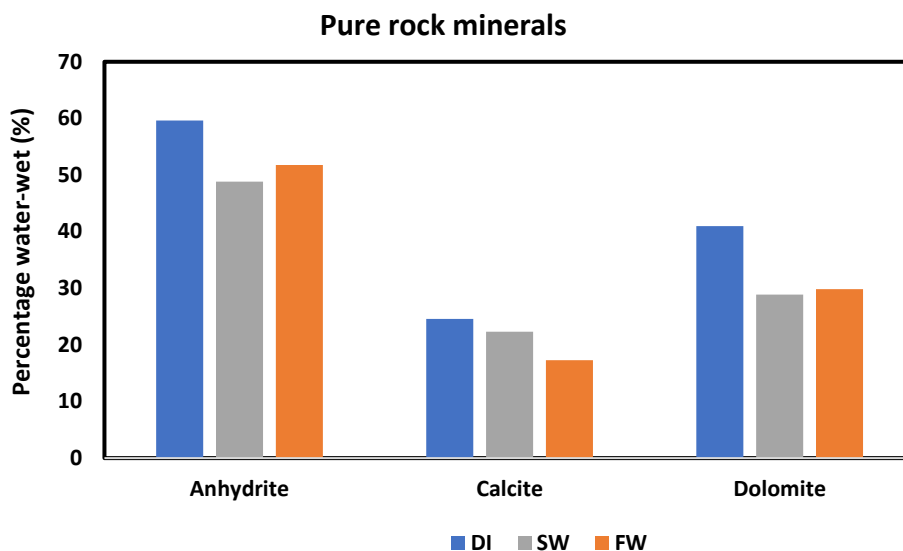


Figure 12. Flotation wettability of pure rock minerals (anhydrite, calcite, and dolomite).

The effect of anhydrite concentration on calcite wettability via flotation measurement is shown in **Figure 4.10**. The water wetness of calcite in DI increases slightly as the anhydrite concentration increases. Similarly, in SW the percentage of water-wet calcite particles are 12.1 %, 13.45 %, 16.5 %, 18.25 %, 22.4 %, and 23.45 % at 1 %, 5 %, 10 %, 15 %, 20 %, and 25 % anhydrite concentrations, respectively. This shows a consistent increase in hydrophilicity with increased anhydrite composition. A similar trend was observed for anhydrite-calcite mixtures in FW. Based on the results of flotation measurements for pure calcite, the amount of water wet calcite grains increases as the salinity of the brine decreases from FW to SW (Mogharab et al., 2022). Overall, anhydrite-calcite mixtures in FW shows lower water wetness compared to DI and SW.

For anhydrite-dolomite mixtures (**Figure 4.11**), a general increase in water wetness is observed in all the fluid types (this is, in DI, SW, and in FW) as the anhydrite content in dolomite rock increases. Highest water wetness is observed in DI followed by SW, while the anhydrite-dolomite mixtures is seen to have the lowest water wetness in FW. This is in line with conclusions from previous literature (Mogharab et al., 2022; Mwangi et al., 2018; Sadeghi et al., 2022).

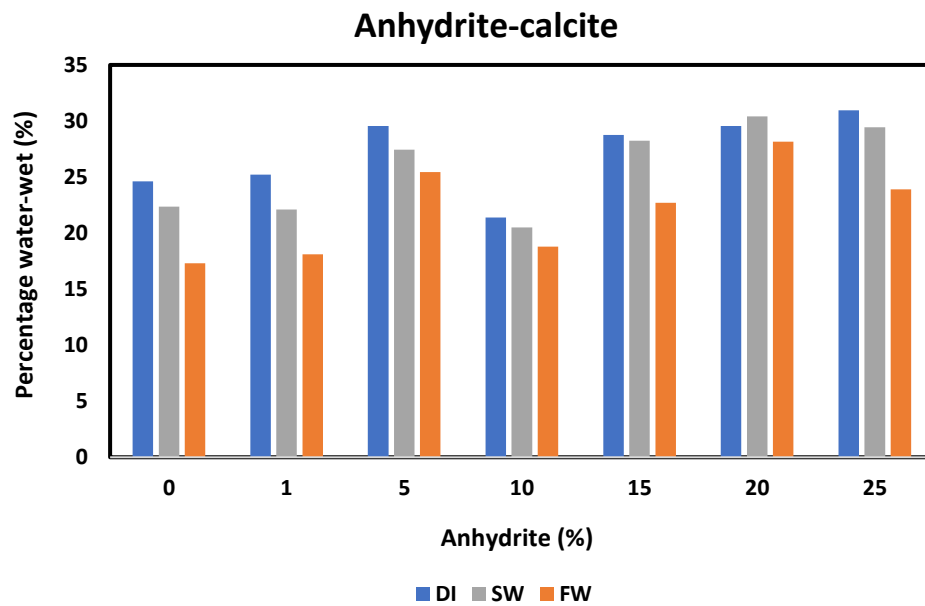


Figure 13. Effect of anhydrite (1 wt.% to 25 wt.%) on calcite flotation wettability.

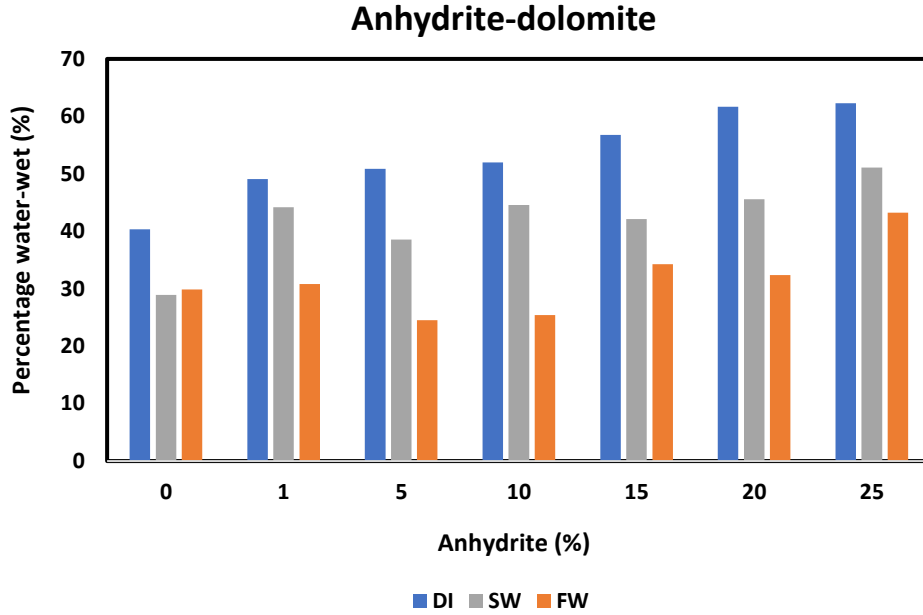


Figure 14. Effect of anhydrite (1 wt.% to 25 wt.%) on dolomite flotation wettability.

4.4.4 Contact angle.

The wettability of pure anhydrite, calcite and dolomite rocks is determined via contact angle measurement in DI, SW, and FW. **Figure 4.12** shows the contact angles of the pure rocks in three different waters. It can be seen from Figure 15a that pure anhydrite rock in DI water is strongly water-wet with contact angle 33° , pure calcite rock is somewhat intermediate-wet (contact angle 85°), while pure dolomite rock is slightly oil-wet (contact angle 102°). Similarly, in sea water, the contact angles of anhydrite, calcite and dolomite are 47° , 92° , and 109° , respectively. This shows strong water wetness for anhydrite, intermediate-wet for calcite and slightly oil-wet for dolomite in sea water (Figure 15b). However, in formation water (Figure 15c), anhydrite is water-wet (contact angle 55°) while calcite and dolomite are oil-wet with contact angle wettability of 113° and 115° , respectively. This results is similar to the findings of previous researchers – Arif et al.

(2020) investigated the influence of rock mineralogy on wettability of carbonates using contact angle measurements, the authors suggested that calcite-based rocks are relatively more hydrophilic compared to dolomitic carbonates, while pure calcite mineral was completely water-wet.

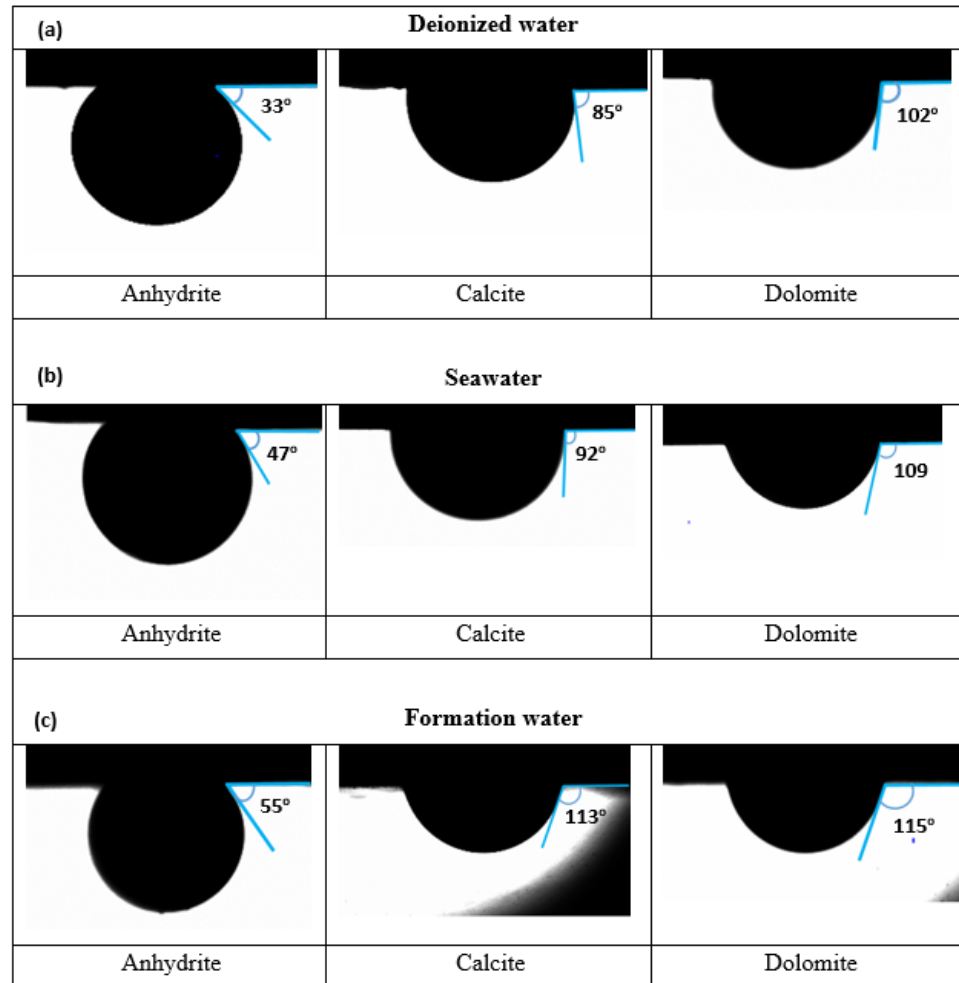


Figure 15. Contact angle of pure anhydrite, calcite and dolomite rocks in de-ionized water, seawater and formation water.

Since pure anhydrite is water-wet in DI, SW and FW, while calcite and dolomite are intermediate- to oil-wet in these fluids, we aim to study the effect of anhydrite composition

in both calcite and dolomite at millimeter scale under different conditions. We thus, measured the wettability via contact angle technique on the synthetic calcite and dolomite rocks having various compositions of anhydrite.

4.4.5 Synthetic rocks composition and minerals distribution

The composition and minerals distribution of the synthetic rocks is analyzed using *QEMSCAN*. This aimed at confirming the compositions and distribution of the anhydrite-calcite and the anhydrite-dolomite in the artificial rock samples. **Table 4.4 & 4.5** shows the anhydrite-calcite and anhydrite-dolomite synthetic rocks composition acquired via *QEMSCAN*, respectively. Although there is slight difference between the anhydrite mixed percentage during synthesis (1 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.%) and the composition acquired via *QEMSCAN*, the disparities are within reasonable range. The distributions of the various rocks minerals for anhydrite-calcite and anhydrite-dolomite synthetic rocks are shown in **Figure 4.4**, it can be seen that the rocks minerals are well dispersed/distributed in the rocks.

Table 4.4. Anhydrite-calcite samples minerals composition acquired via QEMSCAN.

Anhydrite mixed (%)	1	5	10	15	20	25
Rock mineral	Composition by QemScan (%)					
Anhydrite	0.5	4.2	13.7	14.6	19.8	27.5
Dolomite	0.0	0.1	0.2	0.0	0.2	0.0
Calcite	71.4	67.3	66.4	44.7	56.5	49.4

Coesite	28.0	27.2	19.5	39.2	23.3	22.5
Others	0.1	1.2	0.2	1.5	0.2	0.6

Table 4.5. Anhydrite-dolomite samples minerals composition acquired via QEMSCAN.

Anhydrite mixed (%)	1	5	10	15	20	25
Rock mineral	Composition by QemScan (%)					
Anhydrite	1.6	6.5	12.8	16.2	21.3	26.1
Dolomite	69.4	66.5	62.9	59.2	55.7	52.0
Calcite	0.0	0.1	0.2	0.1	0.0	0.2
Coesite	27.8	25.8	22.9	23.2	22.2	20.3
Others	1.2	1.1	1.2	1.3	0.8	1.4

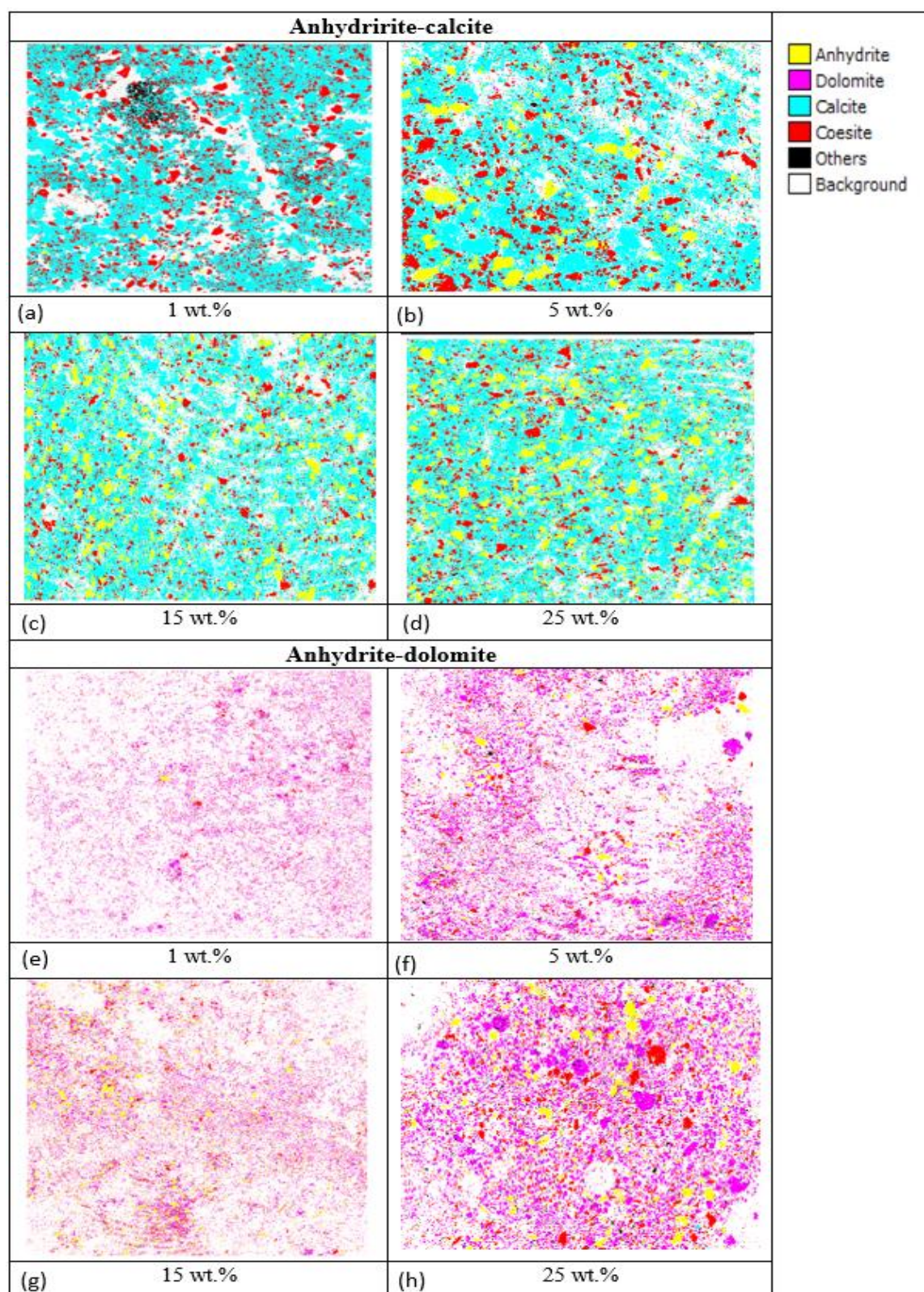


Figure 16. Anhydrite-calcite-dolomite samples compositional analysis by QEMSCAN.

Anhydrite-calcite and anhydrite-dolomite synthetic rocks

The wettability of anhydrite-calcite rocks measured via contact angle in DI, SW and FW is shown in **Figure 4.4**. Generally, the hydrophobicity increases with increase in salinity, at 1 wt.% anhydrite concentration, the contact angles of the anhydrite-calcite are 58°, 67°, and 77°, at 5 wt.% anhydrite concentration, the contact angles are 52°, 56°, and 60°, at 10 wt.% anhydrite concentration, the contact angles are 67°, 71°, and 70°, at 15 wt.% anhydrite concentration, the contact angles are 57°, 61°, and 74°, at 20 wt.% anhydrite concentration, the contact angles are 56°, 60°, and 70°, at 25 wt.% anhydrite concentration, the contact angles are 55°, 58°, and 63° in DI, SW and FW, respectively. Overall, the contact angle, and thus, oil-wetness of the anhydrite-calcite rocks slightly decreases as the anhydrite composition increases from 1 to 25 wt.%.

Similarly, the anhydrite-dolomite rocks in **Figure 4.5** also shows increase in hydrophobicity with increase in salinity, at 1 wt.% anhydrite concentration, the contact angles of the anhydrite-dolomite are 77°, 79°, and 102°, at 5 wt.% anhydrite concentration, the contact angles are 802°, 71°, and 99°, at 10 wt.% anhydrite concentration, the contact angles are 81°, 85°, and 111°, at 15 wt.% anhydrite concentration, the contact angles are 83°, 79°, and 110°, at 20 wt.% anhydrite concentration, the contact angles are 71°, 79°, and 98°, at 25 wt.% anhydrite concentration, the contact angles are 68°, 71°, and 97° in DI, SW and FW, respectively. In general, the contact angle of the anhydrite-dolomite rocks slightly decreases as the anhydrite composition increases from 1 to 25 wt.%.

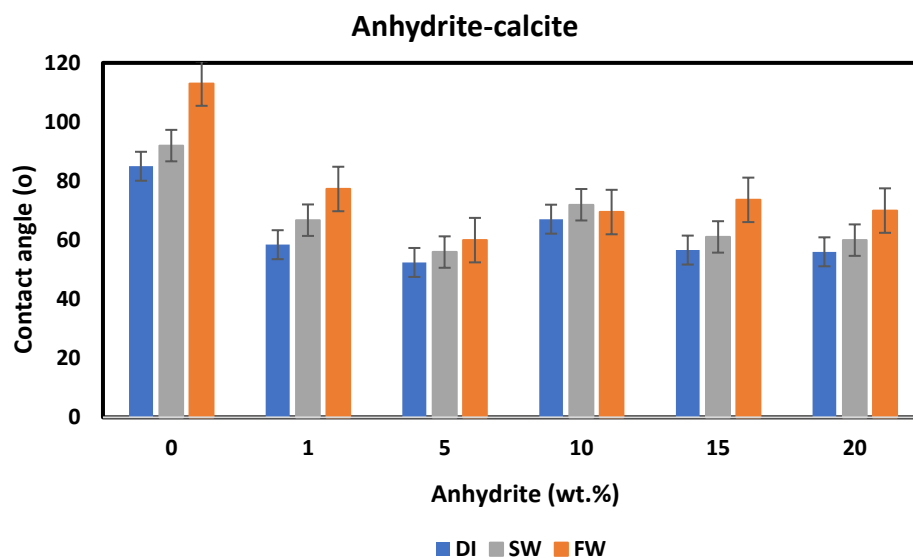


Figure 17. Effect of anhydrite (1 wt.% to 25 wt.%) on calcite contact angle.

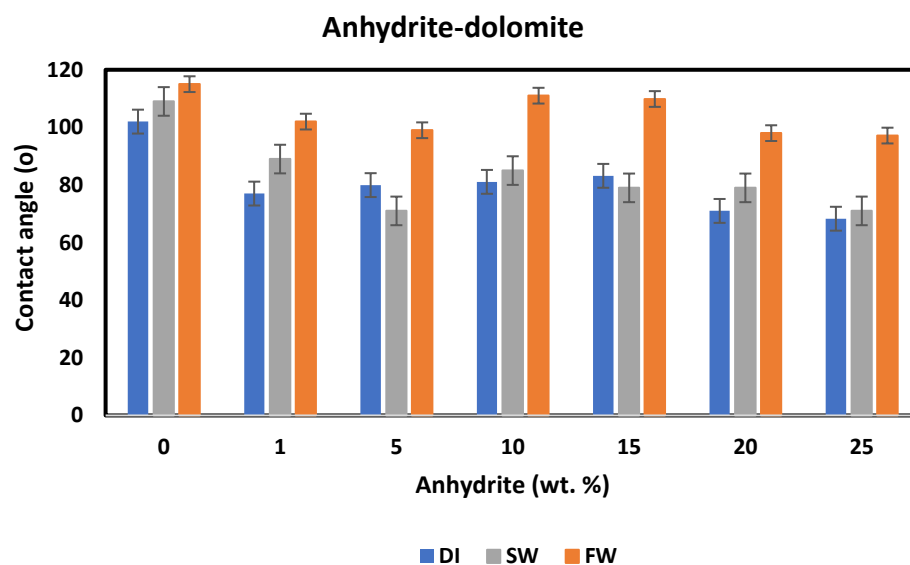


Figure 18. Effect of anhydrite (1 wt.% to 25 wt.%) on dolomite contact angle.

4.5 Summary and Conclusions

Results thus far show that the presence of anhydrite influences the surface charge and thus affects the electrostatic interactions at the rock/fluid interface, and the wetting characteristics of carbonates. However, the change in the zeta potential due to the presence of anhydrite shows no significant difference in terms of the wetting state for both calcite and dolomite surfaces. The zeta potential demonstrates an instable colloidal system which is indicated by a near-zero and low zeta potential values (less than ± 10) of the anhydrite-calcite, and anhydrite-dolomite systems. However, the flotation and contact angle techniques of wettability estimation showed that anhydrite presence has the tendency to alter the wetting state of anhydrite-carbonate-brine-oil systems to more water wet. Similarly, Sadeghi et al. (2022) showed that, in wettability alteration measurements for carbonate minerals, flotation wettability results were consistent with contact angle measurements. This also leads to the conclusion that the presence of the anhydrite can alter the wetting state of these carbonates. Based on the results obtained, we identified and highlighted some of the major findings in the domain of rock wetting behavior and fluid-rock interactions in anhydrite-bearing carbonates, as follows:

- Pure anhydrite is water-wet while calcite and dolomite are intermediate- to oil-wet in DI, SW and FW. However, based on the flotation wettability test, calcite appear less hydrophilic than dolomite particles, in contrast to the observed trend via contact angle technique.
- Anhydrite dissolution and in-situ supply of sulfate ions occur in DI, SW and FW as evident from the general increase in sulfate ions concentration with increased anhydrite content in the anhydrite-calcite and anhydrite-dolomite mixtures.

- The zeta potential values observed in anhydrite-carbonate-brine systems are low; and near-zero (less than ± 10), thus cannot be relied on, with certainty to make conclusions about the propensity of anhydrite to alter the wetting state in anhydrite-carbonate-brine-oil systems.
- Even at wide range of brine pH (2 to 12) and at different anhydrite compositions, the surface charge (via zeta potential measurements) cannot be used to justify the wetting states of neither anhydrite-calcite nor anhydrite-dolomite mixtures. Thus, the zeta potential is not a general and valid candidate to justify the wettability behavior of heterogeneous carbonates.
- Although anhydrite shows no potential to alter the wettability from oil- to water-wet via zeta potential, the flotation and contact angle results shows that its presence notably increases the water wetness in calcite and dolomite formations.
- Generally, the hydrophilicity of anhydrite-carbonate-brine-oil systems as estimated via contact angle and flotation techniques in DI, SW and FW increases with decrease in salinity, and increases as the anhydrite composition increased from 1 to 25 wt.%.

CHAPTER 5

EXPLORING THE IMPACT OF MINERALOGY ON PORE STRUCTURE AND FLUID DYNAMICS IN TIGHT RESERVOIR ROCKS: INSIGHTS FOR ENHANCED OIL RECOVERY AND GAS STORAGE

Summary

The mineralogy, pore structure and fractal characteristics of rock has a great influence on its physical and flow properties. This study investigates the influence of mineralogy, particularly anhydrite relative to dolomite content, on the pore structure, petrophysical characteristics, and fluid flow potential of six rock samples (S-1 to S-6) from a Middle East outcrop reservoir. The main purpose of this research is to give novel perception into the interplay of the rock mineralogy, petrophysical properties, and fluid flow in tight formations, which are candidates for EOR/EGR processes as well as CO₂ subsurface storage. To achieve this, experimental techniques included XRD analysis, routine petrophysical measurements, thin section, SEM-EDS observations, and NMR experiments were performed. In addition, oil recovery potential was also assessed using formation brine spontaneous imbibition, seawater, and surfactant and CO₂ flooding experiments to mimic the primary, secondary, and tertiary oil recovery processes, respectively. Pore structures were categorized into micropores, mesopores, and macropores based on pore sizes and

fluid flow capabilities, and multiscale fractal dimensions were analyzed. Results show that the rocks predominantly consist of anhydrite and dolomite, having varying pore types with broad distributions. Higher dolomite compared to anhydrite content correlates with better reservoir quality. Fractal analysis reveals complex pore structures, with macropores exhibiting medium complexity and mesopores being the most complex. Fractal analysis of the pore structure revealed that no apparent trend was observed for fractal dimension of micropores D1. The fractal dimension of macropores D3 ranged from 2.41 to 2.96, indicating a medium complexity pore structure. The fractal dimension of mesopores D2 is between 2.68 and 2.99, implying that the pore structure of the mesopores is the most complex. Inverse correlations between the fractal dimensions with porosity and permeability were observed. In addition, rocks predominated by anhydrite (S-1 to S-3) showed water-wet behavior, whereas samples (S-4 to S-6), primarily consisting of dolomite, displayed oil-wet characteristics. Moreover, while there was no significant correlation between the cumulative oil recovery achieved in the EOR process and the amount of anhydrite, it was noted that CO₂ flooding proved to be more effective than surfactant flooding in rocks containing anhydrite. The study emphasizes the significance of mineralogy, physical properties, and pore characteristics in selecting recovery methods, particularly during EOR processes. These findings offer a quantitative assessment of microscopic pore structures linked to macroscopic rock properties and oil recovery enhancing our understanding of reservoir dynamics and implications for oil and gas storage.

Keywords: Petrophysics, Reservoir quality, Anhydrite, Tight rocks, Fractal dimension, Gas storage.

5.1 Background

Anhydrite rock is a geological material, which will produce a series of physical and chemical changes upon encountering injected and reservoir fluids, such as dissolution, precipitation, softening, and the salt-induced swelling phenomenon (Isah et al., 2022a; Serafeimidis et al., 2015; Serafeimidis & Anagnostou, 2015). It is important to highlight that about 70% of the global oil fields hosted by carbonate rocks are interbedded with evaporites (Yi-gang, 1981). A substantial portion of the oil fields in the Middle East are situated beneath or between the upper Jurassic anhydrite beds (Omidpour et al., 2023; Yi-gang, 1981). Previous researches have studied the physical and mechanical properties of anhydrite rock under various conditions (Wang et al., 2020), and a chemomechanical processes model in anhydrite rock have been proposed (Huber et al., 2015). Yin & Xie (2019) designed mechanical and acoustic synchronization tests. They acquired the effects of mineral composition on the dynamic and static mechanical properties of the anhydrite rock. Other studies (Isah, Mahmoud, Kamal, Arif, & Al Jawad, 2023; Mogharab et al., 2022; Mohammed, Isah, Al Shehri, Mahmoud, Arif, et al., 2022b) performed series of fluid-rock interaction tests to determine the influence of anhydrite on reservoir rock wettability and fluid behavior related to production.

Anhydrite plays a significant role in various recently discovered hydrocarbon prospects, particularly in anhydrite-bearing carbonate successions, and where it serves as trap seals influenced by the stratigraphic distribution of anhydrite-carbonate facies (Aleali et al., 2013; Amel et al., 2015; El-Tabakh et al., 2004; Mohammed-Sajed & Glover, 2022; Sarg, 2001). Typically occurring interbedded with carbonates, anhydrite is indicative of dry

periods and shallow depositional environments (Aleali et al., 2013; Amel et al., 2015). The Marat Formation, investigated in this study, stands as a prominent example of anhydritized carbonate in the Middle East. While anhydrite cement often negatively impacts reservoir quality by occluding pores and fractures (Mohammed Sajed & Glover, 2020; Warren, 2010), some studies indicate that significant amounts of anhydrite components may not necessarily deteriorate overall reservoir quality (Al-Awwad & Collins, 2013; Gindre-Chanu et al., 2015; Nader et al., 2013). In certain cases, they might even enhance reservoir quality, especially after uplift or late dissolution (Kadkhodaie et al., 2022; Lucia & Ruppel, 1996; Morad et al., 2012; Nader et al., 2013; Ruppel & Bebout, 1996). The influence of anhydrite on reservoir properties has been extensively studied in major Middle Eastern hydrocarbon reservoirs, including the early Triassic Kangan Formation, the Permian Khuff and Dalan formations, the Jurassic Butmah Formation, and the Arab-D and C members of Jurassic Arab formation (Amel et al., 2015; Mohammed-Sajed & Glover, 2022; Mohammed Sajed & Glover, 2020; Morad et al., 2018; Wilson, 1986).

While fluid flows through porous media, the migration of the fluid can bring about changes in the reservoir, potentially leading to modifications in the pore structure due to variations in mineral composition. However, there is limited research on the specific characteristics of alterations in pore structure resulting from the combined influence of rock/fluid interactions and mineralogy (Isah et al., 2022b). Anhydrite holds significance as a vital rock mineral, by nature, it tends to exhibit low permeability and porosity. This characteristic makes it commonly occurred as caprock in reservoirs, playing a crucial role in controlling the movement of fluids within the subsurface. Moreover, the influence of anhydrite on reservoir dynamics can undergo changes due to diagenetic processes. Through

diagenesis, anhydrite or its hydrated form, gypsum, can form within reservoir rocks as cementating, pore filling, or grain coating mineral (Isah et al., 2022a; Mohammed-Sajed & Glover, 2022; Nafisi & Tavakoli, 2023). These diagenetic alterations have substantial implications for reservoir performance (Mohammed Sajed et al., 2021; Omidpour et al., 2023; Rashid et al., 2017; Usman et al., 2020).

The presence of anhydrite in the reservoir rock alters its physical properties, potentially affecting permeability, porosity, and overall fluid flow characteristics (El-Tabakh et al., 2004; Mohammed-Sajed & Glover, 2022; Omidpour et al., 2023). An example that underscores the impact of anhydrite on reservoirs is observed in the Arab-D carbonate reservoir in the Middle East. This reservoir is found to contain a substantial amount of anhydrite, significantly influencing the reservoir's quality and ultimate production potential (Aleali et al., 2013; M. Mahmoud et al., 2021b). The presence of anhydrite in this context can act as a modifying factor, influencing the reservoir's response to reservoir and injected fluids and determining its overall productivity. Quantitatively evaluating the microscopic pore structures of porous rocks, which involves analyzing irregularities in pore shapes and distributions of pore sizes, presents a challenge. The pore structure of rocks can be obtained using the Nuclear magnetic resonance (NMR) T_2 spectrum, as indicated in the previous studies (Gao et al., 2019; Isah et al., 2021b; Yao et al., 2010; Zhang et al., 2019). Nuclear magnetic resonance measurements offer a means to obtain characteristics related to pore structures (Elsayed et al., 2022; Isah et al., 2021a; Wang et al., 2022). The relationship between the NMR relaxation, fractal dimension characteristics, and the pore structure can be analyzed using NMR T_2 distribution data.

Therefore, this study addresses this gap by examining the changes in pore structure in anhydrite-bearing rocks based on different anhydrite content. The investigation includes the analysis of the multiscale fractal dimensions of micropores, mesopores, and macropores, as well as an exploration of the oil recovery potential associated with different mineral compositions. Moreover, limited research has explored the effects of anhydritization on porosity-permeability relationships (Gindre-Chanu et al., 2015; Mohammed-Sajed & Glover, 2022; Warren, 2010). Therefore, this paper represents a study investigating anhydrite content in the Marrat Formation, analyzing the impact of anhydrite fraction and petrophysical properties on pore network and fluid recovery. The study attempts to identify relationships between anhydrite amount and various petrophysical properties (e.g., porosity, permeability, electrical resistivity, and average pore size) for comparison with pore structure and fluid flow potentials. In addition, the research endeavors to examine the positive and negative effects of the amount of anhydrite minerals on reservoir quality and recovery potential, seeking a comprehensive understanding of its overall influence. The findings are then discussed in terms of their implications for the production of oil coupled with CO₂ storage in rock formations. Therefore, the ultimate goal is to comprehend the control that anhydrite has on porosity-permeability and porosity-electrical resistivity relationships, fractal dimension-petrophysical properties relationships, and, consequently, on the fluid flow potential within the formation.

(Pfeifer & Avnir, 1983)(R. Yang et al., 2016)

5.2 Fractal Dimension

Porous sedimentary rocks, being complex geological materials, exhibit numerous irregular pores distributed across various scales (M. Wang et al., 2017). Due to the complex and irregular nature of pore size distribution, which includes pore size, shape, tortuosity, and connectivity, characterizing pore structure quantitatively using the traditional methods or Euclidean geometry is challenging (Wang et al., 2012). Several studies suggested that the pore systems in sedimentary rocks exhibit a fractal nature (Bird et al., 2006; Mandelbrot, 1982; B. Yu & Cheng, 2002). Fractals are described as virtual, self-similar entities that maintain identical appearances regardless of the scale of magnification (Kulesza & Bramowicz, 2014; Mandelbrot, 1982; Schlueter et al., 1997; Xu, 2015), and these self-similar fractal objects can be characterized by the fractal dimension (D) (Y. Ding et al., 2017; Giri et al., 2012; Lai & Wang, 2015; Zheng et al., 2018). Fractal theory establishes the relationship between microscopic pore structures and macro petrophysical parameters such as porosity and permeability (Hu et al., 2012; Zhang et al., 2020). By computing the fractal dimensions of sedimentary rocks, it becomes possible to quantitatively characterize the complexity and heterogeneity of highly disordered pore systems (Cai et al., 2010; K. Li, 2010). Furthermore, the fractal descriptions of pore systems can be applied to predict petrophysical properties such as permeability, wettability, tortuosity, diffusivity, and electrical conductivity (Daigle et al., 2014).

Fractal theory has been employed to provide a quantitative representation of the complexity and heterogeneity in the pore systems in various types of rocks, such as carbonates, sandstone, shale, and coal. The analysis extends to the fractal dimension of micropores, mesopores, and macropores, providing insights into the morphology and heterogeneity of

the pore structure at multiple scales (Isah et al., 2021b; Ma et al., 2019; Z. Ouyang et al., 2016). A higher fractal dimension for micropores implies rougher surfaces, creating more adsorption sites favorable for gas storage (Cai et al., 2010; Jun Liu et al., 2018). In contrast, a higher fractal dimension for macropores (seepage pores) suggests a more complex pore structure with rougher surfaces, potentially hindering fluid flow and migration in the reservoir (F. Yang et al., 2014).

A comprehensive understanding of pore network is essential for grasping the fluids storage and transport characteristics of porous sedimentary rocks (Clarkson et al., 2013). Micropores play a significant role in influencing the fractal dimensions of pore systems. It is the primary causes of heterogeneity in tight rocks, and samples with shorted NMR T_2 relaxation time and unimodal T_2 distribution behaviors have the highest fractal dimension and heterogeneity (Lai et al., 2018). Previous research indicates that when smaller pores, characterized by shorter T_2 relaxation times, dominate the NMR T_2 spectrum, the resulting calculated fractal dimension tends to be high. Conversely, if the NMR T_2 distribution is predominantly composed of longer T_2 components, the associated fractal dimension value generally tends to be lower (Lai et al., 2018; K. Li, 2010).

To explore the evolution of heterogeneity in the pore structure of anhydrite-bearing rocks and its variation in relation to petrophysical properties and flow behavior, the fractal dimension (D) of the pore network was examined using NMR test results. The transverse relaxation time (T_2) of brine in rocks consists of three different components (Coates et al., 1999).

$$\frac{1}{T_2} = \frac{1}{T_{2,B}} + \frac{1}{T_{2,S}} + \frac{1}{T_{2,D}} \quad (1)$$

In eq. (1), the bulk volume, surface, and diffusion transversal relaxation time are in ms. However, as the pore in rock is confined, the T_2 relaxation time is rapid and has a shorter echo time. Hence, T_2 of pore fluids is effectively only influenced by bulk and surface transverse relaxation time. Therefore, the impact of diffusion transverse relaxation time in eq. (1) can be neglected (Coates et al., 1999; Daigle et al., 2014a; Dunn et al., 2002), thus:

$$\frac{1}{T_2} = \frac{1}{T_{2,BULK}} + \frac{1}{T_{2,SURFACE}} \quad (2)$$

Moreover, the surface relaxivity is strongly related to the specific surface to volume ratio of the pores (Anovitz & Cole, 2015; Fleury et al., 2007b; Mitchell & Fordham, 2014). It follows that:

$$\frac{1}{T_2} = \rho \left(\frac{S}{V} \right) = F_g \left(\frac{\rho}{r} \right) \quad (3)$$

where, ρ_2 is the transverse surface relaxivity which is measured in $\mu\text{m/ms}$, and S/V is the pore surface area (μm^2) to volume (μm^3) ratio, F_g is the geometry factor related to pore shape, and r denotes the pore radius. Typically, a higher T_2 value indicate larger pore radius. The area enclosed by the T_2 curve corresponds to the pore volume of the porous medium (Isah et al., 2021a; Xu et al., 2019). The NMR signal provides relative pore size distribution and pore structure, the cumulative volume fraction C_p of pores with radius less than r can be expressed (Westphal et al., 2005; Zhang et al., 2020; Zhang & Weller, 2014; Zhao et al., 2022). The fractal dimensions can be computed using the relationship outlined (Daigle et al., 2014b; Pang et al., 2022; Yao et al., 2010):

$$C_p = \frac{V(r)}{V_s} = \frac{r^{3-D} - r_{min}^{3-D}}{r_{max}^{3-D} - r_{min}^{3-D}} \quad (4)$$

where D is the NMR fractal dimension. But r_{min} is far less than r_{max} . Hence, Eq. (4) can be simplified as

$$C_p = \frac{r^{3-D}}{r_{max}^{3-D}} = \frac{T_2^{3-D}}{T_{2,max}^{3-D}} \quad (5)$$

Taking the logarithm of both sides of Eq. (5), yields

$$\log(C_p) = (3 - D) \log(T_2) + (D - 3) \log(T_{2,max}) \quad (6)$$

In this equation, C_p represents the proportion of the pore volume smaller than the corresponding T_2 value to the total pore volume, and $T_{2,max}$ is the maximum transverse relaxation time. A larger D corresponds to a rougher pore surface and a more complex pore structure.

5.3 Samples and Methods

5.3.1 Samples

The samples for this study were collected from the upper Marrat Formation, prominently exposed in central Saudi Arabia (Al-Hussaini et al., 2021; Al-Mojel et al., 2020; Farouk et al., 2018; Milton, 1967; Powers et al., 1966). This formation is stratigraphically positioned between the Minjur Formation below and the Dhurma Formation (**Figure 5.1**). Early studies on the Marrat Formation identified three distinct members—Lower, Middle, and Upper—each characterized by unique lithological compositions (Figure 5.1). The Lower Member includes glauconitic claystone predominance, the Middle Member is characterized by red clay beds, and the Upper Member is consisting of limestone base, transitioning to interval with interbedded dolostone and evaporite beds (Figure 5.1).

The dolostone and evaporite strata define three shallowing upward cycles, with dolostone indicating relatively deeper environmental conditions and evaporites marking shallower

settings (Figure 5.1). This study focuses on six samples from the lowest of these cycles, evenly distributed between evaporite and dolostone beds to ensure a balanced representation. Three samples were obtained from evaporite layers (identified as S-1, S-2, and S-3 respectively, with S-1 representing the uppermost layer), and the remaining three from dolostone beds (labeled S-4, S-5, and S-6, with S-6 as the lowermost), following a systematic sampling strategy that ensures equal spacing within each layer.

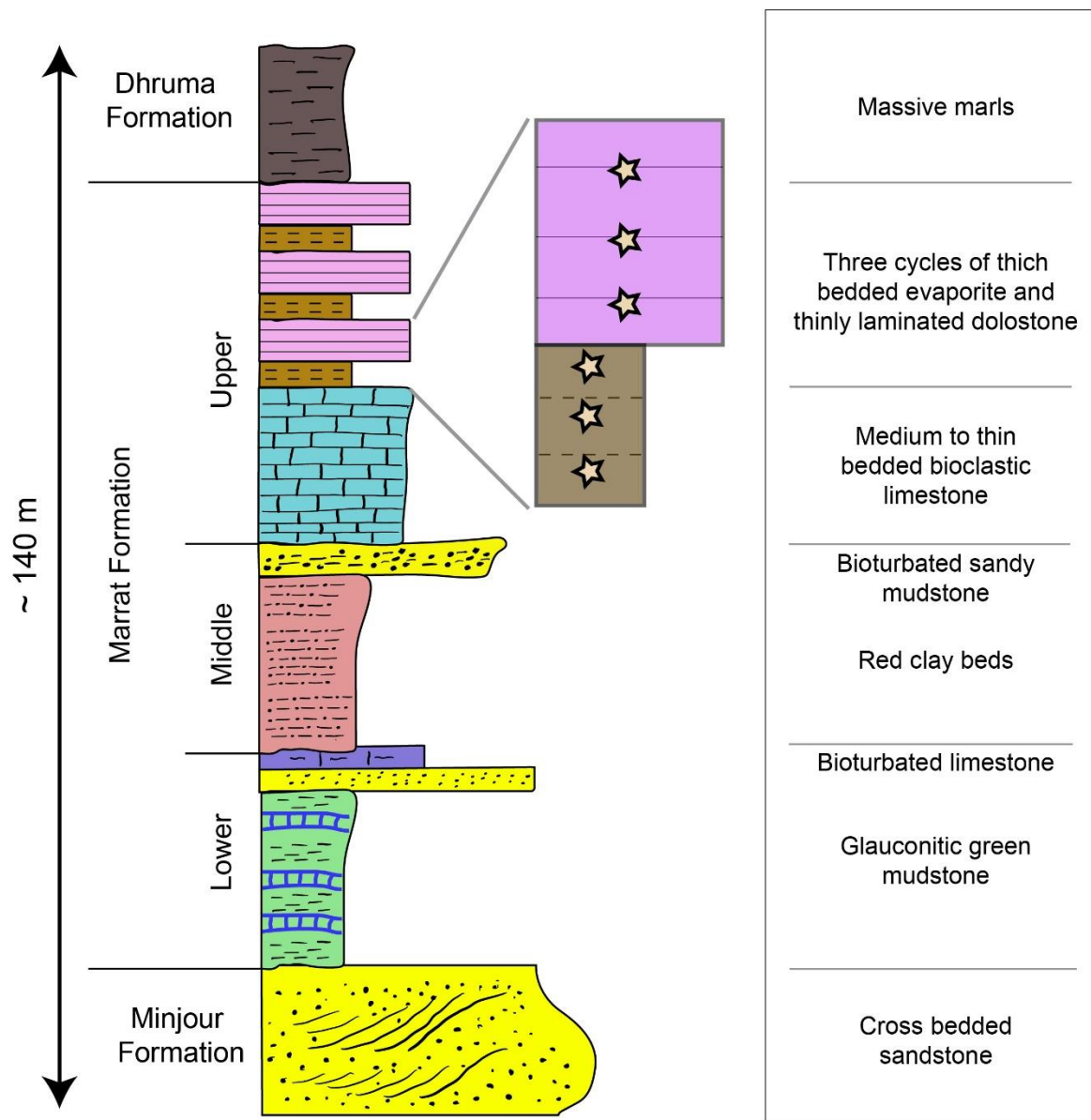


Figure 19. Illustrated stratigraphic section of the Marrat Formation in central Saudi Arabia (Adapted from (Farouk et al., 2018)). This figure presents the lithology and stratigraphic details of the Marrat Formation, highlighting the Upper Marrat Member. Note the location from which the six samples were collected for this study, specifically from the lowest cycle of the three identified cycles of dolostone-evaporite interbedding.

5.3.2 Experiments

To systematically investigate the influence of mineralogy and pore structure on the petrophysical and flow potential of tight carbonate rock samples, a series of experiments were conducted. These included NMR measurements to ascertain pore type and structure through NMR T_2 and fractal characteristics. Additional analyses involved XRD examinations and SEM-EDS observations, with thin section analyses performed to gain insights into the pore/grain characteristics of the samples. The NMR experiments focused on anhydrite-bearing carbonates obtained from the Marrat formation, a Middle Eastern outcrop, utilizing a low magnetic field (2 MHz) NMR system, specifically the Geospec 2.1 rock analyzer from Oxford Instruments. Core samples were introduced into the NMR cell for T_2 relaxation time measurements. The NMR scanning parameters included a Tau value of 0.1 milliseconds, signal-to-noise ratio of 100, and a recycle delay of 11,250 milliseconds. Measurements were conducted on each sample at 100% water saturation ($S_w = 1$) and after desaturation (at S_{ir}) using the centrifuge. Centrifuging is to expel movable water within connected mesopores and macropores using centrifuge equipment at 16,000 RPM for 4 days. The T_2 distribution of NMR was acquired for six samples under both water-saturated and centrifuged conditions. The T_2 distribution curves, under water-saturated and centrifuged conditions were derived. The T_2 cutoff (T_{2C}) is the effective boundary for identifying the free fluid index (FFI) corresponding to macropores (seepage pores) and the bound water irreducible (BWI) corresponding to mesopores and micropores (adsorption pores). This distinction helps differentiate between bound and movable fluids in rock pores. SEM experiments were conducted on anhydrite-bearing samples. Six samples with varying anhydrite compositions underwent SEM-EDS observations using the

Zeiss Laser Crossbeam 550 scanning electron microscopic equipment. In this experiment, samples were divided into small pieces and coated with a thin layer of palladium. The mineral composition of the samples was determined through X-ray diffraction (XRD), employing the D8 DISCOVER X-ray diffractometer for the experiment.

Oil recovery experiments were conducted for two of the rock samples (samples S-5 and S-6), where dolomite predominated in the composition along with substantial amount of anhydrite. The experiments include spontaneous imbibition oil recovery using Amott imbibition cells. Subsequently, the samples underwent seawater flooding, followed by nonionic foaming surfactant (0.025% wt. Triton X-100 solution) and CO₂ injections. These experiments aimed to evaluate the influence of anhydrite composition on oil recovery potential, simulating primary reservoir recovery through spontaneous imbibition of formation brine, as well as secondary recovery via seawater flooding, and tertiary recovery through injection of foaming surfactant and supercritical CO₂.

5.4 Results

5.4.1 Physical properties and Mineralogy

The rock samples' petrophysical properties and mineral composition are outlined in **Table 5.1**. The quantitative analysis of the rocks' mineral composition by XRD reveals that the predominant mineralogy is anhydrite, its content ranges from 9.3 – 99.8%, with dolomite following as the subsequent major component (0 – 90.2%). Traces of other minerals such as calcite, quartz and feldspar were also noticed, and the range of these combined minerals composition is 0. – 3.7%. The XRD results are presented in **Figure 5.2**. Permeability and porosity data (Table 11) indicated that the porosity of the samples is within the range of

0.35% to 6.55%. Although an increase of surrounding rock pressure due to compaction of the rock matrix can also impact the porosity, there is a notable correlation between decreasing anhydrite content and increased dolomite composition, leading to an increase in porosity. The permeability values range from 0.040 to 0.165 mD.

Table 5.1. Dimension and basic properties of the samples.

Sample #	Anhydrite (%)	Dolomite (%)	Others (%)	Diameter (cm)	Length (cm)	Dry	Porosity (%)	Permeability (mD)
						weight (g)		
S-1	99.8	0	0.2	3.769	4.55	115.46	0.35	0.040
S-2	96.9	2.9	0.2	3.746	4.31	106.4	1.46	0.067
S-3	91.1	8.9	0.0	3.762	4.69	119.36	1.78	0.068
S-4	49.5	50.5	0.0	3.740	4.14	103.12	2.38	0.087
S-5	18.2	78.1	3.7	3.789	5.10	143.93	5.15	0.126
S-6	9.3	90.2	0.5	3.823	5.12	90.81	6.55	0.165

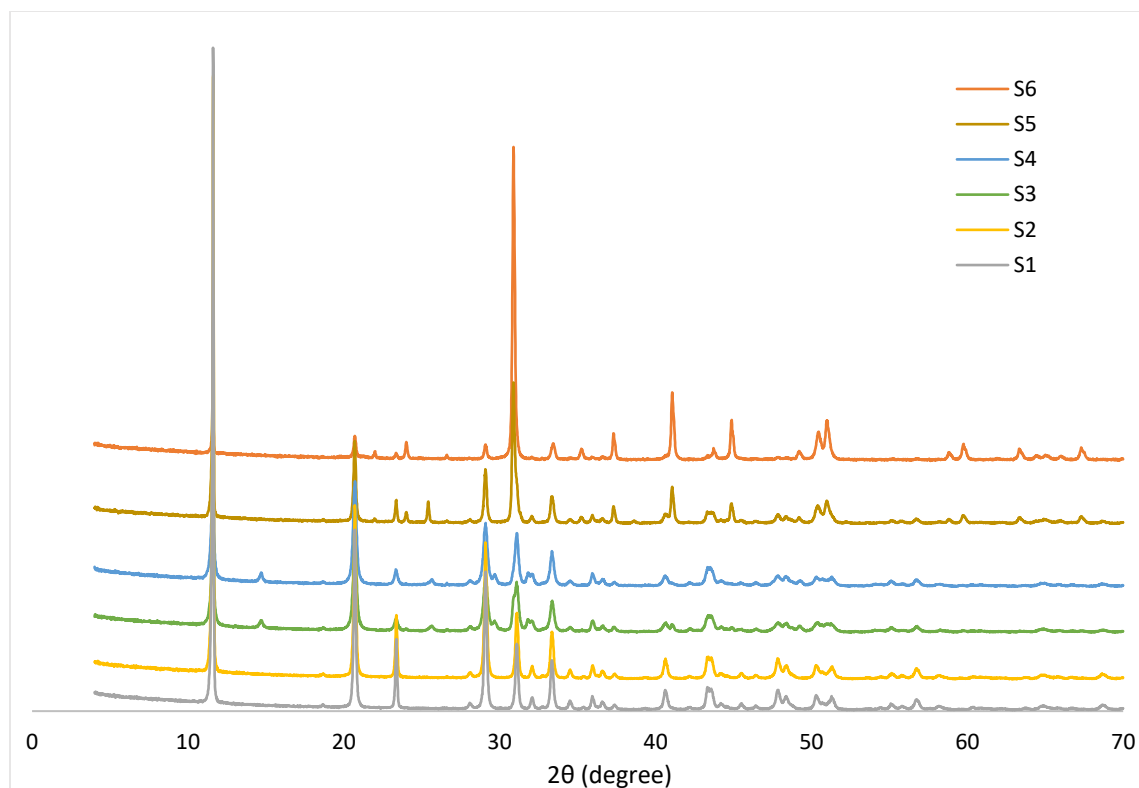


Figure 20. XRD spectra shows the mineralogy of the samples (S-1 to S-6) composed mainly of anhydrite and dolomite.

5.4.2 Pore types and morphology

The petrographic analysis of the studied samples is consistent with the other analyses tools such as XRD and field observations. The dolomite units are mainly composed of skeletal wackestone-packstone to skeletal oncoidal grainstone (**Figure 5.3 D-F**) with variable skeletal grains such as bivalves, gastropods and brachiopods. The lower dolomite unit (S-6) is composed of skeletal oncoidal grainstone that have some visible pores (macropores) in form of moldic and intra-particle pores and micropores within the matrix as well as within some grains. However, anhydrite is occurring as a cement that fills some of the interparticle pores and partial filling of some molds (Figure 5.3 E & F). Passing upward in the section (S-5 & S-4) with increase of anhydrite content, the anhydrite fills the

macropores; interparticle pores as well as the moldic and vuggy pores and leaves only mesopores and micropores, reducing both porosity and permeability (Figure 5.3 C & D). Further passing to the top of the section, the anhydrite content increases, with decrease of dolomite content, and form blocky anhydrite crystals that have no obvious pores (micropores), reducing both porosity and permeability (S-3 to S-1). Similar cases of this diagenetic parasequence were reported in literature where anhydrite had a significant role in porosity and permeability reduction (Abdolmaleki et al., 2016; S. Morad et al., 2012; Nikbin et al., 2021).

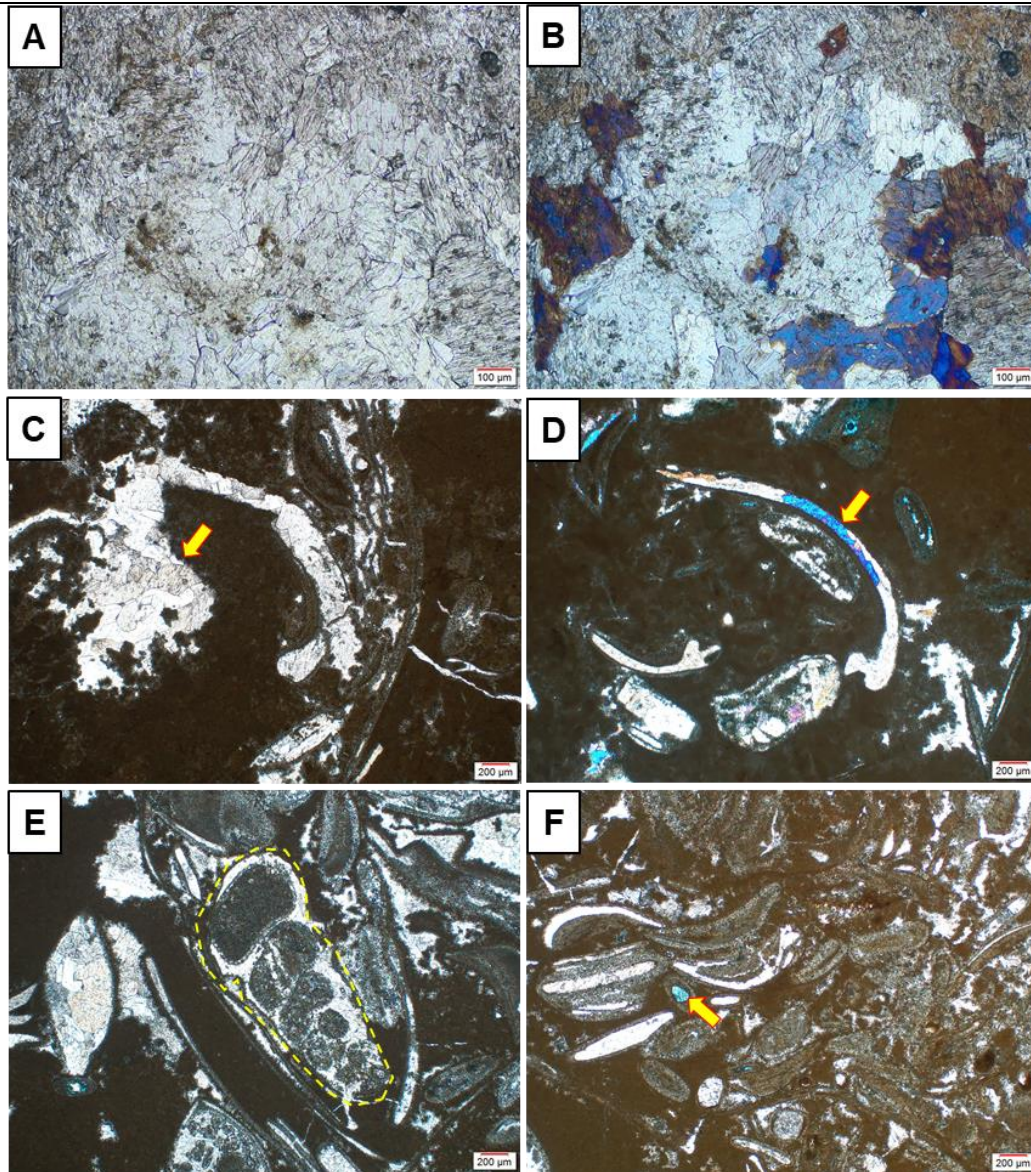
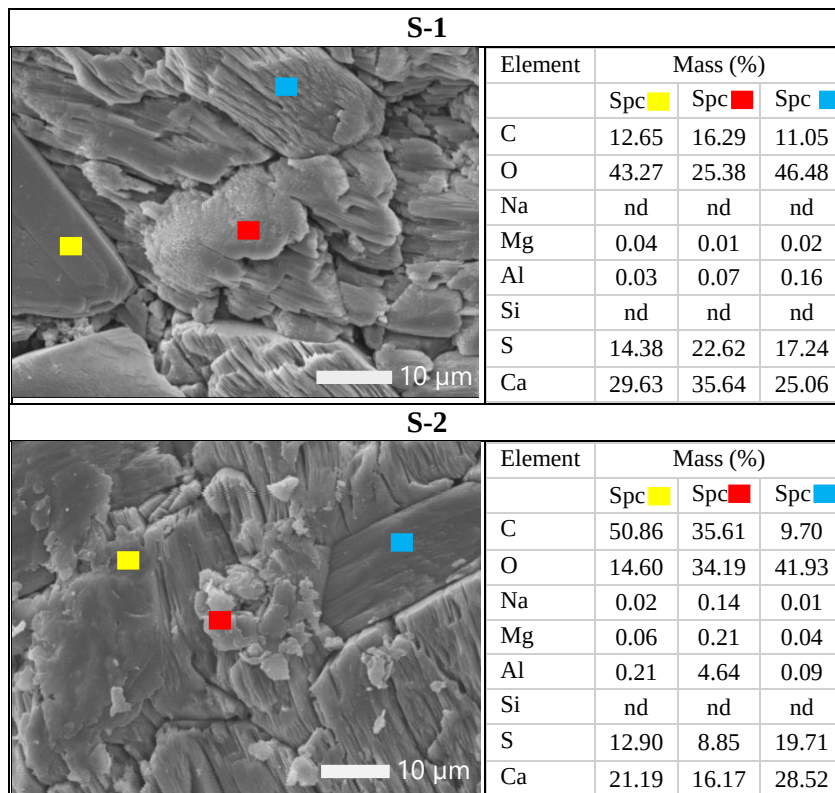


Figure 21. Thin-section photomicrograph of the studied samples. (A) PPL thin-section photomicrograph of sample (S-1) showing the anhydrite blocky crystals with no obvious porosity. (B) XPL of (A). PPL thin-section photomicrograph of anhydrite precipitation within large vug of the dolomite unit (S-4). (D) XPL thin-section photomicrograph showing the anhydrite cement within bivalve skeletal mold (arrow) of sample S-5. (E) PPL thin-section photomicrograph showing gastropod skeletal grain (dotted line) with microporosity within grain chambers of sample S-1. (F) PPL thin-section photomicrograph showing the presence of moldic pores within the skeletal oncoidal grainstone unit (arrow) of sample S-1.

The scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis revealed a variation in mineral composition from the upper to the bottom sections of the sampled intervals (**Figure 5.4**). Specifically, it was observed that moving from the upper section towards the bottom, there is a decrease in anhydrite content accompanied by an increase in dolomite content. This transition is characterized by the formation of blocky anhydrite crystals in the upper sections, which exhibit minimal porosity. However, as one progresses downward through the sections (from S-1 to S-3), there is a shift towards the formation of porous anhydrite-dolomite units, indicating a more heterogeneous composition. Further down the sections (S-4 to S-6), dolomite becomes the predominant mineral component, with reduced anhydrite content compared to the upper sections.



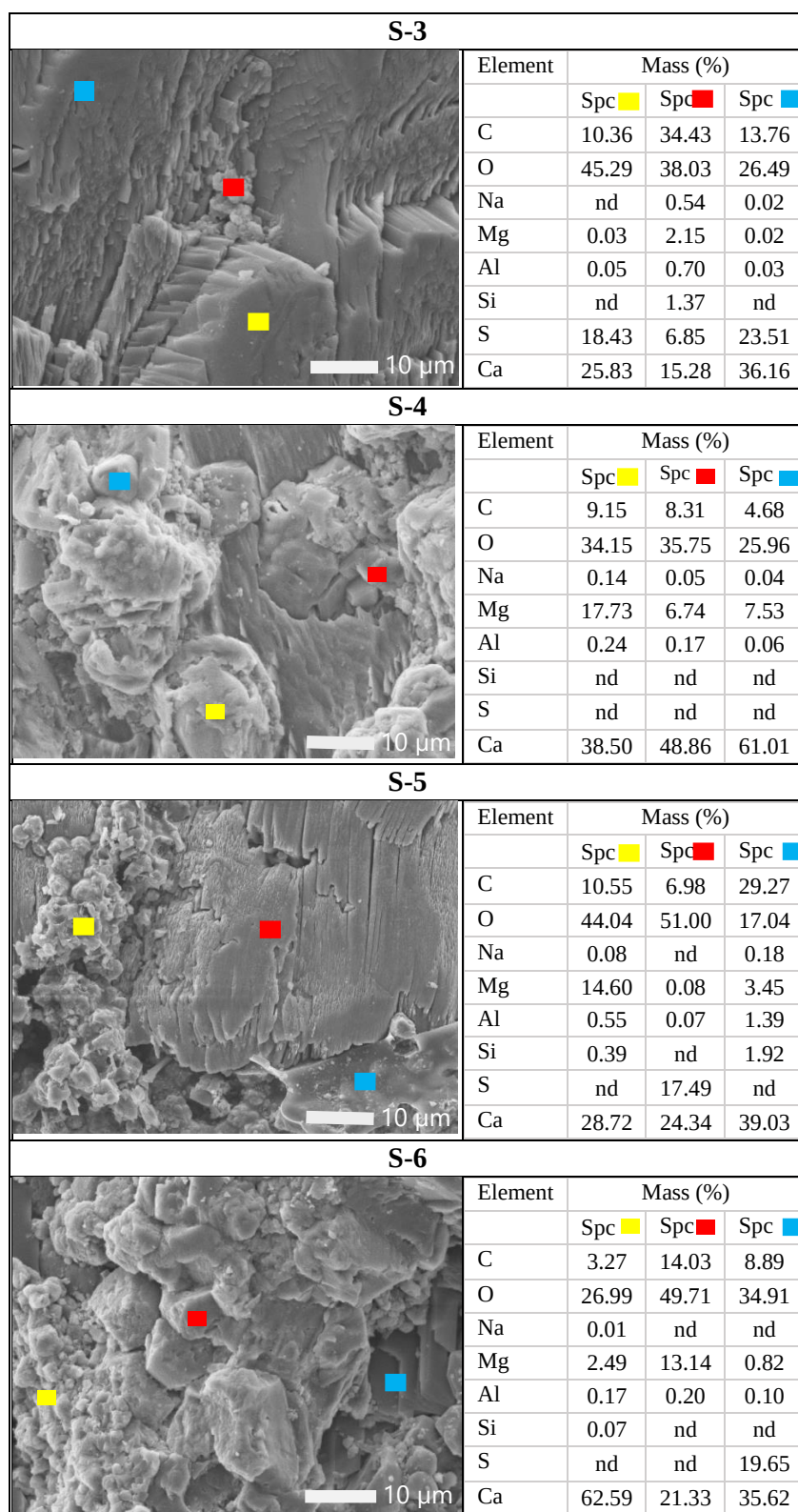
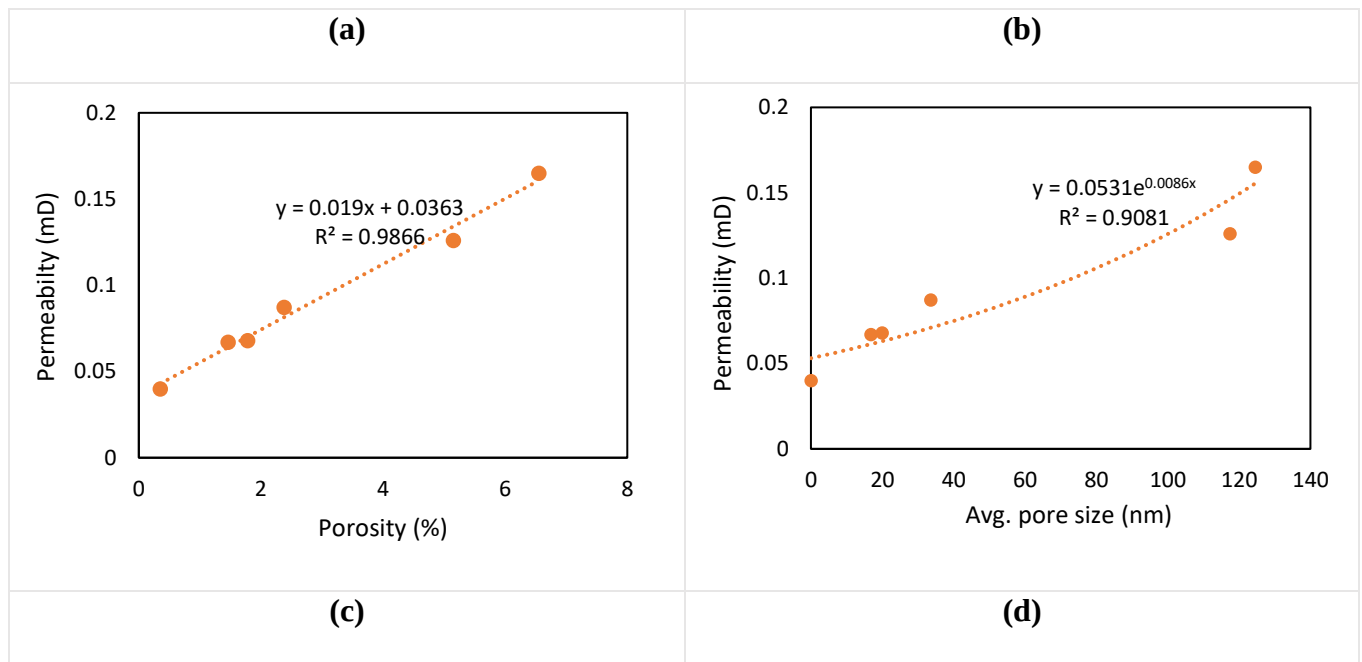


Figure 22. Scanning electron microscope-electron dispersive X-ray spectroscopy (left column) showing the corresponding elemental compositions of the six anhydrite/dolomite samples obtained from the Marrat formation.

5.4.3 Petrophysical properties

The petrophysical properties of the rocks, including porosity, permeability, and electrical resistivity at brine saturated condition, were compared through cross-plots to analyze relationships. Specifically, the relationship between permeability and porosity was found to be linear and positively correlated, with correlation coefficient of 0.9866 as shown in **Figure 5.5a**. Additionally, permeability demonstrated an exponential direct correlation with the average pore size, yielding an R-squared value of 0.9081 (**Figure 5.5b**). Conversely, both permeability and porosity exhibited a linear inverse correlation with electrical resistivity, both with R-squared values greater than 0.81 (**Figure 5.5c and d**). This implies that as the porosity and permeability of the samples increases, the electrical resistivity of the rocks decreases.



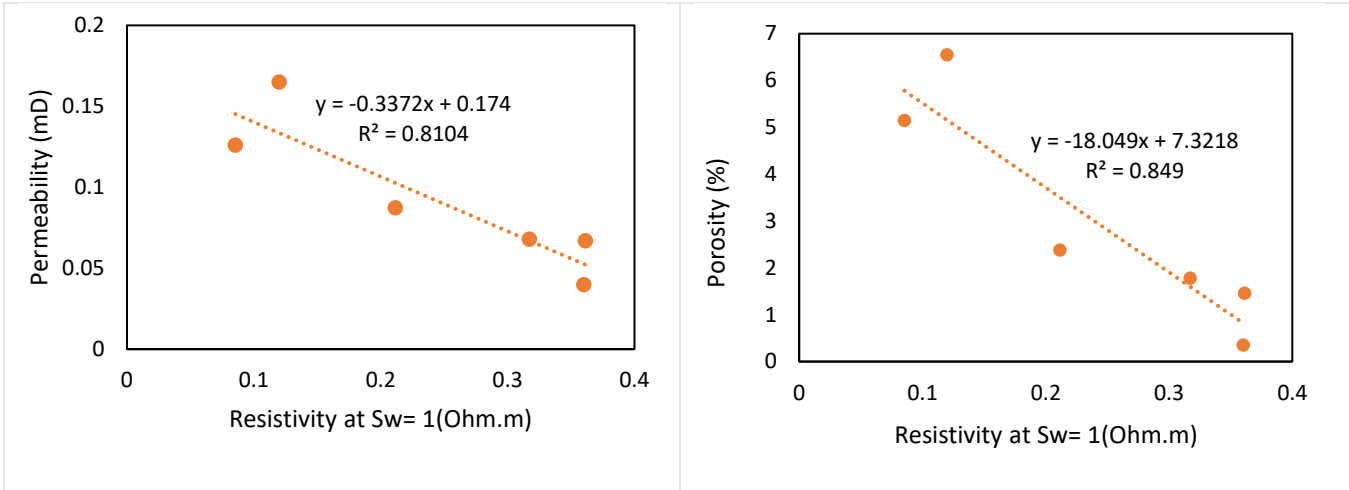


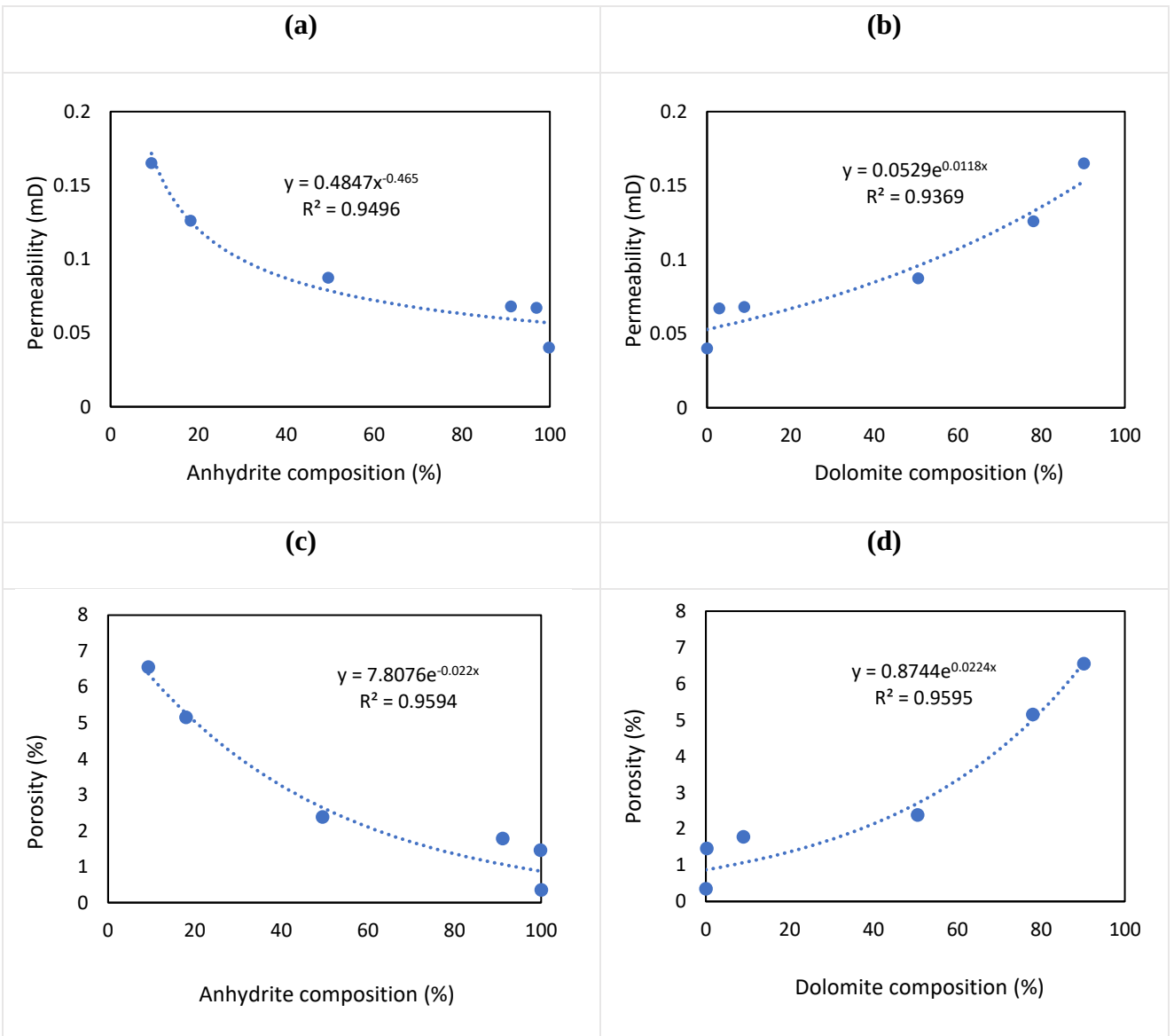
Figure 23. The relationship between the rocks' porosity, anhydrite and dolomite composition, resistivity, average pore size and the log mean of the transverse relaxation time.

5.4.4 Relationships between mineralogy and the physical properties

The lithology of the rock samples, specifically the anhydrite and dolomite content, were compared with the petrophysical parameters of the rocks, including permeability, porosity, and electrical resistivity. For each case, the best-fitting relation was selected for the analysis. As shown in **Figure 5.6a and b**, the permeability of the studied samples demonstrated a power-law inverse correlation with anhydrite content ($R^2 = 0.9496$), while the amount of dolomite exhibited an exponentially direct correlation with permeability, with an R-squared value of 0.9369.

For porosity versus mineralogy, an exponential fit was found to be the most suitable. The porosity of the samples is inversely proportional to anhydrite content and directly proportional to dolomite percentage as illustrated in **Figure 5.6c and d**. The resistivity of the rocks is exponentially correlated to both anhydrite and dolomite content, with a direct correlation for anhydrite and an inverse relationship with dolomite content (**Figure 5.6e and f**). This shows that the reservoir quality, as indicated by the analyzed petrophysical

parameters including porosity, permeability, and electrical resistivity of the rocks decreases as anhydrite content in the rocks increases. This is mainly attributed to the fact that anhydrite precipitate as cement that, at first, fills the interparticle pores, and with more anhydrite concentration other pore types such as inter-particle, moldic vuggy, and fractures will be filled by anhydrite, leading to decrease porosity and permeability significantly. Similar findings were also reported in the literature (Amel et al., 2015; Kadkhodaie et al., 2022; Morad et al., 2012).



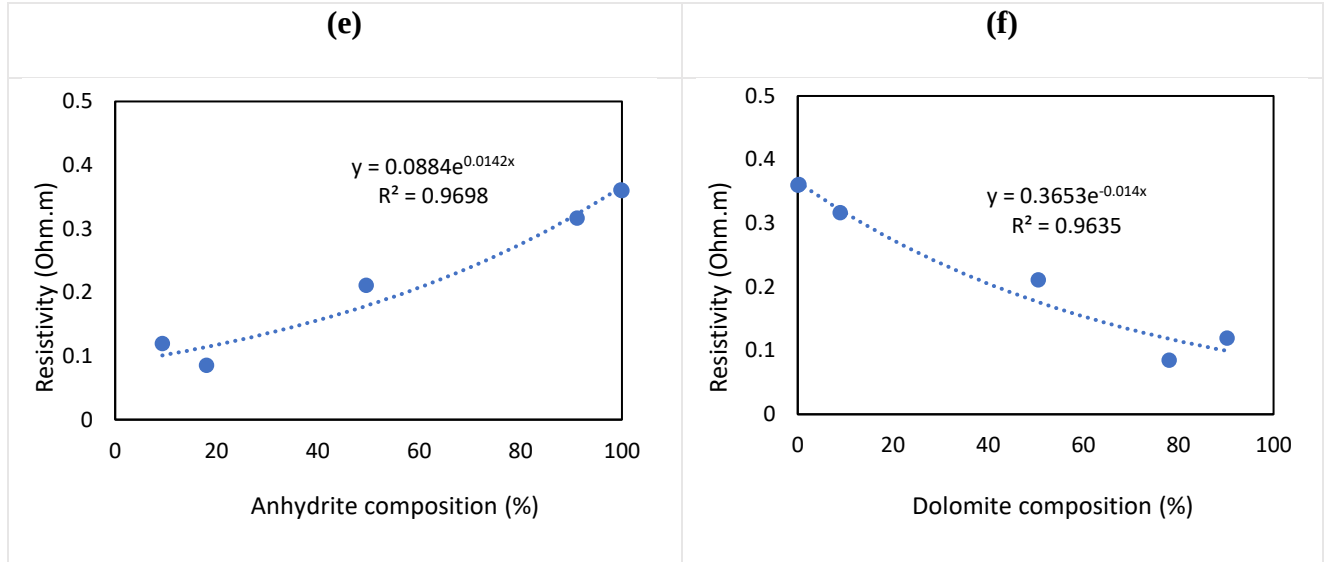


Figure 24. Relationship between the rocks' permeability, anhydrite and dolomite composition, porosity, resistivity, average pore size and the log mean of the transverse relaxation time.

5.4.5 NMR T_2 Relaxation time Distribution

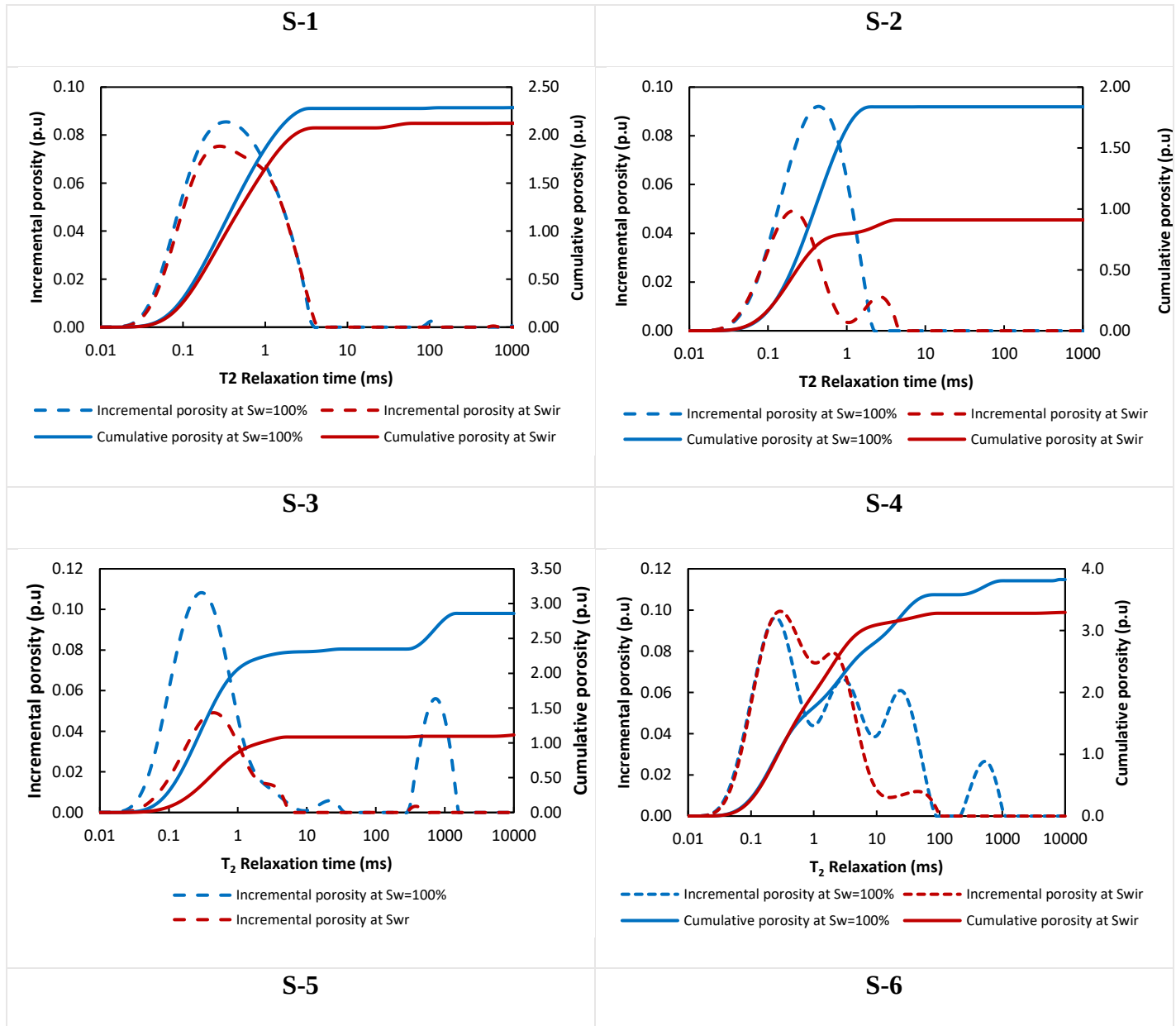
The samples exhibit a noticeable shift of the NMR T_2 curve towards the right, from S-1 through S-6 with decreases anhydrite composition as shown in **Figure 5.7**. The T_2 relaxation time of the spectra varies across different samples: for S-1 and S-2, it ranges from 0.01 to less than 10 ms; for S-3 and S-4, it spans from 0.01 to 1000 ms; and for S-5 and S-6, it extends from 0.01 up to 10000 ms. The amplitude peaks also varies, starting as low as 0.085 p.u for S-1 and up to 0.19 p.u. This shift signifies a gradual enlargement of pore size, corresponding to an increase in the dolomite content in the rocks. Additionally, the pore size distribution ranges from unimodal to multimodal, emphasizing the diverse pore sizes and the considerable heterogeneity in the studied rocks. This observed pattern highlights that the studied rocks are composed of both small and relatively larger pores. Moreover, the diverse mineralogy also controls the relaxation time, for example, in the study by (Heng Wang et al., 2018), the influence of mineralogy on NMR T_2 relaxation time

was observed. They indicated that in carbonates and sandstones, the presence of anhydrite cements leads to reduced NMR T_2 values for both micropores and macropores. The presence of broad pore systems contributes to the complexity observed in the T_2 distribution (Wang et al., 2018).

Moreover, a reduction in anhydrite composition results in a larger area enclosed by the T_2 curve, indicating an increase in the pore space of the rocks due to changes in mineral composition. For the de-saturated rocks, there is a decrease in the signals of the macropores peaks, with some samples, such as S-6, showing complete disappearance of this signal. This is attributed to larger pores being more easily displaced, suggesting that movable fluids reside in these pores.

To further investigate the impact of mineralogical heterogeneity on pore structural changes, the pores can be categorized into micropores, mesopores, and macropores based on the NMR T_2 distribution. Micropores, representing the initial peak in the T_2 spectrum (from the left), are distinguished from the mesopores and macropores, identified as the second and third peaks, respectively, in Figure 5.7. These larger pores are commonly referred to as seepage pores, i.e., the path responsible for fluid flow (Yao et al., 2008). In this classification, NMR signals with a T_2 value less than 1.0 ms ($1.0 < T_2$) are designated as micropores, while signals with a T_2 relaxation time ranging from 1.0 ms to 10.0 ms ($1.0 \leq T_2 \leq 10.0$) are identified as mesopores, specifically adsorption pores. The pore size distribution of the anhydrite-bearing rocks is in the range of 0.01–125 nm shows a multimodal distribution. Both micropores and mesopores have an average pore size of less than 50 nm. Conversely, NMR signals with a T_2 value larger than 10.0 ms ($T_2 > 10$ ms)

correspond to macropores, are seepage pores with pore sizes exceeding 50 nm (Elsayed et al., 2022; Isah et al., 2021b; Ma et al., 2019; Yao et al., 2010).



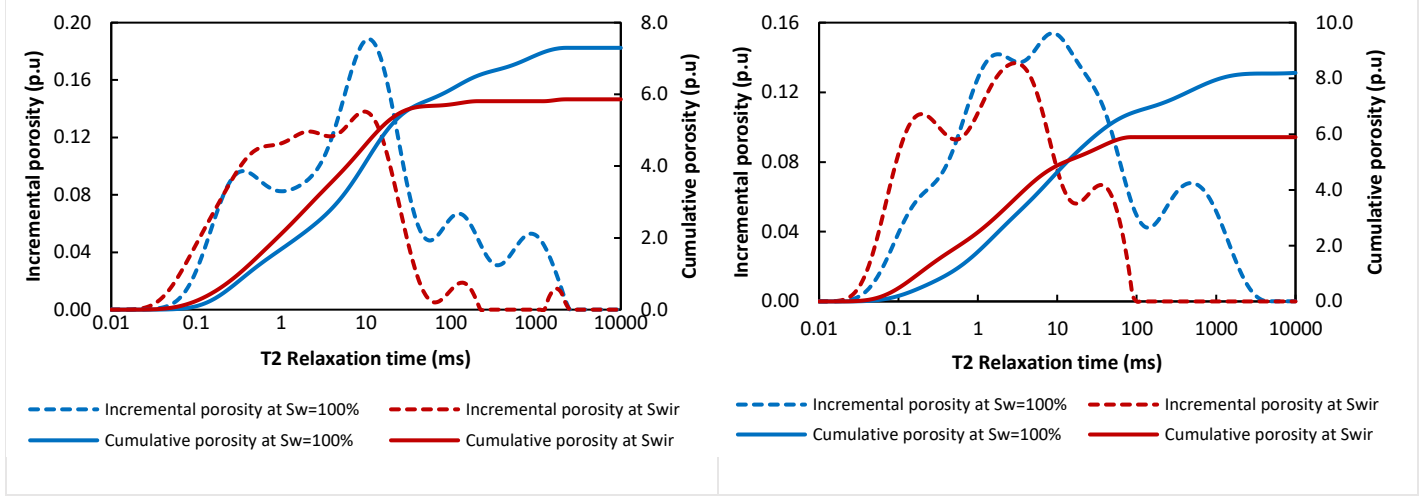


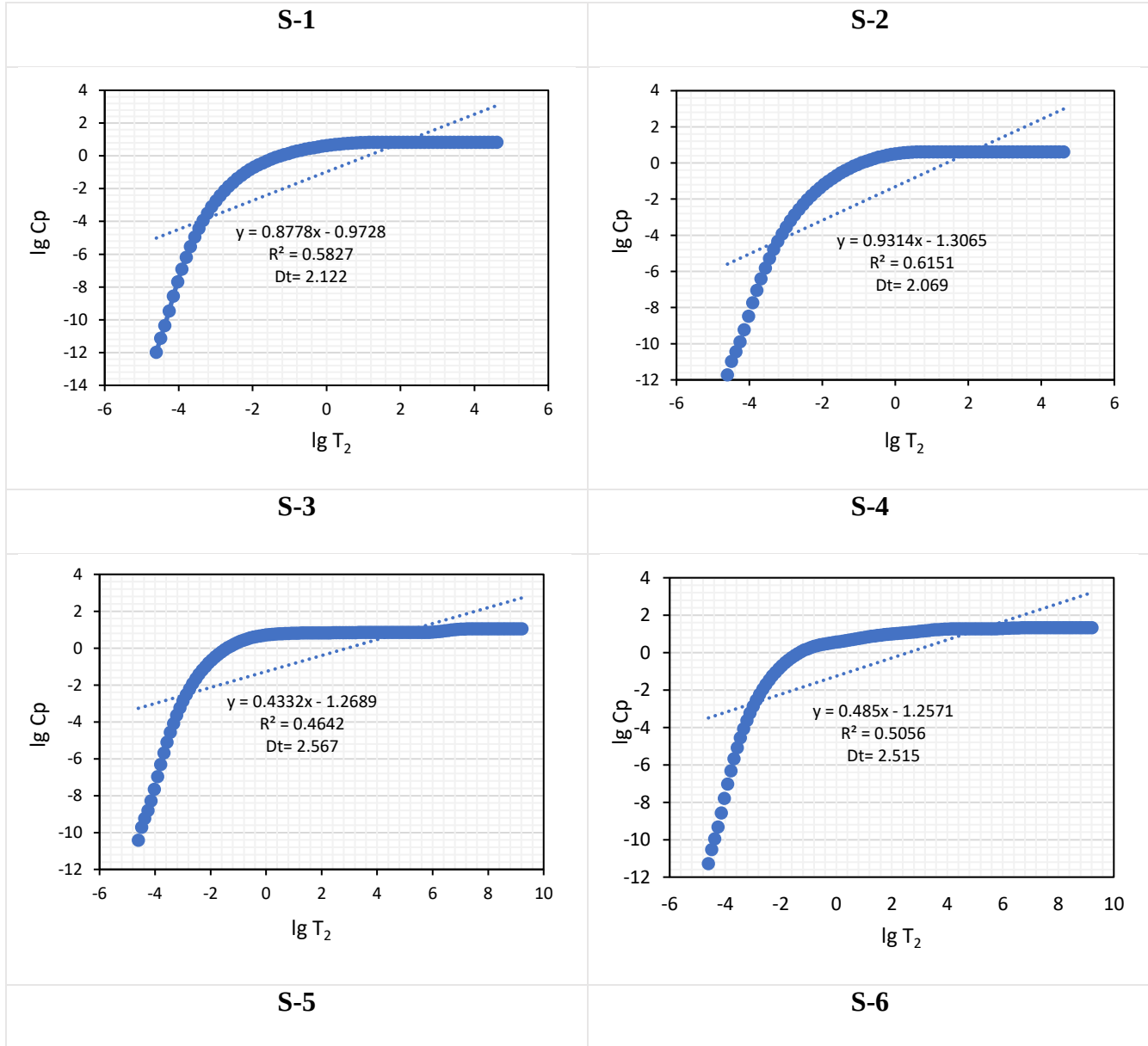
Figure 25. T2 relaxation measurements for the six rock samples at fully brine saturation and after centrifuge displacement test: S1, S2, S3, S4, S5, and S6, where incremental porosity at fully brine saturation (blue line), cumulative porosity at fully brine saturation (blue continues line), cumulative porosity post drainage with air (red continues line), and incremental porosity post drainage with air (red dashed line).

5.5 Discussions

5.5.1 Fractal dimension characteristics using NMR.

Figure 5.8 shows the results of the linear fit of $\log(C_p)$ versus $\log(T_2)$ using Eq. (6). The analysis of D (fractal dimension) for total pores indicates that the R^2 values are relatively low, suggesting a lack of strong correlation. The fitting correlation coefficients range from 0.4642 to 0.6151, suggesting that the pore structure obtained through NMR across the whole scale does not exhibit clear fractal characteristics. This implies that the fractal dimension of the pore structure is not consistent across the entire spectrum of pore radius (Zhou et al., 2022). The poor correlation coefficients indicate the presence of heterogeneity and complexity in the pore structures of the studied rocks. Consequently, for complex pore system, it is deemed unreliable to draw definitive conclusions based on relationships with low R^2 values. Therefore, since NMR can describe the fractal features of wider range of

pore sizes compared to other methods (Zhao et al., 2017). The multiscale fractal dimensions of sub-pores, specifically the micropores, mesopores, and macropores, are subsequently computed and analyzed.



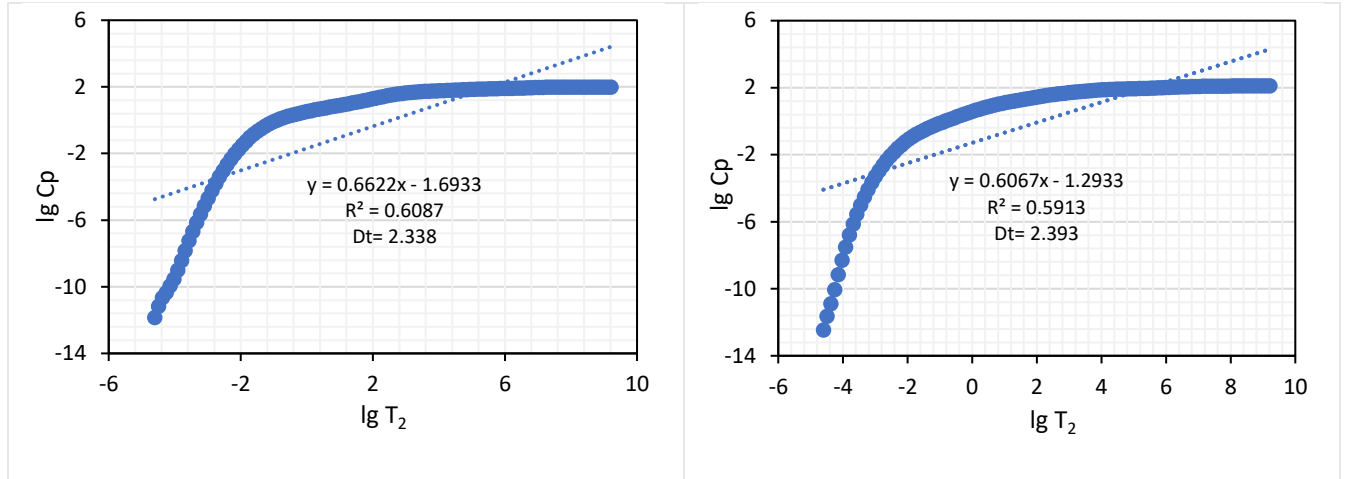


Figure 26. Total NMR fractal dimension (Dt) for the six rock samples at fully brine saturation obtained using NMR method.

The pores in the rock are grouped into three categories based on the pore size, i.e., micropores, mesopores, and macropores. As for the whole sample fractal dimension Dt, it was found that Dt ranges from 2.069 to 2.567 with correlation coefficients that are much lower than those of D1, D2 and D3, implying that the sample has a medium complexity pore structure with fractal characteristics, however the low R^2 value make this unreliable. For the multiscale fractal dimensions, the correlation coefficients are greater than 0.81 in most cases, indicating clear fractal characteristics in macropores (D1), mesopores (D2), and micropores (D3). The D1 values are notably lower than D2 and D3, signifying that mesopores and macropores exhibit greater complexity compared to micropores (Zhang et al., 2023; Zhou et al., 2022). **Table 5.2** and **Figure 5.9** present the multiscale fractal dimensions of micropores, mesopores, and macropores within the rocks. Figure 5.9 shows the results of the linear fit of $\log C_p$ versus $\log(T_2)$ using the NMR method for fractal dimensions of the extracted micropores (D1), mesopores (D2), and macropores (D3). This analysis corresponds to different values of T_2 , representing various pore sizes, structures, and complexity in the pore network. The fractal dimension of macropores and mesopores

are generally larger than the values for the micropores, suggesting a more complex pore structure in the larger pores. Samples S-1 and S-2 uniquely display only two fractal dimensions, D1 for micropores and D2 for mesopores, linked to their bimodal pore size distribution evident in the NMR T_2 relaxation (refer to Figure 5.7 above).

According to fractal geometry theory, the fractal dimensions of pores in rocks typically fall within the range of 2 to 3 (Benoit et al., 1984; Wang et al., 2012; Yao et al., 2010). A fractal dimension closer to the lower limit of 2 suggests a more uniform pore structure, while a value closer to the upper limit of 3 indicates a more complex, irregular pore structure (Z. Ouyang et al., 2016). While typical fractal dimensions based on fractal theory range between 2 and 3 (see above), the fractal dimensions of the micropores (D1) are observed to be consistently less than 2. Therefore, the fractal characteristics of the micropores of the studied rocks are not obvious (Zhao et al., 2022). In contrast, fractal dimensions of mesopores D2 and macropores D3 show significant fractal characteristics. The fractal dimension of mesopores demonstrates a decreasing trend from S-1 to S-6, indicating less complex pore structures within this range.

Fractal dimension of pore hosting the movable fluid (mesopore and macropores) are typically larger than the fractal dimension of the bound fluid (micropores), indicating that the distribution of pores associated with movable fluid is more complex compared to those linked to bound fluid (Jun Liu et al., 2018; Xinhe Shao et al., 2017). This suggests that the pore network related to movable fluid within the tight rock exhibits more evident fractal characteristics compared to the pore network associated with bound fluid. In addition, the fractal dimensions of micropores and macropores exhibit irregular trends, which can be attributed to the complex spatial distribution of minerals in the rock matrix and the varied

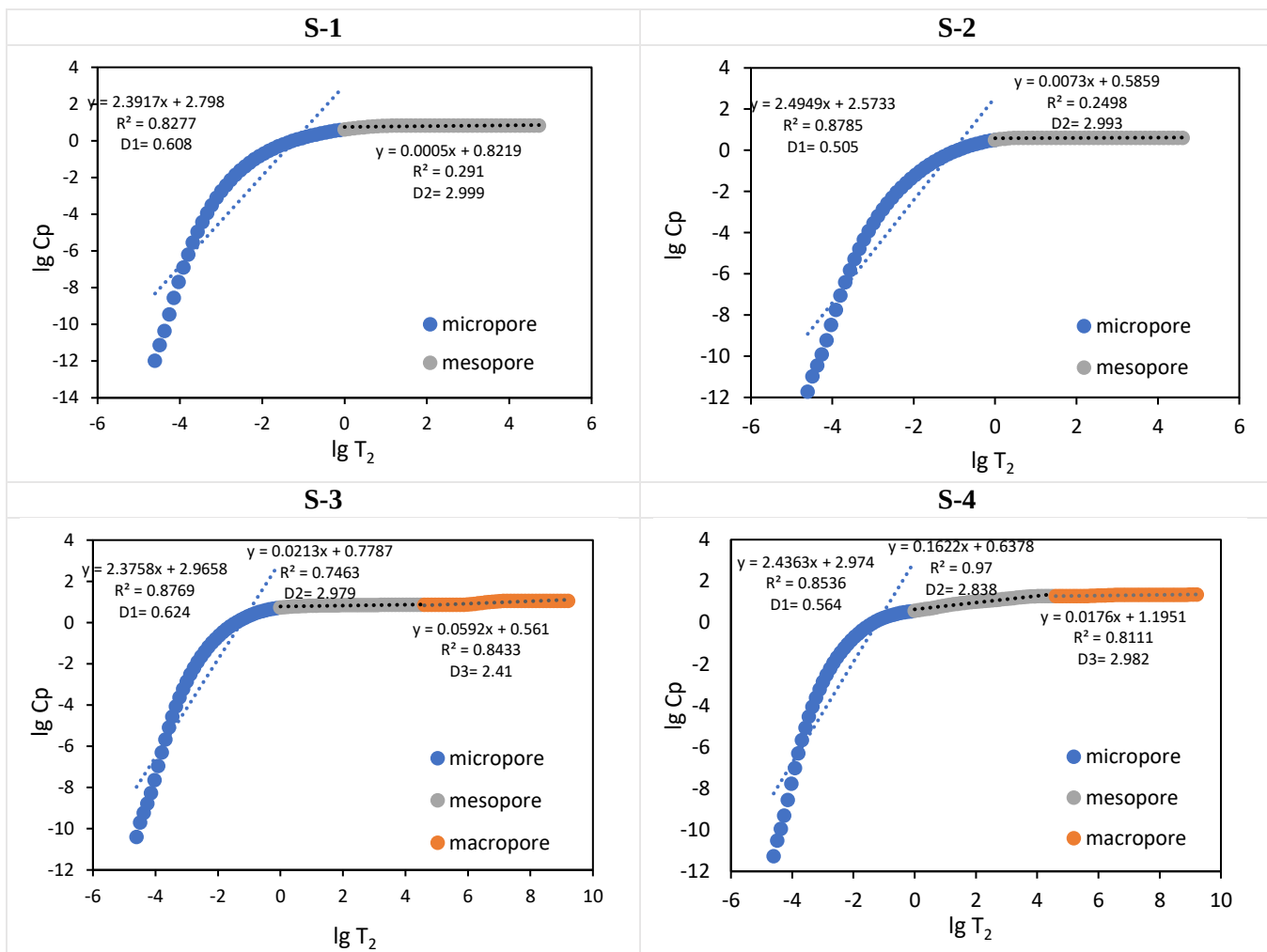
responses of different minerals to NMR relaxation. Alternatively, the irregularities may have resulted from the presence of microcracks or microfractures in the rock, contributing to the porosity of macropores and influencing the observed fractal dimensions.

Table 5.2. Fractal dimensions of the micropores, mesopores and macropores for the rock samples with their corresponding correlation coefficient.

Sample #	Fractal Dimension					
	Micropore (D1)	R ²	Mesopores (D2)	R ²	Macropores (D3)	R ²
S-1	0.608	0.8277	2.999	0.291	-	-
S-2	0.505	0.8785	2.993	0.2498	-	-
S-3	0.624	0.8769	2.979	0.7463	2.410	0.8433
S-4	0.564	0.8536	2.838	0.9700	2.982	0.8111
S-5	0.249	0.9227	2.683	0.9693	2.960	0.8925
S-6	0.498	0.8488	2.724	0.9536	2.958	0.8802

Analyzing Figure 5.9, it follows that the values of D1 and D2 for samples exhibiting a unimodal/bimodal NMR T_2 distribution are higher than those with a multimodal T_2 distribution. Interestingly, samples displaying multimodal behavior exhibit a broader distribution of NMR parameters and fractal dimensions (D1, D2, and D3), indicating a wider distribution of porous material, characterized by the coexistence of small and large pores. In particular, for samples exhibiting unimodal/bimodal T_2 distribution behaviors and a high content of short components (T_2), the fractal dimension of the pore structure tends to approach 3.0. For instance, samples like S-1 and S-2 demonstrate a fractal dimension of 2.999 and 2.993 (Figures 5.9a and b) for D2. It is documented in the previous studies that micropores are the primary contributors to heterogeneity and irregularity in tight rocks, and

the fractal dimensions serve as indicators of the degree of micropore development (Cai et al., 2010; F. Yang et al., 2014). Conversely, samples displaying multimodal behaviors and a high content of long components (T_2) exhibit the lowest fractal dimensions (Lai et al., 2018). Similarly, a study by (Zhang et al., 2019), showed using NMR that based on the fractal theory, the pore structure of macropores is more complex compared to the mesopores. In contrast, the pore structure of micropores corresponds to the least complexity. They indicate that macropores have the most obvious fractal characteristic, followed by mesopores and micropores.



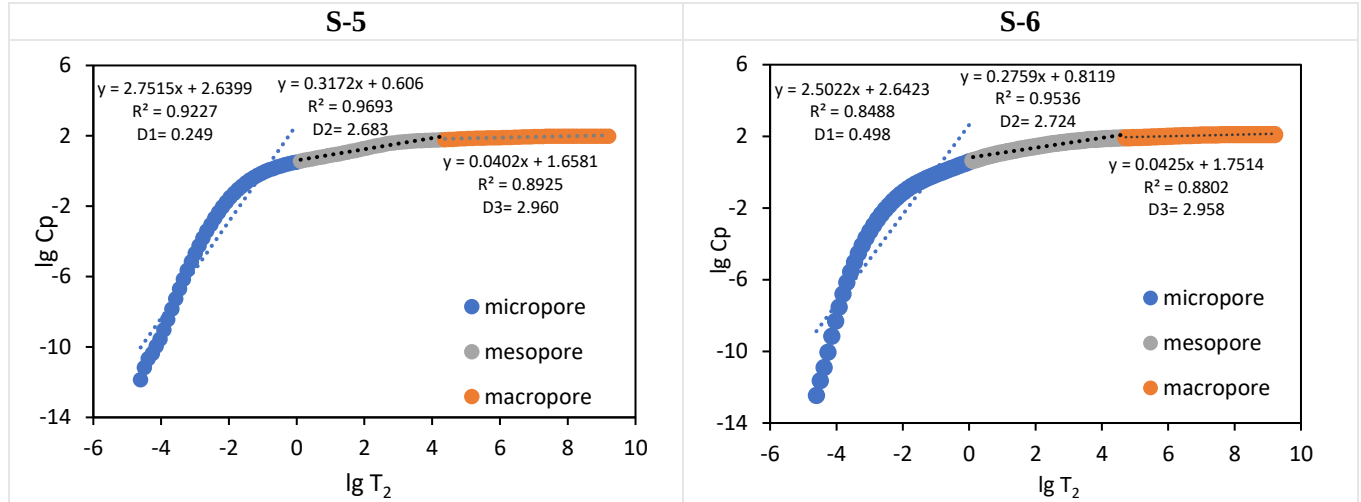


Figure 27. Multi-scale fractal dimensions: micropore (D1), mesopore (D2), and macropore (D3) obtained using NMR T2 relaxation measurements for the six rock samples at fully brine saturation.

5.5.2 Relationships between fractal dimensions and physical properties

A series of plots are used to analyze the relationships between fractal dimensions and petrophysical properties of the rocks as shown in **Figure 5.10**. The fractal dimensions of micropores (D1) and macropores (D3) do not exhibit consistent correlations with the porosity, permeability, electrical resistivity, and average pore size of the rock samples, as indicated by their R-squared values in Figs. 9a through d. This poor correlation is explained by the fact that micropores do not contribute to the flow or storage of movable fluids in the rocks. On the other hand, macropores may consist of microfractures and microcracks, introducing a complex nature to the pore network. There is no apparent correlation between porosity, permeability, and the roughness and complexity of micropores and macropores in this study. Consequently, the relationship between fractal dimensions D1 and D3 with rock permeability is not evident. Thus, the analysis relies more on mesopores, as they host both movable and bound fluids in the rock and considering the excellent correlation coefficients (0.79 to 0.95) displayed.

Similar study by (Zhou et al., 2022), utilizing mercury injection porosimetry (MIP) and NMR experimental data, showed that the contribution to permeability from distinct pore diameters were computed. The findings reveal that the permeability contribution from micropores was negligible and can be ignored. Mesopores accounted for approximately 1–5% of the permeability contribution, while macropores constituted approximately 95–99%, playing a crucial role in determining the fluid flow dynamics. Fractal dimensions are typically associated to the complex nature of micropores, while the presence of mesopores and macropores improves porosity (Jun Liu et al., 2018; F. Yang et al., 2014). Thus, higher porosity can be attributed to a smaller proportion of micropores relative to total pores. Consequently, rocks with high porosity tend to exhibit a lower pore fractal dimension, as observed in Figure 5.10a.

The fractal dimension of mesopores (D_2) shows a linear inverse correlation with porosity and permeability (**Figures 5.10a and b**). The correlation coefficients (R^2) for the fitted curves are 0.0.7862 and 0.8088 for fractal dimension versus porosity and permeability, respectively, indicating a strong correlation D_2 . This implies that as the porosity increases, the fractal dimension decreases, signifying that a higher fractal dimension corresponds to complex pore network development. Similarly, (Zhang et al., 2019) documented that correlation coefficients of micropores, mesopores, and macropores with porosity were 0.75, 0.93 and 0.92, respectively. This indicates that for the three pore subsystems, D_2 has a strong dependence on porosity. With increasing porosity, the fractal dimension of the mesopores decreased. This means that the pore structure of the mesopores became less complex, i.e., more uniform. In another research, the porosity decreases exponentially with the increase of pore structure fractal dimension (C. Hou et al., 2022).

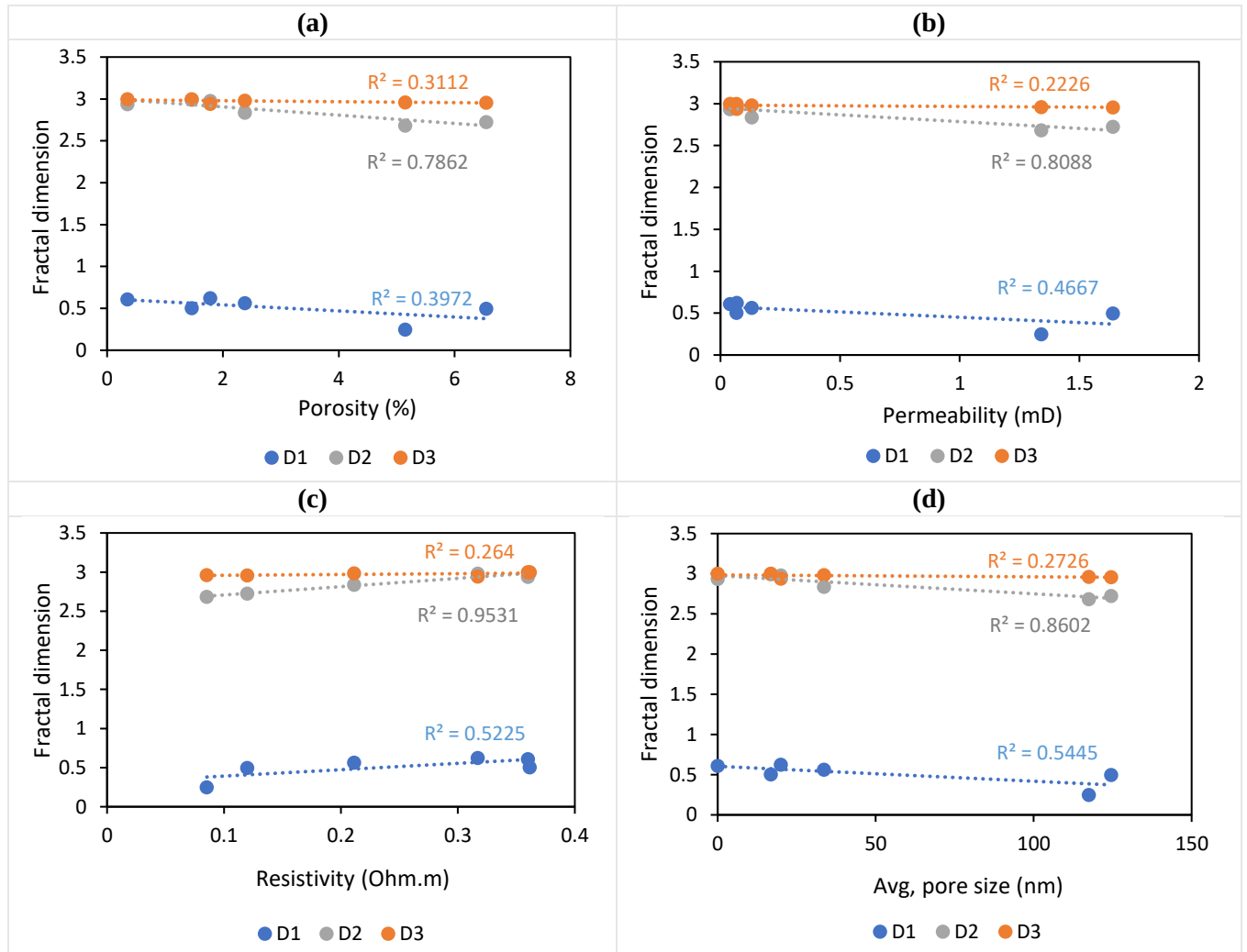


Figure 28. Relationship between the multi-scale fractal dimensions: micropore (D1), mesopore (D2), and macropore (D3) with anhydrite and dolomite compositions, porosity, permeability, resistivity, and average pore size.

The permeabilities of the rock samples decrease proportionally with increase in fractal dimensions, as depicted in Figure 5.10b. The interconnections among micropores, mesopores, macropores, and micro-fractures in the rocks play a crucial role in governing the matrix permeability. The increasing dominance of micropores and mesopores implies that the connecting channels between pores and/or fractures become progressively narrower, resulting in lower permeability (F. Yang et al., 2014). With the fractal dimensions increasing, the permeability contribution of microscale pores and nanoscale

pores in carbonates decreases (Wang et al., 2018; Xu, 2015; Yu & Li, 2011). Consequently, rocks with higher fractal dimensions ($D1$ and $D2$) typically exhibit lower permeability, given that higher fractal dimensions are often associated with an increased presence of micropores and mesopores compared to those with lower fractal dimensions. Moreover, higher porosity and permeability correspond to lower complexity and roughness in the pore structure.

$D2$ is linearly and directly correlated with formation resistivity (Figure 5.10c), indicating improved pore connectivity and reservoir quality. Consistent with the trend observed for the fractal dimension of mesopores regarding porosity and permeability, $D2$ also exhibit a linear inverse relationship with the average pore size of the rocks (Figure 5.10d), implying that larger pore sizes are associated with lower pore structural complexity. Furthermore, the complexity of pore distribution in mesopores is directly linked to porosity, permeability, and average pore size. If there is no mineral filling between the fluid pores, better connectivity corresponds to higher permeability. Thus, carbonate permeability is primarily attributed to the pore size and pore connectivity within the matrix. Additionally, the correlation coefficients in Figure 5.10 indicate that the petrophysical properties of the samples are more sensitively influenced by the structure of mesopores rather than larger macropores. The observed relationships indicate that high complexity of pore networks generally results in poor reservoir quality in tight rocks, whereas the influences on bound-fluid and movable-fluid pore volumes differ (Xinhe Shao et al., 2017).

5.5.3 Relationship between fractal dimensions and mineralogy

The lithology reflects the mineral composition of the rock samples. To investigate the relationship between various mineral compositions and fractal dimensions of distinct pore types (micropores, mesopores, and macropores), comparative diagrams illustrating fractal dimensions and different mineral compositions were plotted (**Figure 5.11**). Anhydrite is the primary mineral component in the samples, with its content varying from 9.3% to 99.8% (see above). The presence of anhydrite in carbonate is associated with diagenesis. Previous studies have indicated that the fractal dimension is either negatively correlated or not correlated with anhydrite content (C. Hou et al., 2022). The results show that the fractal dimension of micropores (D1) shows a linear and direct proportionality to anhydrite content; however, the poor correlation coefficient ($R^2 = 0.3457$) suggests that this relationship is not highly reliable. The fractal dimension of mesopores (D2) exhibits a linear positive correlation with anhydrite composition (Figure 5.11a, grey curve), displaying a strong correlation coefficient ($R^2 = 0.9053$). Conversely, there is no clear connection between the fractal dimension of macropores (D3) and anhydrite content, based on the low R^2 value of 0.2182.

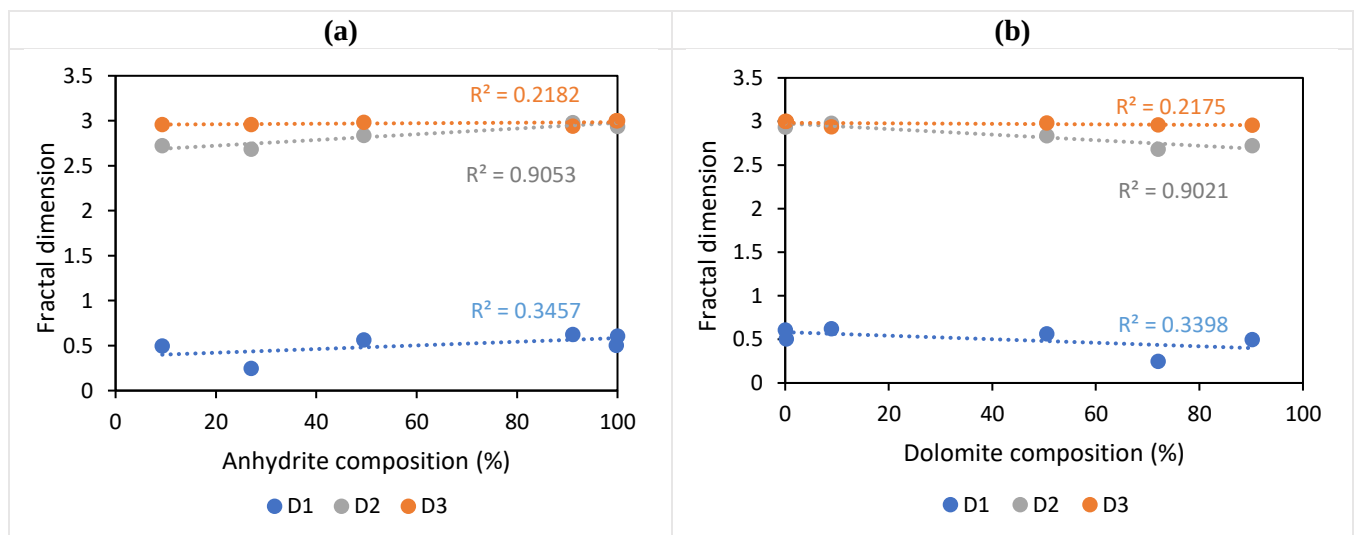


Figure 29. Correlation between the multi-scale fractal dimensions: micropore (D1), mesopore (D2), and macropore (D3) with anhydrite and dolomite compositions, porosity, permeability, resistivity, and average pore size.

Figure 5.11a shows a direct correlation between D2 and anhydrite content, indicating that high content of anhydrite may result in higher complicity of pore network related to movable fluid and bound fluid pores. It's essential to note that mesopores hosts both movable and bound fluids. High anhydrite content increases the complexity of pore distribution in both bound and movable fluids related to mesopores. Thin section analysis reveals that anhydrite content in the samples primarily acts as pore-filling minerals (see Figure 5.3 above). The high anhydrite content reduces the pore space of both bound and movable fluid pores in the rock matrix, leading to an increase in fractal dimension (D2) and higher complexity and roughness. However, anhydrite exhibits lower brittleness and compaction resistance, and a high anhydrite content reduces fracture development, primarily serving as a reservoir cap rock. The high content of anhydrite minerals in carbonate increases matrix heterogeneity and irregular pore morphology, contributing to an increase in the fractal dimension D2 observed. The fractal dimension of micropores and mesopores increases with an increase in anhydrite percentage. The irregular distribution of minerals in the rocks contributes to the uneven and complex pore structure of the pores. Additionally, the presence of anhydrite results in pore filling and the generation of more micropores on the pore surfaces, further enhancing surface roughness and heterogeneity. Similar to the weak correlation observed between the fractal dimension of macropores and anhydrite, there is no evident connection between D3 and dolomite composition ($R^2 = 0.2175$) as depicted in Figure 5.11b. Conversely, for D1 and D2, an opposite trend compared to anhydrite content is noted for dolomite composition. The D1 exhibits a low

R^2 (0.3398). The fractal dimension of mesopores (D2) demonstrates a linear inverse proportionality with dolomite composition (Figure 5.11b, grey curve), showing a strong correlation ($R^2 = 0.9021$). This suggests that rocks with higher dolomite composition display lower complexity and roughness in the mesopores, thus better reservoir quality.

5.6 Evaluation of oil recovery Performance

Despite the large occurrence of anhydrite in carbonates, the influence of reservoir mineralogy, specifically, anhydrite content on recovery enhancement, has not been comprehensively investigated. Understanding the effect of mineralogy in rock/fluid interaction is key to the success of any EOR method (Isah et al., 2022b). The presence of anhydrite and its distribution in rocks is important to precisely evaluate the performance of any IOR/EGR processes. To evaluate the potential for oil recovery in the anhydrite-bearing carbonates, spontaneous imbibition oil recovery and coreflooding experiments were conducted under varied temperature and pressure conditions, employing different fluid displacement processes. This includes spontaneous imbibition of formation brine in the primary recovery, and seawater, surfactant, and CO₂ floodings during the secondary and tertiary recovery processes.

5.6.1 Oil recovery by spontaneous imbibition of formation brine.

The spontaneous imbibition experiment utilized the Amott cells. Initially, the samples (S-5 and S-6) were saturated with formation water using the Vinci automatic saturation system. This involved vacuuming the samples for 3 hours, followed by loading brine using the suction principle. The samples were then pressurized at 3000 psi and left for 3 days to ensure complete saturation. Subsequently, the samples were centrifuged in Arabian

ultralight crude oil to displace the brine, using the ultracentrifuge system at 16000 RPM for 4 days to ensure proper brine displacement by the crude oil. Following this, the samples were aged in the crude oil for two weeks, and the spontaneous imbibition oil recovery was initiated: the cells were filled with formation brine surrounding the rock samples. Oil production was measured using the graduated Amott cells over a two-month period after no oil is being produced, and the recovered oil was measured and recorded.

In the case of sample S-5, the initial oil saturation (S_{oi}) and irreducible water saturation (S_{wir}) were calculated to be 78% and 22%, respectively. The total oil recovery during spontaneous imbibition amounted to 3.8% of the original oil in place (OOIP). For sample S-6, the initial oil and irreducible water saturations are computed as 83% and 17%, respectively. The total oil recovery during spontaneous imbibition for this sample was 5.0% of the original oil in place (OOIP). These results indicate that there is no significant difference in primary oil recovery for the two rock samples with different anhydrite compositions.

5.6.2 Impact of minerals composition on coreflooding EOR

Following the initial recovery through spontaneous imbibition, samples S-5 and S-6 underwent assessment for secondary and tertiary oil recovery potential through two comparable coreflooding experiments. In the secondary recovery phase, the samples were flooded with seawater, followed by surfactant, and CO₂ flooding in the tertiary recovery stage. The coreflooding was conducted at a temperature of 60 °C, with a confining pressure of 5500 psi, and a backpressure of 1500 psi was applied. For both seawater and surfactant flooding, the injection flow rate was maintained at 0.005 cc/min, while CO₂ flooding was

carried out at a rate of 0.05 cc/min. Each sample underwent injection of a total of 18 pore volumes of fluids during these coreflooding experiments. Effluent samples were taken at intervals during the seawater and surfactant flood for ions analysis.

For sample S-5, the overall oil recovery reached 19.7% of the original oil in place (OOIP) after seawater flooding, increased to 23% OOIP after surfactant flooding, and notably rose to 33.9% OOIP at the end of the experiment following the injection of 8 pore volumes (PV) of CO₂ as shown in **Figure 5.12**. This represents a substantial increase of up to 9.9% in recovery attributed to CO₂ flooding, noteworthy is that the CO₂ flooding was performed at supercritical state. **Figure 5.13** shows the oil recovery and pressure gradient profile for sample S-6, the cumulative oil recovery amounted to 23.7% OOIP after seawater flooding, rose to 27.3% OOIP after surfactant flooding, and further increased to 36.9% OOIP after injecting 8 PV of CO₂. Similar to S-5, this signifies a notable increase of up to 9.6 % in recovery following CO₂ flooding. **Table 5.3** provides a summary of the percentage cumulative oil recovery for the different production processes.

Table 5.3. Summary of the cumulative oil recovery for different production processes

Sample #	Primary recovery (%)	Secondary recovery (Seawater flooding) (%)	Tertiary recovery Surfactant flooding (%)	Tertiary recovery (CO ₂ flooding) (%)
S-5	3.8	19.7	23.3	33.9
S-6	5.0	23.7	27.3	36.9

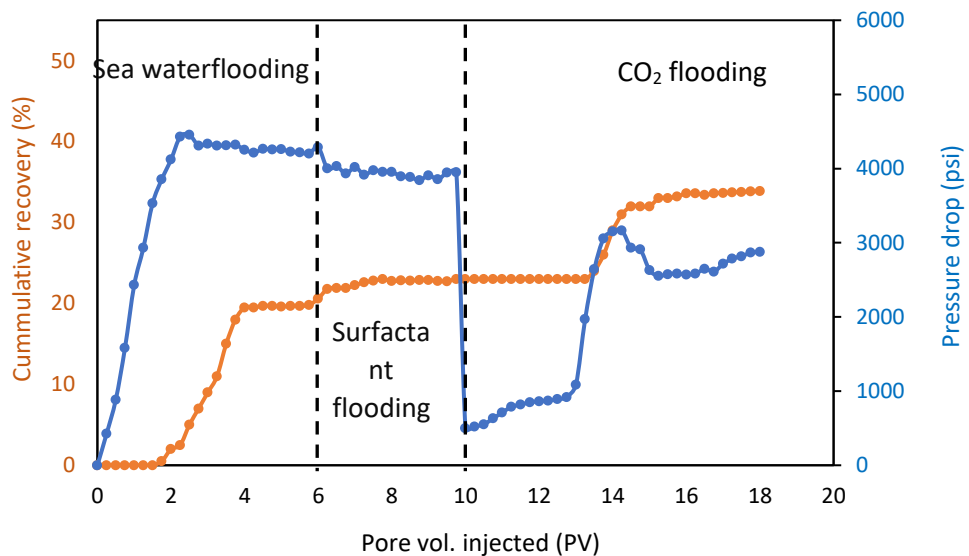


Figure 30. Cumulative oil recovery and pressure gradient profile for sample S-5; 6 pore volumes (PV) of sea water was flooded followed by 4 PV surfactant solution and 8 PV CO₂.

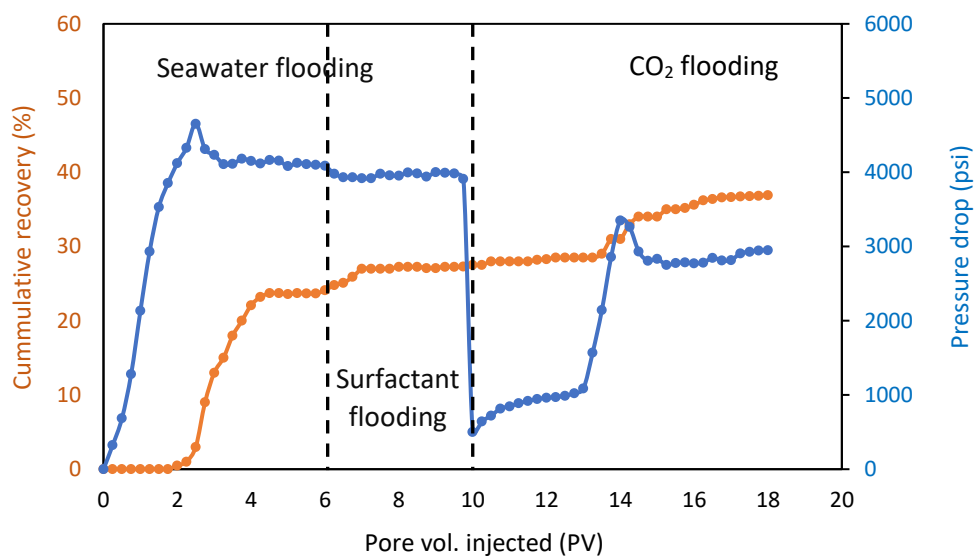


Figure 31. Cumulative oil recovery and pressure gradient profile for sample S-6; 6 pore volumes (PV) of sea water was flooded followed by 4 PV surfactant solution and 8 PV CO₂.

5.6.3 Effluent ions analysis

The ion chromatographic (IC) analysis conducted on the effluent after the primary production experiments in the Amott cells, specifically the brine sample obtained after spontaneous imbibition experiments, was compared with the initial brine. The results indicate that there was no notable change in the concentrations of calcium, magnesium, and sulfate ions. This suggests that there was no significant rock dissolution during the primary recovery phase.

However, an analysis of the effluent during the seawater and surfactant flooding, as shown in **Figure 5.14** (for sample S-5), there is an increase in the concentrations of sulfate (SO_4^{2-}), calcium (Ca^{2+}), and magnesium (Mg^{2+}) ions. This observed increase is attributed to rock dissolution, indicating that the dissolution of the rock leads to increased concentration of these ions in the effluent. This shift in ion concentrations during seawater and surfactant flooding provides valuable insights into the geochemical interaction occurring during these EOR methods. However, despite the increase in sulfate content, the cumulative oil produced was not significant compared to the CO_2 flooding.

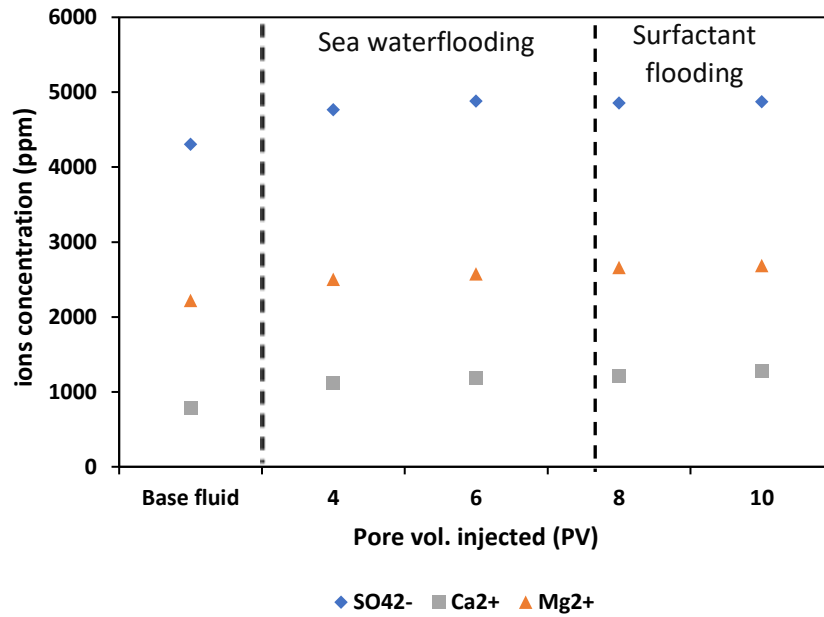


Figure 32. Ionis composition of the effluent sample for seawater and surfactant flooding obtained at predetermined pore volumes injected.

5.6.4 Implications for EOR and CO₂ storage

Considering the role of pore spaces in the storage and flow of oil and gas in reservoirs, the pore system of rocks are categorized based on their sizes and fluid flow capabilities into micropores, mesopores, and micropore. The micropores and some portion of the mesopores, are assotiated with bound or irruducible fluid, also called adsorption pores, while the macropores, with some fraction of the mesopores stores the movable fluids, and are reffered to as the seepage pores. The adsorption pores, characterized by smaller sizes compared to seepage pores, primarily facilitate gas adsorption, influencing the storage and diffusion capacity of reservoirs. Seepage pores, on the other hand, serve as pathways for fluid migration (Wang et al., 2022). The relationships between petrophysical parameters, NMR parameters, mineralogy, and fractal dimensions were analyzed. The work presents the application of rock physical properties and NMR measurements for the understanding

of the microscopic pore structure and heterogeneity of reservoir rocks, particularly for tight carbonates with wide range of anhydrite relative to dolomite content and having experienced extensive diagenetic modifications. Noting that there is a direct relation between increasing dolomitic intervals and the occurrence of anhydrite in reservoirs (Omidpour et al., 2023). The findings from this study show that NMR fractal dimension can be employed as an effective indicator to characterize the pore network of tight anhydrite-bearing carbonates.

While the ions chromatographic analysis of effluent fluid revealed indications of rock dissolution, as evidenced by increased compositions of SO_4^{2-} , Ca^{2+} , and Mg^{2+} , the results in both secondary and tertiary recovery stages demonstrated no significant difference in the oil recovery between samples S-5 and S-6, despite their varying anhydrite content. Notably, in tertiary recovery, a higher cumulative oil production was observed in CO_2 flooding compared to surfactant flooding. This shows that CO_2 injection proves more effective than chemical surfactant flooding in anhydrite-bearing carbonate formation. It is important to address the influence of anhydrite on fractional fluid flow and understand how mineralogical changes affect fractional flow and waterflood recovery of oil. The wettability of the samples was assessed via contact angle measurements, as presented in **Figure 5.15**, rocks predominated by anhydrite exhibited water-wet behavior, whereas the flooded samples (S-5 and S-6), primarily consisting of dolomite, displayed oil-wet characteristics.

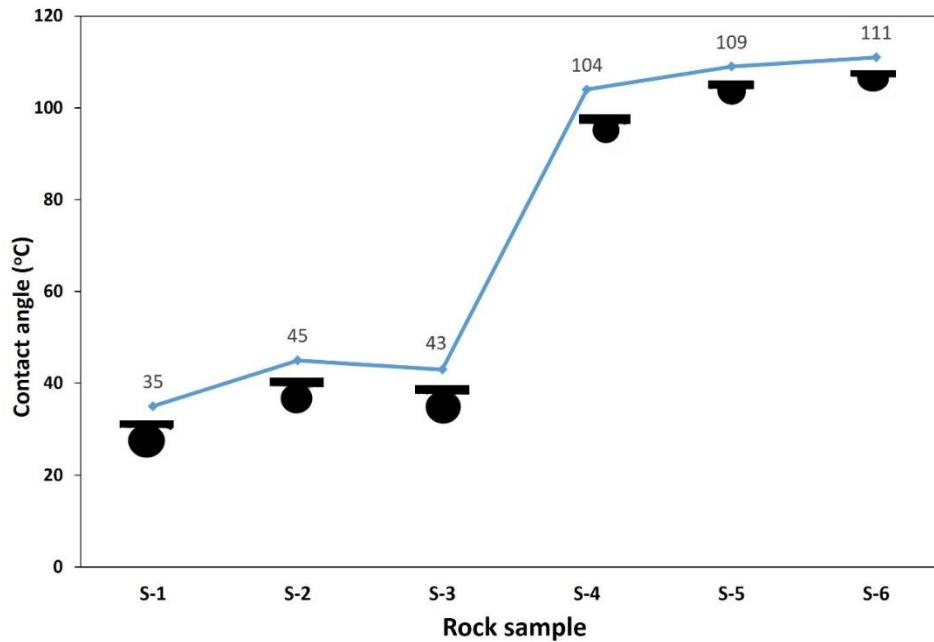


Figure 33. Wettability using contact angle for the rock samples; the top of the section (S-1 to S-3), the dolomite content increases, with decrease in anhydrite content, increasing the oil-wetness, The lower dolomite section (S-4 to S-6) shows oil-wet behavior.

It is known that water-wet rocks have good fractional flow performance yet oil-wet rocks, like dolomite exhibit poorer fractional flow performance (Al-Ibadi et al., 2019; Isah, Mahmoud, Kamal, Arif, & Al Jawad, 2023; Manceau et al., 2015; Noh et al., 2007). This performance typically shows up as early water breakthrough and rapidly increasing water cuts. However, with anhydrite, a water-wet mineral would have the opposite effect on fractional flow; later water breakthrough and not as rapid watercut build (compared to an oil-wet rock). However, having anhydrite in the rock pore space complicates the fractional flow effects of wettability because it is impermeable, however, soluble, and it may form scales that could potentially block the pores and/or pore throats from fluid flow. Therefore, in this sense, the water wetness of anhydrite would be a secondary effect to fractional flow, compared to the impact of pore blocking. The investigation is specifically targeted at

Middle East carbonates as they are predominantly carbonates and are typically waterflooded. This is particularly useful for field practices such as improved oil and gas recovery applications, and for the practicing engineers to better screen these types of reservoirs for waterflooding/EOR processes.

In addition, this approach can serve as a CO₂ storage strategy, integrating enhanced oil recovery (EOR) with CO₂ geo-storage. Concerns about CO₂ emissions, along with the growing demand for energy, necessitate effective strategies to reduce atmospheric CO₂ intensity while simultaneously enhancing the recovery of subsurface hydrocarbon resources in depleted oil reservoirs. The conventional practice of injecting CO₂ to improve hydrocarbon recovery through enhanced displacement, dissolution, and reactive transport, also presents an opportunity for the safe storage of CO₂ in the subsurface. This study emphasizes the combined approach of CO₂ storage and EOR through CO₂ injection. In addition to increasing oil recovery, CO₂ flooding offers the added benefit of CO₂ sequestration, serving as a significant economic incentive for early CO₂ storage initiatives. Therefore, the CO₂ EOR should be considered for production enhancement in the presence of anhydrite, thus the mineralogy, physical properties and pore characteristics are the key criteria in selecting the proper recovery methods. The original rock textures should not be considered as the single important factor controlling the physical and flow properties in tight carbonate reservoir rocks since diagenetic modification can potentially change the depositional rock structure. This work explores the interactions between surfactant EOR and CO₂ in reactive reservoir rock minerals, such as anhydrite. This enhances our understanding of how reservoir rock minerals, particularly anhydrite, influence chemical

and CO₂-based oil recovery processes. Addressing the dual challenge of meeting energy demands while mitigating climate change.

5.7 Conclusions

The pore structure, mineralogy, fractal characteristics and recovery potentials of the tight rocks from an outcrop in the Middle East were studied by SEM-EDS, XRD observations and NMR experiment. Fractal characteristics of the samples were studied by NMR and applied to analyze the mineralogy and physical properties. This study explores the complex relationship between pore structures, rock physical properties and fluid flow within reservoir rocks, focusing on the impact of the mineralogy. The study extends fractal analysis to micropores, mesopores, and macropores in different rocks, providing insights into morphology and heterogeneity at multiscales. Anhydrite's presence in reservoir rocks alters physical properties and reservoir quality, impacting fluid flow. The study examines changes in pore structure of anhydrite-bearing rocks, assessing the implications for oil recovery and potential gas storage. The results show that anhydrite, relative to dolomite content in rock does affect its physical properties and pore structure, and fluid flow characteristics. The relationships between mineralogy, pore system, and electrical properties variation with permeability and porosity were also examined. Multimodal pore size distributions are identified according to the T₂ spectra, indicating a broad pore distribution in the studied samples. Fractal dimensions of the micropores, mesopores and macropores are identified as D1, D2, and D3 with different value ranges, and mesopores possess more obvious fractal characteristics than the micropores and the macropores, the following specific conclusions are drawn:

- (1) Permeability exhibits a strong correlation with porosity (positive correlation), average pore size (positive correlation), and electrical resistivity (negative correlation) with R^2 values greater than 0.81. Similarly, permeability and porosity correlate with the content of anhydrite (negative correlation) and dolomite (positive correlation), ($R^2 > 0.94$).
- (2) The rocks pore distribution is irregular and complex, with multifractal and multimodal characteristics. D1 and D3 are the fractal dimensions of bound fluid pores associated with adsorption pores and movable fluid pores associated with seepage pores, respectively. While D2 is related to both the adsorption and seepage pores that host some portions of bound and movable fluids.
- (3) Rock compositions have different influence on the multiscale fractal characteristics of pores in tight carbonates: The anhydrite content is linearly direct proportional to the multiscale fractal dimensions of the micropores (D1), mesopores (D2) and the macropores (D3), whereas dolomite content is negatively correlated with the multiscale fractal dimensions (D1, D2, and D3).
- (4) Considering the poor correlation coefficients, D1 and D3 have no apparent connection with porosity ($R^2 = 0.2182$ and 0.3457 for D1 and D3, respectively) and permeability ($R^2 = 0.2226$ and 0.4667 for D1 and D3, respectively). While the fractal dimension of mesopores (D2) shows a linear inverse correlation with porosity and permeability. The correlation coefficients (R^2) for the fitted curves are 0.07862 and 0.8088 for fractal dimension versus porosity and permeability, respectively. This implies that as the porosity increases, the fractal dimension decreases, signifying lower pore network complexity in the mesopores.
- (5) Rocks predominated by anhydrite (S-1 to S-3) showed water-wet behavior, whereas samples (S-4 to S-6), primarily consisting of dolomite, displayed oil-wet characteristics.

For the oil recovery analysis, CO₂ injection proves more effective than chemical surfactant flooding in tight anhydrite-bearing carbonate formations.

CHAPTER 6

ENFORCED CO₂ MINERALIZATION IN ANHYDRITE- RICH ROCKS: SrCl₂

Summary

The utilization of subsurface geologic media for carbon capture and storage through mineralization has been recognized as a reliable approach. However, less attention has been given to anhydrite rock type for CO₂ mineralization and storage. Anhydrite-rich rock formations, commonly found in various geological settings, have the potential to serve as natural carbon sinks through the mineralization of CO₂. Therefore, this study aims to investigate the mechanisms and potential of anhydrite-CO₂-brine interactions for carbon storage. The experimental approach involved exposing anhydrite-rich rock to supercritical CO₂-brine environments under varying conditions of fluid composition. For the first time, we conducted novel mineral transformation of an outcrop anhydrite-rich rock sample in static reactor under subsurface conditions of high temperature (60 °C) and pressure (104 bar), in the absence and the presence of SrCl₂ for a one-month period. Mineralogical and geochemical analyses, including, X-ray fluorescence, X-ray diffraction, ions analysis, micro-computed tomography, and mechanical properties were conducted to examine the changes in the rock structure and composition resulting from the interactions. The findings revealed that anhydrite undergoes mineral transformation upon exposure to supercritical CO₂-saturated brine to form stable minerals including calcite, dolomite, magnesite, and

strontianite, which contributes to the long-term storage of CO₂ in the subsurface geologic media. The efficiency and extent of carbon mineralization were found to be influenced by brine composition. Notably, for the CO₂-brine interaction, the carbonation reactions are driven by the coupled dissolution-precipitation mechanism. However, in the presence of Sr²⁺, anhydrite transformation occurs via dissolution-precipitation and diffusion mechanism, the elements diffuse between the solid and the fluid phase. These findings contribute to the understanding of the potential of these formations for carbon storage, opening avenues for further research and the development of effective carbon capture and storage strategies.

Key words: Carbon mineralization, Gas storage, Anhydrite/gypsum, CO₂-brine, Interactions

6.1 Background

The increasing concentration of carbon dioxide (CO₂) in the atmosphere and its contribution to global climate change have sparked a growing interest in carbon capture and storage (CCS) (Ajayi et al., 2019; Boot-Handford et al., 2013; Bui et al., 2018; Gibbins & Chalmers, 2008; L'Orange Seigo et al., 2014; Zhong et al., 2023). Carbon capture and storage by mineralization (CCSM) in subsurface geologic media has been identified as a robust approach in igneous mafic rocks (P. B. Kelemen et al., 2018; Matter et al., 2016a; Parkinson, 2018a; Power et al., 2013a; A. Raza et al., 2022; Zevenhoven et al., 2016). CO₂ mineralization refers to the process of converting CO₂ into a solid form through reactions with suitable geological media, essentially turning it into stone underground. Anhydrite-

rich rock (CaSO_4) have recently gained attention as a potential medium for carbon mineralization due to their high calcium and sulfate content (Forjanes et al., 2020; L. Yu et al., 2019). When exposed to water, anhydrite readily transforms to the more commonly occurring gypsum, ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which further dissociates into its constituents' calcium (Ca^{2+}) and sulfate (SO_4^{2-}) ions (Isah et al., 2022a; J. L. Ricci et al., 2008). It's worth emphasizing that the transformation from anhydrite to gypsum happens via hydration, and this conversion is a gradual process that takes place over extended periods. The released calcium ions tend to react with ionic species such as carbonate ions (CO_3^{2-}) to form minerals precipitates. The anhydrite- CO_2 -brine interactions involves complex geochemical processes that influence the fate of CO_2 and the potential for carbon mineralization. Upon exposure to CO_2 -charged fluid, anhydrite undergoes dissolution, leading to the release of calcium and sulfate ions into the surrounding brine. These released ions subsequently react with dissolved CO_2 to form stable carbonate minerals, thus sequestering CO_2 over geological timescales (Azdarpour et al., 2018; Kelemen et al., 2020; Lee et al., 2012; Wang et al., 2021; Wang et al., 2023).

CCSM can be carried out through two main methods: in-situ and ex-situ approaches. The ex-situ method primarily involves utilizing industrial waste for CO_2 sequestration. The utilization of byproduct gypsum (BG), which is an industrial solid waste, has been explored for carbon dioxide fixation through mineral carbonation. Mineral carbonation of flue gas using industrial BG for CO_2 storage is documented by several authors (de Beer et al., 2014; Lee et al., 2012; Veetil et al., 2021; Wang et al., 2019). Furthermore, additional information regarding BG carbonation can be found elsewhere (Azdarpour, et al., 2015; Wang et al., 2021).

On the other hand, the in-situ method is predominantly applied in subsurface environments, such as depleted oil and gas reservoirs or aquifers, to store CO₂. When reservoir formation or evaporite cap rocks containing gypsum and anhydrite come into contact with carbonate-rich water at a pH range of 5.0 to 7.5 (depending on the CO₂ partial pressure), they are likely to carbonate quickly. In this scenario, evaporite deposits have the potential to be utilized for carbonation, provided there is enough alkalinity to counterbalance the acid released during the process of carbonation (L. Yu et al., 2019). Roncal-Herrero et al. (2017) performed mineral carbonation of anhydrite in static reactor. The authors showed the presence of calcite as the primary component formed on the outer layer of the anhydrite samples undergoing carbonation, starting from the early stages of the process. This observation holds true regardless of the specific surface of the anhydrite being considered. The reaction proceeds through the dissolution of anhydrite and the simultaneous development of calcite crystals. This is evident from the images of anhydrite surfaces, where even after just 1 minute, small calcite crystals were visible, indicating both the dissolution of anhydrite and the formation of calcite crystals (Roncal-Herrero et al., 2017). In most cases, a means of accelerating the carbonation rate is considered. The host rock dissolution rates are slower than the corresponding carbonate precipitation rates, so hastening dissolution is the key to optimization. The dissolution rates of the storage host rock are accelerated by increasing the water-mineral interface area, by altering temperature or pressure, and by adding acid. However, in some cases, base is added to enhance minerals precipitation. Furthermore, the injection of additives could also be helpful in promoting the dissolution and precipitation of minerals along with reaction-induced mechanisms (Oelkers et al., 2008). Accordingly, Ruiz-Agudo et al. (2019) and (Forjanés et al., 2020) carried out

mineral replacement of gypsum by barite (BaSO_4) and celestite (SrSO_4). Their investigation approach involved the addition of BaCl_2 and SrCl_2 solutions in deionized (DI) water prior to each experimental run. The gypsum crystals were held in the aqueous solution for reaction times ranging from 5 min to 168 h. The authors noted the occurrence of distinct layers of barite and celestite. Nevertheless, it's important to highlight that these studies involved only mineral transformation (no carbon mineralization was considered), the conversion of gypsum to barite and celestine during mineral transformation does not involve any CO_2 and no carbonates were formed.

In a different approach, other researchers initially extracted calcium ions using acids from a calcium sulfate source, and subsequently expose it to CO_2 for carbonation (Azdarpour et al., 2015; Raza et al., 2018). In addition, some studies have focused on minerals transformation using aqueous phase (no CO_2 involved) (Forjanes et al., 2020; C. Ruiz-Agudo et al., 2019), while others have used bases to enhance the solution pH and promote carbonate precipitation in the presence of CO_2 (Bang et al., 2014; L. Yu et al., 2019). Some other studies have used other novel ideas, such as in-situ pH swing, to promote divalent ions extraction and carbonate precipitation (Altree-Williams et al., 2017; Azdarpour et al., 2015). **Table 6.1** provides a summary of previous studies on CO_2 /brine/anhydrite-gypsum mineralization under various conditions and reaction duration.

Understanding the anhydrite- CO_2 -brine interactions and their influence on carbon mineralization can aid in the identification of suitable reservoirs for carbon capture and storage projects. The implications of anhydrite- CO_2 -brine interaction for carbon storage is vital for evaluating the suitability of anhydrite-rich formations and evaporite cap rocks as potential carbon sinks. The process of carbon mineralization in anhydrite-rich rock

formations offers the potential for long-term carbon storage, however, the role of SrCl_2 to trigger the CCSM under subsurface conditions has not been investigated.

Therefore, in this study, we aim to investigate the mechanisms and potential of anhydrite- CO_2 -brine interactions for carbon mineralization. Through novel experimental analyses, this work examines the dissolution of anhydrite, the release of calcium and sulfate ions, and the simultaneous formation of other minerals in the presence of supercritical CO_2 and brine. For the first time, we enforce minerals replacement in anhydrite-rich rock for the purpose of CO_2 - geostorage. We conducted anhydrite mineral transformation experiments on an outcrop rock in a static reactor under subsurface conditions of high temperature (60 °C) and pressure (104 bar), both with and without the presence of SrCl_2 salt. The purpose of introducing SrCl_2 is to facilitate the precipitation of strontium carbonate and sulfate. Since strontium sulfate density is about 30% greater than calcium sulfate, this will create additional capacity for geostorage, as well as enhanced reactions and mineralization processes. Thus, the findings from this research is expected to contribute to our understanding of carbon storage potential in anhydrite-rich formations and provide insights for the development of effective CCSM strategies.

Table 6.1. Previous studies on CO_2 /brine/anhydrite-gypsum mineralization under various conditions and reaction duration.

Referenc es	Setu p	Fluid phase	Rock type	Temperatu re /Pressure	Rock/flu id ratio	Reactio n duratio n	Mineral transformati on
(Forjanes et al., 2020)	batch react or	1.5 ml of 0.5 M $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	gypsum	25 °C /1.0 bar	$5 \times 5 \times 2$ mm	5 min to 168 h	Gypsum to celestite and barite (note

		O & BaCl ₂ ·2H ₂ O solutions			fragments		that no CO ₂ was involved in this study)
(Q. Chen et al., 2020)	glass beaker	NaCl and NH ₄ OH solutions, then CO ₂	phosphogypsum	30 °C/ ambient pressure	150µm rock powder	60 – 150 mins	Gypsum transformed to calcite
(C. Ruiz-Agudo et al., 2019)	static reactor	BaCl ₂ solutions (1–250 mM) in 50 ml solution	gypsum	22 °C /1.0 bar	0.095g; 5 × 6 × 1 mm crystals	30 min to 168 h	Gypsum transformed to barite (however, no CO ₂ mineralization was considered)
(L. Yu et al., 2019)	batch reactor	Aqueous 0.1 M Na ₂ CO ₃ ; 0.1 M NaHCO ₃	synthetic gypsum powder	25 °C /1.0 bar	4.8g gypsum in 220ml fluid	287 h	Gypsum transformed to vaterite, calcite and trace aragonite
		Aqueous 0.1 M Na ₂ CO ₃ + 0.2 M NaOH	gypsum powder			189 h	Gypsum transformed to vaterite and calcite
(Azdarpor et al., 2018)	static reactor	CO ₂ up to 70 bar in –DI water	red gypsum	25 to 400 °C /1 to 70 bar	10 g in 50 ml	5 to 120 min	Red gypsum to calcite and siderite
(González-Illanes et al., 2017a)	batch reactor	aqueous Na ₂ CO ₃ and MgCl ₂	anhydrite & gypsum	25 °C /1.0 bar	3x3x1m sample in 2 ml solution	30 min to two months.	Anhydrite & gypsum transformed to calcite and aragonite

(Altree-Williams et al., 2017)	static react or	aqueous Na ₂ CO ₃ and NaHCO ₃	anhydrite	25 – 80 °C /1.0 bar pH 8 – 11.5	10 – 15mg in 5 ml powder	5 min to 28 days.	Anhydrite transformed to calcite and aragonite
(Roncal-Herrero et al., 2017)	static react or	1 ml aqueous 0.5 M Na ₂ CO ₃	anhydrite	25 °C /1.0 bar pH ≈ 11.4	2 × 2 × 1.5 mm fragments	1 min and 1 month	Anhydrite transformed to calcite
(Azdarpor et al., 2015)	static react or	2 M H ₂ SO ₄ , HCl, and HNO ₃ pH was regulated using NH ₄ OH	red gypsum powder	30 to 70 °C /ambient pressure	10 g in 200 ml	5 min to 120 min	Ca ²⁺ and Fe ²⁺ extracted from gypsum for carbon mineralization (by CO ₂ interaction)
(Bang et al., 2014)	static react or	CO ₂ at 0.4, 0.8, and 1.0 L/min + 6 M NaOH in DI	gypsum	Ambient conditions	0.05 – 0.5 M gypsum in 1000 ml		Gypsum transformed to calcite
(Fernández-Díaz et al., 2009)	static react or	1 ml aqueous 0.05 to 0.5 M Na ₂ CO ₃	gypsum	25 °C /1.0 bar	3x3x1m sample in 1 ml solution	1 min to 15 days	Gypsum transformed to vaterite, calcite and aragonite

6.2 Experimental Methodology

6.2.1 Fluids

The experimental brine used in this study was prepared using five distinct salts obtained from Sigma-Aldrich: sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), sodium bicarbonate (NaHCO₃), and sodium sulfate (Na₂SO₄). These

salts were combined in specific proportions to create a synthetic brine solution that closely resembled the composition of seawater found in the Arabian Gulf (Isah, Mahmoud, Kamal, Arif, & Jawad, 2023a). Carbon dioxide (CO₂) of purity 99.9 % is used as the gas phase for the anhydrite-CO₂-brine interactions. The seawater ionic composition is shown in **Table 6.2**.

Table 6.2. Ionic composition of Arabian gulf seawater.

Ions	Concentration (ppm)
Na ⁺	18,300
Ca ²⁺	650
Mg ²⁺	2,110
SO ₄ ²⁻	4,290
Cl ⁻	32,200
HCO ₃ ³⁻	120
TDS	57,670

6.2.2 Rock sample preparation

This study was carried out on a 1.8 by 1.5-inch diameter anhydrite-rich outcrop rock sample. The rock sample initial gas porosity and permeability were 1.46% and 0.068 mD, respectively. The bulk mineralogy of the rock sample was evaluated using X-ray diffraction (XRD). The sample is mainly composed of calcium sulfate (CaSO₄), with traces of other rock minerals such as quartz, dolomite, and calcite. The properties of the sample before CO₂-brine treatments are presented in **Table 6.3**. Initial measurements of the rocks' mineralogical composition, micro-CT imaging, petrophysical properties (porosity and permeability) and geomechanical properties via acoustic measurements and strength tests were performed. The rock sample was then exposed to supercritical CO₂-brine treatment

under high-pressure high-temperature (HPHT) conditions in a static reactor for one month, specifically, at temperature and pressure of 60 °C and 104 bar, respectively. The total volume of the reactor is 1000 cm³. Within this volume, 750 cm³ was filled with brine, about 52 cm³ was occupied by the rock (rock bulk volume), and the remaining space in the reactor was filled with CO₂ at supercritical conditions.

After the CO₂-brine treatment, the assessment of the rocks' mineralogical composition, micro-CT imaging, petrophysical properties (porosity and permeability), geomechanical properties via acoustic measurements and strength tests were repeated. The above procedures were repeated with the same rock sample; however, strontium chloride salt was added (to make 0.1 M SrCl₂ solution) to the brine used in the first CO₂-brine interaction (note that the solution was filtered before use). The rock-CO₂-brine interactions flowchart is presented in **Figure 6.1**.

Table 6.3. Rock properties prior to CO₂-brine treatment.

Parameter	Pre-treatment
Dry weight (g)	119.85
Diameter (mm)	38.04
Length (mm)	46.02
V _p (m/s)	4899
V _{s1} (m/s)	2491
V _{s2} (m/s)	2560
Porosity (%)	1.46
Permeability (mD)	0.067
Grain rho (g/ml)	2.321

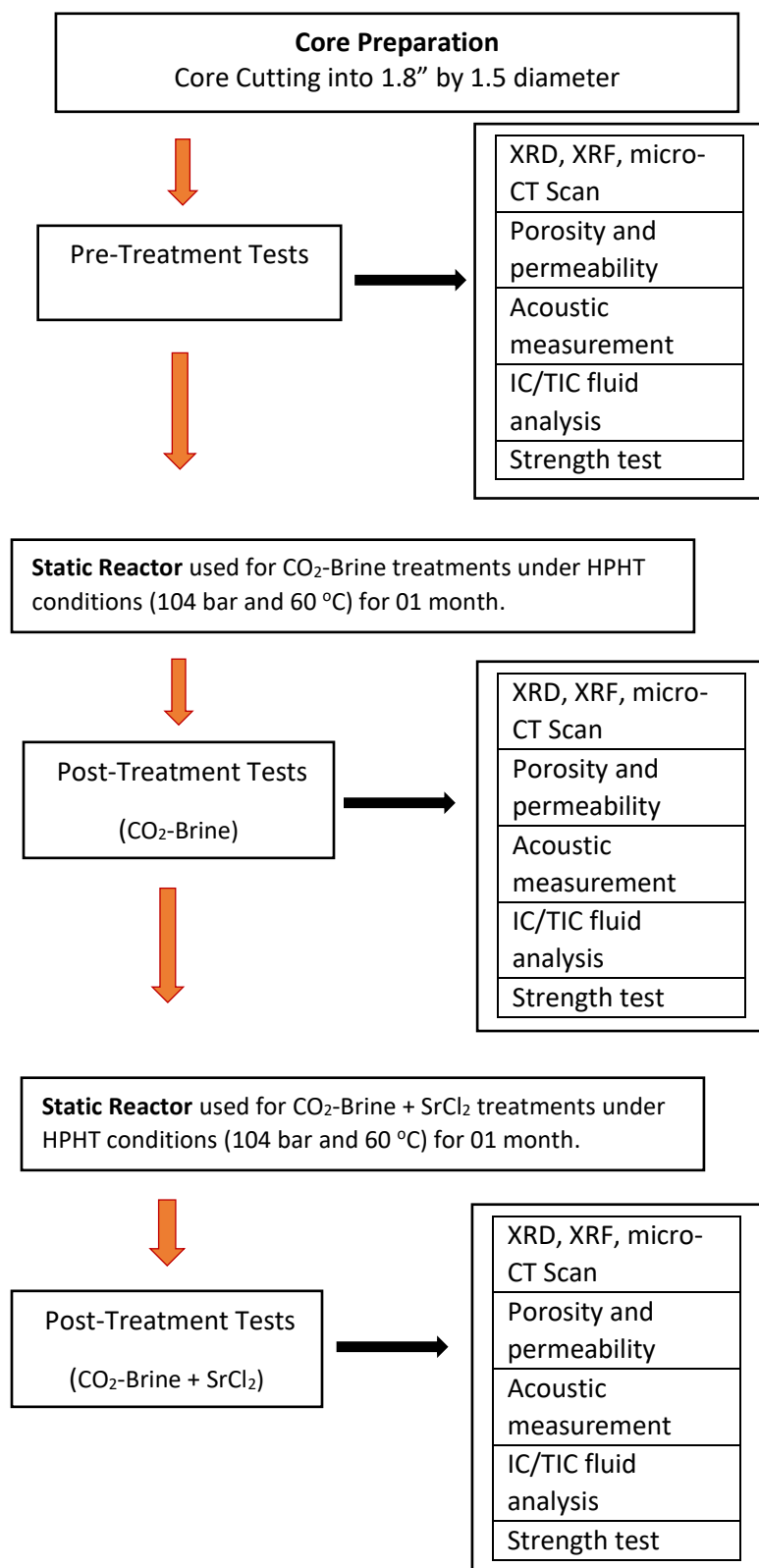


Figure 34. The steps followed and the laboratory experiments that were executed for the rock-CO₂-brine interactions.

6.2.3 Micro-CT Scan and EDX spectroscopy

The micro-CT imaging analysis of the rock pre- and post-CO₂-brine interactions was performed using the Bruker cone-beam helical micro-CT equipment. The helical micro-CT equipment setup used in this study consists of a sample holder, X-rays/light source, and the camera. Micro-CT X-ray imaging employs a pinhole cone-beam geometry, where X-rays are emitted from a small focal point to achieve high resolution. A flat, rectangular X-ray camera detects the emitted X-rays. This imaging technique is referred to as "cone beam" geometry due to its conical shape. The X-ray path forms an angle known as the "cone angle" at the top and bottom of the resulting image. The powdered sample was attached to pin-type stubs to facilitate analysis through electron dispersive X-ray (EDX) spectroscopy. Point-based EDX spectra were acquired using the Zeiss Laser-Crossbeam 550 scanning electron microscopic equipment to observe and assess any alterations after the treatments.

6.2.4 Acoustic measurements and rock strength tests

The geomechanical properties of rock sample were studied through acoustic measurements to evaluate the physical changes of the sample after supercritical CO₂-brine exposure. For the acoustic measurements, the New England Research, Inc. (NER) instruments was employed. The shear wave (V_s) and the compressional wave (V_p) velocities were measured. These parameters were then used to compute the Young's modulus (E), bulk modulus (K) and the Poisson's ratio (ν) for the sample pre- and post-CO₂-brine treatments. Young's modulus (E) is a crucial geomechanical property of rocks that quantifies the

stiffness or resistance of the material to compression or extension caused by applied stress. It is considered a key measure of the rock's rigidity. The Young's modulus of the rock samples is computed before and after CO₂-brine treatments using the compressional and shear waves velocities (V_p and V_s) (Fjær et al., 2008). Poisson's ratio (ν) indicates the relationship between lateral expansion or contraction deformation and long-term extension deformation. For most mineral deposits, Poisson's ratio falls within the range of 0 to 0.5. More rigid, competent, and incompressible rocks generally exhibit lower Poisson's ratios, whereas the opposite is true for less rigid rocks (Domenico, 1984)(Usama Alameedy et al., 2022). The bulk modulus (K) gives the resistance of a substance to uniform compression or volume change when subjected to an applied force or pressure. The rock sample was subjected to a controlled environment, where it was exposed to supercritical CO₂-saturated brine solution at a temperature of 60°C for a duration of one month. Subsequently, a comprehensive characterization technique was employed to analyze the sample and evaluate its response to the exposure. Through the utilization of acoustic techniques, the mechanical properties of the sample were determined, providing valuable insights into the rock's stiffness and elasticity.

$$E = \frac{\rho V_s^2 (3 V_p^2 - 4 V_s^2)}{V_p^2 - V_s^2} \quad (1)$$

$$\nu = \frac{0.5(V_p/V_s)^2 - 1}{(V_p/V_s)^2 - 1} \quad (2)$$

$$K = \frac{E}{3(1 - 2\nu)} \quad (3)$$

While the NER AutoScan scanner, a non-destructive measurement system was used to measure the rock surface hardness (H) pre- and post-CO₂-brine treatments. In AutoScan, the impulse hammer probe serves as a valuable measurement tool for evaluating the elastic stiffness and mechanical strength of rocks. One notable advantage of this probe is its non-destructive nature, as it utilizes millimeter-scale indentations to obtain measurements. Measurement area size is 2 mm with typical measurement times of 10 seconds per point.

6.2.5 IC, TIC and pH measurements

The ion chromatography (IC) was carried out to determine the changes in ionic concentrations in the various fluids under different CO₂-brine interactions. An average of 2 cm³ samples of the supernatant were taken every 48 hours during the experimental run and the ions analysis and pH measurements were performed. Over the one-month period of CO₂-brine interactions, each for CO₂-brine and CO₂-brine+SrCl₂, thirty fluid samples were obtained (15 each for CO₂-brine and CO₂-brine+SrCl₂). These fluids were analysed for rock-CO₂-brine interaction using ion chromatography (IC), and total inorganic carbon (TIC), and pH measurements. It's important to highlight that the brine-CO₂ ratio in the reactor undergoes a slight changes as effluent samples (averaging 2 cm³ per sample) are periodically collected over time from the batch reactor, having a volume of 1000 cm³ (750 cm³ occupied by brine, about 52 cm³ by the rock, and about 200 cm³ was filled with CO₂ at 60 °C and 104 bar).

While this may impact the carbonation process, it's worth noting that the total sampled volume represents less than 5% of the initial brine volume, which does not affect the reaction temperature. Additionally, there was no significant pressure decrease attributed to

the sampling procedure. The final pressure at the end of the reaction remained at 102 bar, indicating only a minor 2-bar drop.

The IC technique was conducted to analyze the ionic composition of the effluent using Metrohm's 930 Compact IC Flex—Compact ion chromatography equipment, while the TIC (Total Inorganic Carbon) analysis for carbonate and bicarbonate ions were determined using Analytikjena's multi N/C 3100 Flow injection TOC analyzer with an accuracy of ± 1.0 ppm and a detection limit up to 0.2 ppm. The pH of the brines and the effluent was measured immediately after sampling (before cooling and CO₂ degassing) using the Thermo Scientific™ Orion Star™ A215 pH/conductivity benchtop multi-parameter meter, with an accuracy of ± 0.002 . **Figure 6.2** shows the schematic of the static reactor system used in this study for rock-CO₂-brine interaction.

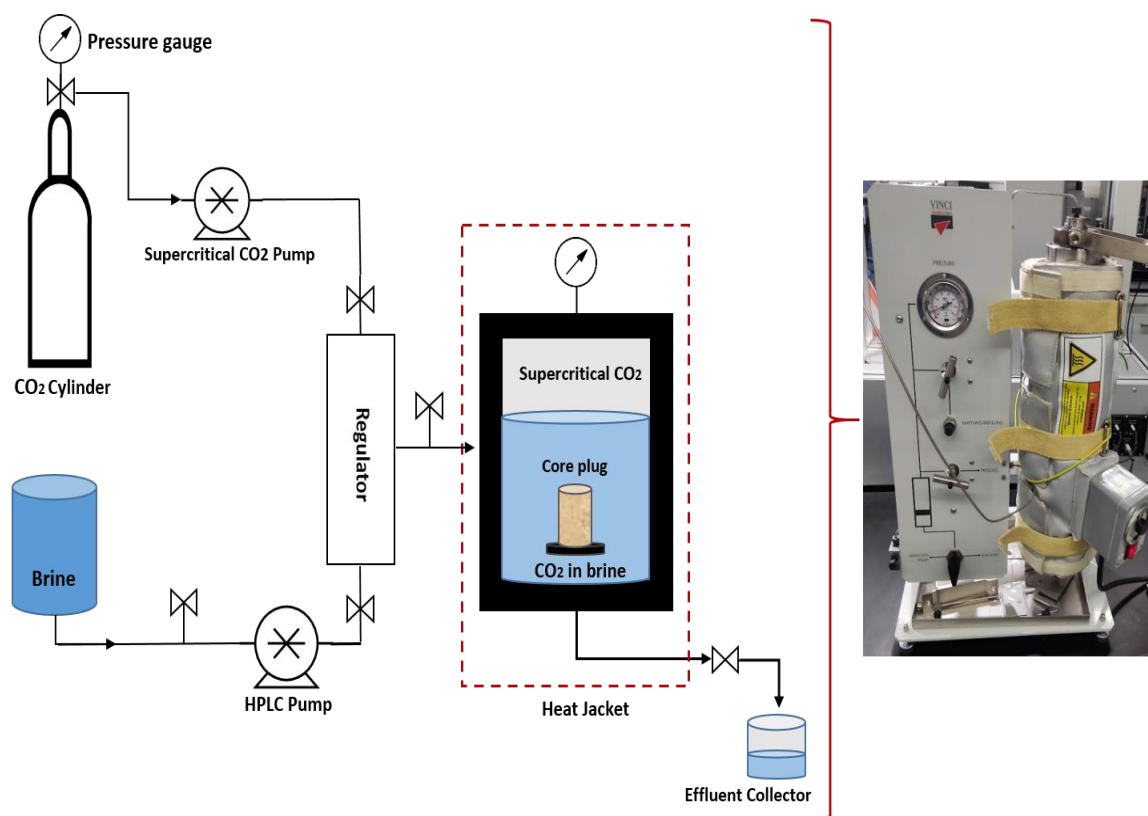


Figure 35. Schematic of the static reactor system used in this study for rock-CO₂-brine interactions.

6.3 Result and Discussion

The photographical images of the rock sample before and after supercritical CO₂-brine treatments show noticeable modification (see **Figure 6.3**), this is attributed to fluids exposure and subsequent compositional alteration via carbon mineralization. Moreover, the process of carbonation progresses from the outer layers towards the inner parts of the rock. This advancement happens through a series of reactions that involve the dissolution of anhydrite and the simultaneous formation of various forms of carbonates (such as aragonite and calcite) through crystallization (Fernández-Díaz et al., 2009).

(a)

(b)

(c)

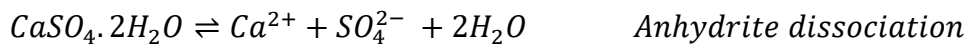


Figure 36. Rock sample before and after supercritical CO₂-brine interactions; (a) before treatment, (b) after CO₂-brine treatment, (c) after CO₂-brine+SrCl₂ treatment.

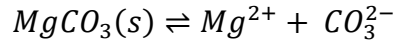
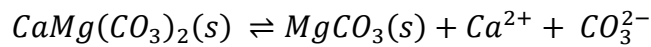
6.3.1 XRD mineralogical analysis

The mineralogical analysis of the rock before and after treatments were carried out using the XRD. The presence of magnesium (Mg^{2+}) and iron (Fe^{2+}) in the anhydrite sample prompted an investigation into the potential formation of magnesium carbonate (MgCO_3) and iron carbonate (FeCO_3). **Table 6.4** presents the mineralogical composition of the anhydrite sample pre- and post CO₂-brine treatments. It is important to highlight that the XRD sample used for analyzing the treated rocks was obtained by carefully and evenly scraping across the outer section of the rock sample. The result of the bulk XRD analysis for the untreated rock indicates that the predominant mineral is anhydrite (CaSO_4), with volume percent of 98 %. In addition, the results show traces of other rock minerals such as quartz, dolomite, calcite, aragonite, and siderite having a volume percent of 0.3 %, 0.8 %, 0.5 %, 0.2 %, and 0.1 %, respectively (**Figure 6.4**). After interaction with supercritical CO₂-saturated brine, the XRD analysis indicates an overall change in minerals composition and formation of new rock minerals. The minerals composition after treatment

with CO₂-saturated brine shows 97.9 % gypsum, while quartz, dolomite, calcite, aragonite, and siderite have volume percent of 0.4 %, 0.3 %, 0.6 %, 0.3 %, and 0.4 %, respectively (see **Figure 6.3**). This indicates a slight decrease in anhydrite and dolomite due to dissolution and minerals replacement with corresponding increase in quartz, calcite, aragonite, and siderite composition. The initial step of the mineral transformation process is the dissolution of anhydrite surfaces, which determines the rate of the overall process. Additionally, a trace of new rock mineral, feldspar is observed after interaction. The formation of trace feldspar, specifically (K-feldspar), is linked to the presence of quartz in the original rock, as quartz provides the necessary silicate ions. Previous research has confirmed that the interaction between CO₂ and brine can induce the dissolution of anhydrite minerals present in rocks, leading to the formation of new minerals (Song et al., 2020; Yu et al., 2019). According to Fernández-Díaz et al. (2009) and (Altree-Williams et al. (2017), when anhydrite interacts with fluids such as CO₂-saturated brine, it can be converted into other mineral in a process known as carbonatation. This transformation leads to the formation of different rock minerals such as aragonite and calcite, as described in references (Altree-Williams et al., 2017; González-Illanes et al., 2017a; L. Yu et al., 2019).



Dolomite undergoes dissolution while simultaneously precipitating a new carbonate mineral through its reaction with water-saturated supercritical carbon dioxide ($ScCO_2$). The process of dolomite dissolution in brine is described through a coupled dissolution-precipitation reactions (Wang et al., 2013; Zhang et al., 2007). The study highlights a unique dissolution behavior in anhydrite and dolomite compared to other carbonates, particularly, calcite tends to dissolve at a higher rate than other carbonates (Pokrovsky et al., 2009). The XRD results confirm that anhydrite generally has higher solubility when compared to carbonates like calcite and dolomite. The implications of this unique behavior on the overall mineral transformations observed in the study are significant. Since anhydrite dissolves more readily, it contributes to the formation of stable minerals like calcite, magnesite, and strontianite when exposed to supercritical CO_2 -saturated brine through the supply of calcium ions. On the other hand, dolomite exhibits a distinctive behavior in which it tends to lose calcium ions through dissolution at a faster rate than magnesium ions when exposed to CO_2 -brine treatment (Zhu et al., 2023). The equilibrium between solid calcium magnesium carbonate ($CaMg(CO_3)_2$) and its dissolved ionic components, calcium ions (Ca^{2+}), magnesium ions (Mg^{2+}), and carbonate ions (CO_3^{2-}) is presented:



Several authors have conducted investigations on the replacement of anhydrite with other rock minerals such as carbonate, and their findings have been documented (Altree-Williams et al., 2017; Fernández-Díaz et al., 2009; González-Illanes et al., 2017a; L. Yu et

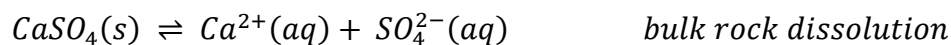
al., 2019). These studies have identified two primary mechanisms involved in the mineral replacement reactions. These mechanisms involve the diffusion of elements between the solids and the fluid phase, where elements are extracted from the solid and necessary elements diffuse into the solid from the interface between the solid and fluid (Pokrovsky et al., 2009; Zhu et al., 2023). The second mechanism is the coupled dissolution-precipitation (CDP), which involves the dissolution of the original mineral and the simultaneous precipitation of the resulting products. These processes are interconnected through a layer of interfacial fluid that separates the two phases, as explained in references (Adegoke et al., 2022) and (Altree-Williams et al., 2017). Likewise, as shown in the study by González-Illanes et al. (2017) and Altree-Williams et al. (2017), the replacement of anhydrite and gypsum involves dissolution and precipitation as the steps that determine the overall rate. Interestingly, the dissolved magnesium in the reacting solutions is found to be incorporated into the pseudomorphs formed, irrespective of the precursor phase (anhydrite or gypsum) or the mineralogical composition of the replacements. Many mineral replacement reactions are driven by fluid-induced dissolution and follow the coupled dissolution-precipitation mechanism.

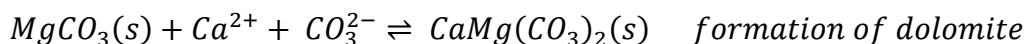
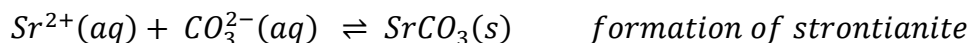
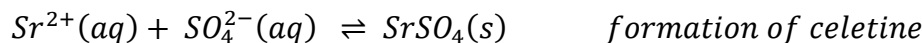
Table 6.4. XRD of the rock sample pre- and post-CO₂-brine treatments.

Minerals	Pre-treatment	Treated with CO₂-saturated brine	Treated with CO₂-saturated brine + SrCl₂
Anhydrite [%]	98.0	97.9	18.8
Pyrite [%]	0.0	0.0	0.4
Quartz [%]	0.3	0.4	0.4
Dolomite [%]	0.8	0.3	1.2

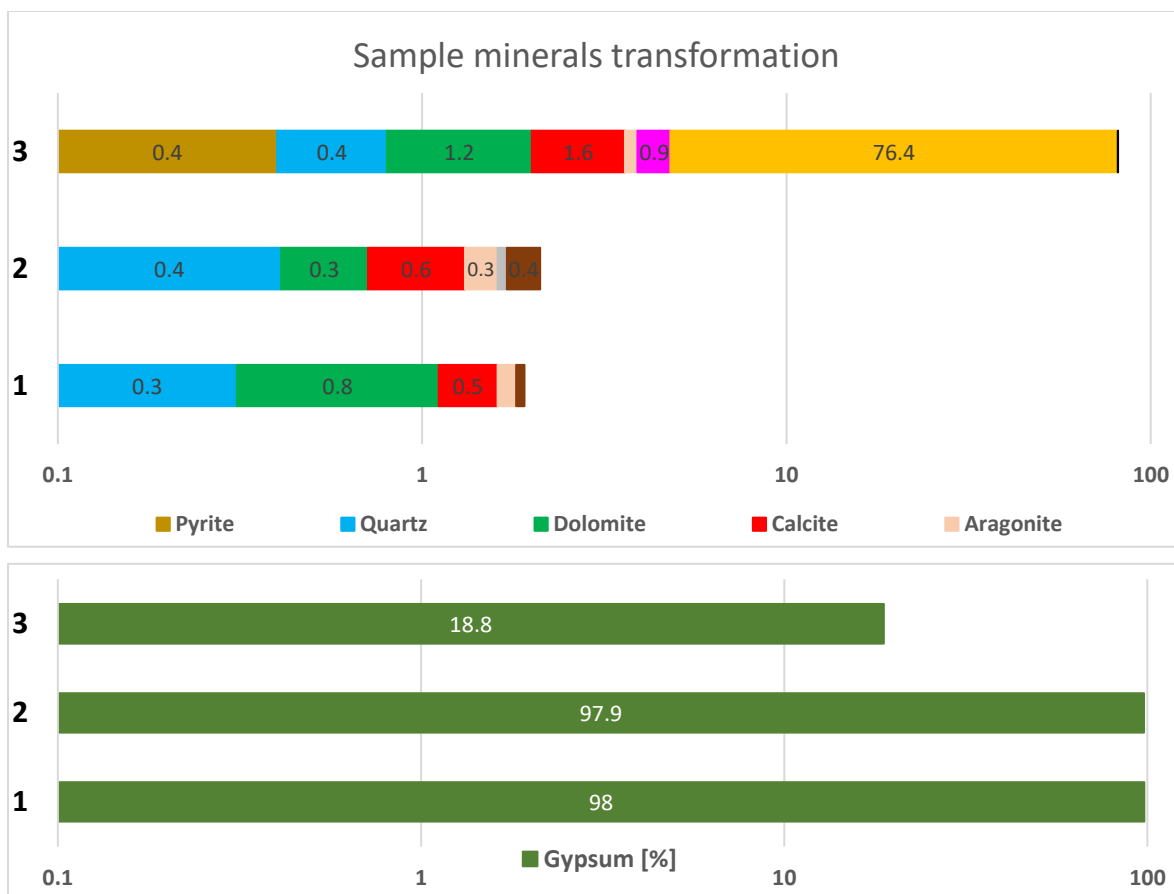
Calcite [%]	0.5	0.6	1.6
Aragonite [%]	0.2	0.3	0.3
Feldspar [%]	0.0	0.1	0.0
Magnesite [%]	0.0	0.0	0.9
Siderite [%]	0.1	0.4	0.0
Celestine [%]	0.0	0.0	76.4
Strontianite [%]	0.0	0.0	0.2
Total	100	100	100

The XRD results for the CO₂-brine interaction in the presence of strontium chloride (SrCl₂) salt shows significant mineralogical alteration in the rock mainly due to carbon mineralization. The minerals composition after treatment with CO₂-saturated brine containing 0.1 M SrCl₂ shows only 18.8 % gypsum, while significant amount of pyrite (FeS₂), dolomite (CaMg(CO₃)₂), calcite (CaCO₃), magnesite (MgCO₃), strontianite (SrCO₃) and celestine (SrSO₄) with volume percent of 0.4 %, 1.2 %, 1.6 %, 0.9 %, and 76.4 %, respectively, resulted. When SrCl₂ is dissolved in brine, complexation reactions can occur between the strontium ions (Sr²⁺) and various ligands or complexing agents present in the brine. These complexation reactions involve the formation of coordination complexes, where the strontium ion is surrounded by ligands. In seawater, mineral precipitation occurs with ions such as carbonate ions (CO₃²⁻) and sulfate ions (SO₄²⁻). These ions interact with Sr²⁺ and form stable complexes. For example, strontium ions can form complexes with carbonate and sulfate ions to create strontium carbonate complexes such as SrCO₃ and SrSO₄ as indicated in the XRD results.





The reaction for bulk rock dissolution represents the equilibrium between solid anhydrite (CaSO_4) and its dissolved ionic components, calcium ions (Ca^{2+}) and sulfate ions (SO_4^{2-}). By reducing the concentration of Ca^{2+} and SO_4^{2-} ions through mineral carbonation (formation of carbonate minerals) and mineralization (formation of celestine), the equilibrium of the reaction is shifted towards the right, resulting in continues dissolution of the rock. The reaction of strontium ion (Sr^{2+}) with the released SO_4^{2-} , leading to the formation of celestine (SrSO_4) mineral is also presented. Given that anhydrite contains Ca ions suitable for carbonate formation, the introduction of Sr ions serves a dual purpose. It leads to the formation of strontianite, a valuable component for CO_2 carbonation, and celestine, which serves to disrupt equilibrium by removing sulfate ions from the products, thereby facilitating the progression of the reaction.



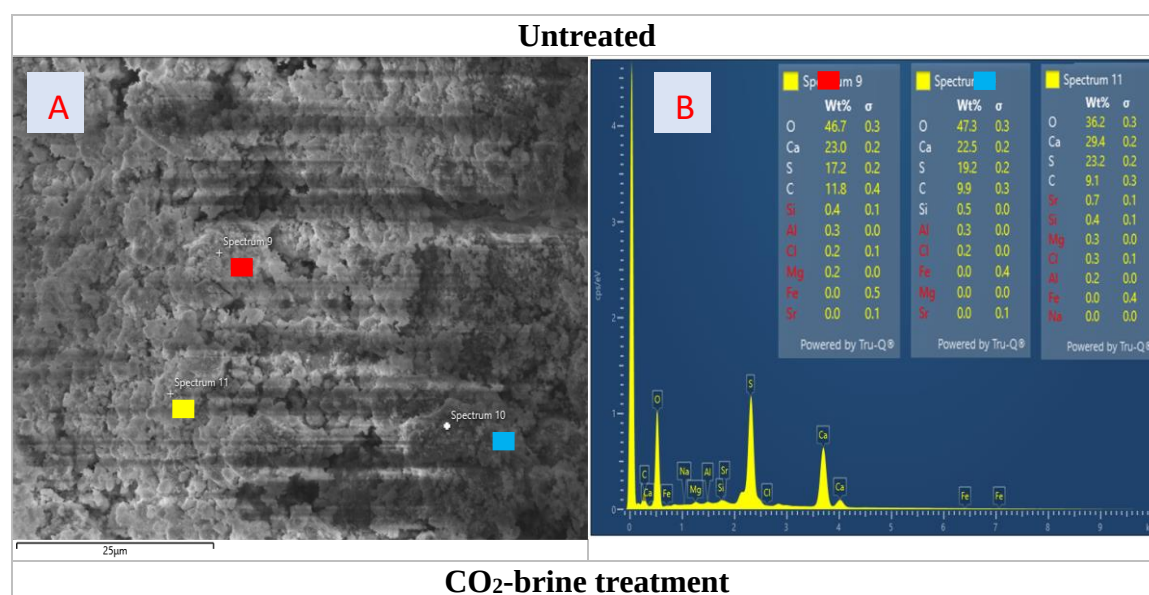
1 → Pre-treatment; 2 → Treated with CO₂– brine; 3 → Treated with CO₂–brine + SrCl₂

Figure 37. XRD mineralogy showing mineralogical compositions before and after supercritical CO₂-brine treatments.

6.3.2 EDX analysis

Point-based Energy-Dispersive X-ray (EDX) spectroscopy was employed to analyze the surface mineralogy of the samples based on their elemental composition. This involved preparing samples by adhering powdered materials onto copper (Cu) tape and subsequently coating them with gold (Au) or platinum (Pt). The analysis focused on three specific points within the untreated samples, those subjected to CO₂-brine treatment, and samples treated with CO₂-brine and SrCl₂. These points are indicated in **Figure 6.5** by red arrows. The

EDX analysis of the untreated sample revealed a predominant composition of oxygen (O), calcium (Ca), sulfur (S), and carbon (C). Additionally, traces of silicon (Si), aluminum (Al), and magnesium (Mg) were detected. This composition aligns with primarily calcium sulfate, as observed in the XRD analysis (refer to section 6.3.1). Upon treatment with CO₂-brine, a noticeable alteration in surface elemental composition was observed. Specifically, there was an increased percentage of calcium (Ca), which can be attributed to the increased presence of calcite and aragonite, as confirmed in the XRD analysis. In the case of samples treated with CO₂-brine in the presence of SrCl₂, there was a notable increase in surface carbon (C) content across all EDX spectra. This increase in carbon content can be linked to the mineralization of carbon into various forms, including calcite, strontianite, dolomite, and magnesite, as elaborated in section 6.3.1 above.



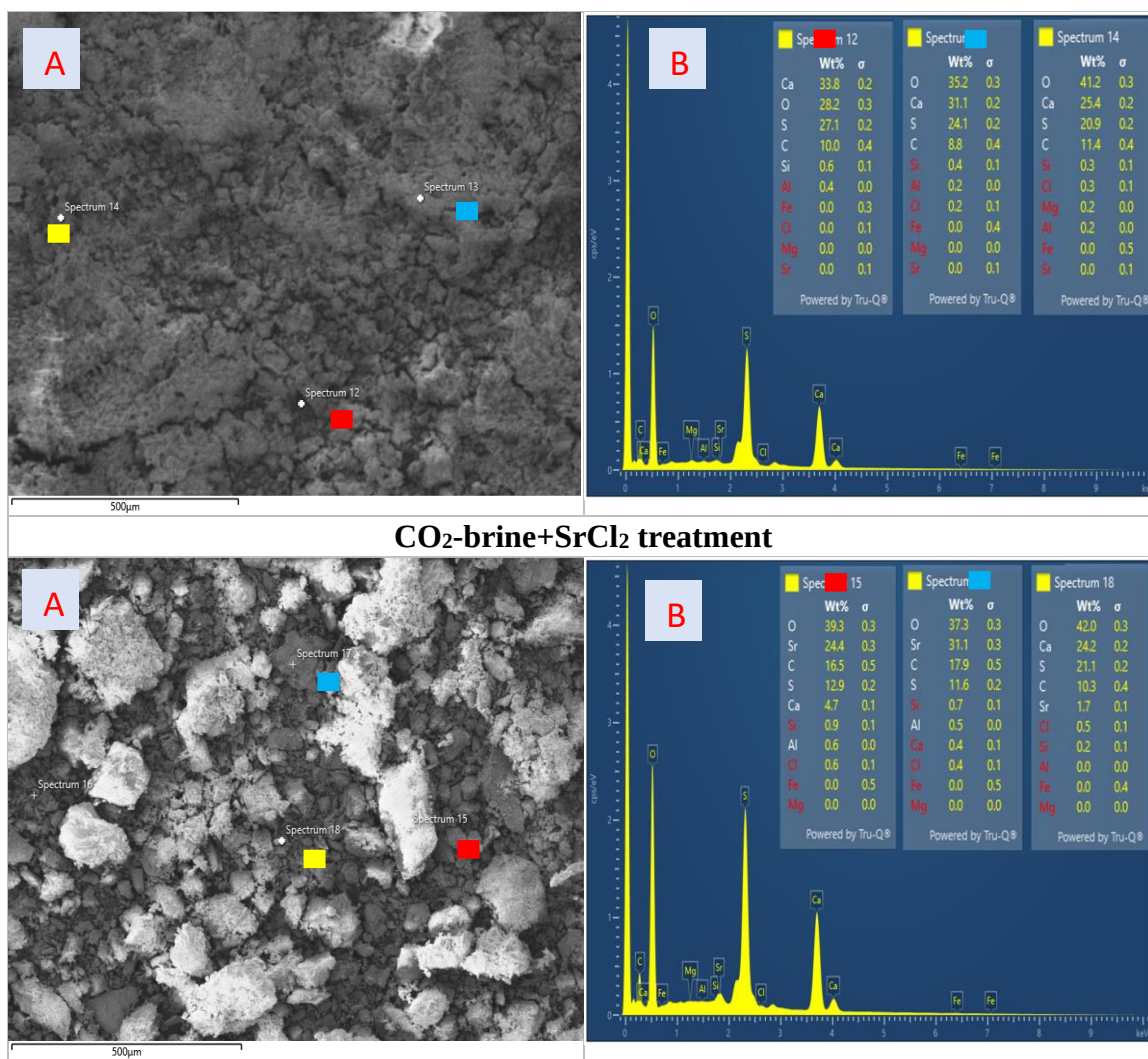


Figure 38. EDX spectroscopy of the elemental composition before and after supercritical CO₂-brine treatments; the colored marks indicate the spectrum points (A); and the corresponding elemental compositions of the points (B) for the untreated, CO₂-brine treatment and CO₂-brine + SrCl₂ treatment.

6.3.3 XRF elemental analysis

Micro-XRF was employed to determine the elemental composition of the sample pre- and post-treatments. The XRF compositional analysis shows that the sample is mainly composed of calcium (Ca) (55.93 wt. %) and sulfur (S) (42.55 wt.%), with traces of other elements including magnesium (Mg), aluminum (Al), silicon (Si), iron (Fe), and strontium

(Sr). The XRF data for the rock sample after CO₂-brine treatments shows modification of the rocks' elemental composition (see **Table 6.5**).

After interaction with supercritical CO₂-saturated brine, the XRF indicates a slight change in elemental composition. The composition after treatment with CO₂-saturated brine showed that Al, Si, K, and Fe increases, this is attributed to the elemental replacements that occurred on the rock surface due to dissolution/precipitation. This is also corroborated in the XRD results where noticeable amount of feldspar (KAlSi₃O₈), quartz (SiO₂), and siderite (FeCO₃) are formed. The XRF analysis of the sample after being exposed to supercritical CO₂-saturated brine with SrCl₂ reveals significant differences in its elemental composition. The dominant elements detected are Sr (52.16 wt.%), Ca (15.86 wt.%), and S (30.59 wt.%). The observed changes in composition can be attributed mainly to mineralogical modifications resulted from the exposure to supercritical CO₂-brine in the presence of SrCl₂, as well as the chemical reactions discussed in the previous section.

Table 6.5. XRF elemental composition (wt.%) of the rock sample pre- and post-supercritical CO₂-brine treatments.

Element	Pre-treatment	Treated with CO₂-saturated brine	Treated with CO₂-saturated brine + SrCl₂
Ca	55.93	54.67	15.86
Mg	0.11	—	0.20
Al	0.38	0.62	—
Si	0.30	0.83	0.34
S	42.55	42.39	30.59
Cl	—	0.23	0.72
K	—	0.31	—

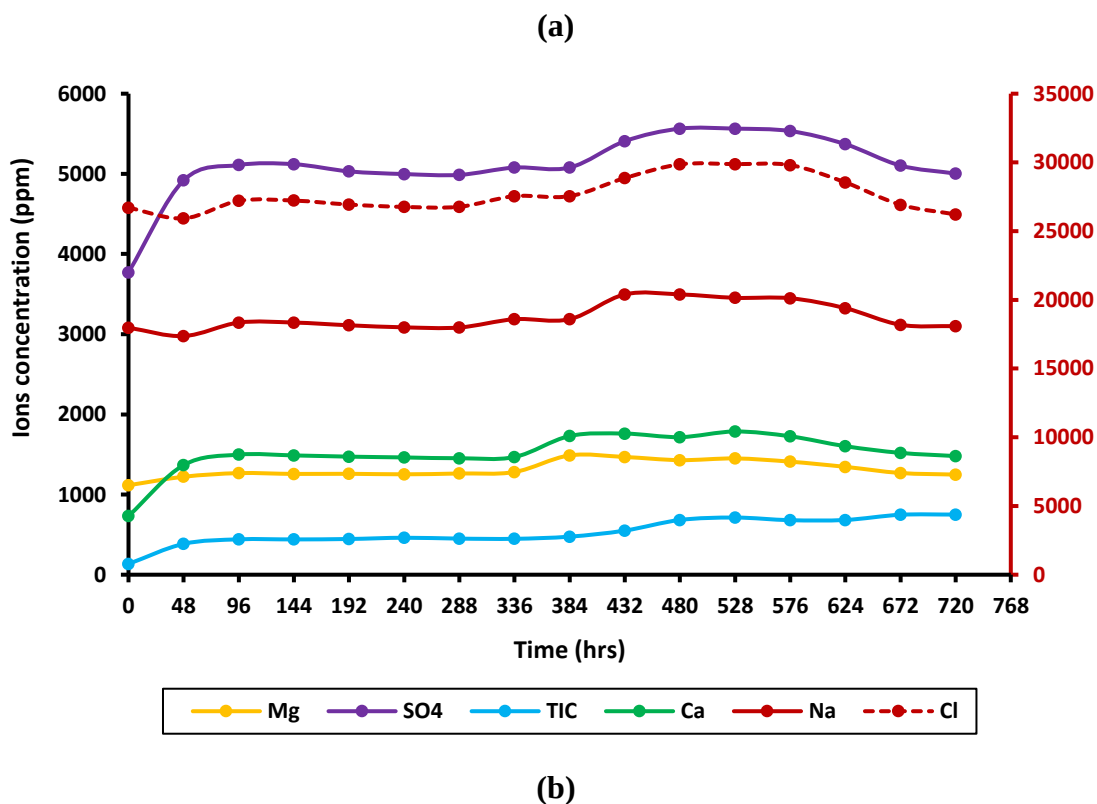
Fe	0.19	0.81	0.13
Sr	0.54	0.16	52.16

6.3.6 IC, TIC and pH analyses

The ionic analysis of the effluents pre- and post-supercritical CO₂-brine treatments provides information about the changes that occur due to dissolution/precipitation of the anhydrite sample in the aqueous phase. **Figure 6.6a** presents the ionic composition of the CO₂-brine effluent, while the pH and conductivity are shown in **Figure 6.6b**. Anhydrite, being the predominant constituent, is chemically reactive and undergoes dissolution and precipitation (Isah et al., 2022a). When in contact with the interacting fluids, several factors influence its solubility, such as temperature and pressure, thus, these influencing factors are kept constant, while salinity and pH, are govern by the resulting interactions (Carlberg & Matthews, 1973; Creaser et al., 2022; Zajacz & Tsay, 2019). The dissolution of anhydrite decreases as the concentration of Ca²⁺ and SO₄²⁻ increases in aqueous phase, this can be observed in **Figure 6.6a** (green and purple curves, respectively). CO₂ is an active gas that has the ability to initiate the dissolution and precipitation of minerals. In addition, it can dissolve in water to generate carbonic acid (H₂CO₃) (Tang, Hu, et al., 2021), which can further dissociates to bicarbonate (HCO₃⁻) and/or carbonate (CO₃²⁻) ions according to the following equilibrium reactions:



Consequently, a gradual increase in the total inorganic carbon (TIC) content in the aqueous phase is observed in **Figure 6.6a** (blue curve), this is also accompanied by a decrease in the pH level due to hydrogen ions (H^+) formed in the solution (see Figure 6.6b). Thus, the acidic medium, in turn, enhances mineral dissolution and the release of ions from the mineral surface. Therefore, for the CO_2 -brine interaction, the mineralization reactions are driven by fluid-induced dissolution and follow the coupled dissolution-precipitation mechanism as evident from the effluent analysis. This involves the dissolution of the original mineral and the simultaneous precipitation of the resulting products.



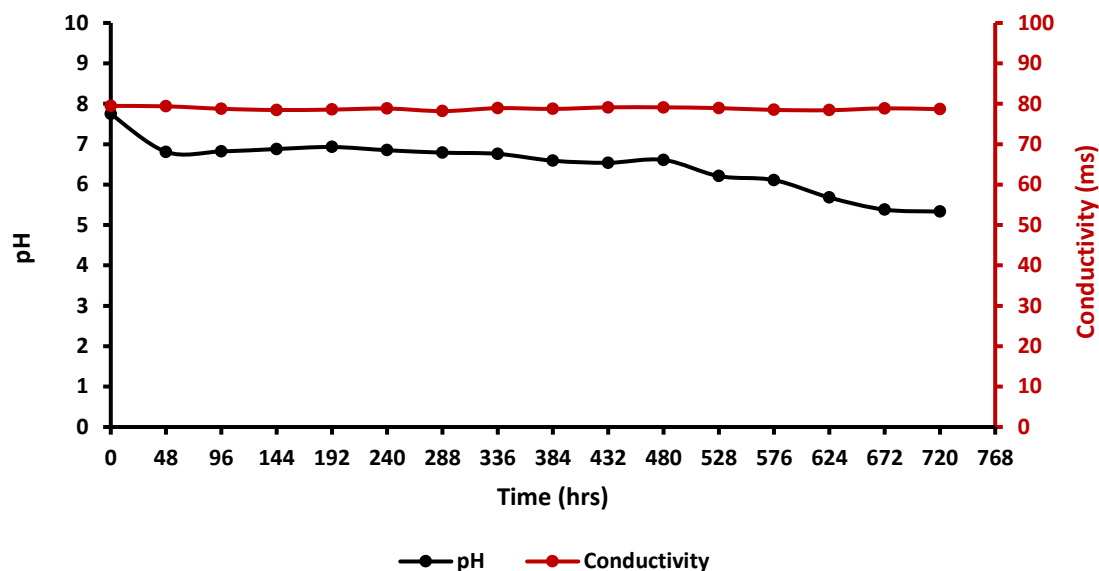
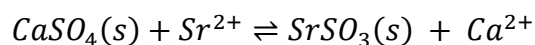


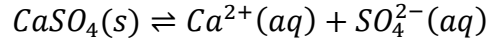
Figure 39. The ionic composition of the effluent of the rock-CO₂-brine interaction.

SrCl₂ dissociates into strontium ions (Sr²⁺) and chloride ions (Cl⁻) in water. The addition of SrCl₂ to seawater leads to change in composition of the seawater, affecting the overall salinity and ion concentrations of the solution. Once in the seawater, the strontium and chloride ions interact with other ions present. These interactions can involve ion exchange, complexation, or precipitation reactions, depending on the specific chemical conditions and concentrations of other ions. Accordingly, this can be one of the possible reasons of the observed reduction in Mg²⁺ concentration of the initial CO₂-charged brine before interaction with the rock. In the presence of Sr²⁺, anhydrite dissolution is often accompanied by Sr/Ca substitution which can be expressed by the following equilibrium equations:

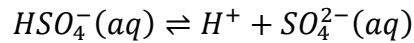
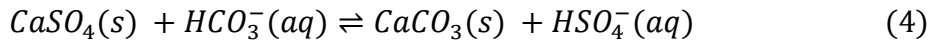


This provide additional Ca²⁺ ions to rock-CO₂-brine system, thus an initial sharp increase in Ca²⁺ concentration is seen in **Figure 6.7a**. The reaction of calcium and carbonate ions

reduces Ca^{2+} ions in the aqueous phase, thus, shifts the reaction equilibrium to the right and more rock will be dissolved with resulting decrease in pH due to additional H^+ ions (see above).



Moreover, solid $CaSO_4$ and bicarbonate ions (HCO_3^-) have the tendency to react, which leads to the formation of solid calcite and hydrogen sulfate ions (An et al., 2021; Worden & Smalley, 1996). In addition, a decrease in the total inorganic carbon (TIC) content of the solution can be attributed to either the consumption of carbonate ions (CO_3^{2-}) through crystallization of carbonates with Ca^{2+} and other divalent ions present during anhydrite dissolution or the removal of bicarbonate ions (HCO_3^-) via the following equation, resulting in the formation of acidic hydrogen sulfate ions (HSO_4^-) and a corresponding decrease in pH.



The ionic composition of the effluent of the rock- CO_2 -brine interaction in the presence of $SrCl_2$ is presented in **Figure 6.7a**. Significantly lower sulfate ions concentration is observed compared to brine without added $SrCl_2$, this is attributed to strontium sulfate crystallization. Moreover, Figure 6.6a displays a slight increase in sulfate ion concentration (purple curve), which shows an initial constant trend. Similarly, the calcium ion concentration (red continuous curve) increases at the start of the interaction, this is due to rock dissolution and subsequent release of Ca^{2+} and SO_4^{2-} into the aqueous phase (see above).

Furthermore, almost all the carbonated CO_3^{2-} in the CO_2 -charged brine is consumed in the carbon mineralization process up to 240 hrs reaction time and then a slight gradual increase is observed (**Figure 6.7a** blue curve). In addition, a decrease in the TIC content is either due to the consumption of CO_3^{2-} by Ca^{2+} released as a result of anhydrite dissolution or the removal of HCO_3^- to form acidic $\text{HSO}_4^-(\text{aq})$ with corresponding decrease in pH, while the fluid conductivity remains unchanged (**Figure 6.7b**).

The slight gradual decline in Ca^{2+} and Mg^{2+} ion concentrations, the stable and non-increasing concentrations of SO_4^{2-} ions and TIC content in the reaction region characterized by the lowest pH (4.33 to 4.44), that is, from 0 to 240 hrs reaction time, suggest that the primary carbonation phase is taking place. This indicates that pH might not be the predominant factor influencing CO_2 mineralization in formations rich in anhydrite. Instead, it is the composition of the brine charged with CO_2 that plays a significant role. As SO_4^{2-} and CO_3^{2-} ions are depleted from the solution, more rock dissolves, leading to enhanced carbon mineralization. Similar conclusion was also reported in the literature (Dai, Wei, Wang, Ma, et al., 2023).

Therefore, the introduction of strontium ions plays a crucial role in the reactions kinetics and subsequent transformation of anhydrite to carbonates and celestine: In the presence of Sr^{2+} , anhydrite replacement occurs via both dissolution-precipitation and diffusion mechanism, the elements diffuse between the solid and the fluid phase. In this case, elements are extracted from the solid and necessary elements diffuse into the solid from the interface between the solid and fluid. This was evident in the relatively higher concentration of Ca^{2+} (extracted from the CaSO_4) coupled with lower ionic concentrations

of SO_4^{2-} , and the TIC content (carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-})) in the reaction effluent when compared to the scenario without Sr^{2+} .

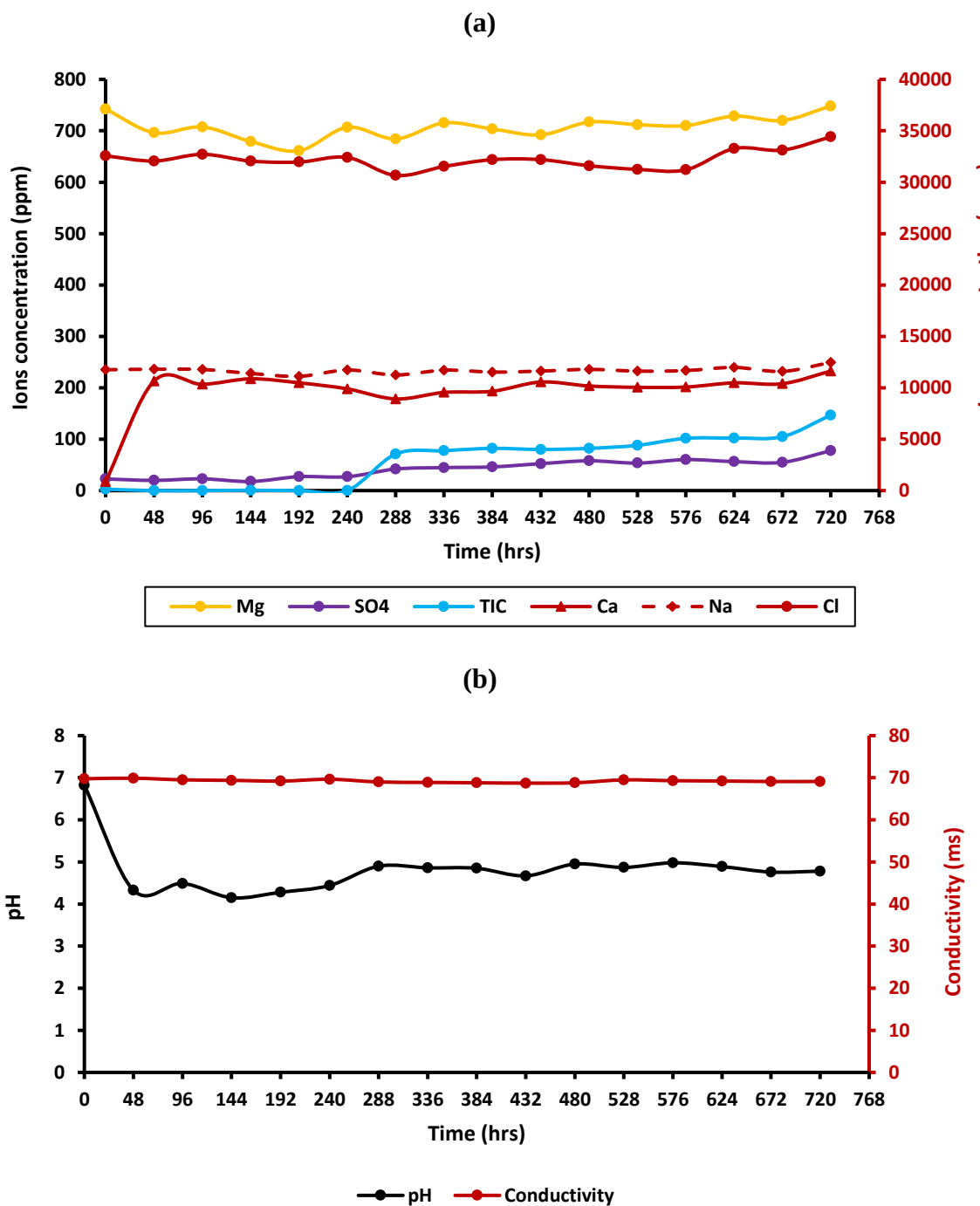
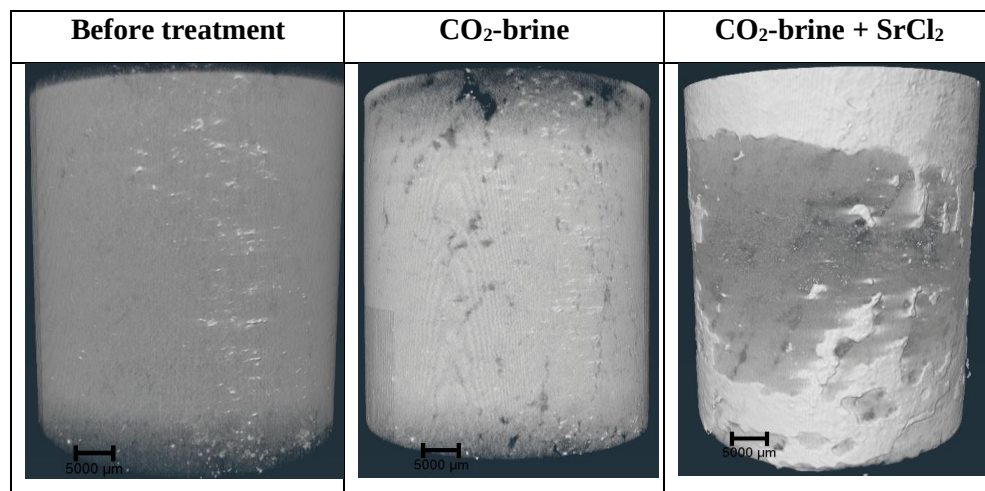


Figure 40. The ionic composition of the effluent of the rock- CO_2 -brine interaction in the presence of $SrCl_2$.

6.3.7 Micro-CT Analysis

The micro-CT scan of the rock sample was conducted both before and after supercritical CO₂-brine treatments. The micro-CT scanning was conducted with specific imaging parameters, including an X-ray voltage of 140 kV, a current of 71 μ A, an exposure time of 3.5 seconds, a total of 2401 projections, a scan duration of 3 hours, a voxel size of 24.95 microns, a circular scan trajectory, and the application of a reconstruction algorithm. The reconstruction process utilized the Filter Back Projection technique, with adjustments for center shift, beam hardening, sample drift corrections, and the application of a Gaussian filter with a kernel size of 0.7. The purpose of this analysis was to examine any changes in the rock's structure and identify potential dissolution effects caused by the CO₂-brine interactions. The results of the micro-CT scan revealed clear evidence of rock dissolution (see **Figure 6.8**). A comparison of the scans before and after the CO₂-brine treatments showed noticeable differences in the rock's morphology. The dissolution process caused certain regions of the rock to undergo material loss, leading to increased pore volume and changes in the overall rock structure.



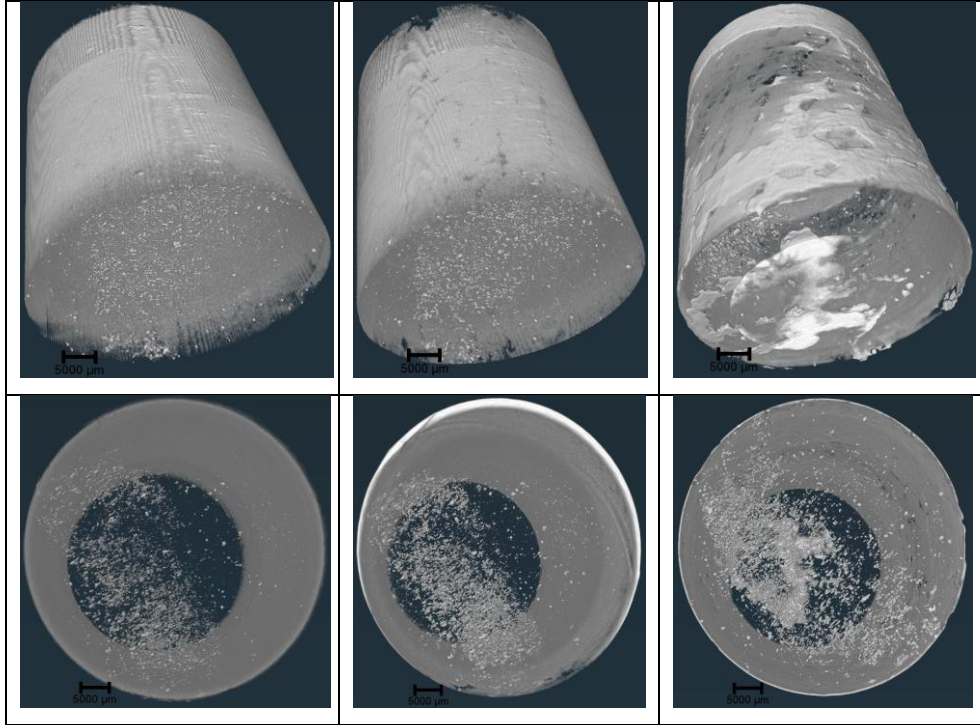


Figure 41. Micro-CT scan of the anhydrite-rich rock sample pre- and post-CO₂-brine interactions (the scale of the images is 5000 μm).

6.4 Geomechanical properties analysis

Geomechanical properties play a crucial role in evaluating the suitability of anhydrite-rich formation as CO₂ storage media, as it determines the rock's ability to securely store CO₂. Rock surface strength, Young's modulus, bulk modulus, and Poisson's ratio are key parameters used to assess the mechanical behavior of the rock sample (Usama Alameedy et al., 2022; Hangx et al., 2009). The mechanical properties of the rock before and after supercritical CO₂ exposure serve as critical factors in evaluating its suitability as potential carbon sinks. A robust rock minimizes the risk of CO₂ leakage and ensures the long-term integrity of the storage site. To assess the geomechanical properties of the rock sample and analyze its physical changes following supercritical CO₂-brine exposure, acoustic measurements were conducted. The shear wave (Vs) and compressional wave (Vp)

velocities were carefully measured. Utilizing these velocity measurements, key parameters such as Young's modulus (E), bulk modulus (K), and Poisson's ratio (ν) were computed for both pre- and post-CO₂-brine treatment conditions. The experimental findings revealed a notable reduction in Young's modulus, decreasing from an initial value of 39.92 MPa to 36 MPa following exposure to CO₂-saturated brine (**Figure 6.9**). Notably, the subsequent exposure to supercritical CO₂-saturated brine supplemented with SrCl₂, further contributed to a reduction in Young's modulus, reaching a final value of 33 MPa. The observed slight decrease in dynamic Young's modulus can be primarily attributed to mineralogical alterations induced by the exposure to supercritical CO₂, as well as the ensuing chemical reactions and associated physical processes. The interactions between the anhydrite-rich rock and supercritical CO₂, including potential dissolution and precipitation of minerals, likely influenced the overall structural integrity and mechanical behavior of the rock (An et al., 2021; Espinoza et al., 2018; Hangx et al., 2009). Moreover, the presence of SrCl₂ in the CO₂-saturated brine solution is believed to have contributed to the observed reduction in Young's modulus, possibly through its influence on the mineralogical changes and stress-strain response of the rock. The mineralogy changes observed through XRD analysis conducted post-treatment shows mineralogy changes happen resulting in mechanical properties changes (see above).

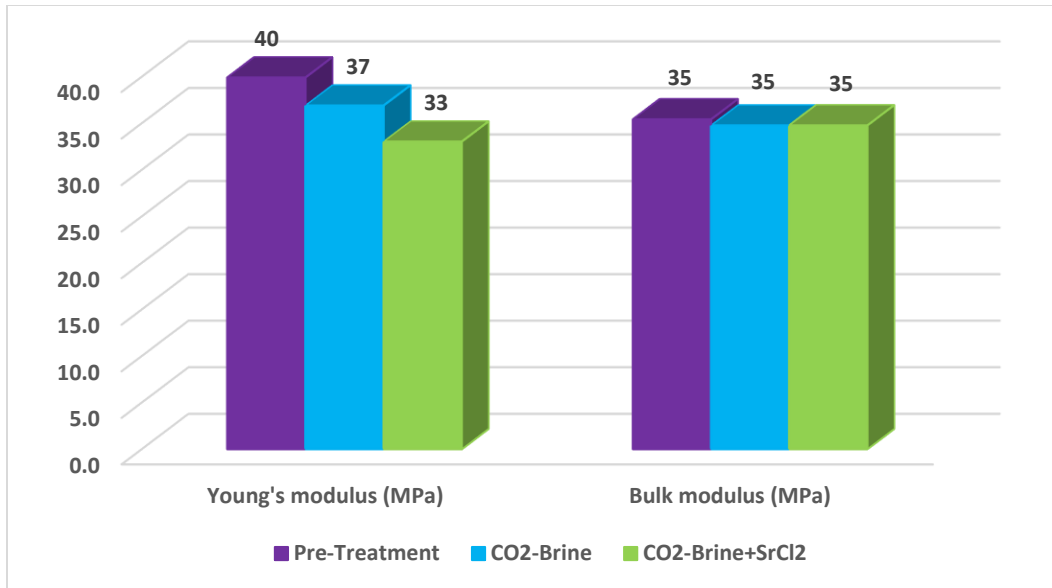


Figure 42. Young's modulus and bulk modulus of anhydrite rock sample pre- and post CO₂-brine interactions.

Furthermore, the bulk modulus was calculated using acoustic data. **Figure 6.9** shows the bulk modulus of the rock. The bulk modulus, which signifies the change in volume or compression in response to applied stress, was initially determined to be 35.42 MPa for untreated anhydrite rock. After exposing the rock sample to supercritical CO₂ saturated brine, a slight reduction in bulk modulus was observed, yielding a measured value of 34.77 MPa. Interestingly, the introduction of SrCl₂ salt into the brine solution prevented any further decrease in bulk modulus. These findings suggest that the inclusion of SrCl₂ may have acted as a stabilizing factor, mitigating the adverse effects of supercritical CO₂-brine exposure on the bulk modulus of rock sample. This observation potentially indicates unaltered response or enhanced stability of the rock under the influence of SrCl₂ in the brine solution.

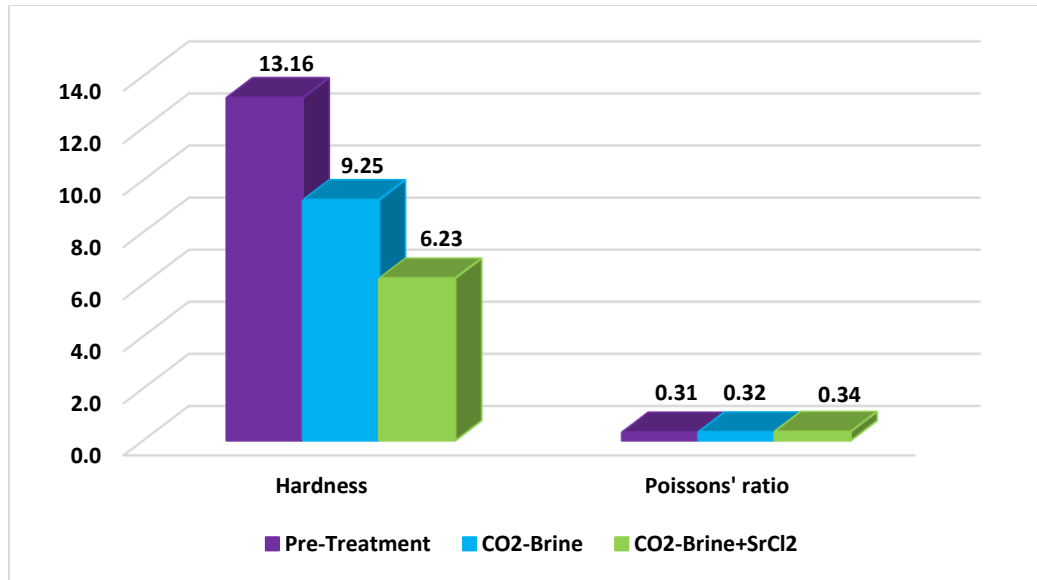


Figure 43. Hardness and poisson's ratio of anhydrite rock sample pre- and post CO₂-brine interactions.

The rock surface hardness (H) was measured before and after the supercritical CO₂-brine exposure using the NER AutoScan instrument (see above). These geomechanical parameters provide valuable insights into the rock sample's structural integrity and mechanical response, allowing for a comprehensive evaluation of its behavior under CO₂-brine conditions. The results revealed a noticeable reduction in hardness, decreasing from an initial value of 13.16 GPa for the untreated sample to 9.25 GPa after exposure to CO₂-saturated brine as shown in **Figure 6.10**. Interestingly, the introduction of SrCl₂ into the brine solution did not lead to an improvement in the strength profile; instead, it further decreased the hardness to 6.23 GPa. This decline in hardness can be attributed to mineralogical changes that occurred during the treatment phase. Similar observation was reported in the previous studies (Aman et al., 2018; S. Kim & Santamarina, 2014; S. Li et al., 2022). The observed reduction in hardness highlights the influence of CO₂ and SrCl₂

on the mechanical properties of anhydrite-rich formation, emphasizing the importance of considering these factors when evaluating its suitability as storage media for CO₂.

Poisson's ratio is a dimensionless material property that quantifies the relationship between transverse strain (lateral contraction or expansion) and axial strain (longitudinal deformation) when a material is subjected to an applied stress (Usama Alameedy et al., 2022; Domenico, 1984). In the context of this study, Poisson's ratio (ν) was computed for both pre- and post-CO₂-brine treatment conditions of the anhydrite-rich rock. The untreated sample exhibited a Poisson's ratio of 0.31. Following treatment with supercritical CO₂-saturated brine, there was a negligible change in Poisson's ratio, with a slight increase to 0.32. Subsequently, when the rock sample was exposed to a solution containing both CO₂ and SrCl₂, there was an additional increase in the Poisson's ratio, resulting in a value of 0.34. This indicates that the interaction with both CO₂ and SrCl₂ in the solution further influenced the lateral contraction or expansion behavior of the rock. This increase in Poisson's ratio indicates that the material became more resistant to volume changes. Essentially, the rock demonstrated an enhanced ability to deform under stress by expanding or contracting perpendicularly to the applied force.

It is worth noting that the changes in Poisson's ratio were relatively small, suggesting that the treatment had a limited effect on the lateral contraction or expansion behavior of the rock (see **Figure 6.11**). Both porosity and permeability of the sample increases after exposure to supercritical CO₂-saturated brine with added SrCl₂. The mineral replacement process is favored by the porosity generated, due to the differences in molar volume and solubility between precursor and product sulfate phases, allowing the progress of the reaction (Isah et al., 2022b; C. Ruiz-Agudo et al., 2019). While there are differences in the

conclusions regarding the trends and extent of porosity and permeability changes, previous research has also indicated that interactions between CO₂ and brine can lead to the dissolution of carbonates in rock formations, resulting in modifications to their porosity and permeability (Carroll et al., 2013; Wang et al., 2021). Studies have shown that the variations in porosity and permeability near injection wells steadily decrease over time (Pan et al., 2016). The alterations in geomechanical properties align with existing literature findings on porosity and permeability. For example, Espinoza et al. (2018) observed about 14% reduction in uniaxial compressive strength in CO₂-treated cores. Rathnaweera et al. (2015) demonstrated a decrease in the damage strength (UCS) of rocks saturated with CO₂-rich water. Typically, the introduction of CO₂ into rock formations leads to a weakening of the rock's strength (Feng et al., 2023). This is primarily attributed to the dissolution and precipitation of rock minerals, which significantly affect the intergranular contacts within the rocks and reduce the bonding energy of the pore structure, ultimately lowering the rocks' strength (Marbler et al., 2013; Song et al., 2023). Thus, these findings provide insights into the petrophysical and mechanical response of the rock under the influence of CO₂ and SrCl₂, contributing to our understanding of its deformation characteristics and potential implications for CO₂ storage applications.

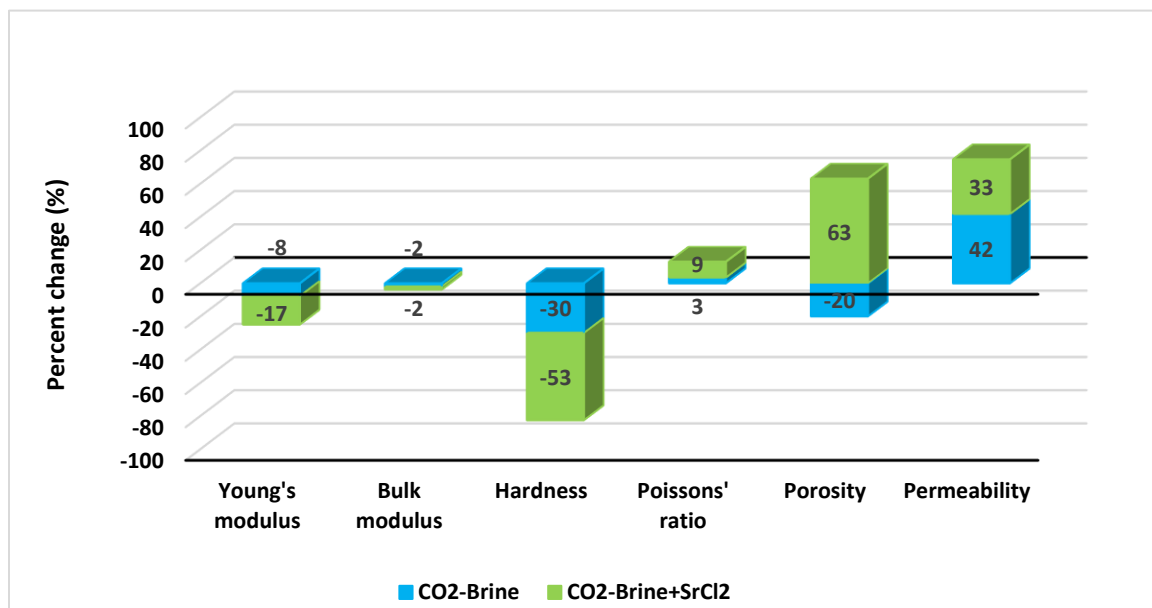


Figure 44. Changes in mechanical and petrophysical properties of the sample after supercritical CO₂-brine interactions.

6.5 Implications for Carbon Storage

Carbon mineralization converts carbon dioxide into stable carbonate minerals through chemical reactions with certain rock formations. This process has significant implications for carbon storage and climate change mitigation. CO₂ mineralization in anhydrite/gypsum offers the potential for long-term and permanent carbon storage. The carbon mineralization in anhydrite-rich formation involves the capture and permanent storage of CO₂ by chemically transforming it into stable rock minerals such as calcite, dolomite, pyrite, magnesite, strontianite, and celestine. By converting CO₂ into solid mineral forms, it effectively locks away carbon dioxide, preventing its release into the atmosphere. Unlike some other carbon capture and storage methods that require ongoing monitoring and maintenance, mineralized CO₂ is stable over geological timescales.

Figure 6.12 shows the total carbon (TC, mg/kg of rock) content in the solid phase before and after supercritical CO₂-brine interactions. The TC in the bulk rock increased after CO₂-brine exposure. The experimental findings revealed a notable increase in the carbon content within the rock. For the untreated sample, the TC was measured at 1473.07 mg/kg of rock, this value increased to 2773.75 mg/kg after exposure to CO₂-saturated brine. Moreover, the subsequent exposure to supercritical CO₂-saturated brine with added SrCl₂ led to a further increase in the TC, reaching a final value of 5132.51 mg/kg. The observed increase in the carbon content is primarily attributed to the extent of carbon mineralization achieved by the respective CO₂-brine treatments, as well as the resulting chemical reactions and associated physical processes. The introduction of SrCl₂ in the aqueous phase shows great potential: The outcome indicates higher carbon mineralization efficiency after CO₂-brine interaction in the presence of aqueous Sr²⁺ compared to treatment with CO₂-brine alone. Carbon mineralization in anhydrite-rich formation shows promising prospects for CO₂ geo-storage and can be employed as a potential strategy for mitigating CO₂ emissions in field scale.

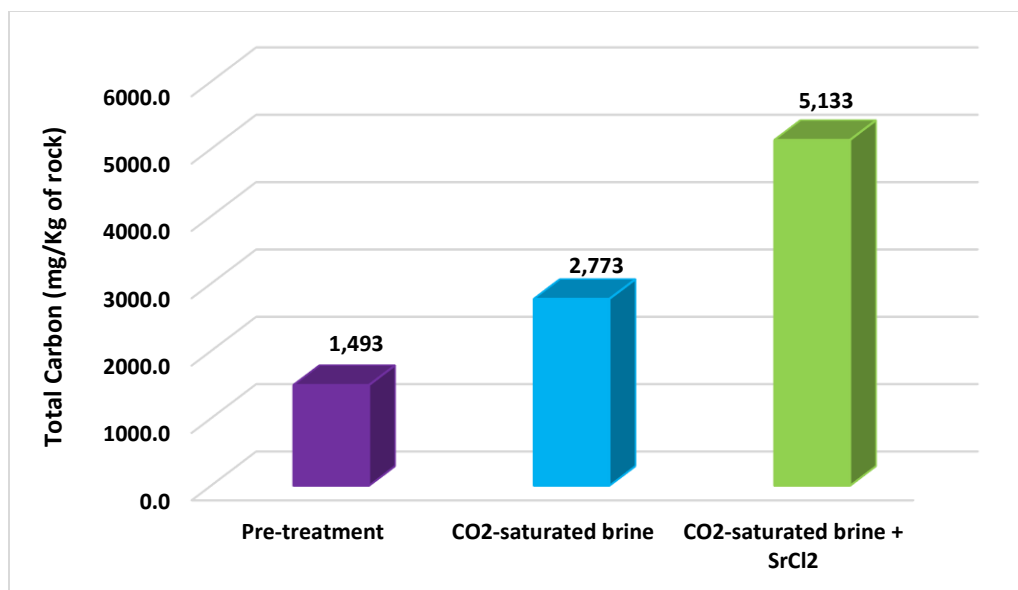


Figure 45. The total carbon (TC, mg/Kg of rock) results in the solid phase before and after supercritical CO₂-brine treatments.

Furthermore, while most of the geomechanical parameters were minimally affected by CO₂-brine exposure, the hardness experienced a notable reduction. However, even after CO₂-brine treatments, the hardness remained relatively high, indicating its potential as a suitable CO₂ geo-storage medium.

A conceptualized schematic of the carbon mineralization in anhydrite-rich formation in the presence of aqueous SrCl₂ is presented in **Figure 6.13**. The purpose of introducing SrCl₂ is to facilitate the precipitation of strontium carbonate and sulfate. Since SrSO₄ density is about 30% greater than CaSO₄, this will create additional capacity for geostorage, as well as enhance reactions and mineralization processes. The generated porosity plays a significant role in facilitating the mineral replacement process, which arises from variations in molar volume and solubility between the original sulfate phases and the resulting products, favoring the mineral replacement process. The geochemical analysis of the reaction effluent demonstrates that the replacement of anhydrite is not solely governed by

the pH; rather, the primary factor is the reaction kinetics that favors dissolution/precipitation reactions. As more sulfate is precipitated due to the introduced Sr^{2+} to form SrSO_4 , Ca^{2+} becomes available for CO_2 mineralization, leading to increased dissolution of anhydrite and simultaneous formation of carbonates (CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, MgCO_3 , and SrCO_3) and celestine (SrSO_4) minerals. Carbonates and the sulfate (SrSO_4) minerals formed during the CO_2 mineralization process are stable and have long-term geological storage potential. They can exist for long time, ensuring the sequestered CO_2 remains securely stored.

Figure 46. Conceptual schematic of carbon mineralization in anhydrite-rich formation in the presence of aqueous SrCl_2 .

In this research, we examined how anhydrite interacts with supercritical CO₂-saturated brine as a means of carbon storage via mineralization. Our experimental approach involved

exposing a sample of anhydrite-rich rock to supercritical CO₂-brine environments, while varying the fluid composition. We conducted anhydrite mineral transformation experiments on an outcrop rock sample in a static reactor under subsurface conditions of high temperature (60 °C) and pressure (104 bar), both with and without the presence of aqueous SrCl₂. To understand the effects of these interactions, we performed mineralogical, geochemical, and geomechanical analyses to observe changes in the composition and structure of the rock.

The results presented herein, demonstrated that under subsurface conditions of temperature and pressure, the replacement of anhydrite with carbonates, followed by the formation of new sulfate mineral, occur through both coupled dissolution-crystallization reactions and elemental diffusion mechanisms. By analyzing XRD data, the reaction effluent, and conducting measurements of TIC on the bulk rock after interactions, several significant findings have been revealed: (i) the initial step of the replacement process is the dissolution of anhydrite surfaces, which determines the rate limitation of the overall process, (ii) for the CO₂-brine interaction, the mineralization reactions are driven by fluid-induced dissolution and follow the coupled dissolution-precipitation mechanism as evident from the effluent analysis. This involves the dissolution of the original mineral and the simultaneous precipitation of the resulting products. (iii) The introduction of strontium ions plays a crucial role in the reactions kinetics and subsequent transformation of anhydrite to carbonates and celestine: In the presence of Sr²⁺, anhydrite replacement occurs via dissolution-precipitation and diffusion mechanism, the elements diffuse between the solid and the fluid phase, where elements are extracted from the solid and necessary elements diffuse into the solid from the interface between the solid and fluid. This was

evident in the relatively higher concentration of Ca^{2+} coupled with lower ionic concentrations of SO_4^{2-} , and the TIC content (H_2CO_3 , HCO_3^- , and CO_3^{2-}) in the reaction effluent when compared to the scenario without Sr^{2+} .

Therefore, this paper presents a novel investigation of the mineral transformation of anhydrite-rich rock obtained from an outcrop. The study explores the kinetics of dissolution, precipitation, and mineralization involved in the replacement process of sulfate (anhydrite) with carbonates (calcite, dolomite, magnesite, strontianite), as well as the formation of an additional sulfate (celestine) mineral. These results contribute to better understanding of the factors controlling the mineral carbonation of CO_2 for carbon geo-storage. By utilizing available rock formations rich in calcium and sulfate ions, large volumes of CO_2 can be mineralized and stored, contributing to significant reductions in greenhouse gas emissions.

CHAPTER 7

ENFORCED CO₂ MINERALIZATION IN ANHYDRITE-RICH ROCKS: BaCl₂

Summary

Carbon dioxide (CO₂) emission is a major contributor to global warming and climate change. Consequently, there is an urgent need to decrease the concentration of CO₂ in the atmosphere and develop reliable methods for its storage. Subsurface carbon mineralization is an effective solution to mitigate atmospheric CO₂ emissions. This study is focused on investigating anhydrite-CO₂-brine interactions as a means of carbon storage in anhydrite-rich reservoirs. To achieve this, we conducted experiments involving anhydrite-rich rock exposed to supercritical CO₂-brine environments. Notably, we conducted a novel mineral transformation of an outcrop anhydrite-rich rock within a static reactor, replicating subsurface conditions of high temperature (333 K) and pressure (104 bar). These experiments were conducted over fifteen days, both in the absence and presence of BaCl₂. A comprehensive suite of mineralogical, elemental, and geochemical analyses was employed, including X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, ion chromatographic (IC) analysis, and micro-computed tomography (micro-CT) assessments. These analyses allowed capturing the changes occurring in the rock's structure and

composition due to the CO₂-brine interactions. The outcomes revealed that anhydrite, when exposed to supercritical CO₂-saturated brine, undergoes a significant mineral transformation. This mineral modification leads to the formation of stable minerals, including calcite, siderite, feldspar, and barite. Consequently, there was an observed increase in total carbon (TC) content of up to 177 % for the CO₂-brine treatment and 266 % for the CO₂-brine + BaCl₂ treatment. These findings provide valuable insights into the potential of anhydrite-based CO₂ storage mechanisms.

Keywords: Carbon mineralization, CO₂ storage, Anhydrite, barium chlorite,

7.1 Background

Carbon dioxide (CO₂) emissions contribute to global warming and climate change. As a result, there is a need to reduce the concentration of CO₂ in the atmosphere and find secure methods for its storage. One approach to address this challenge is subsurface CO₂ storage, which has gained increasing attention in recent years (Alcalde et al., 2018; Bachu, 2008; Baines & Worden, 2004; Caudle et al., 2023; Dou et al., 2023; Hills et al., 2020; Rochelle et al., 2004; S. Yuan et al., 2022; Y. Zhang et al., 2022). This method involves storing CO₂ underground, either in its supercritical form (Alhosani et al., 2020; LI et al., 2023; Pawar et al., 2015) or by transforming it into solid minerals through carbon (Azdarpour et al., 2018; Q. Chen et al., 2020; Dai, Wei, Wang, Zhang, et al., 2023; Gadikota et al., 2020; Matter et al., 2016b; Ostovari et al., 2022; M. Ouyang & Cao, 2023; Parkinson, 2018b; Riffaldi et al., 1996), with the aim of preventing its release into the atmosphere. Carbon mineralization entails injecting CO₂ into underground rock formations along with other

fluids and/or chemicals. Through a series of geochemical reactions, the injected CO₂ interacts with minerals present in the rock, leading to its transformation into various solid rock minerals. This process effectively immobilizes the CO₂ within the geological formation. One of the primary advantages of carbon mineralization is the long-term and safe storage. Once the CO₂ has been solidified into minerals within the rock formation, it can remain stored permanently. Unlike some other CO₂ storage methods, such as traditional reservoirs or geological traps, carbon mineralization reduces concerns about potential leakages and significantly mitigates the need for extensive and ongoing monitoring efforts (Fathy et al., 2023; Madhav et al., 2023; Mouallem et al., 2023; Ostovari et al., 2022).

Utilizing subsurface geological formations such as basalts for CO₂ storage via mineralization has been identified as a dependable approach (Gislason et al., 2010; Jingwen Lu et al., 2024; Mcgrail et al., 2006; Power et al., 2013b; A. Raza et al., 2022; Riffaldi et al., 1996; Romanov et al., 2015). However, there are a few experimental studies in the literature on carbon mineralization in anhydrite-rich rocks to evaluate their potential for subsurface CO₂ storage (Bang et al., 2014; González-Illanes et al., 2017a; Isah et al., 2022a). Anhydrite is chemically reactive and undergoes dissolution and precipitation; therefore, it holds great potential for CO₂ storage via mineralization (Isah et al., 2022a; L. Yu et al., 2019). In particular, Forjanes et al. (2020) investigated brine/anhydrite-gypsum mineralization under various conditions and reaction duration. Gypsum was exposed to 1.5 ml of 0.5 M SrCl₂·6H₂O and BaCl₂·2H₂O solutions in a batch reactor at a temperature of 298 K and 1.0 bar pressure over a wide duration (5 min to 168 h). Their results demonstrated the mineral transformation of gypsum to celestite and barite. Ruiz-Agudo et

al. (C. Ruiz-Agudo et al., 2019) conducted similar experiments in a static reactor at ambient conditions for 30 minutes to 168 hours reaction time and reported the mineral conversion of gypsum to barite.

Recently, several innovative approaches to accelerate CO₂ mineralization have also been reported. For instance, the in-situ pH swing, to promote divalent ions extraction from the precursor rock surface and enhanced carbonate precipitation (Altree-Williams et al., 2017; Azdarpour, Asadullah, Junin, et al., 2015; Fernández-Díaz et al., 2009; Roncal-Herrero et al., 2017; Xu Shao et al., 2024; L. Yu et al., 2019). Chen et al. (Q. Chen et al., 2020) experimentally studied the carbonation of phosphogypsum as a means of CO₂ storage. The experiment was carried out in the presence of NaCl and NH₄OH solutions as pH swing agents, and subsequently 150µm rock powder was exposed to CO₂ in a glass beaker at 303 K and ambient pressure for 60 to 150 minutes. Their results showed a significant transformation of gypsum to calcite. González-Illanes et al. (González-Illanes et al., 2017b) investigated the mineral transformation of anhydrite via batch reactor experiments in the presence of aqueous Na₂CO₃ and MgCl₂ at ambient temperature and pressure. The results revealed a notable transformation of anhydrite and gypsum to calcite and aragonite over the 30-minutes to two months period. Additionally, the study found that mineral transformation occurs even during a short experimental duration.

Thus, it is clear that carbon mineralization represents a promising and environmentally responsible approach to CO₂ storage in subsurface formations. It leverages natural geochemical processes to lock away CO₂ in solid mineral form, ensuring its long-term storage and contributing to efforts to combat global climate change.

Although several experimental studies on carbon mineralization as a means of CO₂ conversion have been conducted on anhydrite and gypsum (Forjanes et al., 2020; Isah et al., 2022a; L. Yu et al., 2019), as well as in basaltic rocks (Hills et al., 2020; P. Kelemen et al., 2019; Matter et al., 2016b; Mohammed et al., 2024). However, there is currently no existing work investigating carbon mineralization and storage capacity specifically for assessing the potential of anhydrite-rich reservoirs for underground CO₂ storage applications. This specific research gap exists in assessing the potential of these reservoirs for underground CO₂ storage applications under subsurface conditions of high temperature and pressure. Therefore, this study aims to explore the mechanisms and potential of anhydrite-CO₂-brine interactions for CO₂ storage. We conducted experiments using an anhydrite-rich rock exposed to supercritical CO₂-brine environments, with variations in fluid composition. The storage capacity and extent of CO₂ mineralization at different fluid compositions were assessed in a batch reactor under reservoir conditions. A noteworthy aspect of our research is the novel mineral transformation of an outcrop anhydrite-rich rock sample within a static reactor, simulating subsurface conditions of high temperature (333 K) and pressure (104 bar), both in the absence and presence of BaCl₂. The addition of BaCl₂ aims to promote the complexation of Ba²⁺ and SO₄²⁻ so more Ca²⁺ will be released for carbonation while sustaining a continuous reaction that includes CaSO₄ dissolution and the formation of carbonate minerals, ultimately enhancing CO₂ mineralization.

7.2 Methods

7.2.1 Fluids: Brine and CO₂

The brine solution was prepared using five salts: sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), sodium bicarbonate (NaHCO₃), and sodium sulfate (Na₂SO₄) (Sigma-Aldrich). These salts were carefully combined in specific proportions to create a synthetic brine solution that closely mimicked the ionic composition of seawater typically found in the Arabian Gulf (Mohammed, Isah, Al Shehri, Mahmoud, Arif, et al., 2022c). High-purity carbon dioxide (CO₂) at 99.9% was employed as the gas phase for brine carbonation and interactions with anhydrite. The ionic composition of the seawater is detailed in **Table 7.1**.

Table 7.1. Ionic composition of Arabian gulf seawater.

Ions	Concentration (ppm)
Na ⁺	18,300
Ca ²⁺	650
Mg ²⁺	2,110
SO ₄ ²⁻	4,290
Cl ⁻	32,200
HCO ₃ ³⁻	120
TDS	57,670

7.2.2 Experimental Procedure

The study was conducted using anhydrite-rich rock and a series of experiments were performed to characterize the rock. The initial gas porosity and permeability of the rock sample were measured at 1.46% and 0.068 mD, respectively. The rock was then cut into sister samples with dimensions measuring 8 and 15 mm in diameter and each 7 mm in

thickness. The 7 by 8 mm samples were used for micro-computed tomography (micro-CT) and scanning electron microscopy- electron dispersive X-ray spectroscopy (SEM-EDS) analysis while the 7 by 15 mm samples were used for other measurements pre- and post-experiments. To assess the bulk mineral composition of the rock, X-ray diffraction (XRD) analysis was performed. The primary constituent of the sample was identified as calcium sulfate (CaSO_4), with amounts of other minerals such as quartz, dolomite, calcite, and scapolite group. The initial properties of the rock before undergoing CO_2 -brine treatments measured: Initial evaluations included measurements of the mineralogical and elemental compositions via XRD and X-ray fluorescence (XRF), Fourier Transform Infrared (FTIR) spectroscopy, micro-CT imaging, and total carbon (TC) content. The FTIR analysis provides information on the changes in functional groups and modifications that occurred during the CO_2 -brine treatments. Micro-CT scans were conducted to quantify the dissolution/precipitation and evaluate the changes in porosity following the interactions. Additionally, TC analysis was employed to determine the carbon content of the rock corresponding to CO_2 mineralization. The subsequent step involved exposing sister rock samples to a supercritical CO_2 -saturated brine treatment under high-pressure high-temperature (HPHT) conditions in the presence and absence of BaCl_2 . The addition of BaCl_2 is to enforce the concurrent precipitation of barium sulfate and carbonate while maintaining a balanced reaction that involves the dissolution of rock and the precipitation of carbonate minerals. This addition of BaCl_2 is a controlled step designed to influence the CO_2 mineralization processes during the rock- CO_2 -brine interaction, thus enhancing the dissolution/precipitation and overall dynamics of the reactions. These treatments were conducted in a 300 ml static reactor (75 vol.% was filled with brine while 25 vol.% was

occupied by supercritical CO₂). The interaction duration is fifteen days, with operating conditions set at a temperature of 333 K and a pressure of 104 bar, while collecting effluent samples at predetermined intervals.

Post CO₂-brine treatment, the series of assessments were repeated. These include the measurement of the rock's mineralogical composition, micro-CT imaging, XRF, FTIR, SEM-EDS, and carbon content for both rock and effluent fluids. Moreover, the same set of procedures was replicated on the other sister rock sample, with the addition of 2.08 wt.% (equivalent to 0.1 M) BaCl₂ salt to the brine used in the initial CO₂-brine interaction. It's worth noting that the solution was filtered before use in the experiments. The flowchart outlining the sequence of rock-CO₂-brine interactions is depicted in **Figure 7.1**.

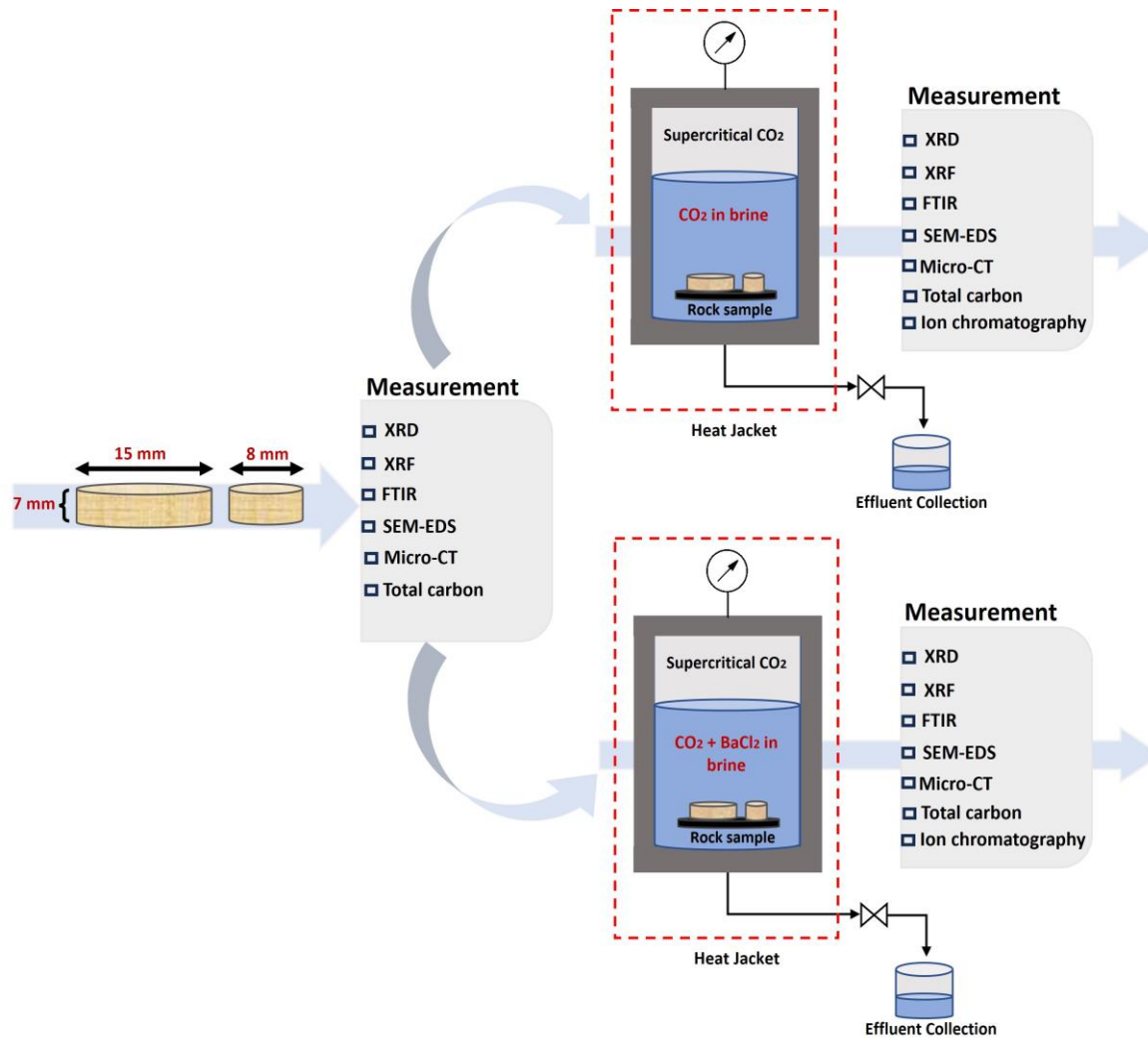


Figure 47. Rock-CO₂-brine interactions experimental flowchart with and without BaCl₂.

7.2.3 Geochemical analysis

To monitor the geochemical changes, 2 ml samples of the effluent were collected approximately three times per week (making a total of 14 ml for seven samples) during the anhydrite-CO₂-brine interactions. While the periodic collection of effluent samples may slightly alter the rock-brine-CO₂ ratio in the reactor and potentially influence the carbonation process, it is important to note that the total sampled volume (approximately

6% of the initial brine volume) has no impact on the reaction temperature. Moreover, the sampling procedure does not lead to a significant pressure decrease; the final pressure at the end of the experiment remains at 101 bar, indicating only a minor 3-bar drop. A required volume of the collected effluent samples was diluted by a factor of 100 using deionized water with a specific resistance of 18.2 M Ω -cm at a temperature of 25°C. This dilution was necessary to ensure that the samples fell within the linear range of the Metrohm's 930 Compact IC Flex-Compact ion chromatography system. After completing the ion chromatography (IC) analysis, a series of peaks corresponding to each ion present in the effluent sample was generated. The area under each peak was considered to be directly proportional to the concentration of the respective ions in the fluid. This proportional relationship was established by comparing the peak areas to known standards with predetermined concentrations.

The analysis of Total Inorganic Carbon (TIC) for carbonate and bicarbonate ions was conducted using Analytikjena's multi-N/C 3100 flow injection TOC analyzer. This analyzer provides results with an accuracy level of ± 1.0 ppm and the capability to detect concentrations as low as 0.2 ppm.

The pH of both the initial brines and the effluent was determined using the Thermo Scientific™ Orion Star™ A215 pH/conductivity benchtop multi-parameter meter, which offers a high level of precision with an accuracy of ± 0.002 .

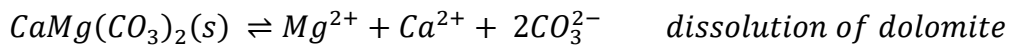
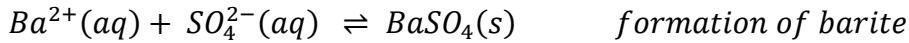
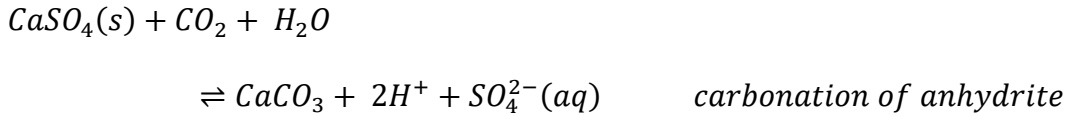
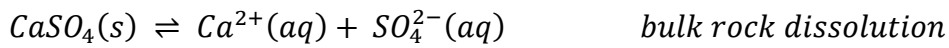
7.3 Results and Discussions

Anhydrite, a mineral composed of calcium sulfate (CaSO₄), can hold great potential in mineral carbonation. This involves the capture and storage of carbon dioxide (CO₂) by

reacting it with minerals to form stable carbonate compounds, effectively removing CO₂ from the atmosphere and storing it in a solid form within subsurface geological formations.

7.3.1 Assessment of Minerals Modification via XRD

The X-ray diffraction analysis of the rock samples exposed to various treatments revealed significant changes in their mineral composition. Anhydrite is chemically reactive and can readily dissolve in water (Isah et al., 2022a). When CO₂ is injected into an underground reservoir (e.g., a depleted oil or gas reservoir or a saline aquifer) or mixed with water and brought into contact with anhydrite-rich rocks or minerals, it can react with the anhydrite to form carbonates (e.g., CaCO₃ and FeCO₃), sulfates (SO₄²⁻), and other rock minerals depending on the fluids composition and rock mineral impurities. The resulting carbonates are stable solid minerals that do not readily dissolve. These minerals can precipitate within the rock formations, effectively locking away the carbon dioxide in a geological reservoir. These reactions can be represented as follows:



As shown in **Figure 7.2**, the primary mineral content of the unaltered sample consisted of 85.4 wt.% anhydrite, 2.2 wt.% calcite, 7.8 wt.% dolomite, about 3.7 wt.% composition of the scapolite group, with traces of quartz, aragonite, feldspar, and siderite. Scapolites represent a group of silicate minerals found in rocks, composed of aluminum, calcium, and sodium silicate, with chlorine, carbonate, and sulfate. This mineral group encompasses various aluminosilicates, including meionite, marialite, and silvialite (Almeida & Jenkins, 2017; Evans et al., 1969). The scapolite occurs in sedimentary, metasedimentary, and igneous rocks depending on the depositional environment. They can be calcic (where calcium is predominant over sodium). These different forms can include carbonate (meionite component, formula as $(\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3))$), sulfate groups (silvialite component, $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)$), or predominant over chlorine (marialite component, $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$) (David K. Teertstra & Sherriff, 1996; Torr  et al., 2018).

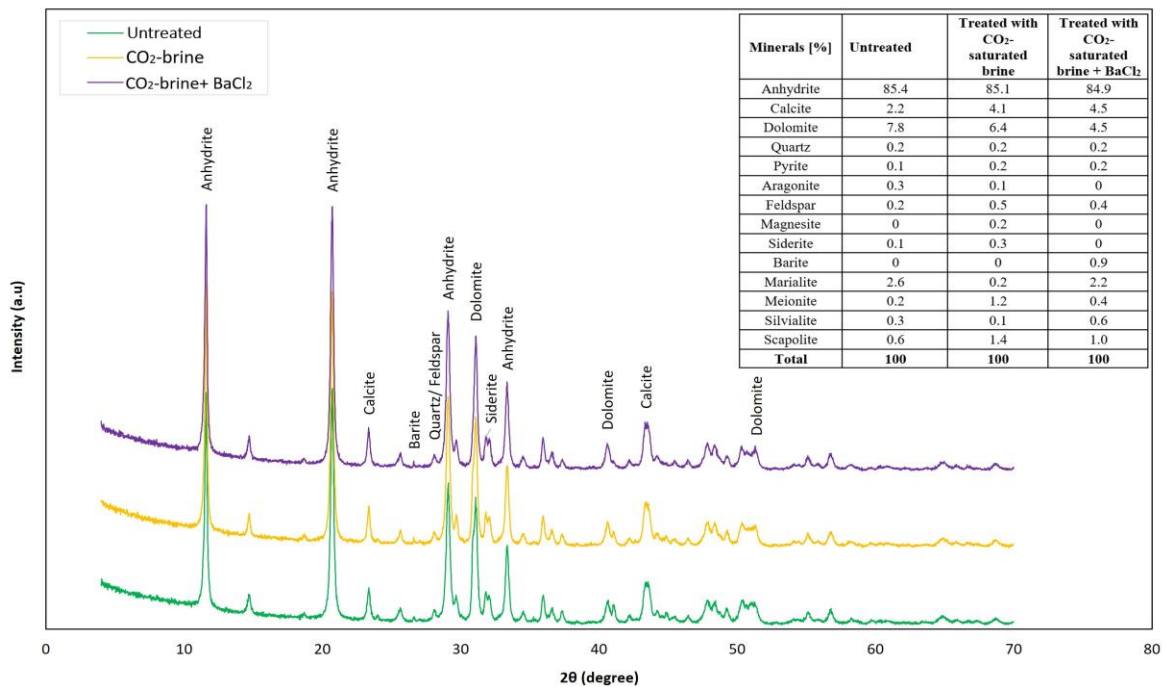


Figure 48. Bulk XRD mineralogy for untreated and CO₂-brine treated rock.

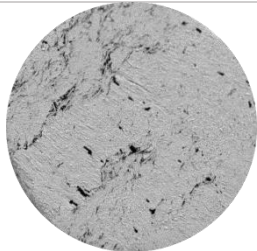
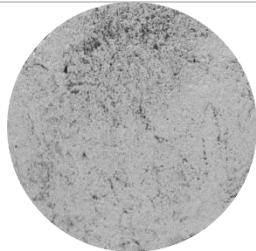
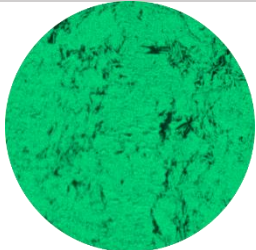
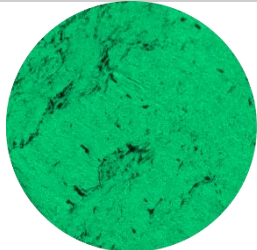
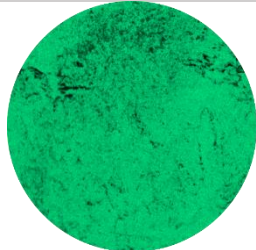
Upon CO₂-brine interaction, a pronounced shift in mineral composition became evident. The most notable transformation occurred in calcite, which saw a significant increase from 2.2 wt.% to 4.1 wt.%, and dolomite, which decreased from 7.8 wt.% to 6.4 wt.%. Notably, the NaCl-scapolite (marialite) decreases from 2.6 wt.% to only 0.2 wt.%, while CaCO₃-scapolite (meionite) increases from 0.2 wt.% to 1.2 wt.%; moreover, the scapolite group (which might contain other members such as mizzonite), increases from 0.6 wt.% to 1.4 wt.%. This shows a significant shift in the minerals' composition after CO₂-brine interaction. It has been indicated that scapolites can transform from one composition to another depending on the environmental conditions (Ellis, 1978; Hamisi et al., 2023; Satish-Kumar et al., 2006; Torró et al., 2018; S. Yuan et al., 2022). Their composition may vary depending on the prevailing condition; for instance, scapolite found in evaporitic settings may be rich in chlorine, whereas non-marine settings might yield carbonate-rich scapolite due to the prevalence of sodium and calcium carbonates rather than halides and sulfates (Mora & Valley, 1989; Vanko & Bishop, 1982). Studies by Teertstra & Sherriff (David K. Teertstra & Sherriff, 1996) and Morrissey & Tomkins (Morrissey & Tomkins, 2020) suggest that Cl-rich scapolites can transform into carbonate-rich forms and vice versa since they form a solid solution. These minerals have been identified as potential carbon dioxide sinks due to their properties (Deer et al., 2013; Newton & Goldsmith, 1975). Additionally, there were increases in the proportions of feldspar and siderite, shifting from 0.2 to 0.5 wt.% and 0.1 to 0.3 wt.%, respectively. This altered mineral composition in the CO₂-brine treated sample strongly suggests the formation of carbonate minerals, with a remarkable increase in its presence. Furthermore, it indicates a slight decrease in aragonite,

and a decline in the weight percentage of dolomite which implies its dissolution from the rock under these conditions.

In the case of the CO₂-brine + BaCl₂ treated sample, the prominent alteration occurred in calcite, it increased from 2.2 wt.% to 4.5 wt.%. In contrast, the composition of dolomite showed a marked reduction from 7.8 wt.% to 4.5 wt.%. The transformation in the scapolite endmembers is not as prominent as in the case of CO₂-brine treatment; the meionite increases from 0.2 wt.% to 0.4 wt.%, while the CaSO₄ endmember (Silvialite) slightly increased from 0.3 wt.% to 0.6 wt.%. Furthermore, there was a slight increase in feldspar from 0.2 to 0.4 wt.%, and the emergence of barite (0.9 wt.%). These observations suggest mineralization and the formation of calcite, barite, and transformation of scapolite endmembers in response to CO₂-brine +BaCl₂ treatment. Meanwhile, the decrease in the weight percentage of dolomite implies its dissolution during exposure to this fluid and conditions. The formation of carbonates favors carbonation, while the dissolution of dolomite promotes de-carbonation. Nevertheless, the most important is the net consumption of CO₂ in the process which is further discussed in the subsequent sections. These changes in mineral composition provide valuable insights into how different treatments affect the rock's mineralogical makeup, which can have significant implications for various geological and engineering applications related to CO₂ storage. This minerals transformation process helps to store the captured CO₂ securely over geological timescales. Once CO₂ is mineralized into carbonates, it is no longer in a gaseous form and is thus stable and immobile. This provides a long-term CO₂ storage solution, as the carbonate minerals can persist for thousands or even millions of years without releasing the stored CO₂ back into the atmosphere.

7.3.2 Elemental Composition by XRF

The principal elements comprising the analyzed rock are calcium and sulfur, with smaller quantities of silicon, aluminum, iron, and magnesium. An X-ray fluorescence analysis of the sample following exposure to supercritical CO₂-saturated brine indicate that the elemental composition remained relatively consistent with the original composition, except for the observable higher intensity of silicon and chlorine (**Figure 7.3**). However, for the CO₂-brine + BaCl₂ treatment, a notable variation was observed. Specifically, there is a distinct presence of barium on the XRF spectrographic map, indicating that barium was introduced into the rock as a result of this particular treatment. This contrast suggests that the introduction of barium chloride (BaCl₂) into the CO₂-brine fluid led to a significant alteration in the rock's elemental composition, manifesting as a noticeable spread of barium on the elemental spectrographic map, presumably due to the complexation of barium and sulfate to form barite as observed in the XRD earlier reported.

Element/Treatment	Untreated	CO ₂ -brine	CO ₂ -brine+BaCl ₂
Calcium (Ca)			
Sulphur (S)			

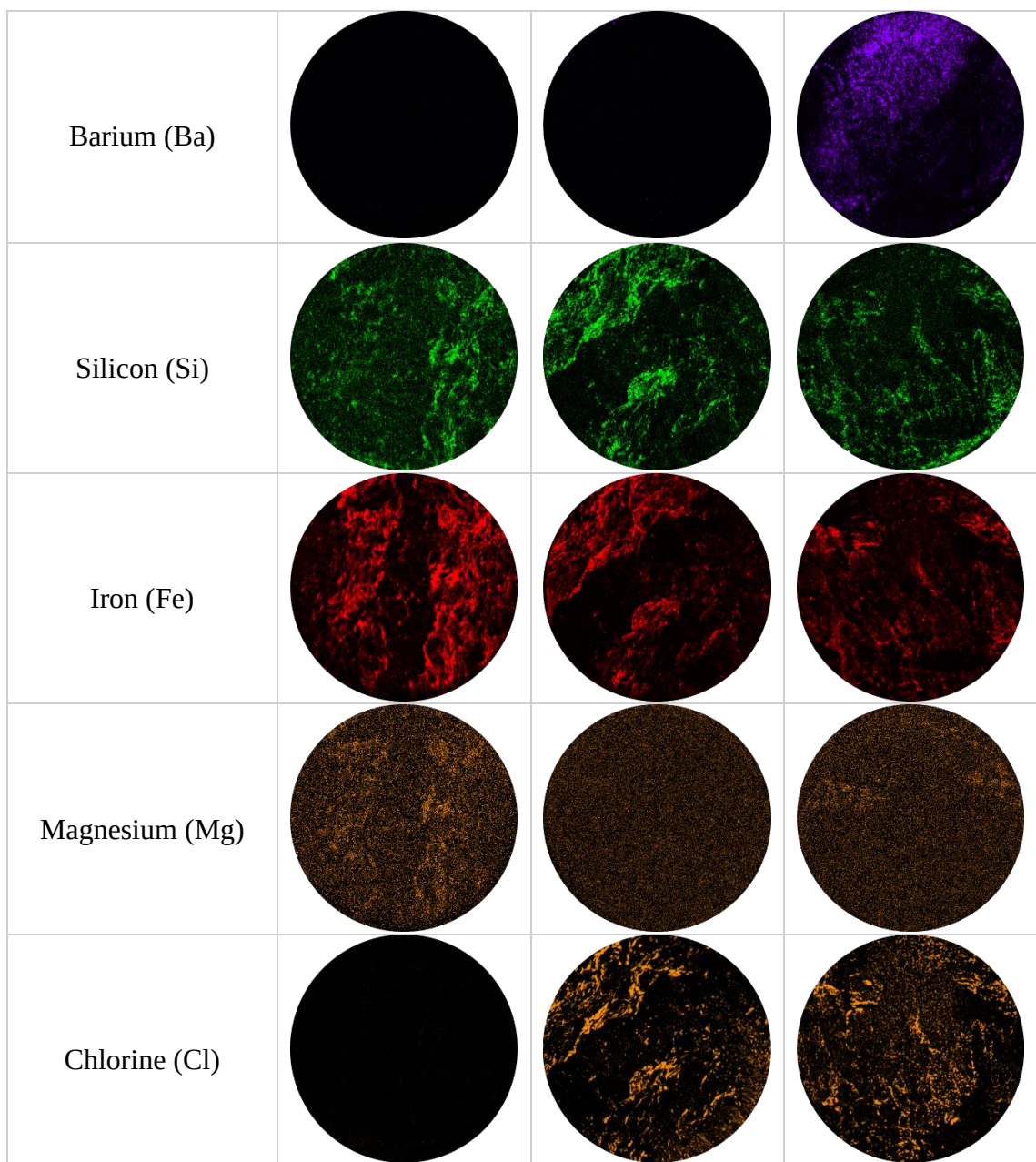


Figure 49. Maps of the dominant elements from X-ray fluorescence (XRF) spectrograph for the untreated, CO₂-brine treated, and CO₂-brine+BaCl₂ treated rock.

7.3.3 SEM Morphology

The scanning electron microscopic (SEM) images provide valuable insights into the structural changes within the three different rock samples: the untreated rock, the rock exposed to supercritical CO₂-saturated brine, and the rock interacted with supercritical

CO₂-saturated brine in the presence of BaCl₂. The SEM images shown in **Figure 7.4** offer a visual distinction among these samples. In the case of the CO₂-brine-rock treatment, the SEM images reveal a notable dissolution and precipitation on the rock surface. This observation aligns well with the results of the geochemical analysis, which suggested that the primary process occurring during CO₂-brine interaction was dissolution and precipitation. The dissolution of the rock surface, as evidenced by the SEM images, corroborates this finding, and underscores the significance of rock-fluid interactions in altering the rock's physical structure. Conversely, for the rock treated with CO₂-brine in the presence of BaCl₂, a different surface morphology emerges. The SEM clearly shows the presence of mineral precipitates on the rock's surface. This indicates that, in this case, the introduction of BaCl₂ to the CO₂-brine-rock system led to predominantly mineral precipitation. These visual observations in the SEM images provide direct evidence of minerals transformation on the rock's surface as a result of the interaction between the fluid and the anhydrite-rich rocks. The dissolution seen in the CO₂-brine-treated sample aligns with geochemical findings, while the clear mineral precipitation in the CO₂-brine + BaCl₂-treated sample highlights the influence of specific chemical additives (BaCl₂) on rock-fluid interactions (Isah et al., 2022b; Tooseh et al., 2018).

Untreated

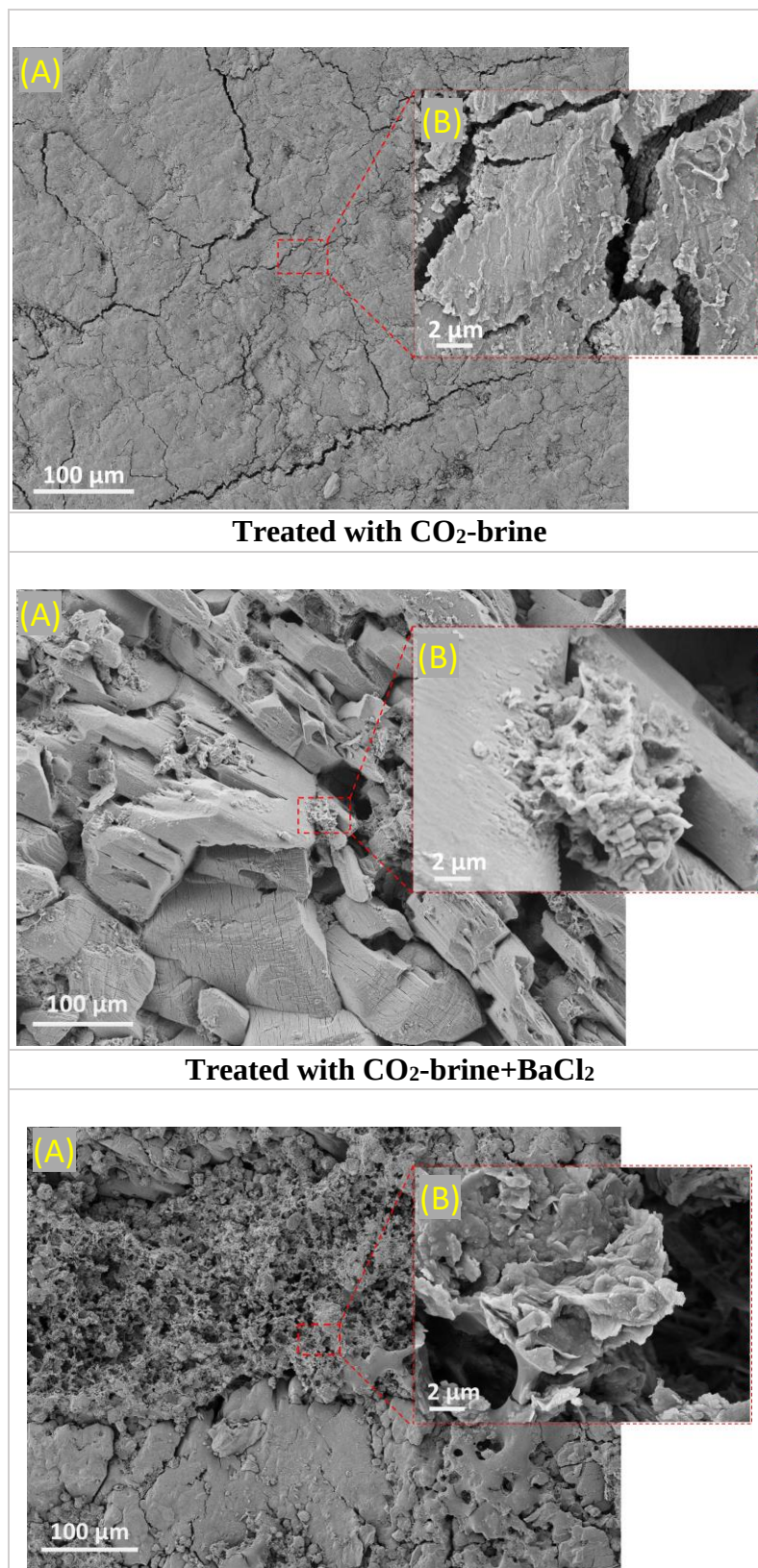


Figure 50. SEM morphology of the rock untreated, and post-CO₂-brine treatments.

7.3.4 SEM-EDS Analysis

The Energy-Dispersive X-ray (EDX) spectroscopy elemental mapping focuses on the key elements present. The results reveal that the untreated rock primarily consists of CaSO_4 with scattered areas of carbonates (indicated by the purple areas) as shown in **Figure 7.5A**. The rationale behind this interpretation lies in the fact that the combination of carbon (in red) and oxygen (in blue) results in a purple color, indicating the presence of carbonates. To further corroborate the presence of carbonates, we refer to the elemental maps in **Figure S1** in the supplementary material. The map (Figure S1g) exhibits an abundance of magnesium in these regions, suggesting that the purple-colored regions contain some carbonates of magnesium, however since no magnesite was observed in the XRD (see above), this potentially represents dolomite. This aligns with the XRD mineralogy findings discussed in the previous section. Additionally, minerals containing aluminum (Al) and silicon (Si) (see aluminum and silicon distribution in **Figure S1d and S1e** of the supplementary material), which are presumed to be aluminosilicate-based exhibited a similar distribution in the carbonate regions, suggesting the presence of carbonate of aluminosilicate, possibly, the scapolite group observed in the XRD. The percentage composition of the elements within the EDX-mapped area is presented in **Figure 7.5b**. The point-based SEM-EDX analysis (**Figure 7.5c**) and the spectrum of elemental composition (**Figure 7.5d**) of the untreated sample also confirm that the untreated sample is primarily composed of CaSO_4 .

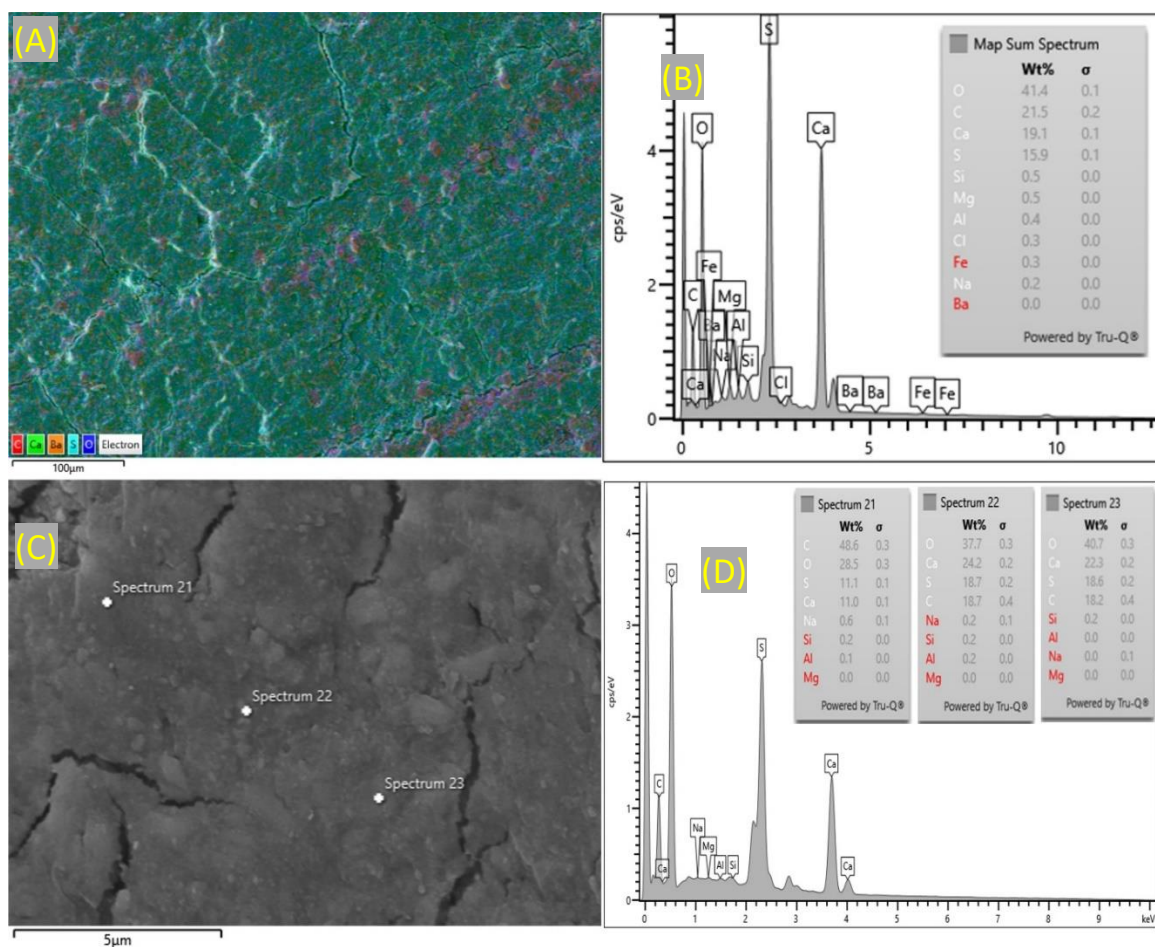


Figure 51. SEM-EDX spectroscopic elemental composition of the untreated rock: (A) EDS layered image, (B) elemental composition of the layered map; (C) point-based SEM-EDS showing the spectrum points, (D) elemental composition of the spectra.

The analysis of the CO₂-brine treated rock revealed notable alteration in minerals. **Figure 7.6a** showed the layered image from the EDS that highlighted considerable presence of carbon (red spots) and carbonates (shown in purple) following the interaction. In **Figure 7.6b**, the elemental map spectrum primarily pointed to the dominance of calcium sulfate. For a more in-depth understanding of the mineral transformation, the point-based SEM-EDS analysis (**Figure 7.6c**) showed that the formed carbonate is composed of aluminum, silicon, chlorine, and sodium, as observed in spectrum 16. Conversely, spectra 18 and 19 (**Figure 7.6d**) primarily represented the host rock (comprising calcium sulfate). In the

supplementary material, **Figure S2** displayed the dissolution of CaSO_4 , indicated by dark areas in **Figure S2a and S1b** for Ca and S. Additionally, there was a notable presence of Al and Si, with traces of Mg, which were evident due to the high intensity of the assigned coloration for these elements in **Figure S2d, S2e, and S2i**, respectively, suggesting the presence of carbonates of aluminosilicate. This information was particularly useful for indicating the presence of the scapolite group.

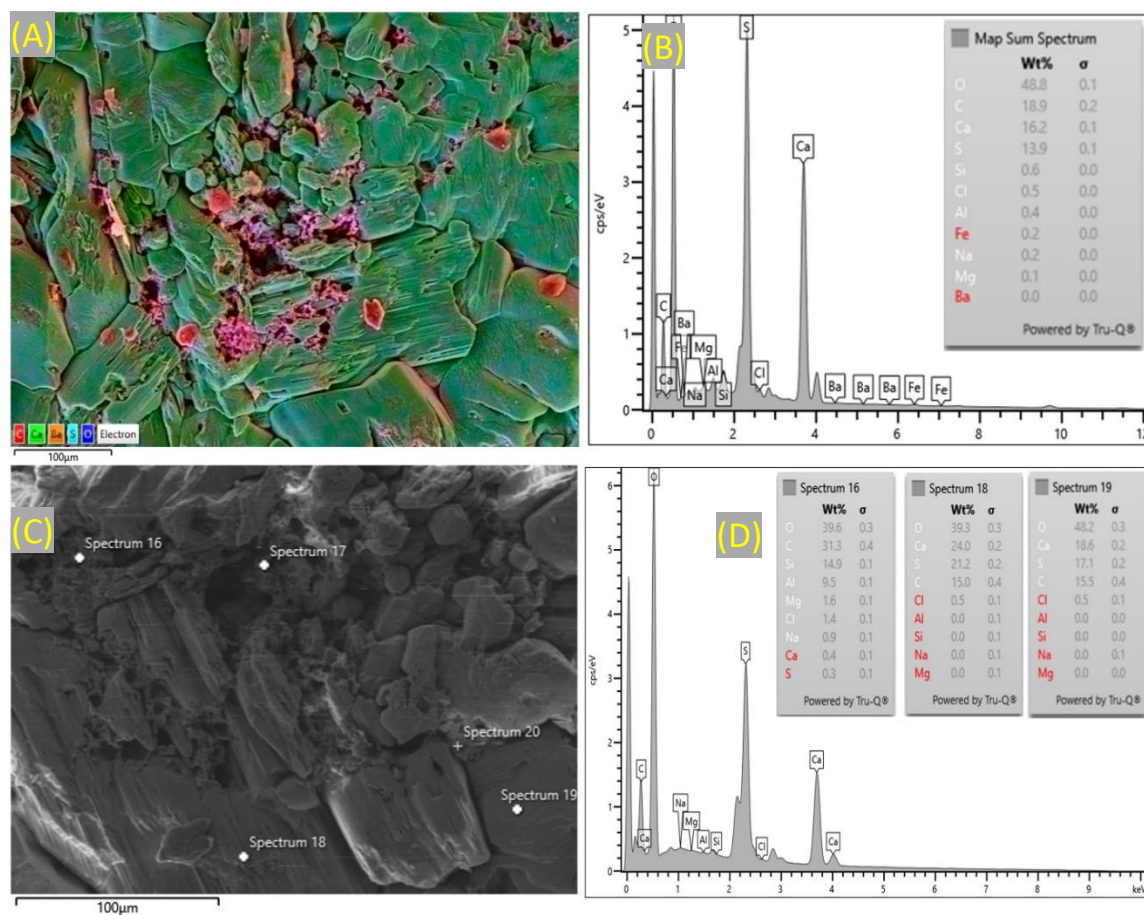


Figure 52. SEM-EDX spectroscopic elemental composition of the CO_2 -brine treated rock: (A) EDS layered image, (B) elemental composition of the layered map; (C) point-based SEM-EDS showing the spectrum points, (D) elemental composition of the spectra.

Figure 7.7 provides a detailed analysis of the elemental composition of the CO₂-brine treated sample in the presence of BaCl₂ using SEM-EDX spectroscopy. Notably, there is a significant presence of carbonates, depicted in purple, while orange-colored regions indicating the presence of barium (**Figure 7.7a**). This observation is further confirmed in **Figure 7.7b**, where the map spectrum displays the elements O, C, Ba, Ca, S, Si, Al, and Cl. This indicates a substantial alteration in the elemental composition of the rock compared to the untreated sample, as shown in **Figure 7.5** above.

Analyzing the point-based SEM-EDS spectra, especially point 8, reveals the precipitation of new minerals primarily composed of C, Ba, O, and S. This new mineral could likely be barium sulfate or carbonates, consistent with the findings in the XRD analysis discussed earlier. Furthermore, the surface morphology and structure of the surface minerals, as observed in **Figure 7.7c**, align with the presence of these new minerals. This correlation is further substantiated by the characteristics of Spectrum 12 and 14 in **Figure 7.7d**, which provide additional evidence of the mineral transformation. Moreover, **Figure S3** in the supplementary material portrays a remarkable alteration in the composition of the sample subjected to CO₂-brine treatment in the presence of BaCl₂. There is an evident replacement of calcium (Ca) and sulfur (S) (**Figure S3a and S3b**) with aluminum (Al), silicon (Si), barium (Ba), and chlorine (Cl), as depicted in **Figure S3d, S3e, S3g, and S3i**, respectively. It's essential to note that the elemental EDS analysis cannot conclusively determine whether the presence of Al, Si, and Cl seen in these figures is due to precipitation resulting from the CO₂-brine interaction or if it is due to the differing dissolution rates that left these elements undissolved, hence displaying higher concentrations. Nonetheless, the primary objective was to verify the changes that occurred post-treatment compared to the untreated

rock. For further validation of the specific functional groups present or formed, an FTIR and the ions analyses were presented in the subsequent sections.

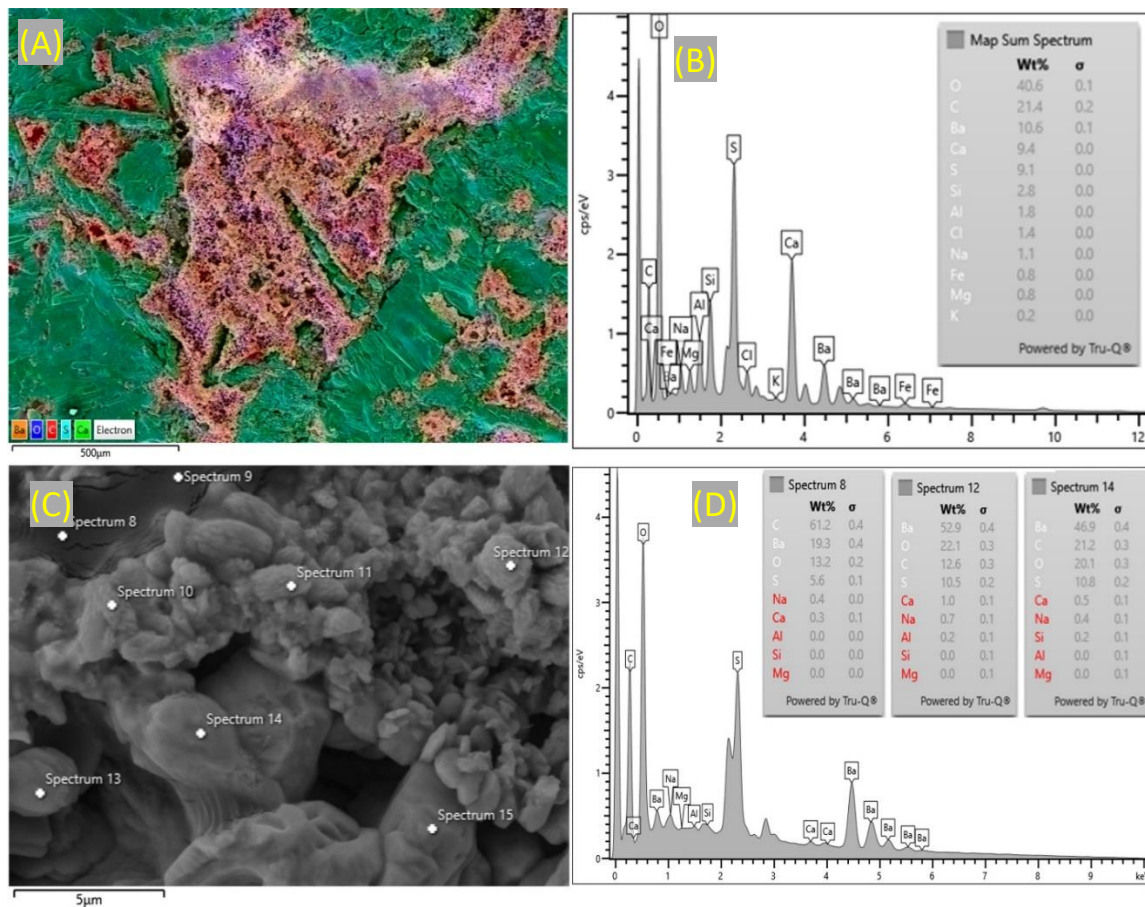


Figure 53. SEM-EDX spectroscopic elemental composition of the CO₂-brine+BaCl₂ treated rock: (A) EDS layered image, (B) elemental composition of the layered map; (C) point-based SEM-EDS showing the spectrum points, (D) elemental composition of the spectra.

7.3.5 FTIR Analysis

We analyzed the spectral domain within the range of 4000 to 500 cm⁻¹ of the FTIR to identify the various species formed or transformed after CO₂-brine interactions. The analysis of FTIR spectra presented in **Figure 7.8** revealed a set of distinct peaks at various wavenumbers, namely 600, 669, 729, 881, 1001, 1111, 1464, 1620, 1684, 2340 - 2360,

2850 - 2930, 3410, and 3541 cm^{-1} . Notably, the presence and intensity of these peaks provide essential insights into the mineral composition and structural changes within the rock after CO_2 -brine interactions. For instance, the anhydrite is characterized by strong bending peaks at 600, 669, and 1111 cm^{-1} is detected in the FTIR spectra. The spectra at 600 and 669 cm^{-1} are attributed to the SO_4 bending in anhydrite (Al Dabbas et al., 2014; Yanyan Chen et al., 2015). The carbonates in the samples were demonstrated by the absorption bands between 3000 and 2850 cm^{-1} , 1620, 1684, and at 881 cm^{-1} , 729 cm^{-1} (Ji et al., 2009).

Additionally, the stretching peaks at 729 cm^{-1} and 881 cm^{-1} corresponds to the presence of dolomite within the sample. The bands at 729 cm^{-1} and 881 cm^{-1} are the characteristic absorption peaks of CO_3^{2-} , which are caused by the bending vibration of CO_3^{2-} in the dolomite structure (Ji et al., 2009; Mroczkowska-Szerszeń et al., 2018; Swayze & Clark, 1990). The band at 729 cm^{-1} is attributed to the in-plane bending mode of CO_3^{2-} in the dolomite structure (Farmer, 1974; M. B. Nguyen et al., 2020; T. T. Nguyen et al., 1991). These FTIR bands illustrate the changes in the amount of dolomite with decreasing trend (peak intensity) from the intact, CO_2 -brine to the CO_2 -brine + BaCl_2 treated rock as observed in the XRD section. The bending peak at 1464 cm^{-1} is indicative of aragonite (Estep et al., 1968), and this peak is most prominent in the untreated rock. Interestingly, this peak disappears entirely in the CO_2 -brine + BaCl_2 treated sample implying no aragonite, aligning with the findings from the XRD analysis discussed the preceding section.

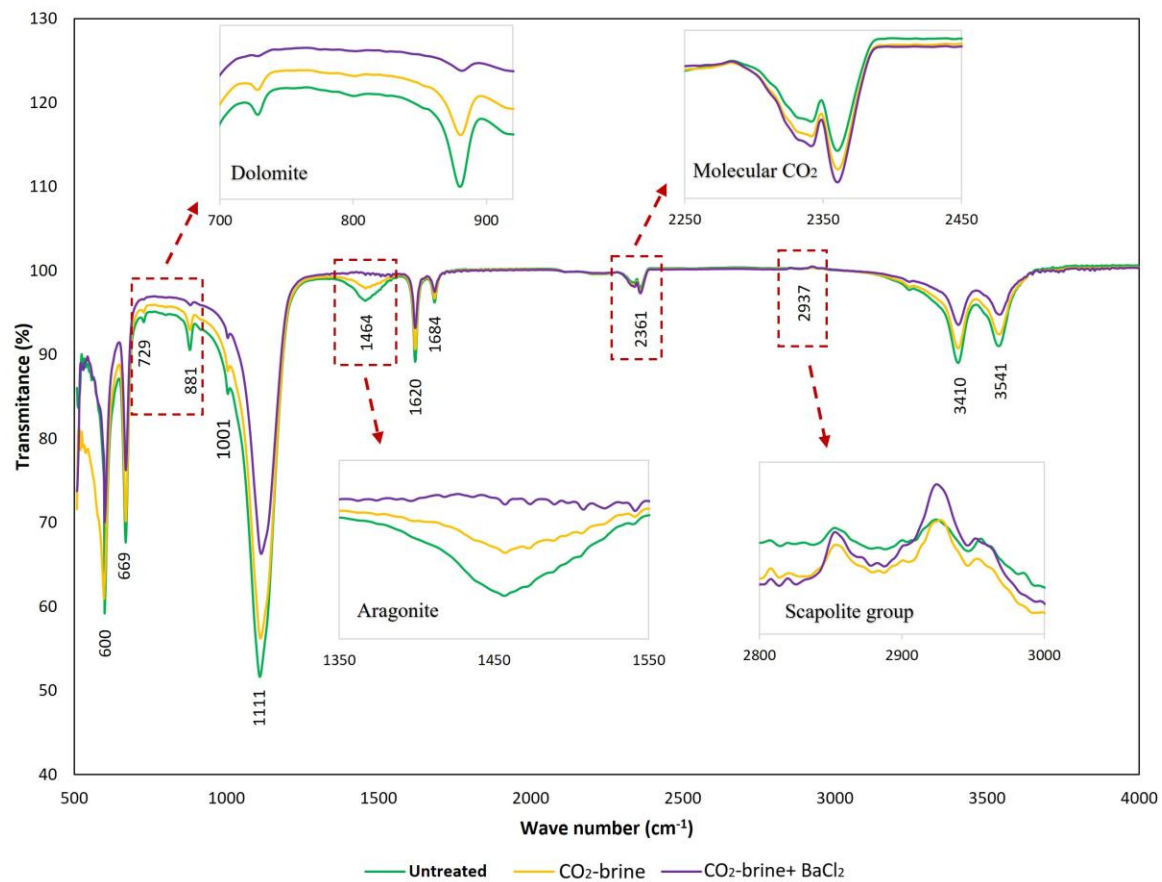


Figure 54. FTIR composition of the untreated rock, and post-CO₂-brine interactions. The zoomed-out spectral domains indicate the changes that occur in the dolomite, aragonite, molecular CO₂, and the scapolite group for the different CO₂-brine treatments.

The FTIR results provide insights on the mineralogical transformations that occurred during the CO₂-brine treatments and their subsequent impact on the sample's composition. Earlier studies have shown that carbon can exist in rocks as molecular CO₂, or as carbonate groups [(CO₃)⁻²] (J. G. Blank et al., 1993). The two peaks at 2342 cm⁻¹ and 2361 cm⁻¹ shows the presence of molecular CO₂ (Della Ventura et al., 2010; Webler et al., 2014). However, the CO₂ antisymmetric stretching vibration (specifically at 2351 cm⁻¹) could also

overlap with the signal of atmospheric, gaseous CO₂, in that case it cannot be easily distinguish (Ni & Keppler, 2013; Schanowski et al., 2023)

The presence of absorption bands within the range of 2800 to 3000 cm⁻¹ is especially useful for indicating the presence of the scapolite group. The absorption peaks at 2885 cm⁻¹ and 2962 cm⁻¹ are attributed to the frequency doubling peak of CO₃²⁻ antisymmetric stretching vibration which is related to the content of scapolite (Rao et al., 2023; Satish-Kumar et al., 2006; Sokolova & Hawthorne, 2008; D. K. Teertstra et al., 1999; P. Yuan et al., 2022). Meanwhile, the band near 2850 cm⁻¹ is linked to calcite (Ji et al., 2009), presumably a CaCO₃-scapolite end-member as shown in the XRD section. The absorption peak at 1001 cm⁻¹ is caused by an aluminosilicate (Rao et al., 2023; Speelman & Schwarcz, 1965), while the band near 1004 cm⁻¹ corresponds to silica vibration (Eniu et al., 2015; Mormone et al., 2011).

Previous studies have found that the character of the carbonate bands in rocks containing aluminosilicate (such as the scapolite) strongly depends on composition. Early investigations conducted by Blank & Brooker (Jennifer G. Blank & Brooker, 1994) and Dixon & Pan (Dixon et al., 1995) highlighted that in NaAl-rich silicate, carbon can exist both as molecular CO₂ and as carbonate groups (Dixon et al., 1995; Fine & Stolper, 1985; Kubicki & Stolper, 1995). Conversely, in Ca and CaMg-rich silicate rock, carbon predominantly exists in the form of carbonate groups. FTIR spectra of CO₂-bearing rocks on the NaAlSi₃O₈-CaAl₂Si₂O₈ join exhibit characteristics transitional between those of the Na- and Ca-rich endmember compositions. The ratio of carbonate to molecular CO₂ increases as the composition shifts from albite (Ab) to anorthite (An), and at a composition of Ab:An of 1:1, all carbon exists as carbonate. The FTIR spectra show bands

corresponding to the asymmetric stretching of CO_3^{2-} around $2850\text{--}2980\text{ cm}^{-1}$ as evidence of carbonation and transformation among the scapolite endmembers (also observed via XRD, as illustrated in **Figure 7.2** above).

7.3.6 Geochemical Analysis

CO_2 is an active gas that can initiate the dissolution and precipitation of minerals. In addition, it can dissolve in water to generate carbonic acid (H_2CO_3) (Tang, Hu, et al., 2021), which can further dissociates to bicarbonate (HCO_3^-) and/or carbonate (CO_3^{2-}) ions according to the following equilibrium reactions:



These species (carbonate and bicarbonate) are collectively categorized as total inorganic carbon (TIC) content in the interacting fluids.

7.3.6.1 CO_2 -Brine-Rock Interactions

Rock-fluid interactions have significant impact on the ion concentration of the effluent brine. In **Figure 7.9a**, we observe the variations in ion concentrations of some key cations: calcium, and sodium for the anhydrite- CO_2 -brine interaction process. The decrease in sodium concentrations implies that the sodium ions were taken onto the mineral surfaces

of the rock. A similar pattern of decreasing concentration of Cl ion is also noticeable, confirming that both Na and Cl were adsorbed by the rock or precipitated on the rock. Interestingly, there is dissolution of the rock's primary mineral component, calcium sulfate, releasing calcium ions into the solution, this is evident from the observed increase in Ca and SO₄ ions concentration of the effluent fluid (**Figure 7.9a and 7.9b**). In addition, the Ca and S distribution in **Figure S2a and S2b** of the supplementary material shows lower concentrations of these elements in some regions on the rock surface, confirming calcium sulfate dissolution. As a result, other calcium-bearing minerals such as calcite precipitate, driving up the calcium concentration as indicated by previous studies (Isah, Mahmoud, Kamal, Arif, & Jawad, 2023b; Minde et al., 2020; Zimmermann et al., 2015).

Figure 7.9b illustrates the sulfate and TIC concentrations in the effluent brine for the anhydrite-CO₂-brine interaction. The sulfate concentration exhibits a slow and gradual increase over time, while TIC concentrations experience a more rapid surge. These changes can be attributed to the dissolution of calcium sulfate (see above) and the precipitation of sulfate-bearing minerals, such as barite, as confirmed by the X-ray diffraction (XRD) analysis. The rapid increase in TIC concentration is primarily linked to the CO₂ dissolution/carbonation of the brine. It's worth noting that the increase in sulfate concentration occurs at a relatively slower rate compared to the rapid increase in TIC concentration. Moreover, both species (TIC and sulfate ions) are being introduced into the fluid (TIC by CO₂ dissolution/carbonation in the brine, while SO₄ is introduced via anhydrite dissolution), as well as being removed by precipitation and mineralization (for carbonate). It is important to note that the increase in TIC of the effluent could suggest a net release of CO₃²⁻ from the rock, as the dissolution of dolomite can release carbonate

ions into the brine. However, if the observed TIC rise resulted from the dissolution of dolomite, there would typically be a concurrent increase in Mg ion concentration in the effluent. Contrarily, the results showed a decrease in Mg ion concentration instead (as depicted in Figure 7.9a). This variation and change in ions concentration highlights the intricacies of the chemical reactions occurring during the anhydrite-CO₂-brine interactions, emphasizing that the dissolution and precipitation processes are not uniform and proceed at different rates.

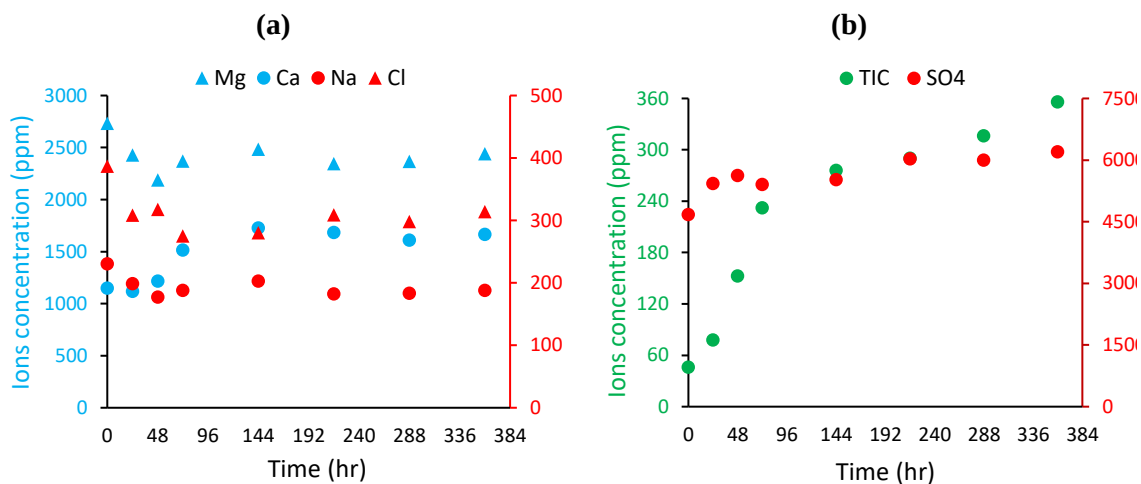


Figure 55. The ionic compositions of the key ions in the effluent of the rock-CO₂-brine interactions.

7.3.6.2 CO₂-Brine+BaCl₂-Rock Interactions

The effluent's ion concentrations of Ca, Na, and Ba ions, along with their initial concentrations (measured at the start of the experiment), are presented in **Figure 7.10a** for the rock-CO₂-brine + BaCl₂ interactions. Notably, the presence of BaCl₂ introduces some distinctive behavior in these ion concentrations compared to the anhydrite-CO₂-brine interactions without BaCl₂. First, there's no significant change observed in the ion concentrations of Na and Ca compared to their initial values. Notwithstanding, an initial

increase in Ca ions concentration suggests dissolution of calcium sulfate (see the Ca and S distribution in **Figure S3a and S3b** of the supplementary material). The presence of BaCl₂ causes slight alteration of the effluent concentrations of these ions. Presumably, there is no precipitation of sodium or chlorine containing components such as halite. Conversely, the concentration of barium ions in the effluent shows a noticeable decrease over time. This decrease is attributed to specific chemical processes occurring in the system: It is primarily linked to the complexation of barium and sulfate ions, culminating in the precipitation of barium sulfate within the rock. As barium sulfate forms and settles within on the rock surface, it reduces the concentration of barium ions in the effluent.

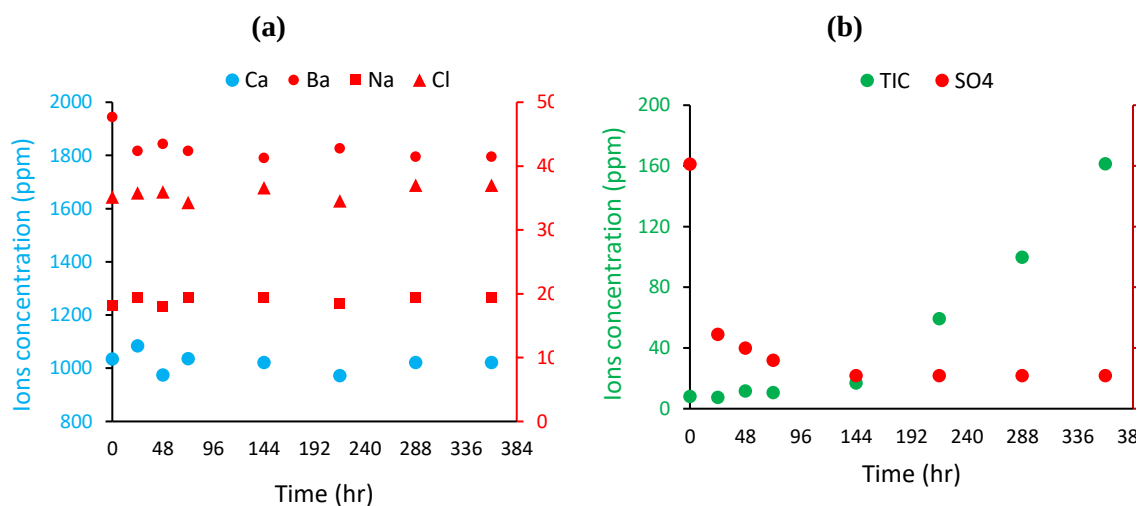


Figure 56. The ionic composition of the effluent of the rock-CO₂-brine interaction in the presence of BaCl₂.

In **Figure 7.10b**, we examine the concentrations of sulfate ion and total inorganic carbon in the effluent during rock-CO₂-brine interactions when BaCl₂ was introduced into the system. It is seen that the sulfate ions' concentration sharply decreases initially and then remains relatively constant over time. This trend can be explained by a combination of

precipitation/dissolution and equilibrium processes. The sharp decrease in SO_4 concentration is a result of sulfate precipitation that predominates anhydrite dissolution. The observed stabilization, beginning after 144 hours of interaction, is thought to result from the concurrent dissolution and precipitation of minerals containing sulfate. This process counteracts the declining trend caused by sulfate precipitation. When BaCl_2 is introduced, it promotes the formation of barium sulfate (BaSO_4) through precipitation. Barium ions from BaCl_2 react with sulfate ions present in the system, leading to the precipitation of barium sulfate as seen in the XRD as discussed earlier.

Unlike sulfate ions, TIC concentration shows a consistent increase over time. This behavior is due to the carbonation of CO_2 in brine. When CO_2 dissolves in water, it forms carbonic acid (H_2CO_3). Carbonic acid, in turn, can dissociate into bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) (see above). As CO_2 continuously dissolves in the brine during the interactions, it leads to the gradual accumulation of these carbonate and bicarbonate species. These chemical changes are fundamental in understanding the complex geochemical reactions in such rock- CO_2 -brine systems.

The rise in TIC concentration in the effluent is a direct consequence of CO_2 dissolution in brine. This increase leads to a decrease in the pH level of the brine, as supported by (Boyd, 2015; Mohammadian et al., 2023; Todd & Peter, 2005). The acidity is a result of the formation of hydrogen ions during CO_2 carbonation. The pH measurement was conducted on the effluent samples immediately after collection, before degassing and cooling. **Figure 7.11** shows that for the CO_2 -brine system, the pH of the brine was 7.41 before the introduction of CO_2 and contact with the rock. However, this value decreased to 4.95 upon encountering CO_2 and the rock. Over time, the pH gradually increased to 5.69 after 360

hours of interaction. In the case of the CO₂-brine + BaCl₂ system, the initial pH of the same brine, with the addition of BaCl₂, was slightly acidic at 6.53. Upon the introduction of CO₂ and interaction with the rock, the pH dropped to 4.93. Subsequently, as reaction progressed, the pH increased to 5.33 at 360 hours. It is important to emphasize that the sudden reduction in pH from 0 to 24 hours interaction time in both cases was due to carbonation of brine as discussed earlier. Nevertheless, the pH gradually increases as the reaction advances, a result of rock dissolution and precipitation, which contributes to a diluting effect on the pH level.

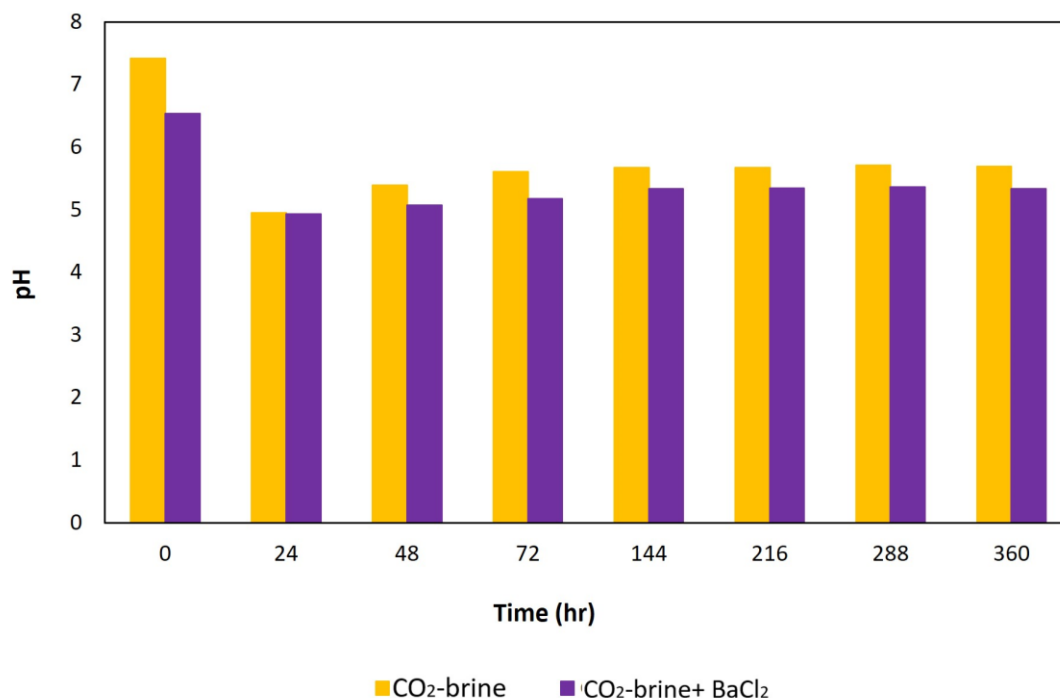


Figure 57. pH of the effluent of the rock-CO₂-brine interactions over 360 hours interaction time.

7.3.7 Micro-CT Analysis

Micro-CT (μ -CT) scans of two similar anhydrite-rich mini-plugs were performed pre and post exposure to CO₂-brine and CO₂-brine+BaCl₂ using the Xradia (Zeiss) Versa 500 μ -

CT equipment. The measured dimensions and mass for the two samples before and after CO₂-brine interactions are tabulated in **Table 7.2**. Comparing the masses before and after interaction, the CO₂-brine treatment showed a more substantial change with a decrease of up to 7.37%, whereas exposure to CO₂-brine with added BaCl₂ exhibited a smaller decrease of 2.45%. However, relying solely on mass changes for a precise conclusion is limited. This implies the potential for either higher dissolution in CO₂-brine treatment than CO₂-brine+BaCl₂ or lower precipitation in CO₂-brine compared to CO₂-brine+BaCl₂ treatment. Yet, this observation aligns with the findings in the SEM and geochemical analysis where higher Ca and SO₄ ions were observed in the reaction effluent (see Figs. 9 and 10 above), signifying higher dissolution in the CO₂-brine treatment.

Table 7.2. Dimensions and mass of the samples before and after CO₂-brine interactions.

Treatment	Length (mm)	Average diameter (mm)	Initial dry mass (g)	Dry mass after interaction (g)	Change in mass (g)
CO ₂ -brine	7.12	8.4	0.6815	0.6313	0.0502 (- 7.37%)
CO ₂ - brine+BaCl ₂	7.25	8.5	0.6762	0.6581	0.0166 (- 2.45%)

A more definitive explanation of these changes will be provided through micro-CT analysis. To quantify the change that resulted from dissolution and precipitation, we analyze the micro-CT scans of the rocks pre- and post CO₂-brine exposure. The voxel resolution was set to 4.5μm for all the scans while ensuring that the entire sample is included in the field of view. An X-ray tube voltage of 140 kV and target current of 64 μA

was used, and 2401 projections were obtained with an exposure time of 3.4 sec. A Filtered Back Projection (FBP) reconstruction algorithm was used to generate the 3D tomogram from the X-ray projections while also performing center shift, beam hardening and sample drift corrections. These images were computationally assessed using PerGeos software (FEI-ThermoFisher) to evaluate the changes in the mineral matrix before and after treatment.

The image processing involved first aligning the orientations of the set of scans for each sample pre- and post-treatment. Followed by registering the two images using normalized mutual information as the metric while keeping the image of the untreated sample as reference. The transformed image was resampled using Lanczos interpolation. The registered images were compared to visually identify the dissolved and precipitated regions. **Figure 7.12** shows the registered 2D μ -CT slices (slice number 80 and 200) for the sample before and after exposure to CO₂-brine (**Figure 7.12a** and **b**, respectively). A blended image (blend of the pre- and post-treatment) of the same 2D slice shows clearly the change occurring in the sample (**Figure 7.12c**). Significant dissolution is observed mainly along the periphery of the treated sample. In **Figure 7.13**, similarly, 2D μ -CT slices are compared for sample before and after exposure to CO₂-brine+BaCl₂. In this case, significant precipitation of high-density mineral (white regions in grayscale image) was seen especially on the surface of the treated sample, whereas dissolution was quite less.

Slice number 80	Slice number 200
-----------------	------------------

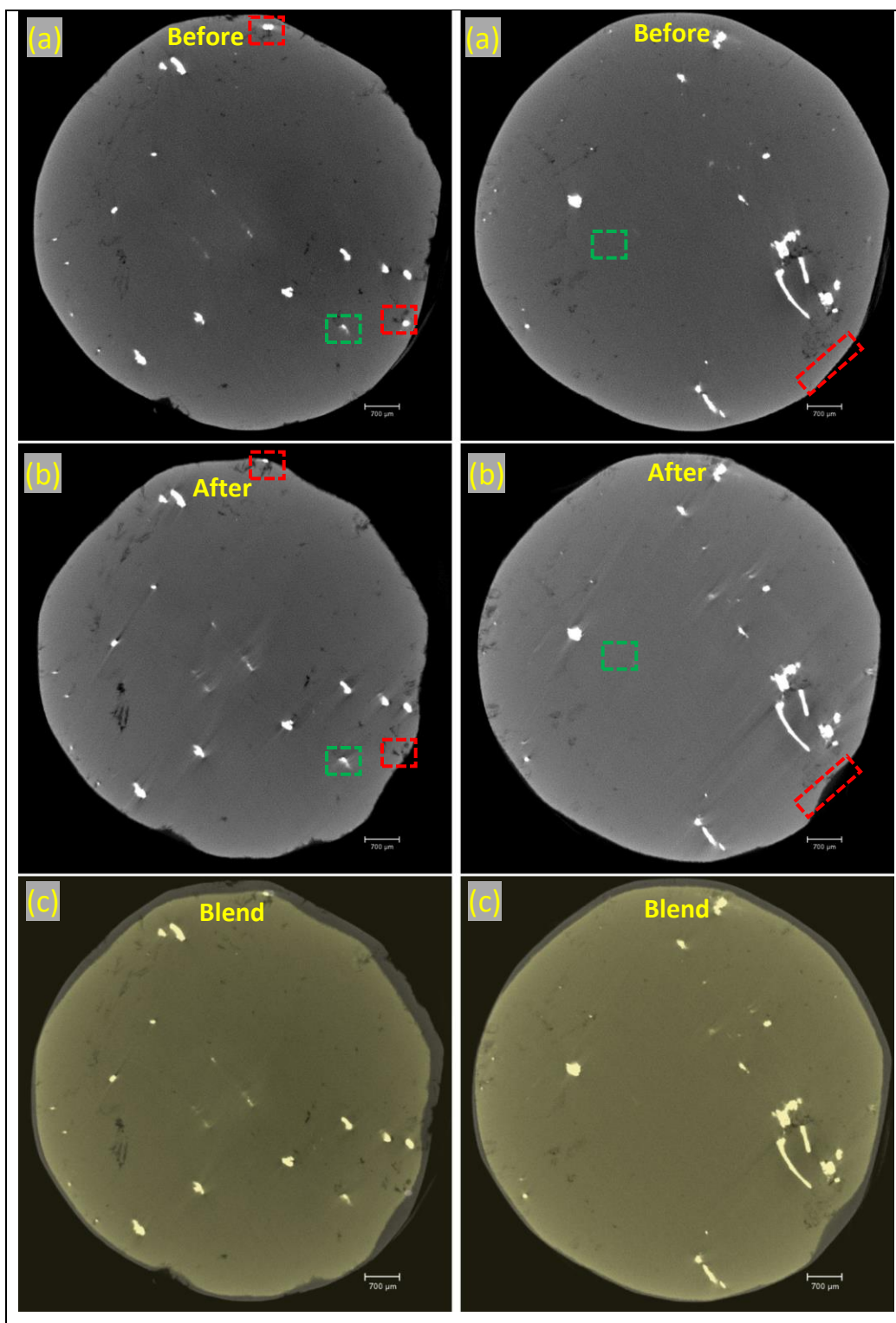


Figure 58. 2D slices from micro-CT images of sample before and after exposure to CO₂-brine. a) pre-exposure 2D μ -CT slice, b) post-exposure 2D μ -CT slice, c) blended image:

Grayscale: pre-, Yellow: post- CO₂-brine. The red boxes show dissolved regions (decrease in intensity) while the green boxes indicate the precipitated regions (increase in intensity of the high-density objects).

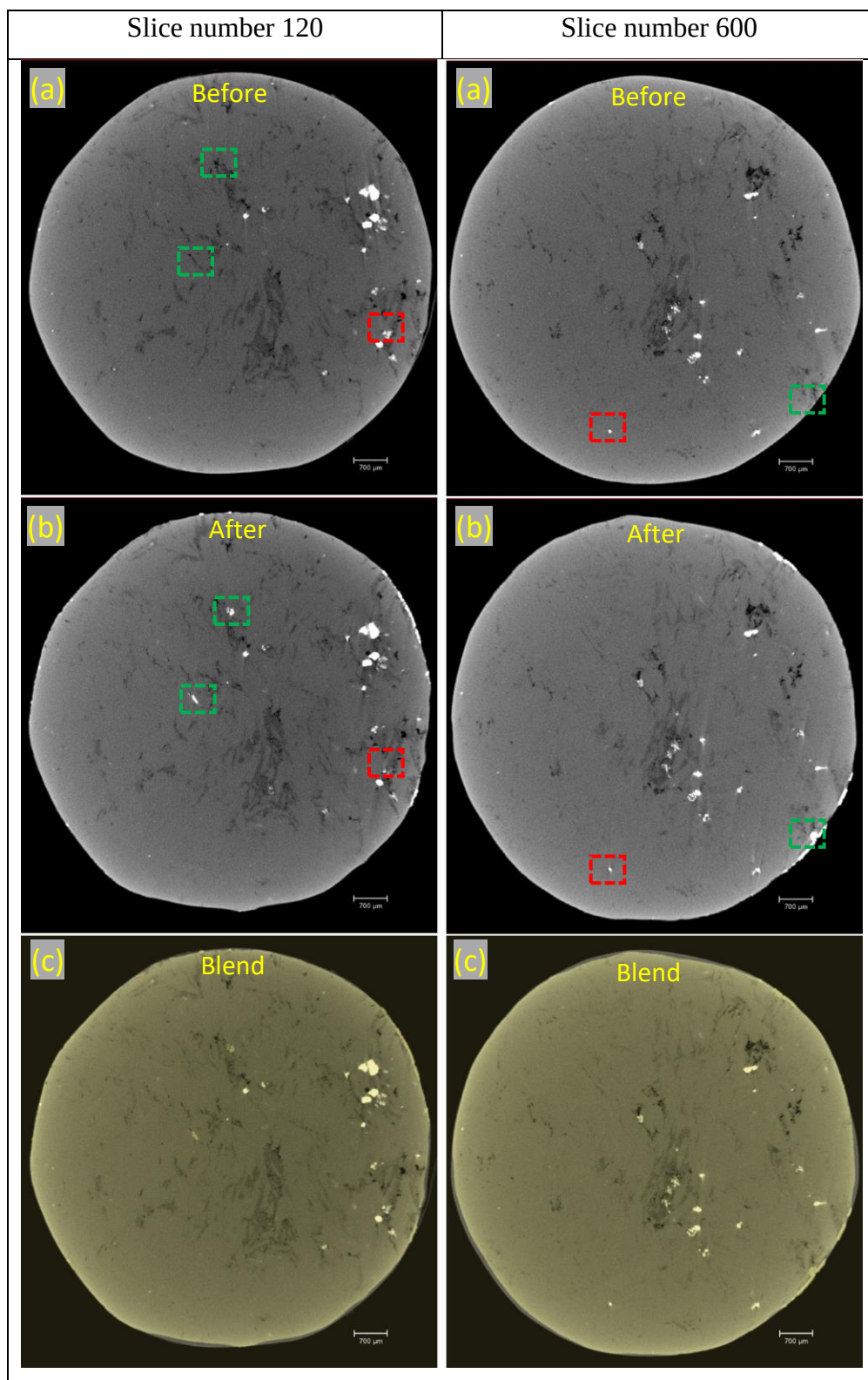


Figure 59. 2D slices from micro-CT images of sample before and after exposure to CO₂-brine+BaCl₂. a) pre-exposure 2D μ -CT slice, b) post-exposure 2D μ -CT slice, c) blended image: Grayscale: pre-, Yellow: post- CO₂-brine+BaCl₂. The red boxes show dissolved

regions (decrease in intensity) while the green boxes indicate the precipitated regions (increase in intensity of the high density objects).

These observations are also validated from **Figure 7.14** and **7.15** for samples treated with CO₂-brine and CO₂-brine+BaCl₂, respectively, where the 3D surface of the samples is compared. The white regions in grayscale images representing high-density material were separately analyzed. As shown in **Figure 7.14**, for supercritical CO₂-brine treatment, an overall decrease was observed in the white regions mainly due dissolution (**Figures 7.14a** and **b**). Little precipitation was observed. In **Figures 7.14c** and **d**, the white regions in the pre-treated sample are shown in blue color and for the post-treated sample in red color. The two images (**Figure 7.14c** and **d**) at different levels of opacity indicate clearly that the change is mostly due to dissolution. However, **Figure 7.15a** and **b** for CO₂-brine+BaCl₂ treatment shows the inverse effect where precipitation is dominant.

An interactive overlay threshold segmentation was performed on the images that were generated from the difference between pre- and post-images (**Figure 7.14c** and **d**). The difference (A-B) of the untreated sample with that of the same sample post treatment indicates the amount of grain dissolution and the other way around (B-A) indicates the amount of grain precipitation occurring between these two timestamps. The volume fractions of the segmented labels were then obtained to compute the amount of grain precipitation and dissolution. **Table 7.3** below lists the computed values. The rock treated with CO₂-brine revealed that the dissolved portion constitutes up to 9.85% of the total volume of the untreated sample, with only 0.91% volume precipitated. In contrast, the rock treated with CO₂-brine+BaCl₂ showed that the dissolved portion accounts for only 2.35%

of the total volume of the untreated sample, while a significant 6.04% volume was precipitated.

Table 7.3. Volume fractions of the segmented labels with computed amount of grain precipitation and dissolution.

Treatment	Dissolved region as % of total volume of pre-treated sample	Precipitated region as % of total volume of pre-treated sample
CO ₂ -brine	9.85%	0.91%
CO ₂ -brine+BaCl ₂	2.35%	6.04%

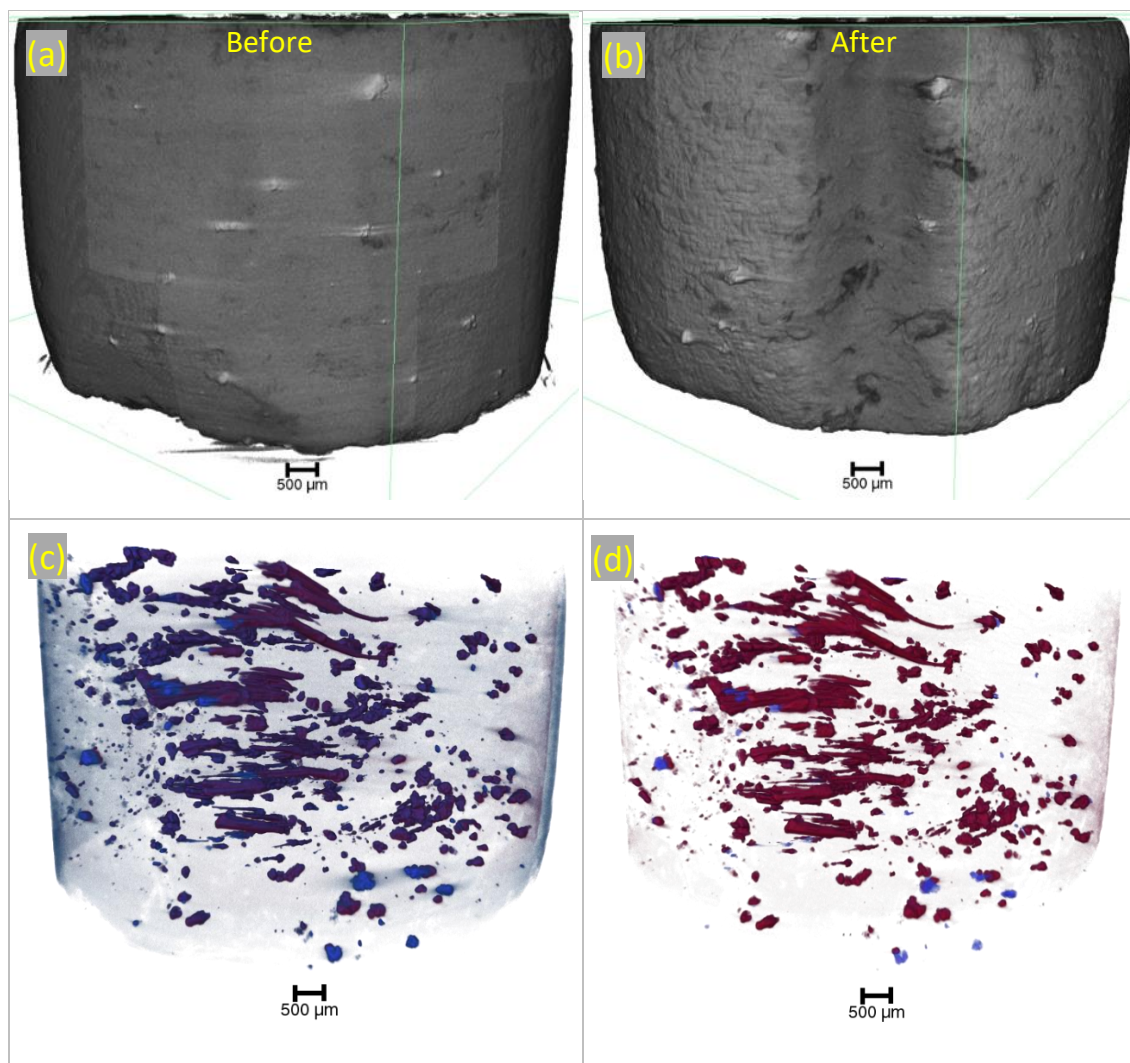


Figure 60. Two perspectives of the 3D image obtained from micro-CT scans comparing the surface pre- (a) and post- (b) CO₂-brine exposure: Mapping together the high-density material; (c) pre-treated sample's region shown in blue color and post-treated samples in red color; (d) shows the same image but with the blue color's opacity reduced to 0.5.

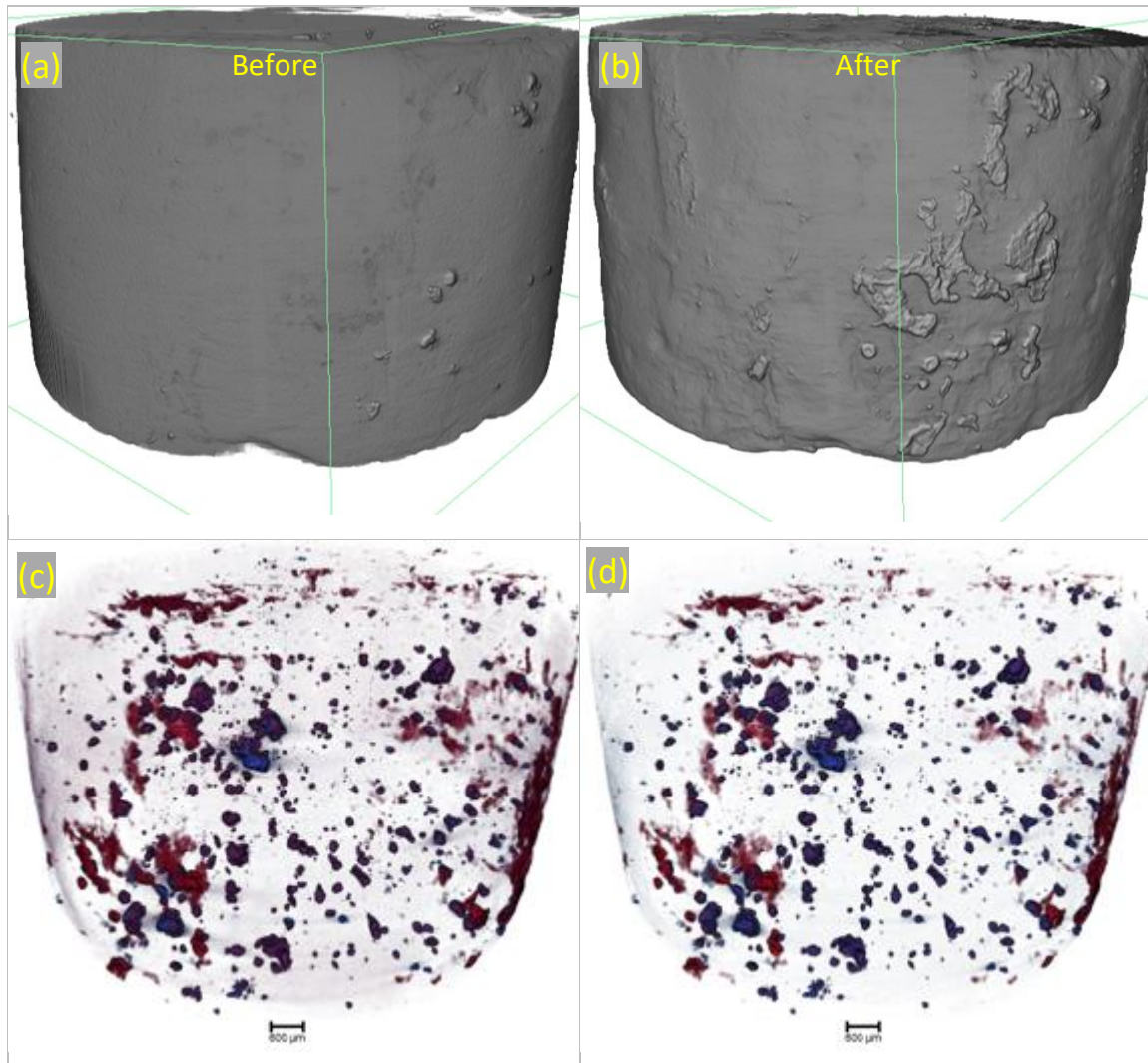


Figure 61. Two perspectives of the 3D image obtained from micro-CT scans comparing the surface pre- (a and c) and post- (b and d) CO₂-brine exposure: Mapping together the high-density material; (c) pre-treated sample's region shown in blue color and post-treated sample's in red color; (d) shows the same image but with the blue color's opacity reduced to 0.5.

7.3.8 Analysis of the Total Carbon Content

The total carbon content (combining both organic and inorganic) of the rock powder was assessed using the elemental solid TOC equipment and it is presented in **Figure 7.16**. The analysis revealed that the untreated rock sample contained approximately 0.348 wt. % total carbon (TC). When exposed to CO₂-brine treatment, the TC content increased to 0.963 wt. % (176.7 % increase in TC). This observed increase is attributed to the mineralization of CO₂ that occurred because of the interaction with supercritical CO₂-saturated brine. This aligns with the findings in the XRD section, where the formation of carbonate minerals, including calcite, was identified. The greater presence of molecular CO₂ (observed in the FTIR section) likely contributed to the rise in TC content in the CO₂-brine treated rock.

Upon treating the sample with supercritical CO₂-brine with added BaCl₂, a higher TC content of 1.275 wt. % (266.4 % increase in TC) was recorded. This substantial increase demonstrates enhanced CO₂ mineralization in comparison to the sample treated solely with CO₂-brine. However, it's important to note that while the addition of BaCl₂ enhances CO₂ mineralization, it may potentially reduce the porosity in comparison to cases without BaCl₂. The formation of barite, facilitated by the addition of BaCl₂, could occupy some pore spaces that might otherwise be available for storing other minerals. This may impact the available pore space for storing minerals formed during the treatment.

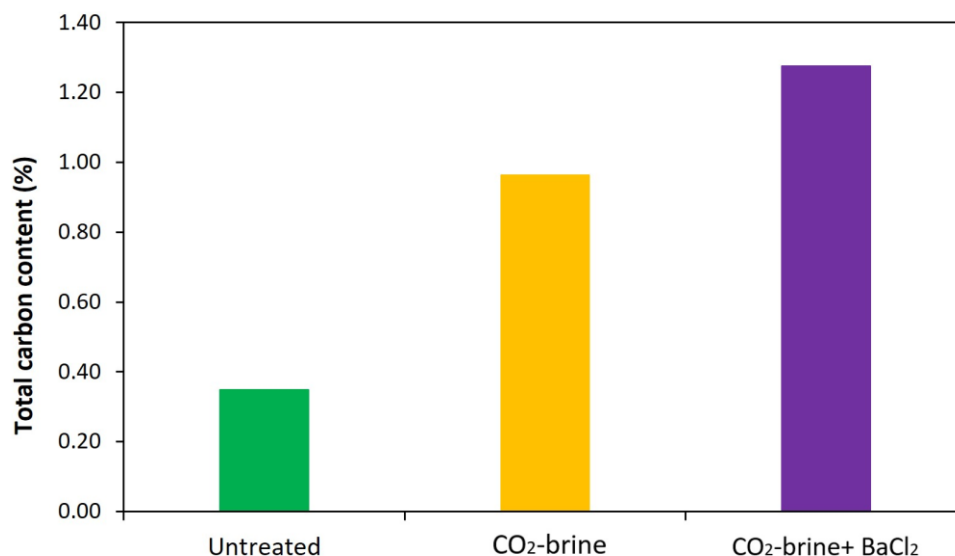


Figure 62. Total carbon content of the untreated, and post-CO₂-brine treated rocks.

7.4 Conclusions

The need to reduce atmospheric carbon dioxide emissions to combat global warming and climate change has led to the exploration of reliable storage methods. Carbon mineralization emerges as a geologically stable and environmentally responsible solution. By converting gaseous CO₂ into solid minerals within subsurface rock formations, this approach offers an effective means of safely storing CO₂. This study delved into the mechanisms and potential of anhydrite-CO₂-brine interactions for carbon storage in anhydrite-bearing reservoirs. Through a series of experiments conducted over fifteen days, including mineral transformation within a static reactor under high-temperature and high-pressure conditions, we obtained valuable insights. The results revealed that anhydrite, when exposed to supercritical CO₂-saturated brine, undergoes a significant mineral transformation, leading to the formation of stable minerals like calcite, siderite, feldspar, and in the presences of barium chlorite, barite. Analytical results showed that the untreated

rock sample had about 0.348 wt.% total carbon (TC), and exposure to CO₂-brine treatment resulted in a TC increase to 0.963 wt.% (176.7 % increase); furthermore, treating the sample with supercritical CO₂-saturated brine with added BaCl₂ led to a higher TC content of 1.275 wt.% (266.4 % increase). These outcomes suggest great potential for CO₂ storage through mineralization in anhydrite-bearing rocks. However, more work is required to understand the compositional dependence of mechanisms of CO₂ mineralization as well as the kinetics of the coupled dissolution/precipitation of anhydrite-rich rocks for carbon subsurface storage. These findings underscore the potential of anhydrite-based CO₂ storage methods and mechanisms, offering promise for addressing the critical challenge of reducing CO₂ emissions and mitigating climate change.

CHAPTER 8

EFFECT OF SULFATE-BASED SCALES ON CALCITE MINERAL SURFACE CHARGE AND ITS IMPLICATIONS ON WETTABILITY: INSIGHTS FROM ZETA-POTENTIAL MEASUREMENTS

Summary

Scales formation and deposition in the subsurface and surface facilities have been recognized as a major cause of flow assurance issues in the oil and gas industry. Sulfate-based scales such as sulfates of calcium (anhydrite, gypsum) and barium (barite) are some of the commonly encountered scales during hydrocarbon production operations. Oilfield scales are a well-known flow assurance problem, which occurs mainly due to the mixing of incompatible brines. Researchers largely focused on the rocks' petrophysical property modifications (permeability and porosity damage) caused by scale precipitation and deposition. Little or no attention is paid to their influence on the surface charge and wettability of calcite minerals. Thus, this study investigates the effect of anhydrite scales' presence on calcite mineral surface charge and their propensity to alter the wetting state of calcite minerals. This was achieved vis-à-vis zeta potential measurement. Furthermore, two modes of scale control (slug and continuous injection) using ethylenediaminetetraacetic

acid (EDTA) were examined to determine the optimal control strategy as well as the optimal inhibitor dosage.

Results showed that the presence of anhydrite scales in a calcite reservoir affects the colloidal stability of the system, thus posing a threat of precipitation, which would result in permeability and porosity damage. Also, the calcite mineral surface charge is affected by the presence of calcium and barium sulfate scales, however, the magnitude of change in the surface charge via zeta potential measurement is insignificant to cause wettability alteration by the mineral scales. Slug and continuous injection of EDTA were implemented, with the optimal scale control strategy being the continuous injection of EDTA solutions. The optimal dosage of EDTA for anhydrite scale control is 5 wt.% and 1 wt.% for the formation water and seawater environments, respectively. Findings from this study further the understanding of not only the scale effects on calcite mineral systems but provide critical insights into the potential of scale formation and their mechanisms of interaction for better injection planning and development of scale control strategy.

Keywords: Sulfate Scales, Calcite Mineral, Wettability Alteration, Scale Control, Precipitation, Chelating Agent.

8.1 Background

Scale formation in subsurface and surface facilities has been recognized as a major concern in oil and gas production operations.(Bader, 2007; Olajire, 2015; Verri et al., 2017) These scales are sulfates such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite), and calcium carbonate. Sulfate scale precipitation and deposition is a serious oilfield operational problem that affects water (brine) injection systems.(P. Abbasi et al., 2020;

Stalker et al., 2003) The most common cause of oilfield scale is the mixing of brines that are incompatible. Brines are said to be incompatible if they interact chemically and precipitate minerals when mixed during water injection.(Bader, 2007) For instance, when seawater with a high concentration of SO_4^{2+} and low concentrations of Ca^{2+} and Ba^{2+} , is mixed with formation brine that contains high concentrations of Ca^{2+} and Ba^{2+} but a low concentration of SO_4^{2+} , this causes precipitation of CaSO_4 and/or BaSO_4 .(P. Abbasi et al., 2020; M. A. Mahmoud, 2014; Peimao Zhang et al., 2006) More so, when seawater is mixed with produced water for injection, scale precipitation is bound to occur (Stalker et al., 2003)

Commonly encountered sulfate scales in the oil and gas industry are barium sulfate (BaSO_4) and calcium sulfate (CaSO_4), which can be anhydrous (anhydrite)(Isah et al., 2022a) or hemihydrate (bassanite).(T. Liu et al., 2019) And unlike the CaSO_4 scale, which has an inverse or retrograde solubility, BaSO_4 solubility increases with temperature.(Isah et al., 2022a; Zarrouk & McLean, 2019) A major concern of the retrograde solubility of CaSO_4 (e.g., anhydrite) is scale formation at elevated temperatures.(Isah et al., 2022a) Although CaSO_4 has a high solubility in water compared to BaSO_4 , under the same conditions, the scales of the two sulfates behave similarly except that the CaSO_4 is more soluble.(K. Abdelgawad et al., 2019; AlAamri et al., 2019) Moreover, some scales are pH-dependent (calcium carbonate, and sulfide scales) while some are not (e.g., calcium, barium, and strontium sulfate scales). Generally, pH-dependent scales are easier to treat than pH-independent scales.(Olajire, 2015; Verri et al., 2017) This is because, pH-dependent scales can be easily treated by acid injection, while this is not suitable for pH-independent scales.(S. Kumar et al., 2018) Thus, it is better to inhibit their occurrence,

which can be achieved using chemical inhibitors such as chelating agents,(K. Abdelgawad et al., 2019; Gamal et al., 2021; M. A. Mahmoud & Abdelgawad, 2015a) regulation of thermodynamic conditions of temperature and pressure, or by proper formulation of injected brine.(Bukuaghangin et al., 2016; Olajire, 2015)

The mechanisms of scale formation in reservoirs are (i) change in pressure and/or temperature, (ii) mixing of incompatible brines with different sulfate and cation (Ca^{2+} and Ba^{2+}) concentrations, and (iii) brine evaporation and consequent increase in salt concentration.(BinMerdhah et al., 2010) These scales impede flow and damage the reservoir and flow equipment,(Mohammed, Al Shehri, Mahmoud, Kamal, Arif, et al., 2022) with the problem more intense at elevated temperatures(AlAamri et al., 2019; Isah et al., 2022a).

Sulfate-based scales limit and block oil and gas production by plugging the pore throats and causing wettability alterations.(Mohammed, Al Shehri, et al., 2021a) In water injection systems, sulfate scales could be deposited on pore walls or plug the pores, thus resulting in formation damage (porosity and permeability reduction), which leads to poor hydrocarbon recovery.(BinMerdhah et al., 2010) Even though sulfate scales also get deposited on rocks and alter their surface properties, most researchers focus on scaling on steel surfaces,(Sanni et al., 2015; Setta & Neville, 2011) and formation damage associated with scale deposition in rocks.(BinMerdhah et al., 2010) BinMerdhah et al.(BinMerdhah et al., 2010) investigated permeability reduction caused by BaSO_4 scales in a sandstone formation. The authors by mixing seawater and formation brine demonstrated that the permeability reductions reported are due to BaSO_4 scales deposition on the pore surface. However, the effect of the deposited scale on the rock's surface wettability was not reported.

Abbasi et al.(P. Abbasi et al., 2020) investigated sulfate precipitation and scale formation in carbonate rock by mixing different injection water with varying concentrations of sulfate and salinity (high and medium sulfate waters, seawater, and low salinity water). The authors showed that the mixing of brine with high SO_4^{2-} content increases the scale precipitation. The authors further employed the use of zeta potential for surface charge chemistry analysis to show that increasing the concentration of SO_4^{2-} and consequently, higher magnitude of sulfate scales alters rock surface wettability into more water wet. However, they concluded that based on the results of the brine compatibility test, SEM, and zeta potential, optimal sulfate content should be defined to minimize the scale formation and obtain a high potential for wetting alteration simultaneously. Nikoo and Malayeri(Nikoo & Malayeri, 2021b) researched the impact of rock surface type and topography during scale formation in scale/brine/rocks interactions. They showed that different rock surfaces have different affinities for CaSO_4 scales. Interfacial interactions between scales and rock surface can be attributed to electrostatic, electrical double-layer, Lifshitz-van der Waals forces, or Lewis acid-base interactions and their magnitude is strongly salinity dependent.(Arsalan et al., 2013, 2015) However, Lewis's acid-base interactions dominate for CaSO_4 scales-rock interaction.

Studies have shown that sulfate scales can alter the surface properties and wetting behavior of rock surfaces.(Bader, 2007; Elkatatny, 2017; Gamal et al., 2021) Although an extensive body of literature is available for bulk precipitation reactions,(Bukuaghangin et al., 2016; Sanni et al., 2015) only a limited number of published articles(P. Abbasi et al., 2020; Chang & Civan, 1997; H.A. Nasr-El-Din & Al-Humaidan, 2001; Taheriotaghsara et al., 2020) focuses on the effect of scales on rock surface chemistry which greatly influences its

wetting behavior. Nikoo and Malayeri,(Nikoo & Malayeri, 2021a) examined sulfate scale/brine/rock interfacial interactions and the rock wettability due to CaSO_4 crystals. The authors used anhydrite, calcite, dolomite, and sandstone for their study and findings showed that the rocks become prone to scale formation and deposition as the fluid salinity and rock surface roughness are increased. Thus, researchers have recently faced the question as to how much surface chemistry and thus the wetting behavior of rocks is affected by sulfate scale deposition during the process of water injection. More so, scale introduction into the reservoir formation by drilling fluid that contains a high concentration of barite has received less attention as to how it affects the near-wellbore wettability. And with this question yet unanswered, it has become important to study and understand the mechanisms of CaSO_4 precipitation and deposition on rocks. This is to be able to precisely predict scale occurrence and control the rock surface characteristics.

To the best of our knowledge, the available published works,(Nikoo & Malayeri, 2021a, 2021b) which have precisely investigated the affinity of rock surface to scale formation are limited. Also, the wettability alteration potential of deposited scales on carbonate rock surfaces has not been investigated. The deposition of sulfate scales may affect the wetting characteristics of the rock surface, which, therefore, influence the ultimate recovery. Another point is the lack of experimental methods to verify the precise wetting potential of scales, their mechanism, and their effect on enhanced oil recovery. Thus, the current study reports systematic research (zeta potential measurements) from the perspective of surface charge by laboratory tests to assess the effect of sulfate-based scales on calcite mineral surface chemistry (charge). This stems from our earlier work,(Mohammed, Al Shehri, et al., 2021a) which revealed that different oilfield operations, as well as scales, affect the net

surface charge of calcite systems. Therefore, results from this study will enhance the understanding of the precise effect of scales on carbonate wettability and its implications in oilfield applications.

8.1.1 Wettability alteration and zeta (ζ) potential

Due to the significant impact, it has on the production capacity, reservoir wettability is a crucial concept in reservoir engineering and has been the focus of numerous studies over the years.(Mohammed et al., 2021) Changes in the pore system (for instance, adsorption), which may be brought on by fluid-fluid interactions, rock-fluid interactions, rock mineralogy, and brine chemistry, have been substantially responsible for wettability alteration.(Mohammed, Al Shehri, et al., 2021c; Mohammed, Al Shehri, Mahmoud, Kamal, & Alade, 2022) These could cause the rock's wettability to change completely or partially. Strong interfacial boundary conditions within the rock system that cause the fluid to be preferentially mobile in the presence of other fluids are what cause reservoir wettability.(Mohan et al., 2011) Therefore, it is mostly caused by a fluid that is either hydrophobic or hydrophilic and adheres to or coats the pore structure, making the carbonate rocks exhibit an oil-wetting state. Most largely confirmed in the literature, wettability alteration of rocks is attributed to the adsorption of the most polar crude oil component (asphaltene).(Mohammed et al., 2021) Asphaltene is said to be the heaviest and most polar crude oil component, soluble in aromatic fluids and insoluble in alkanes.(Mohammed et al., 2021) Because of the electrochemical interactions, asphaltene coats the pore surface and alters its wettability. Furthermore, the rate of asphaltene adsorption is linearly correlated with the change in wettability (Buenrostro-Gonzalez et al., 2004; Clementz,

1982; Gharbi et al., 2017; Ghedan et al., 2010; Ashish Kumar et al., 2016; Leontaritis, 1998; LIN et al., 2018; Mwangi et al., 2018b; Xue et al., 2022; Peimao Zhang et al., 2006) Regarding the relationship between crude oil, asphaltene content, and adsorption, opposing views have been voiced. This could be because the different studies used varying experimental conditions and models, which failed to account for the effect of brine and rock-fluid interactions (Ancheyta et al., 2002; Riazi, 2018; Soulgani et al., 2020).

Since asphaltene is believed to be predominately negatively charged, mineral surfaces must be positively charged for asphaltene adsorption to occur.(Mohammed et al., 2021) We have previously discussed the various minerals found in the reservoir, their surface charges, the composition of the brine, and the forms of salt that can create a mineral surface that can act as a precursor to asphaltene adsorption (Mohammed, Al Shehri, et al., 2021b, 2021c, 2021a; Mohammed, Al Shehri, Mahmoud, Kamal, & Alade, 2022; Mohammed, Al Shehri, Mahmoud, Kamal, Alade, et al., 2022) According to the results of these investigations, the mineral/brine interface must be positively charged for asphaltene adsorption to occur because electrostatic interaction is said to be the primary regulating mechanism.(Du et al., 2022) This consequently changes the wettability. Although various wettability alteration mechanisms have been identified in the literature,(Guo et al., 2020; J. Hao et al., 2019; Tetteh et al., 2020) several factors such as oilfield operations, and ion-specific interactions, affect reservoir wettability.

Multivalent ionic exchange, an electrical double layer (EDL) expansion, electrostatic bond interactions, surface charge alteration, and calcite dissolution are the wettability modification mechanisms connected with carbonate rocks.(Abbas et al., 2021; Crundwell, 2017; Elsaeed et al., 2021; Q. Liu et al., 2021; Mohammed, Al Shehri, et al., 2021c; Tetteh

et al., 2022) This is highlighted by the report of Al-Bayati et al.(Al-Bayati et al., 2022) who described the change in the carbonate rock samples and concluded that the observed recovery was caused by the electrical double layer effect brought on by the injected fluid's reduced ionic strength. Thus, understanding the electrostatic interaction at the rock surface caused by the salinity and composition of the brine is necessary to understand these mechanisms. Because of the mineral dissolution, adsorption of counterions, and formation of chemical complexes, colloidal particles in aqueous solutions acquire charges on their surfaces, experimentally determined vis-à-vis zeta potential measurements. When an electric field is applied to an ionic solution, particles having net charges move with a predetermined velocity, thus, determination of the particles' ζ -potential uses this movement, known as electrophoretic mobility.(Al-Araimi et al., 2021; Awolayo et al., 2018; Derkani et al., 2018) ζ -potential is the potential at a particle's sliding plane in a medium, and its measurement can reveal details about a suspended particle's surface charge, including its nature and size.(Mohammed B. Alotaibi & Nasr-El-Din, 2011; Joekar-Niasar et al., 2019) Additionally, it provides information on a particle's stability and flocculation potential. As a result, it has uses in the production of flocculants and dispersants as well as in water treatment.

ζ -potential values can indicate changes in the state of the surface, such as wettability alterations.(Mohammed, Al Shehri, et al., 2021c) It is a qualitative technique that depicts a change in surface chemistry by reduction or increase in the magnitude and sign of the ζ -potential value. But little or no correlation has been established with wettability other than a change in magnitude and sign of the ζ potential, which could be due to adsorption of fluids on the particle surface or dissolution of ions from the surface. However, studies were

conducted to see if zeta potential may be used as a special indicator of recovery for LSW.(Rodrigues et al., 2022) Streaming potential measurements and core flooding experiments were used by the authors to assess the crude oil/brine/rock system. Results showed that the recovery and ζ -potential of the water/oil and rock/water interfaces are correlated. Therefore, recovery was seen to be beneficial if both interfaces had the same surface charge; yet inferences were reached to the fact that ζ -potential cannot be used as a sole tool for recovery predictions. Thus, at best, it can only be used as a qualitative check, thus, a comparison of wettability alteration using the ζ -potential measurement and the popular Amott–Harvey and USBM methods is not straightforward and can be misleading.(Isah et al., 2022a) Depending on the adsorbing fluid properties and the fluids' propensity to interact with the surface, the ζ -potential can be used as a sign of wettability change. Additionally, the use of ζ -potential measurement in wettability alteration experiments gives researchers insight into wettability changes but does not allow in situ changes to be observed.(Isah et al., 2022b) Furthermore, a thorough understanding of the chemistry of the fluids and surfaces involved in the interactions is necessary to infer the wettability alterations from ζ -potential measurements.

To understand the interactions (intermolecular forces) acting on colloids or charged surfaces in an electrolyte solution, the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory was developed. The DLVO theory is a classical explanation of the intermolecular forces (electrostatic repulsion and van der Waals attraction) responsible for the stability of colloids in a suspension. The effect of crude oil fractions, pH, and salinity on the film thickness on mineral surfaces using the DLVO theory is well documented in the literature.(S. Basu & Sharma, 1997; Subhayu Basu & Sharma, 1996) The principles of thin-

film thickness measurement using AFM were developed in Basu and Sharma's work.(S. Basu & Sharma, 1997) This was done to determine how much these factors affected wettability changes. According to the authors' findings, a decrease in film thickness was seen when both salinity and pH values were reduced. A higher salinity and pH, however, led to a more stable film in the case of the non-polar crude oil fractions. Because glass beads were used in the study and the pH range was only 5.5 – 8.0, these findings have some limitations. They thus give insight into the impact of salt interactions and pH circumstances on wettability alteration. To investigate the impact of altered water chemistry on oil recovery supported by ζ -potential and contact angle measurement, Sanaei et al.(Sanaei et al., 2018) used the DLVO theory and a surface complexation model. With the results showing the dominance of surface charge in the observed recovery, this is to capture the physics of improved recovery in low salinity water flooding. ζ -potential values and a measurement of the contact angle provided additional support for this; nevertheless, the impact of salt was not considered in their analysis. The presence of divalent cations and the sulfate ion is essential for determining surface wetness, according to Tirjoo et al.(Tirjoo et al., 2019) who studied the impact of brine ionic composition on wettability. More specifically, it clarified how to compute the film thickness using the DLVO theory.

8.1.2 Smart and low salinity water

A causative operation that can result in a sulfate scale problem is the injection of smart water. Smart water is a brine whose chemical composition has been altered to achieve ion-specific interactions with the rock/fluid system.(P. Abbasi et al., 2020; Fathi et al., 2011; Prabhakar & Melnik, 2017; Zallaghi & Khaz'ali, 2021) In most cases, the said smart water

contains high and low dosages of SO_4^{2-} and divalent cations, respectively.(P. Abbasi et al., 2020) Smart water differs from low salinity water (LSW), which results from the dilution of formation brine (FW) or seawater (SW) (Taheriotaghsara et al., 2020). These two terms have been erroneously used in the literature(Snosy et al., 2021) however mean two different brine systems. The effect of both brines has gained significant attention recently and continues to be an active area of research. Several studies are available in the literature on smart and LSW water effects on reservoir wettability and oil recovery.(Al-Bayati et al., 2022; Yongqiang Chen et al., 2020; El-Din Mahmoud, 2018; Mosallanezhad & Kalantariasl, 2021; Taheriotaghsara et al., 2020; Yutkin et al., 2018) For example, using AFM, contact angle, and ζ -potential measurements, Al Maskari et al.(Al Maskari et al., 2020) described the impact of pH (caused by mineral dissolution under LSW) on carbonate surface wettability. Findings indicated that the contact angle decreased as pH increased, and this observation was corroborated by an increase in the magnitude of the negative surface charge under the same circumstances. Additionally, the AFM's adhesion test revealed that the adhesion force decreased as pH rose, indicating that the surface's hydrophilicity had increased. Snosy et al.(Snosy et al., 2021) in a thorough investigation of the effect of LSW on carbonate reservoirs concluded that the recovery is controlled by the water's composition rather than its salinity. More so, the concentrations of Na^+ , Mg^{2+} , K^+ , and Cl^- have the largest impact during the secondary recovery stage, whereas K^+ , HCO_3^- , SO_4^{2-} , and the mineralogy are the most important characteristics during the tertiary recovery stage. Similarly, Zekri et al.(Zekri et al., 2021) in an assessment of LSW injection in different wettability states using core flood experiments and effluent analysis, concluded

that the optimum LSW is a function of the wetting state of the rock. Thus, priority should be accorded to the brine composition rather than the salinity level.

In an analysis of the impact of LSW flooding on chalk core samples, Mokhtari et al.(Mokhtari et al., 2022) concluded that 10-fold diluted seawater exhibits greater recovery than FW and SW. Furthermore, the scientists deduced from the ion effluent study that mineral dissolution cannot be the sole mechanism responsible for the observed recovery and that the effect of SO_4^{2-} is not responsible for observed recovery in all situations. More recently, Tetteh et al.(Tetteh et al., 2022) reported using the diffuse layer model (DLM) and triple-layer model (TLM) of surface complexation to model the carbonate rock wettability. The experimental ζ -potential values for the seawater brine used in the investigation were more closely matched by the DLM than by the TLM, according to the results. The computed interaction potential at the interfaces further demonstrated that a low Mg^{2+} and high SO_4^{2-} resulted in a more negative calcite/brine interface. Therefore, to achieve a water-wet state, a more negative interface surface charge is required.

As robust as the research on LSW and smart water is and their implications on oil recovery, it is not without a drawback, which includes sulfate-scale precipitation and salt dispersion. The salt dispersion, which happens when LSW mixes with high salinity water, is one of the downsides of LSW flooding; however, new research suggests that by adding around 200 ppm of polymer, the salt dispersion can be decreased by roughly 70%, resulting in a lower volume of LSW usage.(Darvish Sarvestani et al., 2021) Also, with so many research articles emphasizing the benefits of increased SO_4^{2-} concentration on oil recovery, no attention has been paid to the potential damage it can cause due to sulfate-based scale precipitation, which can result in wettability alterations and permeability damage. Thus, as

stated in the preceding section, this research is aimed at understanding the effect of sulfate-based scales on calcite mineral surface charge and consequent wettability state.

8.2 Materials and Methods

8.2.1 Materials

The rock minerals used in this study include calcite and anhydrite samples with average particle sizes of 8.4 and 8.26 μm for calcite and anhydrite, respectively. All chemicals used in this study were of the American Chemical Society (ACS) reagent grade. The synthetic brine solutions used are with compositions (Table) mimicking the Arabian Gulf seawater (SW) and formation water (FW). The salts used in this study were purchased from Sigma Aldrich (Saint Lois, MO, USA).

Table 8.1: Ionic composition of Arabian gulf formation water (FW) and seawater (SW).(Abdel-Azeim et al., 2021)

Ions	FW (ppm)	SW (ppm)
Na^+	59,491	18,300
Ca^{2+}	19,040	650
Mg^{2+}	2,439	2,110
SO_4^{2-}	350	4,290
Cl^-	132,060	32,200
HCO_3^-	354	120
TDS	213,734	57,670

8.2.2 Sample Preparation for Zeta potential Measurement.

Rocks mineral particles were conditioned in deionized water (DI), seawater (SW), formation water (FW) as well as in mixtures whose pH was modified to mimic oilfield operations. For all samples, the total dissolved mineral particles were 1g, with the

proportion of anhydrite samples to achieve the required ratio added to the calcite mineral sample. After that, 10 mL of fluid was then added to the sample mixture and allowed to stand undisturbed for 24hrs. The pH adjustment of the FW and SW was achieved using 0.1 mM NaOH and nitric acid to avoid surface etching.

8.2.3 Zeta potential measurement and pH measurement

Anton Paar Litesizer 500 (Graz, Austria) machine was used for the sample mixture zeta potential measurements. Before every measurement, the sample mixtures were centrifuged using a Hermle Z326K centrifuge (Gosheim, Germany). Samples were centrifuged at 23 °C for 2 min at 3000 rpm before the zeta potential measurement, sample to be analyzed is taken from the clear supernatant. All reported measurements in this study are within ± 2 mV standard deviation and an average of 20 runs for each sample.

The pH value of the freshly prepared brines and all samples in this study was measured using the Thermo Scientific™ Orion Star™ A215 pH/conductivity benchtop multiparameter meter, with an accuracy of ± 0.002 .

8.3 Results and Discussions

The effect of sulfate-based scales on calcite mineral surface charge is investigated using zeta potential measurement. To provide a holistic picture of the effects, the influence of the varying proportions (wt.%) of the scales (anhydrite) on calcite surface chemistry is explored. As an initial step, the pH of the fluids (DI and synthetic brines) used in this study was recorded. The pH values were 7.64, 7.65, and 6.27 for DI, SW, and FW, respectively. These pH values are the benchmark against which all reported pH values are compared in this study. This is so, to infer governing mechanisms responsible for the observed surface charges.

8.3.1 Calcite in DI, FW, and SW

The surface charge of calcite mineral is first studied to serve as a benchmark against which the effect of scales would be compared. The zeta potential of calcite minerals in DI, SW, and FW is shown in **Figure 63**. **Figure 63** shows that the calcite mineral in DI and SW is negatively charged while it shows a positive charge in FW. To understand the mechanism responsible for the observed surface charge, the initial and final pH values are critical. In the case of DI water, the initial pH was recorded as 7.64, however, after calcite mineral conditioning in DI water, the resulting pH of the Calcite/DI mixture was 8.50. This points to the fact that the H^+ and OH^- in the case of DI water are potential determining ions (PDIs). Also, the increase in pH from 7.64 to 8.50 shows that the dominant interaction is due to the H_{water} and O_{calcite} interactions, resulting in more OH_{water} in the system, thus, the shift in pH. In the case of SW and FW, no pH change is observed, which indicates that the H^+ and OH^- are not PDIs. Furthermore, this implies that the surface charge development of the calcite mineral in SW and FW is due to their respective fluid composition (ions).

In the case of SW (Figure 63), the calcite mineral is negatively charged however the magnitude of the charge is small. The negative surface charge can be attributed to the presence of anions (Cl^- and SO_4^{2-}) in SW, especially the SO_4^{2-} . However, the low magnitude of the charge can be attributed to the competitive interaction of the cations (Na^+ , Ca^{2+} , and Mg^{2+}) with the calcite surface. Although due to the high SO_4^{2-} concentration in SW, the surface remains negatively charged, however, this can be easily reversed by a change in the fluid composition. The reported calcite mineral surface charge in SW agrees with the report of Rodrigues et al. (Rodrigues et al., 2022) who studied the effect of controlled salinity flooding on the oil-water-carbonate system. Furthermore, our

observations differ slightly from the report of Belhaj et al.(Belhaj et al., 2022) who reported a higher magnitude of surface charge value even though both cases agree on the nature (negative surface charge) of the calcite mineral surface charge in SW. This disparity can be attributed to the fact that the samples used in their study contain quartz and dolomite which resulted in an increased negative surface charge. However, in our study, pure calcite minerals were used. Similarly, our observation is corroborated by the report of Kasha et al.(Kasha et al., 2021) The authors used old and unaged limestone samples and zeta potential measurements to describe the interactions of PDIs (Mg^{2+} , Ca^{2+} , and SO_4^{2-}) on limestone. According to the authors' findings, SO_4^{2-} dominates in creating and maintaining a negative surface charge for both aged and unaged samples when additional PDIs are present. The case of FW is like that of SW, in that no pH change was observed. However, the FW has more cation concentration than SW and has ten (10) times less SO_4^{2-} compared to SW. Thus, the surface charge of calcite in FW is positive due to the adsorption of cations on the calcite surface. Figure 63 also shows that increased salinity affects the resulting surface charge of calcite minerals, thus, salinity reduction may hold the key to the control of the mineral surface charge. This agrees with the report of Tetteh et al.(Tetteh et al., 2022) which demonstrated that increase in the cation concentration results in reduced negative surface charge. More so, an increase in cation concentration results in the formation of a salt layer on the calcite mineral surface.(Koleini et al., 2021).

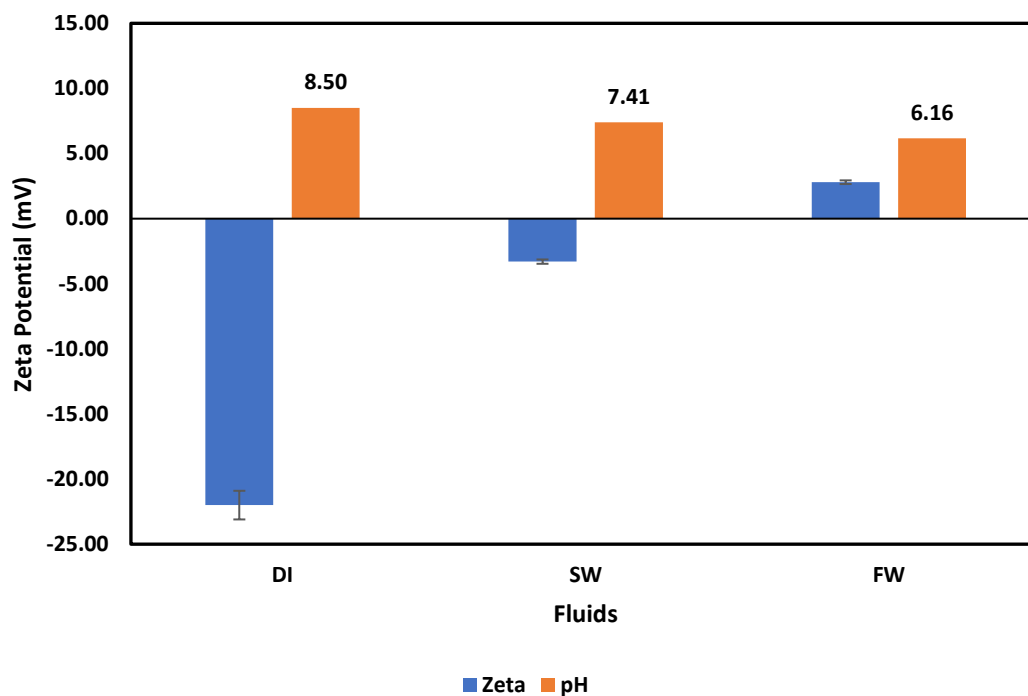
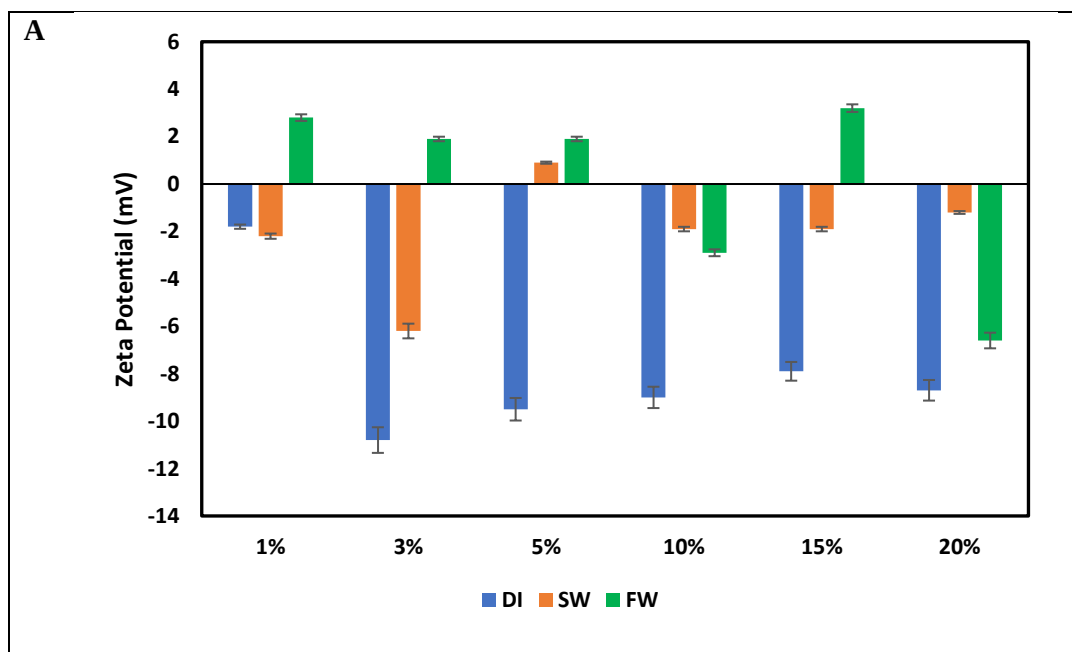


Figure 63. Calcite Mineral surface charge in DI, SW, and FW.

8.3.2 Effect of anhydrite scale on calcite mineral surface charge

Anhydrite scales form due to acid sulfate water and calcium present in the reservoir (Cope et al., 1985) and like calcite, its solubility decreases with increased temperature (Zarrouk & McLean, 2019). The effect of anhydrite (1 – 20 wt.%) on the surface charge of calcite minerals is shown in **Figure 64**. In the case of DI water (Figure 64A), the calcite mineral is observed to remain negatively charged as in Figure 63 without the effect of anhydrite, however, the magnitude of the surface charge is reduced due to the presence of the anhydrite scale. The lowest magnitude of surface charge is observed at 1 wt.% anhydrite concentration; however, above this concentration (3 – 20 wt.%), the surface charge magnitude increased to approximately –10 mV. The surface charge at 1 wt.% can be attributed to the dominance of the Ca^{2+} at low anhydrite concentration however, above 1

wt.%, the SO_4^{2-} dominated the interactions thus the increased negative surface charge as the anhydrite scale concentration increases. Notably, no significant pH changes (Figure 64B) are observed with an increase in the anhydrite scale concentration except at 15 wt.%, which explains the reduction in the zeta potential value. Furthermore, except at an anhydrite concentration of 1wt.%, the same surface charge is observed, which implies the complete coverage of the active sites on the calcite surface by the anhydrite scale. This also points to the fact that the anhydrite scale has the most impact on the calcite surface charge when present at low concentrations (< 3 wt.%).



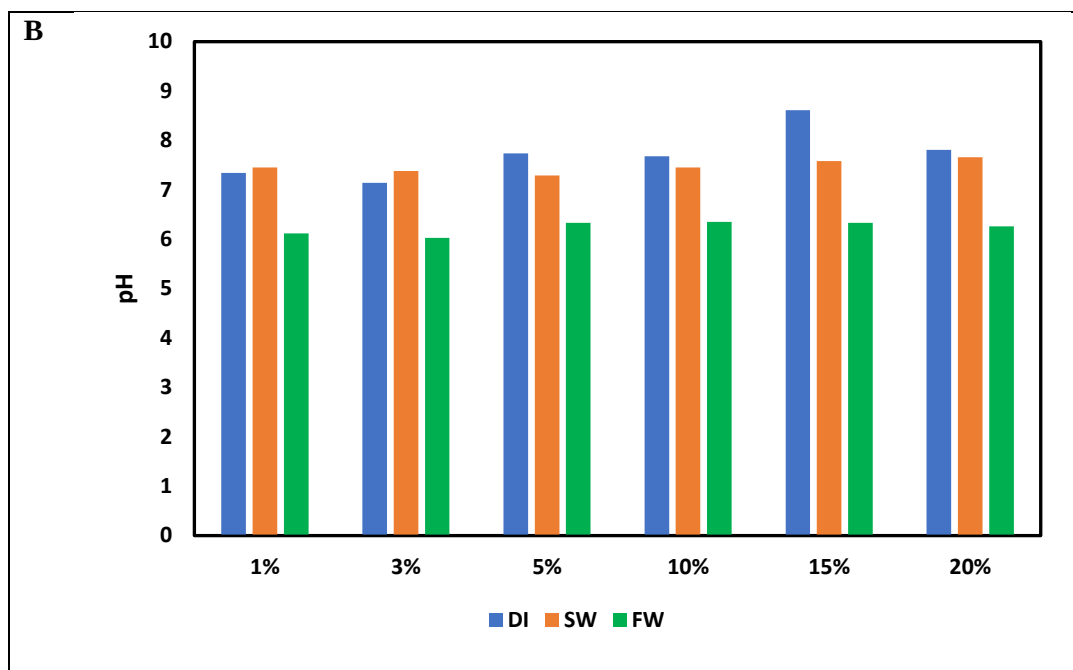


Figure 64. Effect of anhydrite scale on calcite mineral surface charge. (A) zeta potential values of calcite/anhydrite mixtures in varying fluids. (B) pH value of the mixtures after 24hr. conditioning. The X-axis represents fluids (DI, SW, and FW) in which the mineral was conditioned.

The cases of SW and FW differ from that of DI water in that they have dissolved ions as shown in Table . Also, from the pH values (Figure 64B), no change is observed thus, the observed effect on the calcite mineral surface charge is due to the ionic composition of the brines. In the case of SW, at 1 wt.% anhydrite, a slight reduction in the calcite mineral surface charge is observed from a value of -3.3 mV without anhydrite (Figure 63) to -2.2 mV in the presence of anhydrite (Figure 64A). Even though the SO_4^{2-} concentration in SW was high, its effect only became pronounced at 3 wt.% anhydrite concentration. As the anhydrite scale concentration increased to 5 wt.%, a charge reversal due to counter adsorption of the Ca^{2+} present in the system or collapse of the double-layer with increased SO_4^{2-} density is observed. Furthermore, an increase in the anhydrite scale concentration beyond 10 wt.% (i.e., 15 and 20 wt.%) does not increase the negative charge magnitude.

This can be attributed to the saturation of the calcite surface with adsorbed SO_4^{2-} . In the case of FW, a positive surface charge is observed at anhydrite concentrations of 1 – 5 wt.% and 15 wt.%, with a negative surface charge observed at 10 and 20 wt.%. This is attributed to the adsorption of cations in the FW on the surface and the counterbalance of the SO_4^{2-} from the anhydrite scale by the cations. Therefore, the effect of the anhydrite scale on calcite mineral surface charge shows that except in the case of FW, the calcite mineral is negatively charged due to the sulfate ion from the scale. More so, the low values of the zeta potential show that the presence of the anhydrite scale possesses no wettability alteration potential and does not in itself possess the capability to alter the wetting state of the calcite mineral.

8.3.3 Effect of oilfield operations

Oilfield operations, which include drilling, stimulations, waterflooding, low salinity and polymer injections, etc. are implemented during the life of a field. These operations induce pH change around the wellbore, which impacts fluid interactions at the mineral/fluid interfaces. (Mohammed, Al Shehri, Mahmoud, Kamal, Alade, et al., 2022) Thus, the effect of such pH changes along with the presence of scales is explored in this section.

The effect of anhydrite (1 – 25 wt.%) and oilfield-induced pH on the calcite mineral surface charge is shown in **Figure 65**. Also shown in this figure is the surface charge of calcite due to these two factors in different fluids (DI, SW, and FW). In the case of DI water, regardless of the concentration of the anhydrite scale, the surface charge of calcite is observed to be negative; however, the magnitude varies with the scale concentration. Figure 65A depicts the case of 1 wt.% anhydrite/calcite mixture in different fluids. In the case of DI (Figure

65A), at pH values of 5 and 6, an average surface charge value of -4 mV is observed; however, with the decrease in the pH towards the acidic pH region, a reduction in the charge magnitude is recorded. This can be attributed to the interaction of the H^+ with the calcite mineral surface. Furthermore, the sudden increase in the charge magnitude at pH 1, is caused by the compression of the double layer due to high H^+ density. On the other hand, the reduction in the surface charge at pH values 9 – 11 is due to the compression of the double-layer with an increase in OH^- as the pH increases. The provided explanation is plausible because in an electrolyte solution, when two charged surfaces (mineral surface and ions) and the electrical double layers (EDLs) that accompany them approach one another, the EDLs initially start to overlap resulting in the compression of the interfacial boundary before eventually collapsing under confinement.(Zachariah et al., 2016) Altering the pH or the salt concentration offers other ways, as in our case to change the interfacial populations and chemical potentials, and hence the relative stability of these structural components. Therefore, as earlier stated, the behavior of the calcite mineral in the DI water environment is controlled by the PDIs (H^+ and OH^-). In the case of SW, intermittent charge reversal is observed at pH values of 5 – 12. This can be attributed to the interplay between cation adsorption and sulfate ion adsorption as no observable pH change is recorded. However, in the acidic pH range (pH 1 – 4), the decrease in the negative surface charge is due to H^+ ion interaction with the surface. In the case of FW, an all-positive surface condition is observed across all pH. This can be attributed to the high cation concentration in FW. Most probably, Na^+ , Mg^{2+} , and Ca^{2+} , however, the effect of the pH becomes apparent at the alkaline pH range with the reduction in the positive charge magnitude. This is corroborated by the work of Chen et al.(Yongqiang Chen et al., 2020) who investigated

the effect of pH and Ca^{2+} on the calcite/brine interface charge. The authors alluded that at any given pH, the surface species distribution varies thus, the effect of pH on the calcite/brine interface charge is due to the varying distribution of hydration sites ($>\text{CO}_3^-$ and CaOH_2^+) on the calcite surface. Furthermore, calcite surface interactions with the ions are dependent on adsorption reaction which is significantly reduced due to high sulfate content (Mosallanezhad & Kalantariasl, 2021).

The case of 5 wt.% anhydrite is depicted in Figure 65B and as can be observed, the surface charge is positive. In the case of SW, the highest magnitude of positive charge is recorded at pH 5, with a reduction in the surface charge magnitude observed as the pH value tends toward the acidic pH region. This reduction can be attributed to the compression of the double layer due to an increase in H^+ density as the pH approaches a value of 1. On the alkaline pH region, with an increase in pH, the surface charge magnitude reduces due to OH^- interaction with the surface; however, at a pH value of 12, charge reversal is observed. In the case of FW (Figure 65B), a similar trend as in SW is observed however the dominance of double-layer compression is more pronounced. Evident from Figure 65A – F, is the fact that with an increase in the anhydrite concentration, the surface charge across the pH values becomes positive, so a combined effect of induced pH and anhydrite concentration is what results in the surface charge reversal with the dominant mechanisms being ion-adsorption and electrical double layer compression.

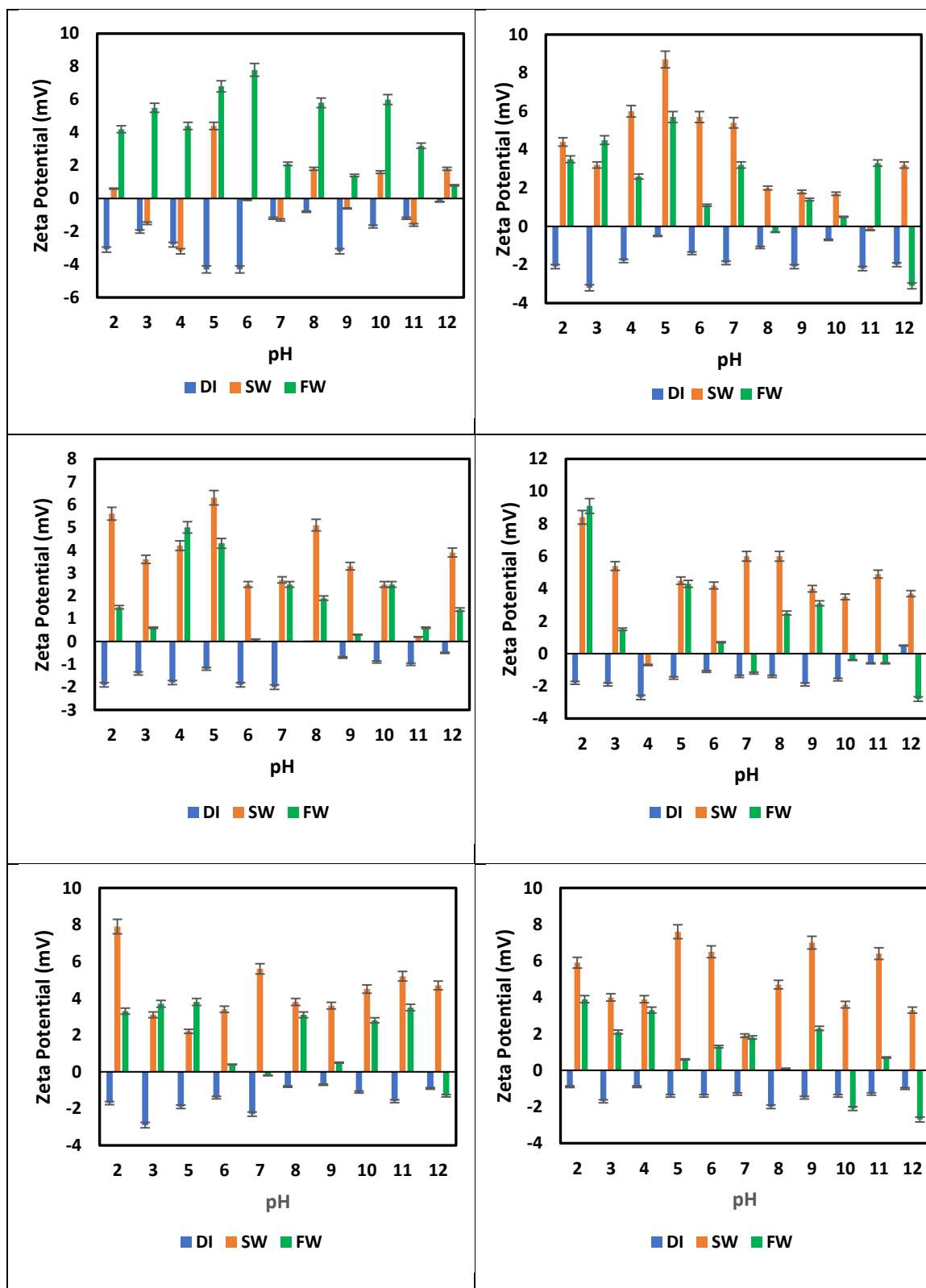


Figure 65. Effect of Oilfield induced pH and anhydrite scale on calcite mineral surface charge. A-F represents 1, 5, 10, 15, 20, and 25 wt.% anhydrite/calcite sample mixture, respectively.

8.3.4 Scale Control

Formation damage due to scales is remedied by the injection of fluids to dissolve the deposited scale,(Fredd & Fogler, 1998; Kremieniewski et al., 2021; Mohamed et al., 2020; Siddig et al., 2022) stabilize the formation and alter the wetting state of the rock.(M. Mahmoud et al., 2021b; M. A. Mahmoud, 2014; Hisham A. Nasr-El-Din et al., 2007) Another mechanism of scale control is the use of chelating agents which chelate specific ions from the rock surface and prevent their precipitation or deposition.(Mohammed, Mahmoud, Al Shehri, Kamal, & Alade, 2022) Of the several chelating agents, the most used is the ethylenediaminetetraacetic acid (EDTA). EDTA is reported to prevent anhydrite scale as well as alter the wetting state of the rock (Fredd & Fogler, 1998)

Hassan and AL-Hashim(Hassan & Al-Hashim, 2020b) reported the surface charge modification of the carbonate system using EDTA chelating agents (1, 3, 5, and 10 wt.%). The authors analyzed the changes using ion concentration analysis via inductively coupled plasma-optical emission spectrometry (ICP-OES), and recovery evaluation using core flooding and spontaneous imbibition tests. Furthermore, nuclear magnetic resonance (NMR) was also used to evaluate the potential damage to the sample due to chelating agent treatment. Findings showed that the carbonate sample surface charge can be reversed to negative vis-à-vis the chelating agent. Also, an increase in chelating agent concentration results in an increased negative surface charge. The authors also alluded based on the ICP analysis, that the surface charge modification is attributed to Ca^{2+} dissolution or chelating from the carbonate surface. This was further corroborated by the recovery measurements from the imbibition test and core flooding experiments.

Mady et al.(Mady et al., 2021) report the use of organophosphorus, nitrogen-free scale inhibitors for calcite minerals. The authors conducted a compatibility test, efficiency evaluation, Density Functional Theory (DFT), solid-state computations as well environmental friendliness examination of the proposed fluids. In comparison to the commercial inhibitors, the nitrogen-free scale inhibitors performed well, with the distance and number of $\text{PO}(\text{OH})_2$ and COOH on the inhibitor backbone suggested to control the performance. Recently, a technique of converting anhydrite to calcite via a chelating agent was reported(M. Mahmoud et al., 2021b) however, in this study, the varying concentration of EDTA was employed to control the scale effect on the calcite mineral surface charge. This is to ascertain the optimal EDTA concentration required for anhydrite scale inhibition. Furthermore, the mechanism responsible for the EDTA interaction was investigated using ion concentration analysis. Therefore, to evaluate whether the dominant mechanism is ion chelating or wettability alteration, the concentration of Ca^{2+} and Ba^{2+} were monitored in our study.

To understand the effect of EDTA solutions in chelating the cations from the mineral surface, 1g of the minerals (calcite, anhydrite) were conditioned in EDTA of different concentrations (1, 5, and 10 wt.%). After 24hrs, the mixture was sonicated, and a sample was taken from the clear supernatant. The samples were then analyzed for concentrations of Ca^{2+} and Ba^{2+} in the EDTA solution chelated from the mineral surfaces. This is to establish and affirm the earlier reports by Mahmoud et al.(M. Mahmoud et al., 2021b) **Figure 66** shows the results of the ion concentration analysis for the minerals. The effectiveness of the EDTA solution in chelating cations from the mineral surfaces is in the

order anhydrite > calcite. More so, the amount of cations chelated by the EDTA solutions increases with an increase in EDTA concentrations in the cases of calcite and anhydrite.

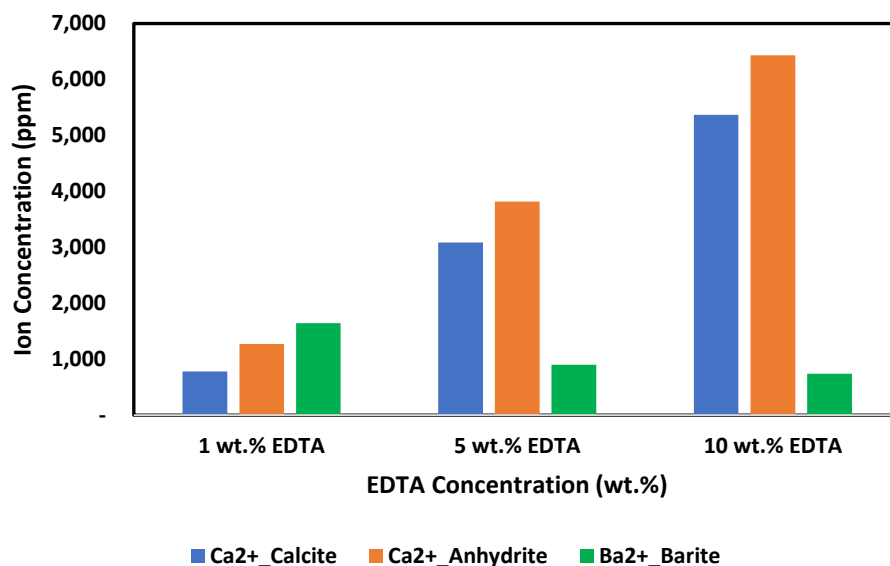


Figure 66. Ion concentration analysis.

Two modes (**Figure 67**) of EDTA implementation (slug (Figure 67A) and continuous injection (Figure 67B)) and environment (primary and secondary production stage) were evaluated in this study. The primary and secondary production in this study means EDTA injection (slug or continuous) was implemented in the native reservoir state (FW) and after seawater injection commenced, respectively. In the case of slug injection, the EDTA contacts the mineral once, whereas, in the case of continuous injection, the mineral is contacted multiple times.(Mohammed, Mahmoud, Al Shehri, Kamal, & Alade, 2022)

8.3.5 Slug injection.

Error! Reference source not found. shows the zeta potential values of the effect of EDTA (1, 5, and 10 wt. %) slug solution on the calcite/anhydrite systems in FW and SW

environments. In the case of a calcite/anhydrite system in the FW environment (**Error! Reference source not found.**A), the highest magnitude of negative charge is -15.8 mV. This is in the case of 1 wt.% EDTA slug being applied to a calcite/anhydrite system with 1 wt.% anhydrite. For a calcite system with a 1wt.% anhydrite scale, the optimum EDTA concentration for slug treatment is 1 wt. %. This is because increased EDTA concentrations to 5 and 10 wt.% result in a lower magnitude of negative surface charge. This can be attributed to the compression of the double layer. Also, from the zeta potential values at 5 and 10 wt.% EDTA slug application, it can be inferred that there exists a limit to the double layer compression, beyond which the increased concentration of EDTA has no further effect. This is evident in the fact that the same value of surface charge results regardless of the increased EDTA concentration from 5 – 10 wt.%. For a calcite rock with a 5 wt.% anhydrite scale system, a lower magnitude of negative surface charge results compared to the case of a 1 wt.% anhydrite scale. This is because, with a more anhydrite scale, more Ca^{2+} , which is a PDI is introduced into the system. Moreover, the highest magnitude of negative surface charge was observed in the case of 1 wt.% EDTA slug, with a reduction in surface charge observed with an increase in EDTA concentration. This decrease in surface charge is due to the compression of the double layer and in this case (5 wt.% anhydrite), slug treatment with as much as 10 wt.% EDTA solution is not sufficient to improve the colloidal stability of the system.

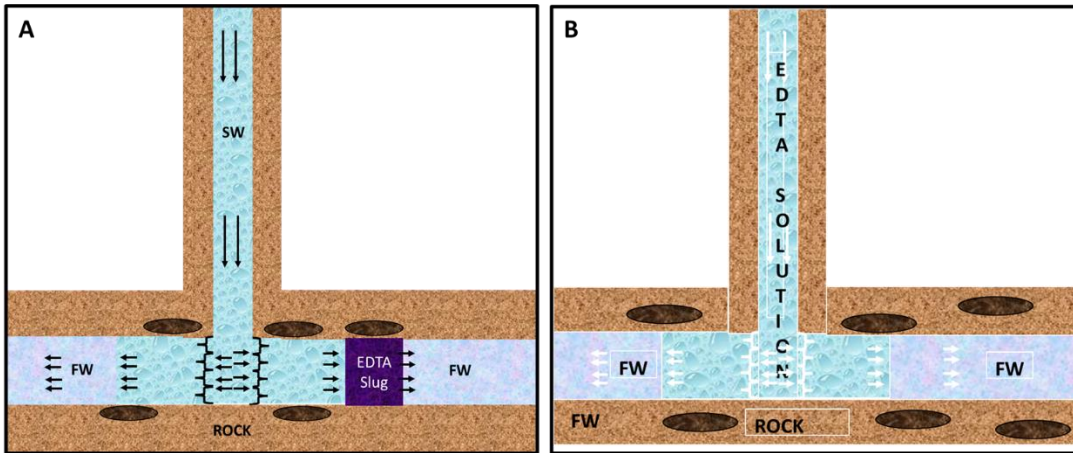


Figure 67: Mode of chelating agent injection. (A) slug injection. (B) Continuous injection.

With an increase in the anhydrite scale concentration to 10 wt.%, a positively charged surface results with all tested EDTA concentrations (1–10 wt.%) ineffective in reversing the calcite/anhydrite system surface charge. Thus, in the FW environment, the application of slug treatment is not effective due to the observed low negative and positive surface charges. This is attributed to the high concentration of cations in FW, which reduces the effect of the EDTA chelating agent on the calcite/anhydrite system. The effect of EDTA slug treatment on the calcite/anhydrite system in the SW environment, which has less cation concentration compared to FW is represented in **Error! Reference source not found**.B. In the case of a calcite system with a 1wt.% anhydrite scale, an increase in EDTA solution concentration is observed to improve the negative charge magnitude of the system. This agrees with the report of Hassan and Al-Hashim(Hassan & Al-Hashim, 2020b) who reported carbonate

A	B
---	---

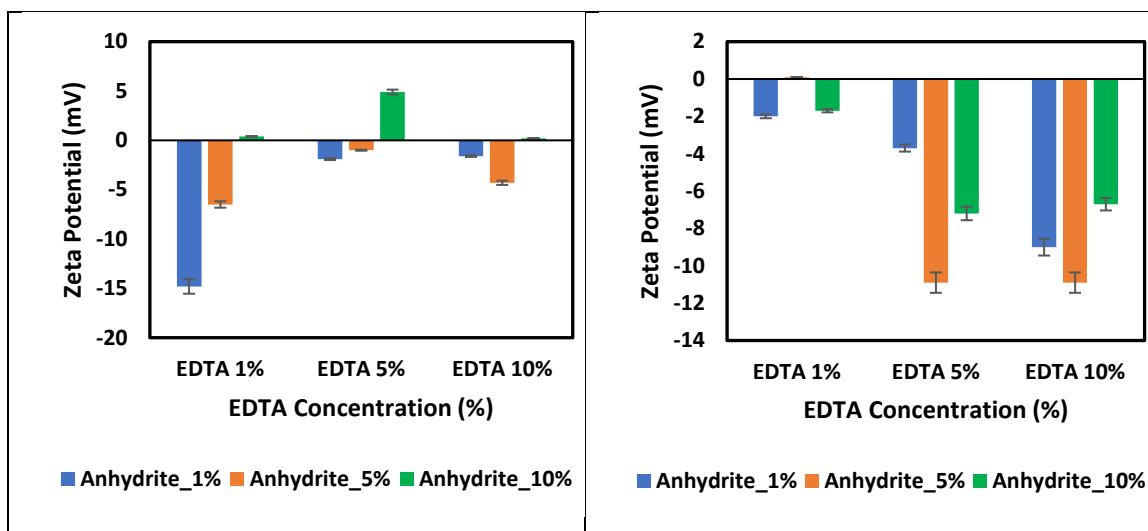


Figure 68. Effect of slug injection on scale control. A and B: zeta potential values for anhydrite/calcite case scenario in FW and SW, respectively.

system surface charge modification using an EDTA chelating agent. In the cases of 5 and 10 wt.% anhydrite concentrations, the optimum EDTA concentration for slug treatment was determined to be 5 wt.%. This is because a further increase in EDTA concentration above 5 wt.% showed an insignificant difference. Thus, in the SW water environment, calcite systems with 1 wt.% and above 5 wt.% anhydrite require 10 wt.% and 5 wt.% EDTA solutions for slug treatment, respectively.

8.3.6 Continuous injection

Continuous injection (see Figure 67B above) of chelating agents into the formation is the alternative to slug injection. This often requires a low dosage of chemical for economic concerns; thus, the most efficient chemical is that whose optimal concentration is exceptionally low and efficient. This is achieved by dosing the SW injected into the formation with the required chemical dosage. In this study, we investigate the use of 1 –

10 wt.% EDTA for continuous injection in a calcite scale system of varying scale concentration (1, 5, and 10 wt.%).

Error! Reference source not found. shows the effect of continuous injection of 1, 5, and 10 wt.% EDTA on the anhydrite/calcite system of 1, 5, and 10 wt.% anhydrite. Also shown in this figure is the effect of the EDTA chelating agent in different environments (FW (**Error! Reference source not found.**A – C) and SW (**Error! Reference source not found.**D – F)).

In the FW environment (**Error! Reference source not found.**A – C), the optimum EDTA concentration to achieve the highest magnitude of negatively charged surface is 1 wt.%, 1 wt.%, and 5 wt.% for 1, 5, and 10 wt.% anhydrite/calcite systems, respectively. In an economic view, 1 wt.% EDTA is optimal for low anhydrite scale conditions, whereas, for higher scale percentages (10 >=), 5 wt.% continuous injections will suffice. On the other hand, in SW (**Error! Reference source not found.**D – F) environment, 1 wt.% EDTA continuous injection is the optimal injection dosage regardless of the anhydrite scale percentage. Thus, once SW injection has started, the dosage of the injected SW with 1 wt.% EDTA solution helps improve the colloidal stability against precipitation. This also ensures surface conditions that would not serve as precursor for polar crude oil compounds adsorption. Thus, an operational strategy to minimize wettability alteration and formation damage.

A	B
---	---

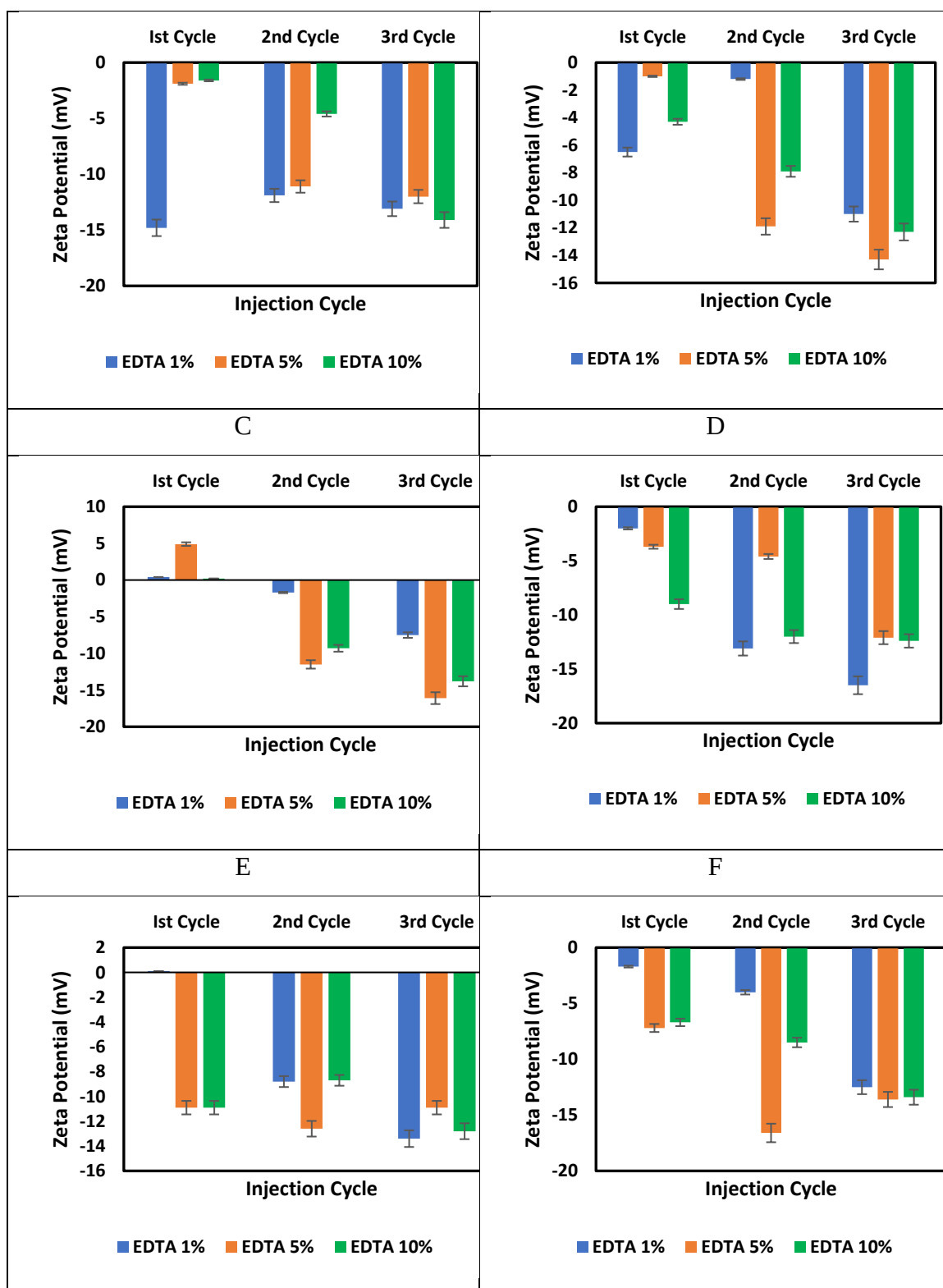


Figure 69. Effect of continuous EDTA chelating agent injection on the calcite/scale surface charge. (A – C) and (D – F) represent 1, 5, and 10 wt.% anhydrite/calcite system in FW and SW environments, respectively.

8.4 Wettability alteration

Results thus far show that the presence of scales affects the surface charge of calcite minerals and thus affects the calcite mineral interactions. As earlier presented in the preceding section, for wettability alteration to occur due to the adsorption of crude oil polar compounds, the calcite surface charge must be opposite that of asphaltene which is said to be negatively charged. The results of the effect of sulfate scale on calcite mineral surface charge (Figure 64 & 8.3) showed that the presence of the scales makes the surface negatively charged except in the case of anhydrite in the FW environment. Thus, if the surface is negatively charged, wettability alteration due to the asphaltene molecule is mitigated. However, the change in the zeta potential due to the presence of the scales possesses the threat of precipitation. The threat of scale precipitation is due to the instability of the colloidal system which is depicted by a near-zero and low zeta potential values (less than ± 10) of the calcite/scale systems. This also leads to the inference that the presence of the scale does not affect the wettability of the calcite system, however, possesses a threat of permeability and porosity damage. Additionally, the injection of EDTA solution as a scale control method enhanced the magnitude of the system's negative surface charge, thus, improving the calcite surface's ability to mitigate changes in wettability brought on by asphaltene adsorption.

Wettability alteration assessment using, for instance, the contact angle method was difficult to achieve in this study. The difficulties encountered that prevented the report of wettability alteration vis-à-vis contact angle measurements in this study involved making a core plug with scales at the proper percentage compositions. The samples must be heated and

compressed under high pressure to create a core plug from the powder. The core plugs would after that be cut into chips to quantify the contact angle. Additionally, cementing materials are employed to bind the powdered samples together to create the core plugs, and according to this study, a cementing material concentration of greater than 30 weight percent is needed. This, in our opinion, would affect the recorded contact angle. To reduce the cementing material's influence on surface contacts, a different study is devoted to the creation of representative core plugs.

8.5 Conclusions

The impact of sulfate-based scale (anhydrite) on calcite mineral surface charge is investigated in this study. Also, the effect of pH-inducing oilfield operations, as well as an evaluation of the optimal concentration of chelating agent for scale control, is presented. Based on our findings, the following conclusions are reached.

The presence of sulfate-based scales in calcite-rich formation results in precipitation-prone conditions even though the surface charge may be negative.

Sulfate-based scales do not by themselves induce wettability alteration as they create a calcite mineral surface (negatively charged) that is inhibitive of asphaltene adsorption.

The combined effect of sulfate scales and pH-inducing oilfield operations creates a positively charged calcite surface prone to polar crude oil compound adsorption and would consequently cause wettability alterations.

Chelating agents are good candidates for sulfate-based scale control, with the best operational strategy being the continuous injection of chelating agents.

The optimal concentrations of EDTA for control of anhydrite scale in FW and SW environments are 5 wt.% and 1 wt.% for continuous injection strategy.

CHAPTER 9

EFFECT OF SURFACE ROUGHNESS AND INTERFACIAL TENSION (IFT) OF ROCK WETTABILITY

Summary

Surface roughness at the grain-pore interface plays a critical role in various petroleum applications, influencing pore fractal characteristics, rock physical properties such as permeability, and fluid flow and distribution within porous media. The wetting behavior of rock is highly dependent on its root mean square (RMS) roughness, which, in turn, affects overall fluid dynamics. Despite its importance, the comprehensive effect of surface roughness and interfacial tension (IFT) on rock wettability remains insufficiently investigated. This study compares the wettability change with RMS roughness of pure, nonporous, and impermeable calcite substrates with that of conventional carbonate rock (Indiana limestone) under varying IFT conditions (ranging from 0.4 mN/m to 50 mN/m achieved by surfactant addition at different concentrations).

Different sandpaper grit sizes were employed for mechanical polishing to achieve different surface roughness levels for both conventional calcite and nonporous, nonpermeable calcite substrates. Five rock samples were polished using diamond lapping foils (0.5 μm , 2 μm , 9 μm , 15 μm , and 55 μm) to attain different surface roughness levels, and RMS roughness measurements were conducted at different spots on the polished surfaces of

Indiana limestone, specifically on the grain surface and around the pores. Surfactant was added to obtain 3 different IFT values, 50.33 mN/m at 0 wt%, 4.64 mN/m at 0.005 wt%, and 0.40 mN/m at 0.1 wt%. Dynamic contact angle measurements were conducted on the prepared two types of calcite substrates at 3 different IFT conditions. The results indicate that the RMS roughness of nonporous calcite substrates (ranging from 28 nm for 0.5 μm polishing foil, to 145 nm for 55 μm sandpaper) is comparable to that measured on the grain surface of conventional Indiana limestone (37.3 nm for 0.5 μm to 270.6 nm for 55 μm grit size). However, RMS roughness around the pores on the Indiana limestone surface is significantly larger than that of the nonporous calcite substrate, suggesting that pore presence in the rock increases microscale surface roughness. Peak to Valley (P-T) roughness also showed similar trend. Contact angle measurements revealed that lower IFT and surface roughness exhibit greater oil-wetting characteristics. A smoother surface appeared to increase the instability of the drop and the obtained contact angle values. Moreover, the nonporous calcite exhibits greater surface hardness than the conventional carbonate measured by nanoindentation. However, wettability via contact angle does not show any correlation with the nanomechanical hardness of the rock surfaces, even under varying interfacial tension conditions. This study sheds light on the complex interactions between surface roughness, interfacial tension, and rock wettability, contributing to a deeper understanding of fluid-rock interactions in porous media.

Key words: Surface roughness, Interfacial tension, Wettability, Nanoindentation, Contact angle

9.1 Experiments

Contact angle measurement is the most used technique for evaluating surface wettability. Ideally, the measurement should be conducted on a homogenous, atomic smooth, flat surface. However, when studying the contact angle in the oil/water/rock system, the rock surface is inhomogeneous and rough. The impact of surface roughness has been found to have a profound influence on the obtained angle values. Dynamic contact angle measurement captures the contact angle values while the drop shape undergoes a continuous change. A consistent dynamic contact angle value indicates either the minimum or maximum Gibbs free energy. However, with a rough surface, it is difficult to reach a steady dynamic contact angle or a consistent static contact angle value.

This work aims to study the impact of roughness and interfacial tension (IFT) on the dynamic contact angle measurement. The measurements were conducted using the DSA25B manufactured by KRUSS at room conditions. n-decane was chosen to represent oil. Deionized water was used as the surrounding phase. n-decane was injected through a manual syringe to form a droplet on the rock surface. The detected contact angle changed along the manually increased droplet volume. Angle values were recorded by the software.

9.2 Results and Discussion

Figure 9.1 presents the optical images and root mean square (RMS) roughness of Iceland spar for various polishing. The surface topographic images in both 2D and 3D are shown. The samples were polished using sandpapers with grit sizes of 55 μm (1), 15 μm (2), 9 μm (3), 2 μm (4), and 0.5 μm sample with roughness #5. Smoother surfaces were obtained with smaller sandpaper micron sizes. The surface roughness ranges from 28.3 nm for 0.5 μm polishing foil to 145 nm for 55 μm foil.

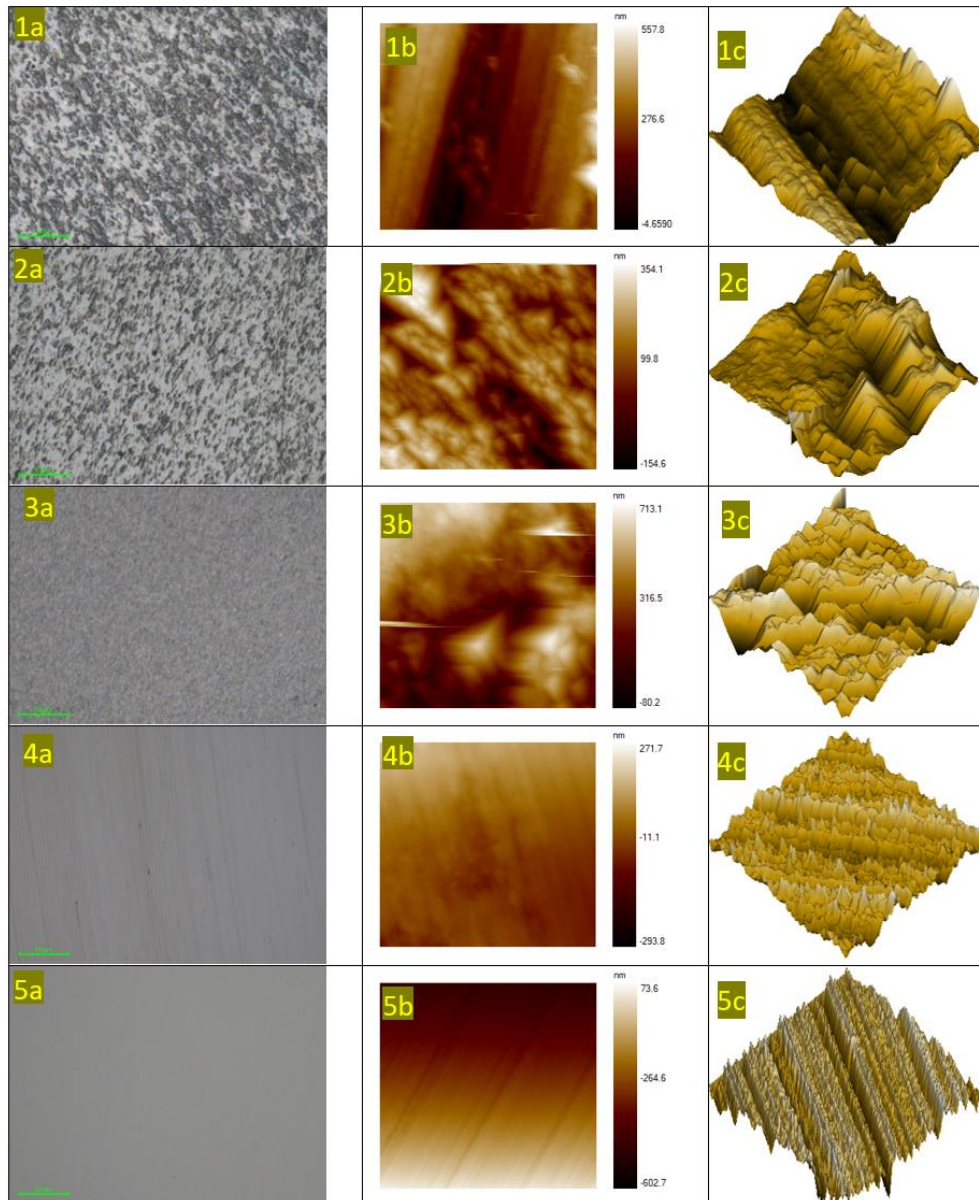


Figure 70. Nonporous-nonpermeable calcite: a) optical images, b) and c) are surface topographic images in 2D and 3D, respectively. Polished with 55 μm (1), 15 μm (2), 9 μm (3), 2 μm (4), and 0.5 μm sandpapers (5).

For the porous and permeable Indiana rock sample, two different surface roughness measurements were performed for each surface polishing, that is, the RMS surface roughness is measured on the grain surfaces and around the pores of the samples surface.

Figure 9.2 and **Figure 9.3** show the optical images and surface roughness of the Indiana limestone samples on the grain surfaces and around the pores, respectively.

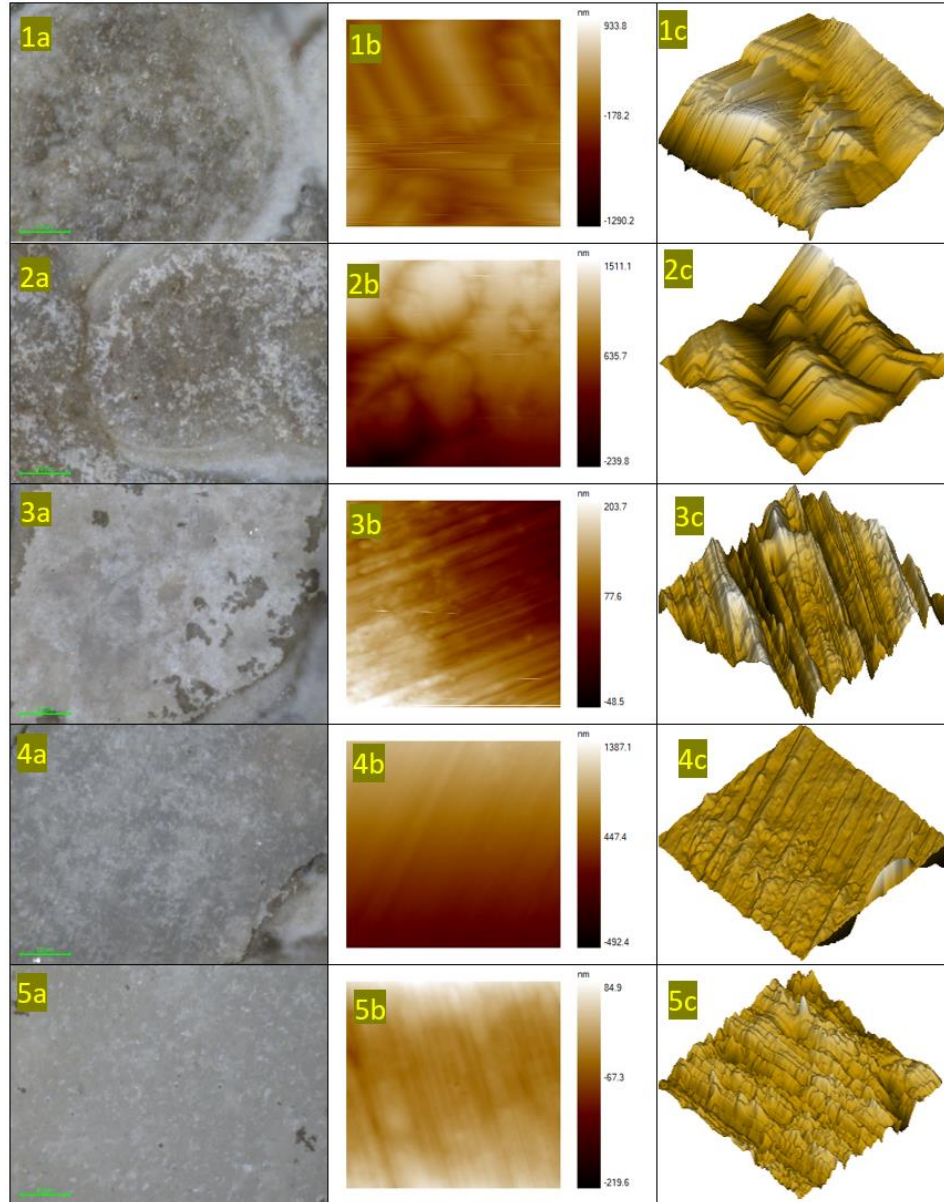


Figure 71. Indiana limestone: roughness of the grain surface; a) optical images, b) and c) are surface topographic images in 2D and 3D, respectively. Polished with 55 μm (1), 15 μm (2), 9 μm (3), 2 μm (4), and 0.5 μm sandpapers (5).

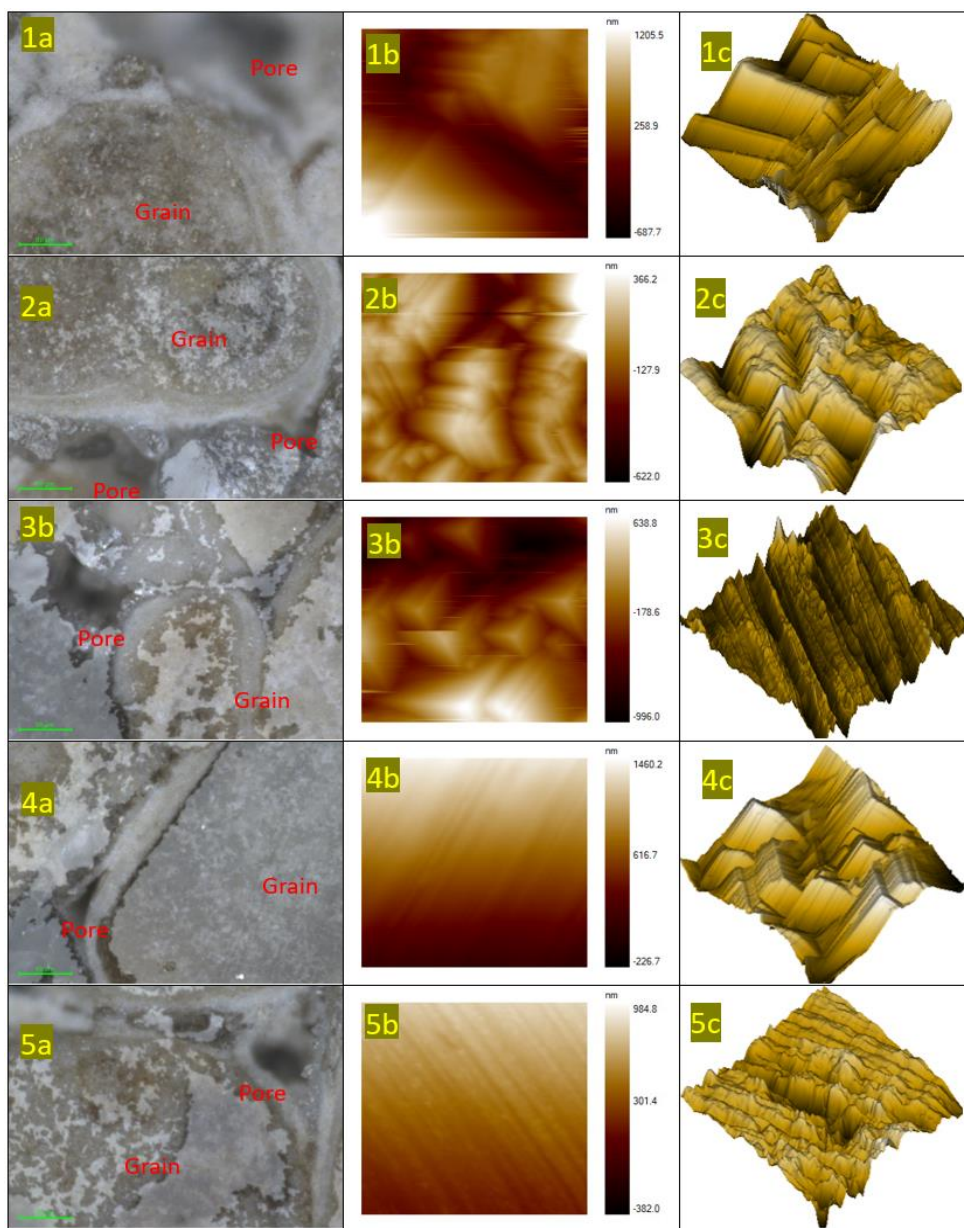


Figure 72. Indiana limestone: roughness around the pore spaces; a) optical images, b) and c) are surface topographic images in 2D and 3D, respectively. Polished with 55 μm (1), 15 μm (2), 9 μm (3), 2 μm (4), and 0.5 μm sandpapers.

The data presented in **Figure 9.4** highlights similarities and differences in surface roughness between nonporous-nonpermeable calcite (Iceland spar) and Indiana limestone (ILS). The surface roughness of the Iceland spar and the grain surface of the limestone appear similar, suggesting comparable surface textures. However, the RMS roughness of

the limestone around its pores consistently exceeds that of both the limestone grain surface and the nonporous calcite. This disparity indicates that the presence of pores significantly influences the surface topography of the limestone. Such variations in surface roughness may have implications for other surface properties, such as surface energy and wetting behavior. The increased roughness around pores suggests a more complex and heterogeneous surface, which could affect interactions with fluids.

The Peak to Valley (P-T) roughness against sandpaper size for the Iceland spar (nonporous-nonpermeable calcite) and Indiana limestone (ILS) are also computed and tabulated in **Table 9.1 and Figure 9.5**, and this shows similar trend observed in the RMS roughness with polishing foil micron size.

Table 9.1. Roughness and sandpaper size for the Indiana limestone (ILS) and the nonporous-nonpermeable calcite.

Sample	Sandpaper		Porous Indiana LS				Iceland spar (Non-Porous Calcite)	
	Micron size		Around the pores		Grain surface		Surface	
	Grit	(μm)	RMS (nm)	P-T (nm)	RMS (nm)	P-T (nm)	RMS (nm)	P-T (nm)
1	280	55	442	2081	270.6	1367.7	145	813.9
2	1200	15	368	1697.4	198.1	1065.6	94.5	597.6
3	1800	9	374.4	1383.1	59.9	265.4	81.2	620.9
4	9000	2	331	1634.8	46.2	516.6	34.9	547.8
5	60000	0.5	349.1	1224.9	37.3	197	28.3	181.3

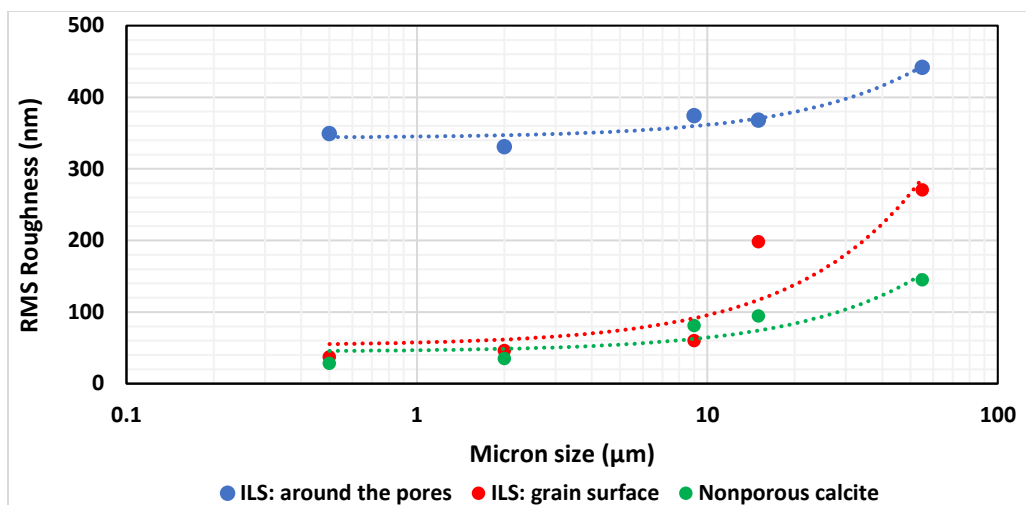


Figure 73. Root mean square (RMS) roughness against sandpaper size for the Indiana limestone (ILS) and the nonporous-nonpermeable calcite.

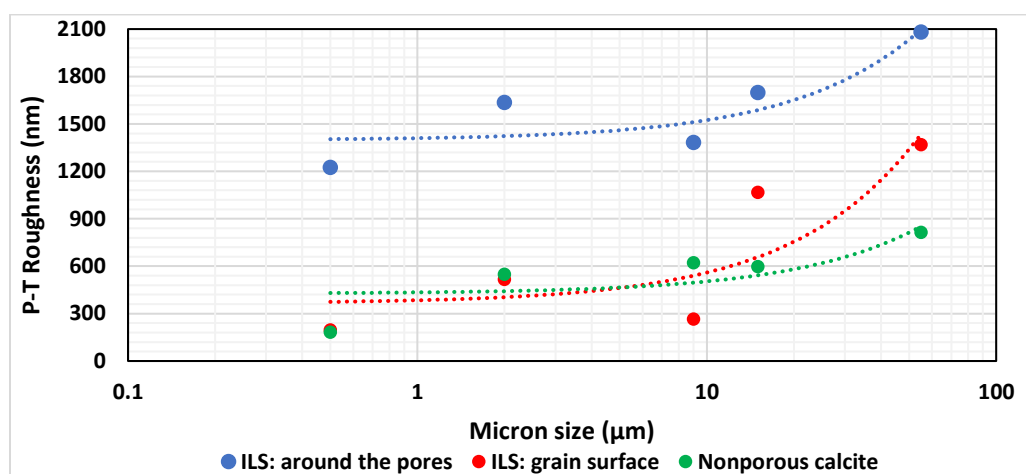
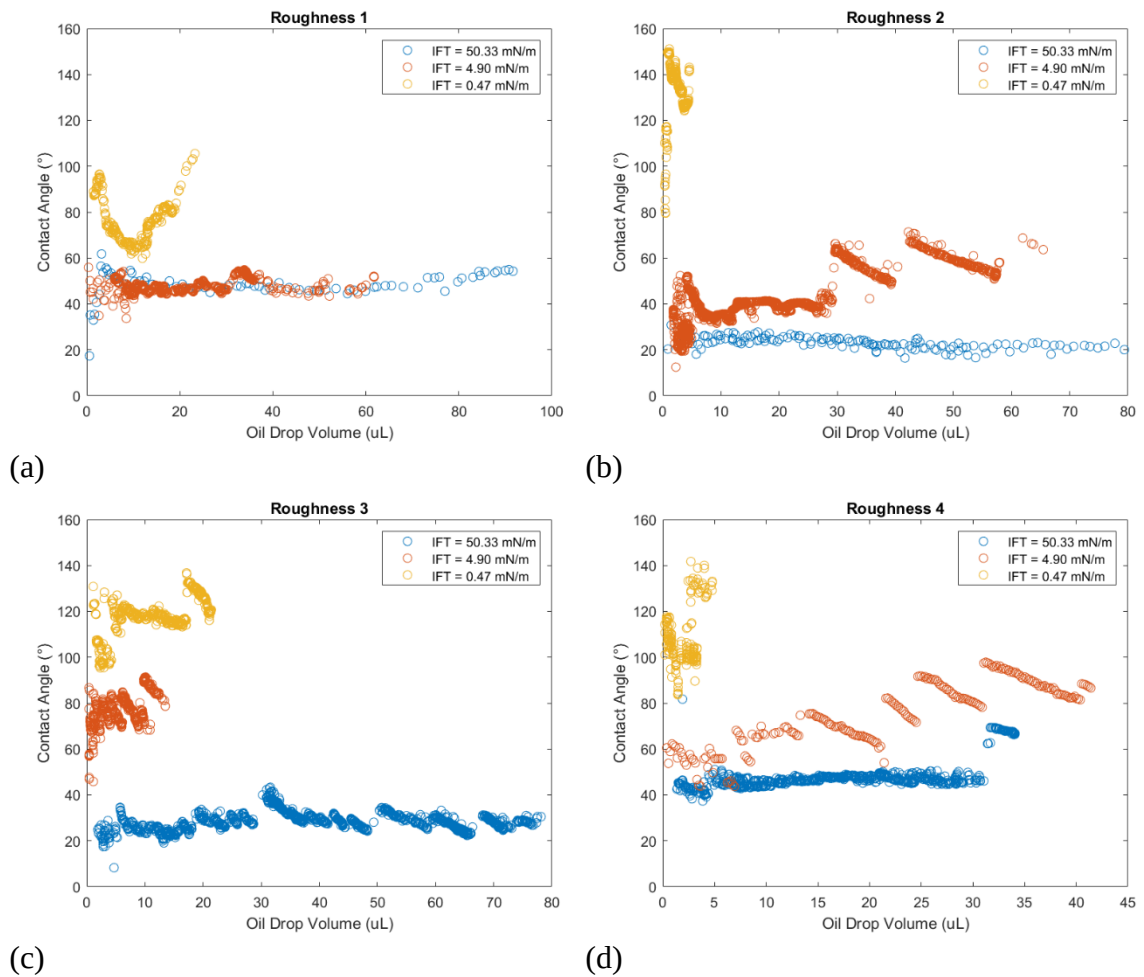


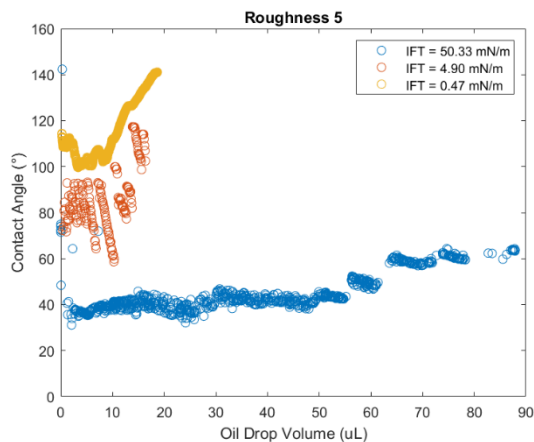
Figure 74. Peak to Valley (P-T) roughness against sandpaper size for the Indiana limestone (ILS) and the nonporous-nonpermeable calcite.

9.2.1 Iceland spar contact angle results

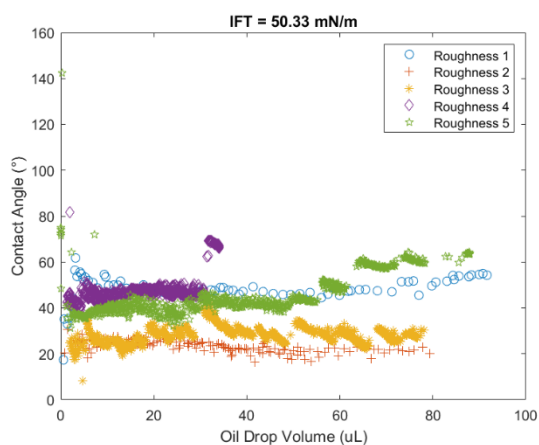
According to **Figure 75**, a higher oil/water IFT value appears to maintain a more stable contact angle value. The measured contact angle value at the same drop volume is larger at a lower IFT. The contact angle hysteresis becomes more significant when the IFT is lower, and the roughness is smaller. At the same IFT condition, a higher roughness

generally means a more stable contact angle value. The measured contact angle value appeared to be strongly dependent on the volume of the oil drop. When the drop size is smaller than 5 μL , the contact angle value is very unstable. When the drop size is in the range of 5~10 μL , the value starts stabilizing. As the drop volume continues to increase, contact angle hysteresis becomes more significant, resulting in a stepwise increase.

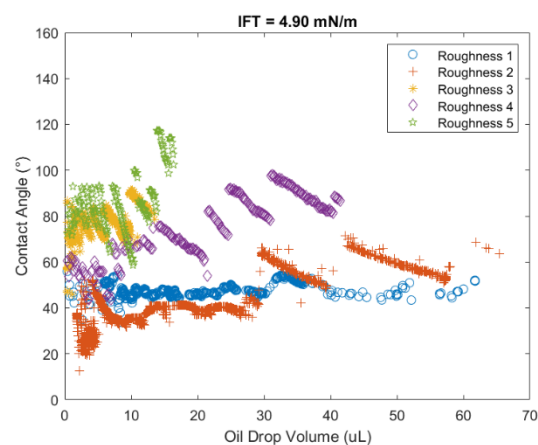




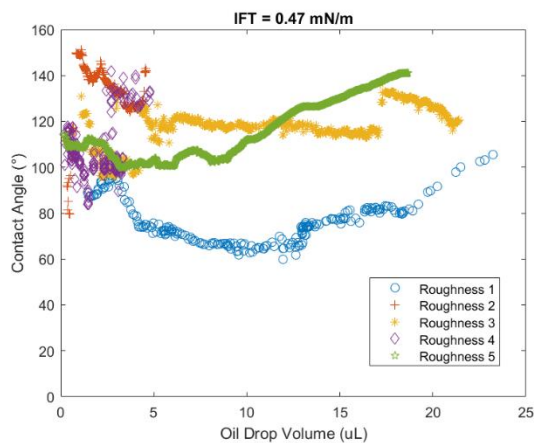
(e) Figure 75 Contact angle values at 3 different IFT levels for 5 Iceland spar samples of different roughness.



(a)



(b)



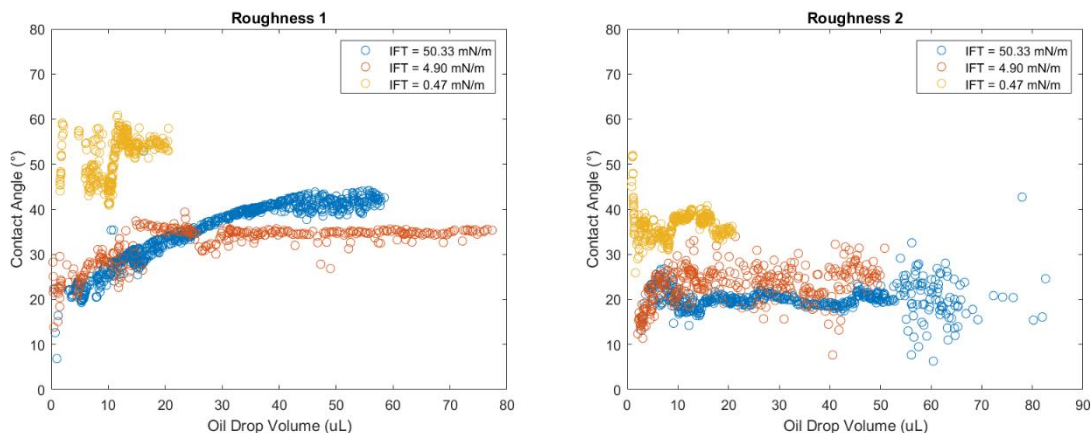
(c)

Figure 76 Contact angle values of 5 Iceland spar samples of different roughness at 3 different IFT levels.

9.2.2 Indiana limestone contact angle results

Based on the results displayed, Impact of roughness is that, a higher roughness gives a more stable contact angle (**Figure 9.8**). At Roughness 1, the contact angle curve. This emphasize the importance of taking into account the surface roughness and IFT variations in wettability assessments.

This statement underscores two critical considerations in dynamic contact angle measurements. Firstly, it emphasizes that contact angle measurements with droplet volumes less than 5~10 μL may be unreliable. This indicates that extremely small droplets may not provide accurate or consistent contact angle readings, likely due to challenges in achieving stable droplet shapes or difficulties in accurately measuring the contact line. Secondly, it points out that gravity begins to exert a noticeable effect on larger droplets. When droplet volumes are too high, the force of gravity can distort the droplet shape, leading to inaccuracies in the measured contact angle. This highlights the importance of carefully controlling droplet size and volume in contact angle measurements to ensure reliable and accurate results.



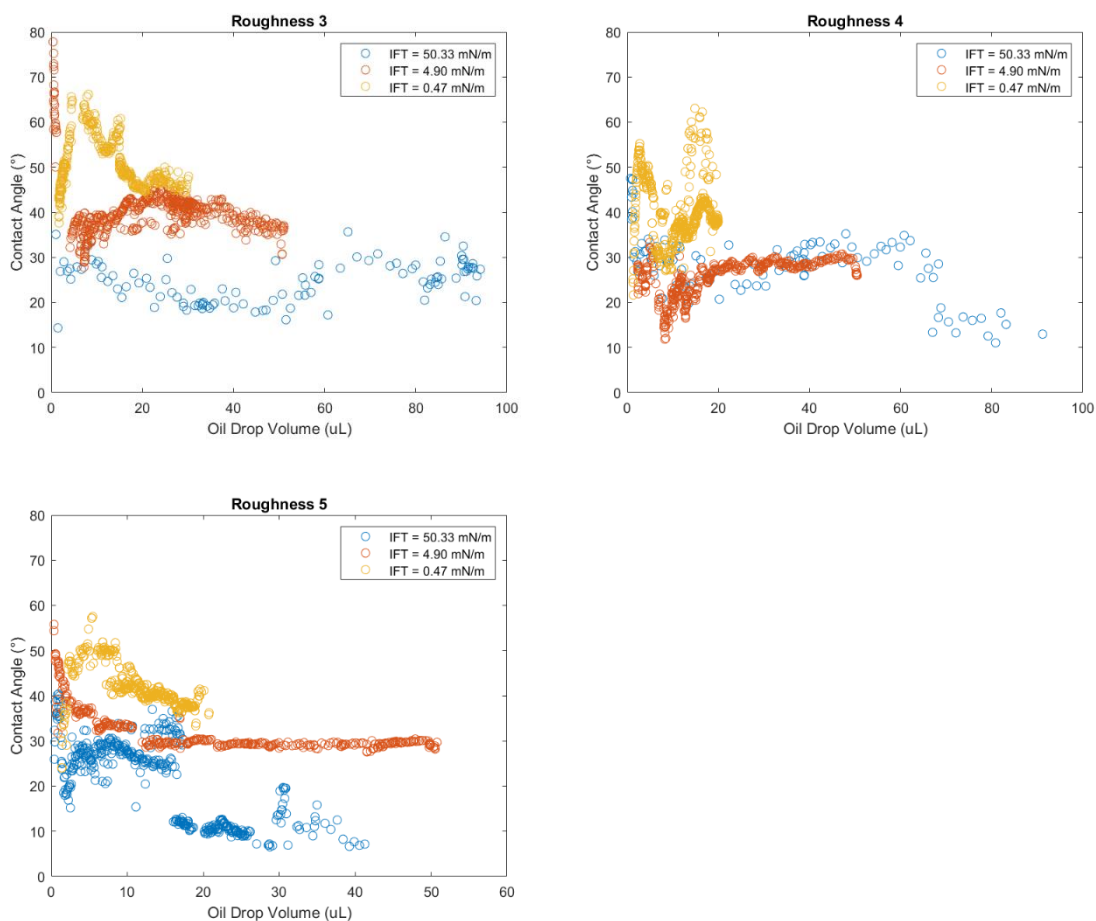
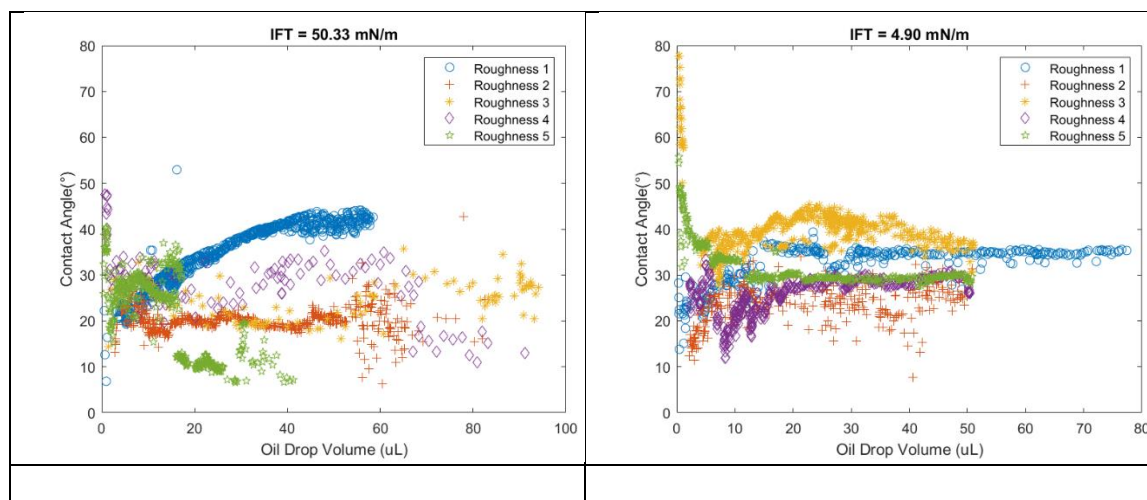


Figure 77. Contact angle values at 3 different IFT levels for 5 Indiana limestone samples of different roughness.



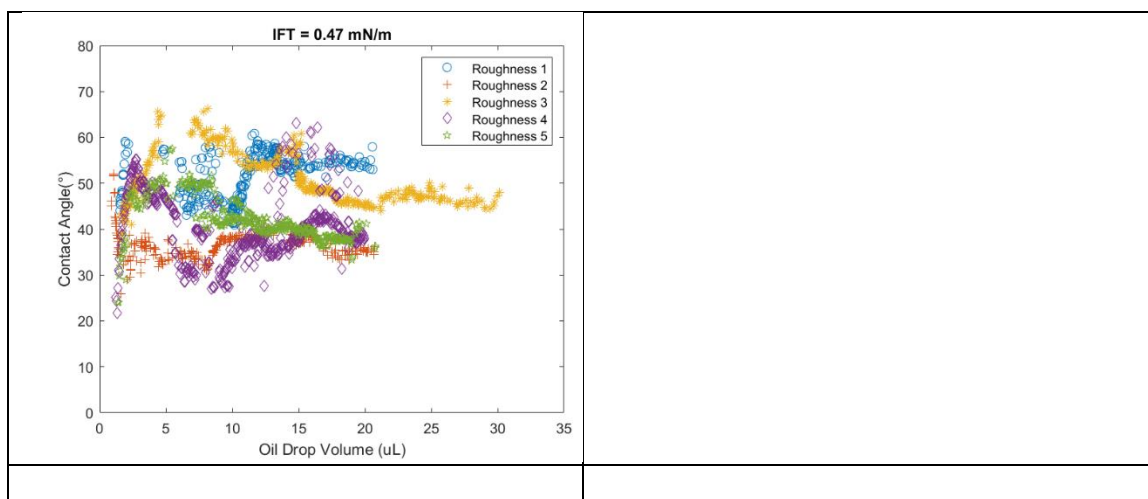


Figure 78. Contact angle values of 5 Indiana limestone samples of different roughness at 3 different IFT levels.

9.3 Conclusions

The findings suggest that the root mean square roughness of nonporous calcite substrates, ranging from 28 nm for 0.5 μm polishing foil to 145 nm for 55 μm sandpaper, closely resembles that measured on the grain surface of conventional Indiana limestone, which ranges from 37.3 nm for 0.5 μm to 270.6 nm for 55 μm grit size. However, the RMS roughness around the pores on the Indiana limestone surface is notably larger than that of the nonporous calcite substrate, indicating that the presence of pores in the rock increases microscale surface roughness. The Peak to Valley (P-V) roughness also shows a similar trend.

Contact angle measurements demonstrate that lower interfacial tension (IFT) and surface roughness lead to greater oil-wetting characteristics. Notably, a smoother surface seems to enhance the instability of the drop and the obtained contact angle values. Additionally, the nonporous calcite exhibits greater surface hardness than the conventional carbonate as measured by nanoindentation. Despite this, wettability, as determined by contact angle,

does not exhibit any correlation with the nanomechanical hardness of the rock surfaces, even under varying interfacial tension conditions. This study provides insights into the intricate interplay between surface roughness, interfacial tension, and rock wettability, contributing to a deeper comprehension of fluid-rock interactions in porous media.

References

- Abbas, A. H., Pourafshary, P., Wan Sulaiman, W. R., Jaafar, M. Z., & Nyakuma, B. B. (2021). Toward Reducing Surfactant Adsorption on Clay Minerals by Lignin for Enhanced Oil Recovery Application. *ACS Omega*, *acsomega.1c01342*.
<https://doi.org/10.1021/acsomega.1c01342>
- Abbasi, G. R., Al-Yaseri, A., Isah, A., Keshavarz, A., & Iglaue, S. (2021). Influence of Rock Wettability on THF Hydrate Saturation and Distribution in Sandstones. *The Journal of Physical Chemistry C*, *125*(31), 17323–17332. <https://doi.org/10.1021/ACS.JPCC.1C03940>
- Abbasi, P., Abbasi, S., & Moghadasi, J. (2020). Experimental investigation of mixed-salt precipitation during smart water injection in the carbonate formation. *Journal of Molecular Liquids*, *299*, 112131. <https://doi.org/10.1016/J.MOLLIQ.2019.112131>
- Abbasi, S., & Khamsehchi, E. (2021). Experimental investigation of competitive mechanisms of precipitation and dissolution due to seawater and low salinity water injection in carbonate reservoirs. *Journal of Molecular Liquids*, *324*, 114767.
<https://doi.org/10.1016/J.MOLLIQ.2020.114767>
- Abbaszadeh, M., Nasiri, M., Sciences, M. R.-E. E., & 2016, U. (2016). Experimental investigation of the impact of rock dissolution on carbonate rock properties in the presence of carbonated water. *Springer*. <https://doi.org/10.1007/s12665-016-5624-3>
- Abdel-Azeim, S., Sakthivel, S., Kandiel, T. A., & Kanj, M. Y. (2021). Specificity and Synergy at the Oil–Brine Interface: New Insights from Experiments and Molecular Dynamics Simulations. *Energy & Fuels*, *35*(18), 14647–14657. <https://doi.org/10.1021/acs.energyfuels.1c02133>
- Abdelgawad, K., Mahmoud, M., Elkatatny, S., & Patil, S. (2019). Effect of calcium carbonate on barite solubility using a chelating agent and converter. *Proceedings - SPE International Symposium on Oilfield Chemistry, 2019*. <https://doi.org/10.2118/193566-ms>
- Abdelgawad, K. Z., Mahmoud, M., Elkatatny, S., Abdulraheem, A., & Patil, S. (2019). Reaction Kinetics and Coreflooding Study of High-Temperature Carbonate Reservoir Stimulation Using GLDA in Seawater. *Energies* 2019, Vol. 12, Page 3407, *12*(18), 3407.
<https://doi.org/10.3390/EN12183407>
- Abdolmaleki, J., Tavakoli, V., & Asadi-Eskandar, A. (2016). Sedimentological and diagenetic controls on reservoir properties in the Permian–Triassic successions of Western Persian Gulf, Southern Iran. *Journal of Petroleum Science and Engineering*, *141*, 90–113.
<https://doi.org/10.1016/J.PETROL.2016.01.020>
- Adegoke, I. A., Xia, F., Deditius, A. P., Pearce, M. A., Roberts, M. P., & Brugger, J. (2022). A new mode of mineral replacement reactions involving the synergy between fluid-induced solid-state diffusion and dissolution-reprecipitation: A case study of the replacement of bornite by copper sulfides. *Geochimica et Cosmochimica Acta*, *330*, 165–190.
<https://doi.org/10.1016/J.GCA.2021.04.017>
- Aghamir-Baha, S. (2014). *Measurment of polymer concentration and optimization of sludge dewatering using UV-VIS spectroscopy*. May, 127.

- Ajayi, T., Awolayo, A., Gomes, J. S., Parra, H., & Hu, J. (2019). Large scale modeling and assessment of the feasibility of CO₂ storage onshore Abu Dhabi. *Energy*, 185, 653–670. <https://doi.org/10.1016/J.ENERGY.2019.07.052>
- Al-Araimi, S., Karimi, M., & Al-Maamari, R. S. (2021). Experimental Investigation of the Effect of Acid and Base on Wettability Alteration of a Calcite Surface. *Energy & Fuels*, 35(15), 11869–11883. <https://doi.org/10.1021/acs.energyfuels.1c01167>
- Al-Awwad, S. F., & Collins, L. B. (2013). Carbonate-platform scale correlation of stacked high-frequency sequences in the Arab-D reservoir, Saudi Arabia. *Sedimentary Geology*, 294, 205–218. <https://doi.org/10.1016/J.SEDGEO.2013.05.015>
- Al-Balushi, M. A., Karimi, M., & Al-Maamari, R. S. (2020). Impact of Acid and Base Numbers and Their Ratios on Wettability Alteration of the Calcite Surface. *Energy and Fuels*, 34(1), 245–257. <https://doi.org/https://doi.org/10.1021/acs.energyfuels.9b03538>
- Al-Bayati, A., Karunarathne, C. I., Al Jehani, A. S., Al-Yaseri, A. Z., Keshavarz, A., & Iglaier, S. (2022). Wettability Alteration during Low-Salinity Water Flooding. *Energy & Fuels*, 36(2), 871–879. <https://doi.org/10.1021/acs.energyfuels.1c03728>
- Al-Hussaini, A., Alnazghah, M., Al-Ramadan, K., Fallatah, M., & Polo, C. (2021). Asymmetrical wave-dominated siliciclastic shorelines with evidence of along-strike variability of sedimentary processes: A revised interpretation for the Toarcian Marrat red beds, central Arabia. *Marine and Petroleum Geology*, 126, 104915. <https://doi.org/10.1016/J.MARPETGEO.2021.104915>
- Al-Ibadi, H., Stephen, K. D., & Mackay, E. (2019). Insights into the fractional flow of low salinity water flooding in the light of solute dispersion and effective salinity interactions. *Journal of Petroleum Science and Engineering*, 174, 1236–1248. <https://doi.org/10.1016/J.PETROL.2018.12.001>
- Al-Mahrooqi, S. H., Grattoni, C. A., Moss, A. K., & Jing, X. D. (2003). An investigation of the effect of wettability on NMR characteristics of sandstone rock and fluid systems. *Journal of Petroleum Science and Engineering*, 39(3–4), 389–398. [https://doi.org/10.1016/S0920-4105\(03\)00077-9](https://doi.org/10.1016/S0920-4105(03)00077-9)
- Al-Mahrooqi, S. H., Grattoni, C. A., Muggeridge, A. H., Zimmerman, R. W., & Jing, X. D. (2006). Pore-scale modelling of NMR relaxation for the characterization of wettability. *Journal of Petroleum Science and Engineering*, 52(1–4), 172–186. <https://doi.org/10.1016/j.petrol.2006.03.008>
- Al-Mojel, A., Razin, P., Le Nindre, Y. M., & Dera, G. (2020). Shallow-marine depositional sequences in a transgressive mixed siliciclastic-carbonate system: The Early Jurassic Marrat Formation from central Saudi Arabia. *Journal of African Earth Sciences*, 167, 103429. <https://doi.org/10.1016/J.JAFREARSCI.2019.02.011>
- Al-Shalabi, E. W., Sepehrnoori, K., & Pope, G. (2014). Geochemical interpretation of low salinity water injection in carbonate oil reservoirs. *Proceedings - SPE Symposium on Improved Oil Recovery*, 2(December), 998–1020. <https://doi.org/10.2118/169101-ms>
- Al-Shalabi, E. W., Sepehrnoori, K., & Pope, G. (2015). Geochemical Interpretation of Low-Salinity-Water Injection in Carbonate Oil Reservoirs. *SPE Journal*, 20(06), 1212–1226.

<https://doi.org/10.2118/169101-PA>

- Al-Shirawi, M., Karimi, M., & Al-Maamari, R. S. (2021). Impact of carbonate surface mineralogy on wettability alteration using stearic acid. *Journal of Petroleum Science and Engineering*, 203, 108674. <https://doi.org/10.1016/J.PETROL.2021.108674>
- Al-Yaseri, A. Z., Lebedev, M., Barifcani, A., & Iglaue, S. (2016). Receding and advancing (CO₂ + brine + quartz) contact angles as a function of pressure, temperature, surface roughness, salt type and salinity. *The Journal of Chemical Thermodynamics*, 93, 416–423. <https://doi.org/10.1016/J.JCT.2015.07.031>
- Al Dabbas, M., Eisa, M. Y., & Kadhim, W. H. (2014). Estimation of gypsum-calcite percentages using a Fourier transform infrared spectrophotometer (FTIR), in Alexandria Gypsiferous Soil-Iraq. *iasj.Net*, 55(4B), 1916–1926. <https://www.iasj.net/iasj/download/d36860e7a0c46f9d>
- Al Maskari, N. S., Almobarak, M., Saeedi, A., & Xie, Q. (2020). Influence of pH on Acidic Oil-Brine-Carbonate Adhesion Using Atomic Force Microscopy. *Energy and Fuels*, 34(11), 13750–13758. <https://doi.org/10.1021/acs.energyfuels.0c02494>
- Al Maskari, N. S., Sari, A., Saeedi, A., & Xie, Q. (2019). Influence of Surface Roughness on the Contact Angle due to Calcite Dissolution in an Oil-Brine-Calcite System: A Nanoscale Analysis Using Atomic Force Microscopy and Geochemical Modeling. *Energy and Fuels*, 33(5), 4219–4224. <https://doi.org/10.1021/ACS.ENERGYFUELS.9B00739>
- AlAamri, J., AlDahlan, M., Al-Otaibi, F. M., & Al-Ghamdi, A. (2019). Evaluation of a New Barium Sulfate Dissolver and the Effect of the Presence of Calcium Carbonate in the Dissolution Rate. *Society of Petroleum Engineers - Abu Dhabi International Petroleum Exhibition and Conference 2019, ADIP 2019*. <https://doi.org/10.2118/197360-MS>
- Alameedy, U, Alhaleem, A. A., Isah, A., Al-Yaseri, A., Mahmoud, M., & Salih, I. S. (2022). Effect of Acid Treatment on the Geomechanical Properties of Rocks: An Experimental Investigation in Ahdeb Oil Field. *Journal of Petroleum Exploration and Production Technology, Accepted for Publication*.
- Alameedy, Usama, Alhaleem, A. A., Isah, A., Al-Yaseri, A., Mahmoud, M., & Salih, I. S. (2022). Effect of acid treatment on the geomechanical properties of rocks: an experimental investigation in Ahdeb oil field. *Journal of Petroleum Exploration and Production Technology*, 12(12), 3425–3441. <https://doi.org/10.1007/S13202-022-01533-X/TABLES/6>
- Alcalde, J., Flude, S., Wilkinson, M., Johnson, G., Edlmann, K., Bond, C. E., Scott, V., Gilfillan, S. M. V., Ogaya, X., & Stuart Haszeldine, R. (2018). Estimating geological CO₂ storage security to deliver on climate mitigation. *Nature Communications* 2018 9:1, 9(1), 1–13. <https://doi.org/10.1038/s41467-018-04423-1>
- Aleali, M., Rahimpour-Bonab, H., Moussavi-Harami, R., & Jahani, D. (2013). Environmental and sequence stratigraphic implications of anhydrite textures: A case from the Lower Triassic of the Central Persian Gulf. *Journal of Asian Earth Sciences*, 75, 110–125. <https://doi.org/10.1016/J.JSEAES.2013.07.017>
- Alhammadi, A. M., Alratrout, A., Singh, K., Bijeljic, B., & Blunt, M. J. (2017a). In situ characterization of mixed-wettability in a reservoir rock at subsurface conditions. *Scientific*

- Reports* 2017 7:1, 7(1), 1–9. <https://doi.org/10.1038/s41598-017-10992-w>
- Alhammad, A. M., Alratrout, A., Singh, K., Bijeljic, B., & Blunt, M. J. (2017b). In situ characterization of mixed-wettability in a reservoir rock at subsurface conditions. *Scientific Reports* 2017 7:1, 7(1), 1–9. <https://doi.org/10.1038/s41598-017-10992-w>
- Alhassawi, H., & Romero-Zerón, L. (2015). Novel surfactant delivery system for controlling surfactant adsorption onto solid surfaces. Part II: Dynamic adsorption tests. *Canadian Journal of Chemical Engineering*, 93(8), 1371–1379. <https://doi.org/10.1002/cjce.22231>
- Alhosani, A., Scanziani, A., Lin, Q., Raeini, A. Q., Bijeljic, B., & Blunt, M. J. (2020). Pore-scale mechanisms of CO₂ storage in oilfields. *Scientific Reports* 2020 10:1, 10(1), 1–9. <https://doi.org/10.1038/s41598-020-65416-z>
- Ali, M., Awan, F. U. R., Ali, M., Al-Yaseri, A., Arif, M., Sánchez-Román, M., Keshavarz, A., & Iglauer, S. (2021). Effect of humic acid on CO₂-wettability in sandstone formation. *Journal of Colloid and Interface Science*, 588, 315–325. <https://doi.org/10.1016/J.JCIS.2020.12.058>
- Almeida, K. M. F., & Jenkins, D. M. (2017). Stability field of the Cl-rich scapolite marialite. *American Mineralogist*, 102(12), 2484–2493. <https://doi.org/10.2138/AM-2017-6132>
- AlOtaibi, F., AlOsaimi, F., Sanni, M., Kokal, S., Ali, R., & Alhashboul, A. (2017). Remaining Oil Saturation Measurements for CO₂-EOR Pilot in Saudi Arabia. *Society of Petroleum Engineers - SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition 2017*, 1963–1994. <https://doi.org/10.2118/188146-MS>
- Alotaibi, M. B., Nasralla, R. A., & Nasr-El-Din, H. A. (2011). Wettability Studies Using Low-Salinity Water in Sandstone Reservoirs. *SPE Reservoir Evaluation & Engineering*, 14(06), 713–725. <https://doi.org/10.2118/149942-PA>
- Alotaibi, Mohammed B., & Nasr-El-Din, H. A. (2011). Electrokinetics of Limestone Particles and Crude-Oil Droplets in Saline Solutions. *SPE Reservoir Evaluation & Engineering*, 14(05), 604–611. <https://doi.org/10.2118/151577-PA>
- AlQuraishi, A. A., AlHussinan, S. N., & AlYami, H. Q. (2015). *Efficiency and Recovery Mechanisms of Low Salinity Water Flooding in Sandstone and Carbonate Reservoirs*. OnePetro.
- AlRatrout, A., Blunt, M. J., & Bijeljic, B. (2018). Wettability in complex porous materials, the mixed-wet state, and its relationship to surface roughness. *Proceedings of the National Academy of Sciences of the United States of America*, 115(36), 8901–8906. <https://doi.org/10.1073/PNAS.1803734115>
- AlSada, A., & Mackay, E. (2017). Low Salinity Water Flooding Possible Mechanisms and the impact of Injected Sulphate variation on Oil Recovery in Carbonate Reservoirs: Compositional Modelling Approach. *Society of Petroleum Engineers - SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition 2017*, 1216–1228. <https://doi.org/10.2118/187980-MS>
- Altree-Williams, A., Pring, A., Ngothai, Y., & Brugger, J. (2017). The Carbonatation of Anhydrite: Kinetics and Reaction Pathways. *ACS Earth and Space Chemistry*, 1(2), 89–100. https://doi.org/10.1021/ACSEARTHSPACECHEM.6B00012/ASSET/IMAGES/LARGE/SP-2016-00012V_0013.JPEG

- Aman, M., Espinoza, D. N., Ilgen, A. G., Major, J. R., Eichhubl, P., & Dewers, T. A. (2018). CO₂-induced chemo-mechanical alteration in reservoir rocks assessed via batch reaction experiments and scratch testing. *Greenhouse Gases: Science and Technology*, 8(1), 133–149. <https://doi.org/10.1002/GHG.1726>
- Amel, H., Jafarian, A., Husinec, A., Koeshidayatullah, A., & Swennen, R. (2015). Microfacies, depositional environment and diagenetic evolution controls on the reservoir quality of the Permian Upper Dalan Formation, Kish Gas Field, Zagros Basin. *Marine and Petroleum Geology*, 67, 57–71. <https://doi.org/10.1016/J.MARPETGEO.2015.04.012>
- Amirmoshiri, M., Zhang, L., Puerto, M. C., Tewari, R. D., Bahrim, R. Z. B. K., Farajzadeh, R., Hirasaki, G. J., & Biswal, S. L. (2020). Role of Wettability on the Adsorption of an Anionic Surfactant on Sandstone Cores. *Langmuir*, 36(36), 10725–10738. <https://doi.org/10.1021/acs.langmuir.0c01521>
- An, S., Erfani, H., Hellevang, H., & Niasar, V. (2021). Lattice-Boltzmann simulation of dissolution of carbonate rock during CO₂-saturated brine injection. *Chemical Engineering Journal*, 408, 127235. <https://doi.org/10.1016/J.CEJ.2020.127235>
- Ancheyta, J., Centeno, G., Trejo, F., Marroquín, G., García, J. A., Tenorio, E., & Torres, A. (2002). Extraction and characterization of asphaltenes from different crude oils and solvents. *Energy and Fuels*, 16(5), 1121–1127. <https://doi.org/10.1021/EF010300H/ASSET/IMAGES/MEDIUM/EF010300HE00004.GIF>
- Anderson, W. G. (1986). Wettability Literature Survey- Part 2: Wettability Measurement. *Journal of Petroleum Technology*, 38(11), 1246–1262. <https://doi.org/10.2118/13933-PA>
- Anovitz, L. M., & Cole, D. R. (2015). Characterization and Analysis of Porosity and Pore Structures. *Reviews in Mineralogy and Geochemistry*, 80(1), 61–164. <https://doi.org/10.2138/RMG.2015.80.04>
- Ansah, E. O., Nguele, R., Sugai, Y., & Sasaki, K. (2019). Predicting the antagonistic effect between albite-anorthite synergy and anhydrite on chemical enhanced oil recovery: effect of inorganic ions and scaling. <https://doi.org/10.1080/01932691.2019.1659149>, 42(1), 21–32. <https://doi.org/10.1080/01932691.2019.1659149>
- Arif, M., Abu-Khamsin, S. A., & Iglauer, S. (2019). Wettability of rock/CO₂/brine and rock/oil/CO₂-enriched-brine systems: Critical parametric analysis and future outlook. *Advances in Colloid and Interface Science*, 268, 91–113. <https://doi.org/10.1016/J.CIS.2019.03.009>
- Arif, M., Abu-Khamsin, S. A., Zhang, Y., & Iglauer, S. (2020). Experimental investigation of carbonate wettability as a function of mineralogical and thermo-physical conditions. *Fuel*, 264, 116846. <https://doi.org/10.1016/J.FUEL.2019.116846>
- Arif, M., Jones, F., Barifcani, A., & Iglauer, S. (2017). Electrochemical investigation of the effect of temperature, salinity and salt type on brine/mineral interfacial properties. *International Journal of Greenhouse Gas Control*, 59, 136–147. <https://doi.org/10.1016/J.IJGGC.2017.02.013>
- Arsalan, N., Buiting, J. J., & Nguyen, Q. P. (2015). Surface energy and wetting behavior of reservoir rocks. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 467,

107–112. <https://doi.org/10.1016/J.COLSURFA.2014.11.024>

- Arsalan, N., Palayangoda, S. S., Burnett, D. J., Buiting, J. J., & Nguyen, Q. P. (2013). Surface energy characterization of carbonate rocks. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 436, 139–147. <https://doi.org/10.1016/J.COLSURFA.2013.06.004>
- Ausbrooks, R., Hurley, N. F., May, A., & Neese, D. G. (1999). Pore-size distributions in vuggy carbonates from core images, NMR, and capillary pressure. *Proceedings - SPE Annual Technical Conference and Exhibition, OMEGA*, 139–152. <https://doi.org/10.2523/56506-ms>
- Austad, T., Shariatpanahi, S. F., Strand, S., Aksulu, H., & Puntervold, T. (2015a). Low Salinity EOR Effects in Limestone Reservoir Cores Containing Anhydrite: A Discussion of the Chemical Mechanism. *Energy and Fuels*, 29(11), 6903–6911. <https://doi.org/10.1021/acs.energyfuels.5b01099>
- Austad, T., Shariatpanahi, S. F., Strand, S., Aksulu, H., & Puntervold, T. (2015b). Low Salinity EOR Effects in Limestone Reservoir Cores Containing Anhydrite: A Discussion of the Chemical Mechanism. *Energy and Fuels*, 29(11), 6903–6911. https://doi.org/10.1021/ACS.ENERGYFUELS.5B01099/ASSET/IMAGES/LARGE/EF-2015-01099B_0014.JPEG
- Austad, T., Shariatpanahi, S. F., Strand, S., Black, C. J. J., & Webb, K. J. (2012). Conditions for a low-salinity Enhanced Oil Recovery (EOR) effect in carbonate oil reservoirs. *Energy and Fuels*, 26(1), 569–575. <https://doi.org/10.1021/ef201435g>
- Awolayo, A., Sarma, H., & Nghiem, L. (2018). Brine-Dependent Recovery Processes in Carbonate and Sandstone Petroleum Reservoirs: Review of Laboratory-Field Studies, Interfacial Mechanisms and Modeling Attempts. *Energies*, 11(11), 3020. <https://doi.org/10.3390/en11113020>
- Azdarpour, A., Afkhami Karai, M., Hamidi, H., Mohammadian, E., & Honarvar, B. (2018). CO₂ sequestration through direct aqueous mineral carbonation of red gypsum. *Petroleum*, 4(4), 398–407. <https://doi.org/10.1016/J.PETLM.2017.10.002>
- Azdarpour, A., Asadullah, M., Junin, R., Mohammadian, E., Hamidi, H., Daud, A. R. M., & Manan, M. (2015). Extraction of calcium from red gypsum for calcium carbonate production. *Fuel Processing Technology*, 130(C), 12–19. <https://doi.org/10.1016/J.FUPROC.2014.09.034>
- Azdarpour, A., Asadullah, M., Mohammadian, E., Hamidi, H., Junin, R., & Karai, M. A. (2015). A review on carbon dioxide mineral carbonation through pH-swing process. *Chemical Engineering Journal*, 279, 615–630. <https://doi.org/10.1016/J.CEJ.2015.05.064>
- Bachu, S. (2008). CO₂ storage in geological media: Role, means, status and barriers to deployment. *Progress in Energy and Combustion Science*, 34(2), 254–273. <https://doi.org/10.1016/J.PECS.2007.10.001>
- Bader, M. S. H. (2007). Sulfate removal technologies for oil fields seawater injection operations. *Journal of Petroleum Science and Engineering*, 55(1–2), 93–110. <https://doi.org/10.1016/J.PETROL.2006.04.010>
- Bai, S., Kubelka, J., & Piri, M. (2021). Wettability alteration by Smart Water multi-ion exchange in carbonates: A molecular dynamics simulation study. *Journal of Molecular Liquids*, 332, 115830. <https://doi.org/10.1016/J.MOLLIQ.2021.115830>

- Baines, S. J., & Worden, R. H. (2004). The long-term fate of CO₂ in the subsurface: Natural analogues for CO₂ storage. *Geological Society Special Publication*, 233, 59–85. <https://doi.org/10.1144/GSL.SP.2004.233.01.06>
- Bakhshian, S., Rabbani, H. S., Hosseini, S. A., & Shokri, N. (2020). New Insights Into Complex Interactions Between Heterogeneity and Wettability Influencing Two-Phase Flow in Porous Media. *Geophysical Research Letters*, 47(14), e2020GL088187. <https://doi.org/10.1029/2020GL088187>
- Bang, J. H., Kim, W., Song, K. S., Jeon, C. W., Chae, S. C., Cho, H. J., Jang, Y. N., & Park, S. J. (2014). Effect of experimental parameters on the carbonate mineralization with CaSO₄·2H₂O using CO₂ microbubbles. *Chemical Engineering Journal*, 244, 282–287. <https://doi.org/10.1016/J.CEJ.2014.01.072>
- Basu, S., & Sharma, M. M. (1997). Investigating the role of crude-oil components on wettability alteration using atomic force microscopy. *Proceedings - SPE International Symposium on Oilfield Chemistry, September*, 203–211. <https://doi.org/10.2118/37231-ms>
- Basu, Subhayu, & Sharma, M. M. (1996). Measurement of Critical Disjoining Pressure for Dewetting of Solid Surfaces. *Journal of Colloid and Interface Science*, 181(2), 443–455. <https://doi.org/10.1006/jcis.1996.0401>
- Bauer, D., Youssef, S., Fleury, M., Bekri, S., Rosenberg, E., & Vizika, O. (2012). Improving the Estimations of Petrophysical Transport Behavior of Carbonate Rocks Using a Dual Pore Network Approach Combined with Computed Microtomography. *Transport in Porous Media*, 94(2), 505–524. <https://doi.org/10.1007/s11242-012-9941-z>
- Belhaj, A. F., Singh, N., & Sarma, H. K. (2022, March). Understanding the Interactions at Rock-Water and Oil-Water Interfaces during Controlled-Salinity Water Flooding. *Day 4 Fri, March 25, 2022*. <https://doi.org/10.4043/31656-MS>
- Benoit, B. M., Dann, E. P., & Alvin, J. P. (1984). Fractal character of fracture surfaces of metals. *Nature* 1984 308:5961, 308(5961), 721–722. <https://doi.org/https://doi.org/10.1038/308721a0>
- BinMerdhah, A. B., Yassin, A. A. M., & Muherei, M. A. (2010). Laboratory and prediction of barium sulfate scaling at high-barium formation water. *Journal of Petroleum Science and Engineering*, 70(1–2), 79–88. <https://doi.org/10.1016/J.PETROL.2009.10.001>
- Binnig, G., Quate, C. F., & Gerber, C. (1986). Atomic force microscope. *Physical Review Letters*, 56(9), 930–933. <https://doi.org/10.1103/PHYSREVLETT.56.930/FIGURE/1/THUMB>
- Bird, N., Díaz, M. C., Saa, A., & Tarquis, A. M. (2006). Fractal and multifractal analysis of pore-scale images of soil. *Journal of Hydrology*, 322(1–4), 211–219. <https://doi.org/10.1016/J.JHYDROL.2005.02.039>
- Blank, J. G., Stolper, E. M., & Carroll, M. R. (1993). Solubilities of carbon dioxide and water in rhyolitic melt at 850°C and 750 bars. *Earth and Planetary Science Letters*, 119(1–2), 27–36. [https://doi.org/10.1016/0012-821X\(93\)90004-S](https://doi.org/10.1016/0012-821X(93)90004-S)
- Blank, Jennifer G., & Brooker, R. A. (1994). Experimental studies of carbon dioxide in silicate melts; solubility, speciation, and stable carbon isotope behavior. *Reviews in Mineralogy and Geochemistry*, 30(1), 157–186.

- Blunt, M. J., Lin, Q., Akai, T., & Bijeljic, B. (2019). A thermodynamically consistent characterization of wettability in porous media using high-resolution imaging. *Journal of Colloid and Interface Science*, 552, 59–65. <https://doi.org/10.1016/J.JCIS.2019.05.026>
- Bonto, M., Eftekhari, A. A., & Nick, H. (2019). A Calibrated Model for the Carbonate-Brine-Crude Oil Surface Chemistry and its Effect on the Rock Wettability, Dissolution, and Mechanical Properties. *Society of Petroleum Engineers - SPE Reservoir Simulation Conference 2019, RSC 2019*, 10–11. <https://doi.org/10.2118/193865-MS>
- Boot-Handford, M. E., Abanades, J. C., Anthony, E. J., Blunt, M. J., Brandani, S., Mac Dowell, N., Fernández, J. R., Ferrari, M. C., Gross, R., Hallett, J. P., Haszeldine, R. S., Heptonstall, P., Lyngfelt, A., Makuch, Z., Mangano, E., Porter, R. T. J., Pourkashanian, M., Rochelle, G. T., Shah, N., ... Fennell, P. S. (2013). Carbon capture and storage update. *Energy & Environmental Science*, 7(1), 130–189. <https://doi.org/10.1039/C3EE42350F>
- Boyd, C. E. (2015). pH, Carbon Dioxide, and Alkalinity. *Water Quality*, 153–178. https://doi.org/10.1007/978-3-319-17446-4_8
- Brady, P. V., & Thyne, G. (2016a). Functional Wettability in Carbonate Reservoirs. *Energy and Fuels*, 30(11), 9217–9225. <https://doi.org/10.1021/ACS.ENERGYFUELS.6B01895>
- Brady, P. V., & Thyne, G. (2016b). Functional Wettability in Carbonate Reservoirs. *Energy and Fuels*, 30(11), 9217–9225. https://doi.org/10.1021/ACS.ENERGYFUELS.6B01895/ASSET/IMAGES/LARGE/EF-2016-01895G_0010.JPEG
- Brattekkås, B., & Fernø, M. A. (2016). New Insight from Visualization of Mobility Control for Enhanced Oil Recovery Using Polymer Gels and Foams. *Chemical Enhanced Oil Recovery (CEOR) - a Practical Overview, October*. <https://doi.org/10.5772/64586>
- Broseta, D., Tonnet, N., & Shah, V. (2012). Are rocks still water-wet in the presence of dense CO₂ or H₂S? *Geofluids*, 12(4), 280–294. <https://doi.org/10.1111/J.1468-8123.2012.00369.X>
- Buchgraber, M., Kavscek, A. R., & Castanier, L. M. (2012). A Study of Microscale Gas Trapping Using Etched Silicon Micromodels. *Transport in Porous Media*, 95(3), 647–668. <https://doi.org/10.1007/s11242-012-0067-0>
- Buenrostro-Gonzalez, E., Lira-Galeana, C., Gil-Villegas, A., & Wu, J. (2004). Asphaltene precipitation in crude oils: Theory and experiments. *AIChE Journal*, 50(10), 2552–2570. <https://doi.org/10.1002/aic.10243>
- Bui, M., Adjiman, C. S., Bardow, A., Anthony, E. J., Boston, A., Brown, S., Fennell, P. S., Fuss, S., Galindo, A., Hackett, L. A., Hallett, J. P., Herzog, H. J., Jackson, G., Kemper, J., Krevor, S., Maitland, G. C., Matuszewski, M., Metcalfe, I. S., Petit, C., ... Mac Dowell, N. (2018). Carbon capture and storage (CCS): the way forward. *Energy & Environmental Science*, 11(5), 1062–1176. <https://doi.org/10.1039/C7EE02342A>
- Bukuaghangin, O., Sanni, O., Kapur, N., Huggan, M., Neville, A., & Charpentier, T. (2016). Kinetics study of barium sulphate surface scaling and inhibition with a once-through flow system. *Journal of Petroleum Science and Engineering*, 147, 699–706. <https://doi.org/10.1016/J.PETROL.2016.09.035>
- Bultreys, T., Boone, M. A., Boone, M. N., De Schryver, T., Masschaele, B., Van Hoorebeke, L., &

- Cnudde, V. (2016). Fast laboratory-based micro-computed tomography for pore-scale research: Illustrative experiments and perspectives on the future. *Advances in Water Resources*, 95, 341–351. <https://doi.org/10.1016/j.advwatres.2015.05.012>
- Bultreys, T., Van Hoorebeke, L., & Cnudde, V. (2015). Multi-scale, micro-computed tomography-based pore network models to simulate drainage in heterogeneous rocks. *Advances in Water Resources*, 78, 36–49. <https://doi.org/10.1016/j.advwatres.2015.02.003>
- Cai, J., Yu, B., Zou, M., & Mei, M. (2010). Fractal analysis of invasion depth of extraneous fluids in porous media. *Chemical Engineering Science*, 65(18), 5178–5186. <https://doi.org/10.1016/J.CES.2010.06.013>
- Cao, D., Wang, J., Han, M., & Alshehri, A. J. (2015). Comprehensive Effects on the Propagation of Surfactant and Polymer Flow. *Spe Enhanced Oil Recovery Conference [Eorc] (Kuala Lumpur, Malaysia, 8/11-13/2015) Proceedings*.
- Carbillet, L., Heap, M. J., Baud, P., Wadsworth, F. B., & Reuschlé, T. (2021). Mechanical Compaction of Crustal Analogs Made of Sintered Glass Beads: The Influence of Porosity and Grain Size. *Journal of Geophysical Research: Solid Earth*, 126(4), e2020JB021321. <https://doi.org/10.1029/2020JB021321>
- Carlberg, B. L., & Matthews, R. R. (1973). Solubility of Calcium Sulfate in Brine. *All Days*. <https://doi.org/10.2118/4353-MS>
- Carroll, S., Hao, Y., Smith, M., & Sholokhova, Y. (2013). Development of scaling parameters to describe CO₂–rock interactions within Weyburn-Midale carbonate flow units. *International Journal of Greenhouse Gas Control*, 16, S185–S193. <https://doi.org/10.1016/J.IJGGC.2012.12.026>
- Caudle, B., Taniguchi, S., Nguyen, T. T. H., & Kataoka, S. (2023). Integrating carbon capture and utilization into the glass industry: Economic analysis of emissions reduction through CO₂ mineralization. *Journal of Cleaner Production*, 416, 137846. <https://doi.org/10.1016/J.JCLEPRO.2023.137846>
- Chandrasekhar, S., & Mohanty, K. K. (2013). Wettability Alteration with Brine Composition in High Temperature Carbonate Reservoirs. *Proceedings - SPE Annual Technical Conference and Exhibition*, 3, 2416–2432. <https://doi.org/10.2118/166280-MS>
- Chandrasekhar, Sriram, Sharma, H., & Mohanty, K. K. (2018). Dependence of wettability on brine composition in high temperature carbonate rocks. *Fuel*, 225, 573–587. <https://doi.org/10.1016/J.FUEL.2018.03.176>
- Chang, F. F., & Civan, F. (1997). Practical model for chemically induced formation damage. *Journal of Petroleum Science and Engineering*, 17(1–2), 123–137. [https://doi.org/10.1016/S0920-4105\(96\)00061-7](https://doi.org/10.1016/S0920-4105(96)00061-7)
- Chen, Q., Ding, W., Sun, H., Peng, T., & Ma, G. (2020). Indirect mineral carbonation of phosphogypsum for CO₂ sequestration. *Energy*, 206, 118148. <https://doi.org/10.1016/J.ENERGY.2020.118148>
- Chen, Yanyan, Zou, C., Mastalerz, M., Hu, S., Gasaway, C., & Tao, X. (2015). Applications of Micro-Fourier Transform Infrared Spectroscopy (FTIR) in the Geological Sciences—A Review. *International Journal of Molecular Sciences* 2015, Vol. 16, Pages 30223-30250,

16(12), 30223–30250. <https://doi.org/10.3390/IJMS161226227>

Chen, Yongqiang, Ubaidah, A., Elakneswaran, Y., Niasar, V. J., & Xie, Q. (2020). Detecting pH and Ca²⁺ increase during low salinity waterflooding in carbonate reservoirs: Implications for wettability alteration process. *Journal of Molecular Liquids*, 317, 114003.

<https://doi.org/10.1016/j.molliq.2020.114003>

Chen, Yongqiang, Xie, Q., Sari, A., Brady, P. V., & Saeedi, A. (2018). Oil/water/rock wettability: Influencing factors and implications for low salinity water flooding in carbonate reservoirs. *Fuel*, 215, 171–177. <https://doi.org/10.1016/J.FUEL.2017.10.031>

Civan, F. (2015). *Reservoir formation damage*.

https://books.google.com/books?hl=en&lr=&id=MO6cBAAQBAJ&oi=fnd&pg=PP1&dq=Civan,+F.,+2015.+Reservoir+formation+damage.+Gulf+Professional+Publishing.&ots=Wrmbo_NzMF&sig=7HCPOpZokbZ-IFzKR8UOb-VI9Z8

Clarkson, C. R., Haghsheenas, B., Ghanizadeh, A., Qanbari, F., Williams-Kovacs, J. D., Riazi, N., Debuhr, C., & Deglint, H. J. (2016). Nanopores to megafactures: Current challenges and methods for shale gas reservoir and hydraulic fracture characterization. *Journal of Natural Gas Science and Engineering*, 31, 612–657. <https://doi.org/10.1016/j.jngse.2016.01.041>

Clarkson, C. R., Solano, N., Bustin, R. M., Bustin, A. M. M., Chalmers, G. R. L., He, L., Melnichenko, Y. B., Radliński, A. P., & Blach, T. P. (2013). Pore structure characterization of North American shale gas reservoirs using USANS/SANS, gas adsorption, and mercury intrusion. *Fuel*, 103, 606–616. <https://doi.org/10.1016/J.FUEL.2012.06.119>

Clementz, D. M. (1982). Alteration of Rock Properties by Adsorption of Petroleum Heavy Ends: Implications for Enhanced Oil Recovery. *SPE Enhanced Oil Recovery Symposium*, 4. <https://doi.org/10.2118/10683-MS>

Clerke, E. A., Mueller, H. W., Phillips, E. C., Eyvazzadeh, R. Y., Jones, D. H., Ramamoorthy, R., & Srivastava, A. (2008). Application of Thomeer Hyperbolas to decode the pore systems, facies and reservoir properties of the Upper Jurassic Arab D limestone, Ghawar field, Saudi Arabia: A “Rosetta Stone” approach. *GeoArabia*, 13(4), 113–160.

Clogston, J. D., & Patri, A. K. (2011). Zeta potential measurement. *Methods in Molecular Biology (Clifton, N.J.)*, 697, 63–70. https://doi.org/10.1007/978-1-60327-198-1_6

Coates, G. R., Xiao, L., & Prammer, M. G. (1999). NMR logging : principles and applications. *Gulf Publishing Company: Houston, TX*. <https://cir.nii.ac.jp/crid/1130282271026258560>

Cope, D. M., Bogie, I., Harvey, C. C., Menzies, A. J., & Garcia, S. E. (1985). Calculation of Calcite and Anhydrite Scaling Potential in Geothermal Wells. *7th Geothermal Workshop*, 1985.

Creaser, E. C., Steele-MacInnis, M., & Tutolo, B. M. (2022). A model for the solubility of anhydrite in H₂O-NaCl fluids from 25 to 800 °C, 0.1 to 1400 MPa, and 0 to 60 wt% NaCl: Applications to hydrothermal ore-forming systems. *Chemical Geology*, 587, 120609. <https://doi.org/10.1016/J.CHEMGEO.2021.120609>

Crundwell, F. K. (2017). On the Mechanism of the Dissolution of Quartz and Silica in Aqueous Solutions. *ACS Omega*, 2(3), 1116–1127. <https://doi.org/10.1021/acsomega.7b00019>

Cui, G., Wang, Y., Rui, Z., Chen, B., Ren, S., & Zhang, L. (2018). Assessing the combined influence

- of fluid-rock interactions on reservoir properties and injectivity during CO₂ storage in saline aquifers. *Energy*, 155, 281–296. <https://doi.org/10.1016/J.ENERGY.2018.05.024>
- Curbelo, F. D. S., Santanna, V. C., Neto, E. L. B., Dutra, T. V., Dantas, T. N. C., Neto, A. A. D., & Garnica, A. I. C. (2007). Adsorption of nonionic surfactants in sandstones. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 293(1–3), 1–4. <https://doi.org/10.1016/j.colsurfa.2006.06.038>
- Curtis, M. E., Sondergeld, C. H., Ambrose, R. J., & Rai, C. S. (2012). Microstructural investigation of gas shales in two and three dimensions using nanometer-scale resolution imaging. *AAPG Bulletin*, 96(4), 665–677. <https://doi.org/10.1306/08151110188>
- Dai, X., Wei, C., Wang, M., Ma, R., Song, Y., Zhang, J., Wang, X., Shi, X., & Vandeginste, V. (2023). Interaction mechanism of supercritical CO₂ with shales and a new quantitative storage capacity evaluation method. *Energy*, 264, 126424. <https://doi.org/10.1016/J.ENERGY.2022.126424>
- Dai, X., Wei, C., Wang, M., Zhang, J., Wang, X., Shi, X., & Vandeginste, V. (2023). Understanding CO₂ mineralization and associated storage space changes in illite using molecular dynamics simulation and experiments. *Energy*, 283, 128467. <https://doi.org/10.1016/J.ENERGY.2023.128467>
- Daigle, H., Johnson, A., & Thomas, B. (2014a). Determining fractal dimension from nuclear magnetic resonance data in rocks with internal magnetic field gradients. *https://doi.org/10.1190/Geo2014-0325.1*, 79(6), D425–D431. <https://doi.org/10.1190/Geo2014-0325.1>
- Daigle, H., Johnson, A., & Thomas, B. (2014b). Determining fractal dimension from nuclear magnetic resonance data in rocks with internal magnetic field gradients. *https://doi.org/10.1190/Geo2014-0325.1*, 79(6), D425–D431. <https://doi.org/10.1190/Geo2014-0325.1>
- Daigle, H., Thomas, B., Rowe, H., & Nieto, M. (2014). Nuclear magnetic resonance characterization of shallow marine sediments from the Nankai Trough, Integrated Ocean Drilling Program Expedition 333. *Journal of Geophysical Research: Solid Earth*, 119(4), 2631–2650. <https://doi.org/10.1002/2013JB010784>
- Dang, T. Q. C., Chen, Z., Nguyen, T. B. N., & Bae, W. (2014). Investigation of isotherm polymer adsorption in porous media. *Petroleum Science and Technology*, 32(13), 1626–1640. <https://doi.org/10.1080/10916466.2010.547910>
- Darvish Sarvestani, A., Rostami, B., & Mahani, H. (2021). Polymer-Enhanced Low-Salinity Brine to Control In Situ Mixing and Salt Dispersion in Low-Salinity Waterflooding. *Energy & Fuels*, 35(13), 10540–10550. <https://doi.org/10.1021/acs.energyfuels.1c00871>
- Das, S., Katiyar, A., Rohilla, N., Nguyen, Q. P., & Bonnetcaze, R. T. (2020). Wettability Alteration and Adsorption of Mixed Nonionic and Anionic Surfactants on Carbonates. *Langmuir*, 36(50), 15410–15422. https://doi.org/10.1021/ACS.LANGMUIR.0C03022/SUPPL_FILE/LA0C03022_SI_001.PDF
- de Beer, M., Maree, J. P., Liebenberg, L., & Doucet, F. J. (2014). Conversion of calcium sulphide to calcium carbonate during the process of recovery of elemental sulphur from gypsum

- waste. *Waste Management*, 34(11), 2373–2381.
<https://doi.org/10.1016/J.WASMAN.2014.07.010>
- Deer, W. A., Howie, R. A., & Zussman, J. (2013). An Introduction to the Rock-Forming Minerals. *An Introduction to the Rock-Forming Minerals*. <https://doi.org/10.1180/DHZ>
- Deglint, H. J., Clarkson, C. R., DeBuhr, C., & Ghanizadeh, A. (2017a). Live Imaging of Micro-Wettability Experiments Performed for Low-Permeability Oil Reservoirs. *Scientific Reports*, 7(1), 1–13. <https://doi.org/10.1038/s41598-017-04239-x>
- Deglint, H. J., Clarkson, C. R., DeBuhr, C., & Ghanizadeh, A. (2017b). Live Imaging of Micro-Wettability Experiments Performed for Low-Permeability Oil Reservoirs. *Scientific Reports* 2017 7:1, 7(1), 1–13. <https://doi.org/10.1038/s41598-017-04239-x>
- Dehaghani, A. H. S., Hosseini, M., Tajikmansori, A., & Moradi, H. (2020). A mechanistic investigation of the effect of ion-tuned water injection in the presence of cationic surfactant in carbonate rocks: An experimental study. *Journal of Molecular Liquids*, 304, 112781. <https://doi.org/10.1016/J.MOLLIQ.2020.112781>
- Delgado, A. V., González-Caballero, F., Hunter, R. J., Koopal, L. K., & Lyklema, J. (2007). Measurement and interpretation of electrokinetic phenomena. *Journal of Colloid and Interface Science*, 309(2), 194–224. <https://doi.org/10.1016/j.jcis.2006.12.075>
- Della Ventura, G., Bellatreccia, F., Marcelli, A., Cestelli Guidi, M., Piccinini, M., Cavallo, A., & Piochi, M. (2010). Application of micro-FTIR imaging in the Earth sciences. *Analytical and Bioanalytical Chemistry*, 397(6), 2039–2049. <https://doi.org/10.1007/S00216-010-3811-8/METRICS>
- Derkani, M., Fletcher, A., Abdallah, W., Sauerer, B., Anderson, J., & Zhang, Z. (2018). Low Salinity Waterflooding in Carbonate Reservoirs: Review of Interfacial Mechanisms. *Colloids and Interfaces*, 2(2), 20. <https://doi.org/10.3390/colloids2020020>
- Ding, H., & Rahman, S. (2017). Experimental and theoretical study of wettability alteration during low salinity water flooding-an state of the art review. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 520, 622–639.
<https://doi.org/10.1016/J.COLSURFA.2017.02.006>
- Ding, H., & Rahman, S. R. (2018). Investigation of the Impact of Potential Determining Ions from Surface Complexation Modeling [Research-article]. *Energy and Fuels*, 32(9), 9314–9321.
<https://doi.org/10.1021/acs.energyfuels.8b02131>
- Ding, Y., Weller, A., Zhang, Z., & Kassab, M. (2017). Fractal dimension of pore space in carbonate samples from Tushka area (Egypt). *Arabian Journal of Geosciences*, 10(17), 1–12.
<https://doi.org/10.1007/S12517-017-3173-Z/METRICS>
- Dixon, J. E., Stolper, E. M., & Holloway, J. R. (1995). An Experimental Study of Water and Carbon Dioxide Solubilities in Mid-Ocean Ridge Basaltic Liquids. Part I: Calibration and Solubility Models. *Journal of Petrology*, 36(6), 1607–1631.
<https://doi.org/10.1093/OXFORDJOURNALS.PETROLOGY.A037267>
- Domenico, S. N. (1984). Rock lithology and porosity determination from shear and compressional wave velocity. *Geophysics*, 49(8), 1188–1195.
<https://doi.org/10.1190/1.1441748>

- Dou, L., Sun, L., Lyu, W., WANG, M., GAO, F., GAO, M., & JIANG, H. (2023). Trend of global carbon dioxide capture, utilization and storage industry and challenges and countermeasures in China. *Petroleum Exploration and Development*, 50(5), 1246–1260. [https://doi.org/10.1016/S1876-3804\(23\)60463-X](https://doi.org/10.1016/S1876-3804(23)60463-X)
- Du, C., Li, D., Shi, C., Du, Z., Han, W., Zhu, Y., Dong, H., Fan, X., & Wang, C. (2022). Study on the association driving force of low temperature coal tar asphaltenes. *Journal of Molecular Structure*, 1254, 132361. <https://doi.org/10.1016/j.molstruc.2022.132361>
- Dunn, K. J. D., Bergman, J., & Latorraca, G. A. (2002). *Nuclear Magnetic Resonance: Petrophysical and Logging Applications - Google Books*. Pergamon Oxford, U.K.,. [https://doi.org/10.1016/S0950-1401\(02\)80001-](https://doi.org/10.1016/S0950-1401(02)80001-)
- El-Din Mahmoud, M. A. (2018). Effect of Chlorite Clay-Mineral Dissolution on the Improved Oil Recovery From Sandstone Rocks During Diethylenetriaminepentaacetic Acid Chelating-Agent Flooding. *SPE Journal*, 23(05), 1880–1898. <https://doi.org/10.2118/189988-PA>
- El-Tabakh, M., Mory, A., Schreiber, B. C., & Yasin, R. (2004). Anhydrite cements after dolomitization of shallow marine Silurian carbonates of the Gascoyne Platform, Southern Carnarvon Basin, Western Australia. *Sedimentary Geology*, 164(1–2), 75–87. <https://doi.org/10.1016/J.SEDGEO.2003.09.003>
- Elkhatatny, S. (2017). New Formulation for Iron Sulfide Scale Removal. *SPE Middle East Oil and Gas Show and Conference, MEOS, Proceedings, 2017-March*, 1809–1821. <https://doi.org/10.2118/183914-MS>
- Ellis, D. E. (1978). Stability and phase equilibria of chloride and carbonate bearing scapolites at 750°C and 4000 bar. *Geochimica et Cosmochimica Acta*, 42(8), 1271–1281. [https://doi.org/10.1016/0016-7037\(78\)90121-7](https://doi.org/10.1016/0016-7037(78)90121-7)
- Elsaeed, S. M., Zaki, E. G., Omar, W. A. E., Ashraf Soliman, A., & Attia, A. M. (2021). Guar Gum-Based Hydrogels as Potent Green Polymers for Enhanced Oil Recovery in High-Salinity Reservoirs. *ACS Omega*, 6(36), 23421–23431. <https://doi.org/10.1021/acsomega.1c03352>
- Elsayed, M., Isah, A., Hiba, M., Hassan, A., Al-Garadi, K., Mahmoud, M., El-Husseiny, A., & Radwan, A. E. (2022). A review on the applications of nuclear magnetic resonance (NMR) in the oil and gas industry: laboratory and field-scale measurements. *Journal of Petroleum Exploration and Production Technology* 2022 12:10, 12(10), 2747–2784. <https://doi.org/10.1007/S13202-022-01476-3>
- Emadi, A., & Sohrabi, M. (2013). Visual Investigation of Oil Recovery by Low Salinity Water Injection: Formation of Water Micro-Dispersions and Wettability Alteration. *Proceedings - SPE Annual Technical Conference and Exhibition*, 6, 4168–4182. <https://doi.org/10.2118/166435-MS>
- Eniu, D., Gruian, C., Vanea, E., Patcas, L., & Simon, V. (2015). FTIR and EPR spectroscopic investigation of calcium-silicate glasses with iron and dysprosium. *Journal of Molecular Structure*, 1084, 23–27. <https://doi.org/10.1016/J.MOLSTRUC.2014.12.020>
- Esfandyari, H., Shadizadeh, S. R., Esmaeilzadeh, F., & Davarpanah, A. (2020). Implications of anionic and natural surfactants to measure wettability alteration in EOR processes. *Fuel*, 278, 118392. <https://doi.org/10.1016/J.FUEL.2020.118392>

- Eslahati, M., Mehrabianfar, P., Isari, A. A., Bahraminejad, H., Manshad, A. K., & Keshavarz, A. (2020). Experimental investigation of Alfalfa natural surfactant and synergistic effects of Ca^{2+} , Mg^{2+} , and SO_4^{2-} ions for EOR applications: Interfacial tension optimization, wettability alteration and imbibition studies. *Journal of Molecular Liquids*, 310, 113123. <https://doi.org/10.1016/J.MOLLIQ.2020.113123>
- Espinoza, D. N., Jung, H., Major, J. R., Sun, Z., Ramos, M. J., Eichhubl, P., Balhoff, M. T., Choens, R. C., & Dewers, T. A. (2018). CO_2 charged brines changed rock strength and stiffness at Crystal Geyser, Utah: Implications for leaking subsurface CO_2 storage reservoirs. *International Journal of Greenhouse Gas Control*, 73, 16–28. <https://doi.org/10.1016/J.IJGGC.2018.03.017>
- Estep, P. A., Kovach, J. J., & Karr, C. (1968). Quantitative Infrared Multicomponent Determination of Minerals Occurring in Coal. *Analytical Chemistry*, 40(2), 358–363. <https://doi.org/10.1021/AC60258A006>
- Evans, B. W., Shaw, D. M., & Haughton, D. R. (1969). Scapolite stoichiometry. *Contributions to Mineralogy and Petrology*, 24(4), 293–305. <https://doi.org/10.1007/BF00371272/METRICS>
- Falat, J., Fehr, A., Telmadarreie, A., & Bryant, S. (2020). High-Resolution Inline Density Measurements: Insight on Multiphase Flow and Transport Phenomena in Porous Media. *E3S Web of Conferences*, 146, 1–11. <https://doi.org/10.1051/e3sconf/202014601005>
- Farmer, V. C. (1974). the infrared spectra of minerals. *Mineralogical Society Monograph*, 4, 331–363. <https://cir.nii.ac.jp/crid/1571417124190337792>
- Farouk, S., Al-Kahtany, K., El-Sorogy, A., & El-Motaal, E. A. (2018). High-frequency cycles and sequence stratigraphy of the lower Jurassic Marrat Formation, central Saudi Arabia. *Marine and Petroleum Geology*, 98, 369–383. <https://doi.org/10.1016/J.MARPETGEO.2018.08.030>
- Fathi, S. J., Austad, T., & Strand, S. (2011). Water-Based Enhanced Oil Recovery (EOR) by “Smart Water”: Optimal Ionic Composition for EOR in Carbonates. *Energy & Fuels*, 25(11), 5173–5179. <https://doi.org/10.1021/ef201019k>
- Fathy, A., Arif, M., Adila, A. S., Raza, A., & Mahmoud, M. (2023). A Numerical Study of Mineral Dissolution in Deep Heterogeneous Carbonate Reservoirs: Implications for CO_2 Geo-sequestration. *Society of Petroleum Engineers - SPE Reservoir Characterisation and Simulation Conference and Exhibition 2023, RCSC 2023*. <https://doi.org/10.2118/212632-MS>
- Fedrizzi, R. M., Ceia, M. A. R. de, Misságia, R. M., Santos, V. H., & Lima Neto, I. (2018). Artificial carbonate rocks: Synthesis and petrophysical characterization. *Journal of Petroleum Science and Engineering*, 163, 303–310. <https://doi.org/10.1016/J.PETROL.2017.12.089>
- Feng, Y., Zhang, S., Ma, C., Liu, F., Mosleh, M. H., & Shin, H. (2023). The role of geomechanics for geological carbon storage. *Gondwana Research*, 124, 100–123. <https://doi.org/10.1016/J.GR.2023.07.003>
- Fernández-Díaz, L., Pina, C. M., Astilleros, J. M., & Sánchez-Pastor, N. (2009). The carbonatation of gypsum: Pathways and pseudomorph formation. *American Mineralogist*, 94(8–9), 1223–1234. <https://doi.org/10.2138/AM.2009.3194>

- Ferreira, V. H. S., & Moreno, R. B. Z. L. (2020). Polyacrylamide Adsorption and Readsorption in Sandstone Porous Media. *SPE Journal*, 25(1), 497–514. <https://doi.org/10.2118/199352-PA>
- Fine, G., & Stolper, E. (1985). The speciation of carbon dioxide in sodium aluminosilicate glasses. *Contributions to Mineralogy and Petrology*, 91(2), 105–121. <https://doi.org/10.1007/BF00377759/METRICS>
- Fink, D. H., & Thomas, G. W. (1964). X-Ray Studies of Crystalline Swelling in Montmorillonites. *Soil Science Society of America Journal*, 28(6), 747–750. <https://doi.org/10.2136/SSSAJ1964.03615995002800060021X>
- Fjær, E., Holt, R. M., Horsrud, P., & Raaen, A. M. (2008). *Petroleum Related Rock Mechanics*. Elsevier. https://books.google.co.uk/books?hl=en&lr=&id=l6CfasFxyzYC&oi=fnd&pg=PP1&ots=nYW0HQuEZ9&sig=_geL1vZ9R5iR6_B9B_LxQ1kFIG4&redir_esc=y#v=onepage&q&f=false
- Fleury, M., Santerre, Y., & Vincent, B. (2007a). Carbonate rock typing from nmr relaxation measurements. *48th Annual Logging Symposium 2007*, 1–14.
- Fleury, M., Santerre, Y., & Vincent, B. (2007b). *Carbonate Rock Typing From NMR Relaxation Measurements*. OnePetro. <https://dx.doi.org/>
- Forjanés, P., Astilleros, J. M., & Fernández-Díaz, L. (2020). The Formation of Barite and Celestite through the Replacement of Gypsum. *Minerals 2020, Vol. 10, Page 189, 10(2)*, 189. <https://doi.org/10.3390/MIN10020189>
- Foroutan, S., & Moghadas, J. (2013). A Neural Network Approach to Predict Formation Damage Due to Calcium Sulphate Precipitation. *SPE - European Formation Damage Conference, Proceedings, EFDC, 2*, 714–725. <https://doi.org/10.2118/165157-MS>
- Fredd, C. N., & Fogler, H. S. (1998). Alternative Stimulation Fluids and Their Impact on Carbonate Acidizing. *SPE Journal*, 3(1), 34–40. <https://doi.org/10.2118/31074-pa>
- Frenier, W. W., Fredd, C. N., & Chang, F. (2001). Hydroxyaminocarboxylic Acids Produce Superior Formulations for Matrix Stimulation of Carbonates at High Temperatures. *Proceedings - SPE Annual Technical Conference and Exhibition*, 3315–3330. <https://doi.org/10.2118/71696-MS>
- Gadikota, G., Matter, J., Kelemen, P., Brady, P. V., & Park, A. H. A. (2020). Elucidating the differences in the carbon mineralization behaviors of calcium and magnesium bearing aluminosilicates and magnesium silicates for CO₂ storage. *Fuel*, 277, 117900. <https://doi.org/10.1016/J.FUEL.2020.117900>
- Galindo, K., Guimarães, L., Lins, C., Lima, A., Santos, Y., & Gomes, I. (2021). Minerals Dissolution Effect on the Mechanical Properties of Synthetic Carbonatic Rocks under a Reactive Fluid Injection. *Asrjetsjournal.Org*, 79(1), 15–43. https://www.asrjetsjournal.org/index.php/American_Scientific_Journal/article/view/6710
- Gamal, H., Al-Afnan, S., Elkatatny, S., & Bahgat, M. (2021). Barium sulfate scale removal at low-temperature. *Geofluids*, 2021. <https://doi.org/10.1155/2021/5527818>
- Gao, H., & Li, H. (2015). Determination of movable fluid percentage and movable fluid porosity in ultra-low permeability sandstone using nuclear magnetic resonance (NMR) technique.

- Journal of Petroleum Science and Engineering*, 133, 258–267.
<https://doi.org/10.1016/j.petrol.2015.06.017>
- Gao, H., Wang, C., Cao, J., He, M., & Dou, L. (2019). Quantitative study on the stress sensitivity of pores in tight sandstone reservoirs of Ordos basin using NMR technique. *Journal of Petroleum Science and Engineering*, 172, 401–410.
<https://doi.org/10.1016/j.PETROL.2018.09.083>
- Gell, E. M., Walley, S. M., & Braithwaite, C. H. (2019). Review of the Validity of the Use of Artificial Specimens for Characterizing the Mechanical Properties of Rocks. *Rock Mechanics and Rock Engineering*, 52(9), 2949–2961. <https://doi.org/10.1007/S00603-019-01787-8/FIGURES/15>
- Gharbi, K., Benyounes, K., & Khodja, M. (2017). Removal and prevention of asphaltene deposition during oil production: A literature review. *Journal of Petroleum Science and Engineering*, 158(March), 351–360. <https://doi.org/10.1016/j.petrol.2017.08.062>
- Ghedan, S., Canbaz, C. H., Boyd, D., Mani, G., & Haggag, M. (2010). Wettability profile of a thick carbonate reservoir by the new rise in core wettability characterization method. *Society of Petroleum Engineers - 14th Abu Dhabi International Petroleum Exhibition and Conference 2010, ADIPEC 2010*, 3, 2203–2217.
- Ghosh, P., & Mohanty, K. K. (2019). Study of Surfactant–Polymer Flooding in High-Temperature and High-Salinity Carbonate Rocks. *Energy & Fuels*, 33(5), 4130–4145.
<https://doi.org/10.1021/ACS.ENERGYFUELS.9B00407>
- Gibbins, J., & Chalmers, H. (2008). Carbon capture and storage. *Energy Policy*, 36(12), 4317–4322. <https://doi.org/10.1016/J.ENPOL.2008.09.058>
- Gindre-Chanu, L., Warren, J. K., Puigdefabregas, C., Sharp, I. R., Peacock, D. C. P., Swart, R., Poulsen, R., Ferreira, H., & Henrique, L. (2015). Diagenetic evolution of Aptian evaporites in the Namibe Basin (south-west Angola). *Sedimentology*, 62(1), 204–233.
<https://doi.org/10.1111/SED.12146>
- Giri, A., Tarafdar, S., Gouze, P., & Dutta, T. (2012). Fractal pore structure of sedimentary rocks: Simulation in 2-d using a relaxed bidisperse ballistic deposition model. *Journal of Applied Geophysics*, 87, 40–45. <https://doi.org/10.1016/J.JAPPGEO.2012.09.002>
- Gislason, S. R., Wolff-Boenisch, D., Stefansson, A., Oelkers, E. H., Gunnlaugsson, E., Sigurdardottir, H., Sigfusson, B., Broecker, W. S., Matter, J. M., Stute, M., Axelsson, G., & Fridriksson, T. (2010). Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. *International Journal of Greenhouse Gas Control*, 4(3), 537–545. <https://doi.org/10.1016/J.IJGGC.2009.11.013>
- Gogoi, S. B. (2011). Adsorption-Desorption of Surfactant for Enhanced Oil Recovery. *Transport in Porous Media*, 90(2), 589–604. <https://doi.org/10.1007/s11242-011-9805-y>
- Gomari, K. A. R., Hamouda, A. A., & Denoyel, R. (2006). Influence of sulfate ions on the interaction between fatty acids and calcite surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 287(1–3), 29–35.
<https://doi.org/10.1016/j.colsurfa.2006.03.018>
- Gomez, J. S., Chalaturnyk, R. J., & Zambrano-Narvaez, G. (2019). Experimental Investigation of

- the Mechanical Behavior and Permeability of 3D Printed Sandstone Analogues Under Triaxial Conditions. *Transport in Porous Media*, 129(2), 541–557.
<https://doi.org/10.1007/S11242-018-1177-0>
- González-Illanes, T., Borrero, M. T., Herráez, M. M., Pimentel, C., & Pina, C. M. (2017a). Pseudomorphic Replacement of Mg-Ca Carbonates after Gypsum and Anhydrite. *ACS Earth and Space Chemistry*, 1(3), 168–178.
https://doi.org/10.1021/ACSEARTHSPACECHEM.7B00027/ASSET/IMAGES/LARGE/SP-2017-00027H_0012.JPEG
- González-Illanes, T., Borrero, M. T., Herráez, M. M., Pimentel, C., & Pina, C. M. (2017b). Pseudomorphic Replacement of Mg-Ca Carbonates after Gypsum and Anhydrite. *ACS Earth and Space Chemistry*, 1(3), 168–178.
https://doi.org/10.1021/ACSEARTHSPACECHEM.7B00027/ASSET/IMAGES/LARGE/SP-2017-00027H_0012.JPEG
- Gou, Q., Xu, S., Hao, F., Yang, F., Zhang, B., Shu, Z., Zhang, A., Wang, Y., Lu, Y., Cheng, X., Qing, J., & Gao, M. (2019). Full-scale pores and micro-fractures characterization using FE-SEM, gas adsorption, nano-CT and micro-CT: A case study of the Silurian Longmaxi Formation shale in the Fuling area, Sichuan Basin, China. *Fuel*, 253(66), 167–179.
<https://doi.org/10.1016/j.fuel.2019.04.116>
- Gregersen, C. S., Kazempour, M., & Alvarado, V. (2013). ASP design for the Minnelusa formation under low-salinity conditions: Impacts of anhydrite on ASP performance. *Fuel*, 105, 368–382. <https://doi.org/10.1016/J.FUEL.2012.06.051>
- Guo, H., & Kovscek, A. R. (2019). Investigation of the effects of ions on short-range non-DLVO forces at the calcite/brine interface and implications for low salinity oil-recovery processes. *Journal of Colloid and Interface Science*, 552, 295–311.
<https://doi.org/10.1016/j.jcis.2019.05.049>
- Guo, H., Nazari, N., Esmailzadeh, S., & Kovscek, A. R. (2020). A Critical Review of the Role of Thin Liquid Films for Modified Salinity Brine Recovery Processes. *Current Opinion in Colloid & Interface Science*, 50, 101393. <https://doi.org/10.1016/j.cocis.2020.101393>
- Hamisi, J., Etschmann, B., Tomkins, A., Pitcairn, I., Pintér, Z., Wlodek, A., Morrissey, L., Micklethwaite, S., Trcera, N., Mills, S., & Brugger, J. (2023). Complex sulfur speciation in scapolite – Implications for the role of scapolite as a redox and fluid chemistry buffer in crustal fluids. *Gondwana Research*, 121, 418–435.
<https://doi.org/10.1016/J.GR.2023.05.005>
- Han, M., Fuseni, A., Zahrani, B., & Wang, J. (2014). Laboratory study on polymers for chemical flooding in carbonate reservoirs. *Society of Petroleum Engineers - SPE EOR Conference at Oil and Gas West Asia 2014: Driving Integrated and Innovative EOR*, 655–670.
<https://doi.org/10.2118/169724-ms>
- Hangx, S., Spiers, C., & Peach, C. (2009). The mechanical behavior of anhydrite and the effect of CO₂ injection. *Energy Procedia*, 1(1), 3485–3492.
<https://doi.org/10.1016/J.EGYPRO.2009.02.140>
- Hao, J., Mohammadkhani, S., Shahverdi, H., Esfahany, M. N., & Shapiro, A. (2019). Mechanisms of smart waterflooding in carbonate oil reservoirs - A review. *Journal of Petroleum Science*

- and Engineering, 179, 276–291. <https://doi.org/10.1016/J.PETROL.2019.04.049>
- Hao, X., Abu-Al-Saud, M., Ayirala, S., & Elakneswaran, Y. (2021). Influence of carbonate impurities on smartwater effect: Evaluation of wettability alteration process by geochemical simulation. *Journal of Molecular Liquids*, 340, 117165. <https://doi.org/10.1016/J.MOLLIQ.2021.117165>
- Hassan, A. M., & Al-Hashim, H. S. (2020a). Oil Recovery Mechanisms During Sequential Injection of Chelating Agent Solutions Into Carbonate Rocks. *Journal of Energy Resources Technology*, 142(1). <https://doi.org/10.1115/1.4044226>
- Hassan, A. M., & Al-Hashim, H. S. (2020b). Surface charge study of EDTA interaction with carbonate rock during chelating agent flooding. *Journal of Petroleum Science and Engineering*, 191, 107163. <https://doi.org/10.1016/J.PETROL.2020.107163>
- Hill, H. J., Helfferich, F. G., Lake, L. W., Reisberg, J., & Pope, G. A. (1977). Cation Exchange and Chemical Flooding. *JPT, Journal of Petroleum Technology*, 29, 1336–1338. <https://doi.org/10.2118/6642-PA>
- Hills, C. D., Tripathi, N., & Carey, P. J. (2020). Mineralization Technology for Carbon Capture, Utilization, and Storage. *Frontiers in Energy Research*, 8. <https://doi.org/10.3389/FENRG.2020.00142/FULL>
- Hirasaki, G. J., Miller, C. A., & Puerto, M. (2011). Recent advances in surfactant EOR. *SPE Journal*, 16(4), 889–907. <https://doi.org/10.2118/115386-PA>
- Hou, B., Jia, R., Fu, M., Wang, Y., Bai, Y., & Huang, Y. (2018). Wettability Alteration of an Oil-Wet Sandstone Surface by Synergistic Adsorption/Desorption of Cationic/Nonionic Surfactant Mixtures. *Energy & Fuels*, 32(12), 12462–12468. <https://doi.org/10.1021/ACS.ENERGYFUELS.8B03450>
- Hou, C., Jin, X., & He, J. (2022). Investigation on the Microscopic Deterioration Characteristics of Anhydrite Rock Exposed to Freeze–Thaw Cycles. *International Journal of Geomechanics*, 22(4), 04022013. [https://doi.org/10.1061/\(ASCE\)GM.1943-5622.0002328](https://doi.org/10.1061/(ASCE)GM.1943-5622.0002328)
- Hu, Q., Ewing, R. P., & Dultz, S. (2012). Low pore connectivity in natural rock. *Journal of Contaminant Hydrology*, 133, 76–83. <https://doi.org/10.1016/J.JCONHYD.2012.03.006>
- Huber, T., Pimentel, E., & Anagnostou, G. (2015). Experimental Investigations for the Modelling of Chemo-mechanical Processes in Anhydritic Rock. *Energy Procedia*, 76, 87–95. <https://doi.org/10.1016/J.EGYPRO.2015.07.853>
- Huq, F., Haderlein, S. B., Cirpka, O. A., Nowak, M., Blum, P., & Grathwohl, P. (2015). Flow-through experiments on water–rock interactions in a sandstone caused by CO₂ injection at pressures and temperatures mimicking reservoir conditions. *Applied Geochemistry*, 58, 136–146. <https://doi.org/10.1016/J.APGEOCHEM.2015.04.006>
- Iglauer, S. (2017). CO₂–Water–Rock Wettability: Variability, Influencing Factors, and Implications for CO₂ Geostorage. *Accounts of Chemical Research*, 50(5), 1134–1142. <https://doi.org/10.1021/ACS.ACCOUNTS.6B00602>
- Isah, A., Adebayo, A. R., Mahmoud, M., Babalola, L. O., & El-Husseiny, A. (2021a). Drainage mechanisms in gas reservoirs with bimodal pores – A core and pore scale study. *Journal of*

- Natural Gas Science and Engineering*, 86, 103652.
<https://doi.org/10.1016/j.jngse.2020.103652>
- Isah, A., Adebayo, A. R., Mahmoud, M., Babalola, L. O., & El-Husseiny, A. (2021b). Drainage mechanisms in gas reservoirs with bimodal pores – A core and pore scale study. *Journal of Natural Gas Science and Engineering*, 86, 103652.
<https://doi.org/10.1016/J.JNGSE.2020.103652>
- Isah, A., Adebayo, A. R., Mahmoud, M., Babalola, L. O., & El-Husseiny, A. (2021c). Characterization of Fluid Drainage Mechanism at Core and Pore Scales: an NMR Capillary Pressure–Based Saturation Exponent Prediction. *Society of Petroleum Engineers - SPE Europec Featured at 82nd EAGE Conference and Exhibition, EURO 2021*, 2, 205176.
<https://doi.org/10.2118/205176-MS>
- Isah, A., Arif, M., Hassan, A., Mahmoud, M., & Iglauer, S. (2022a). A systematic review of Anhydrite-Bearing Reservoirs: EOR Perspective, CO₂-Geo-storage and future research. *Fuel*, 320, 123942. <https://doi.org/10.1016/J.FUEL.2022.123942>
- Isah, A., Arif, M., Hassan, A., Mahmoud, M., & Iglauer, S. (2022b). Fluid–rock interactions and its implications on EOR: Critical analysis, experimental techniques and knowledge gaps. *Energy Reports*, 8, 6355–6395. <https://doi.org/10.1016/J.EGYR.2022.04.071>
- Isah, A., Mahmoud, M., Kamal, M. S., Arif, M., & Al Jawad, M. (2023). Multiscale Wettability Characterization of Anhydrite-Rich Carbonate Rocks: Insights into Zeta Potential, Flotation, and Contact Angle Measurements. *SPE Reservoir Evaluation & Engineering*, 26(03), 592–610. <https://doi.org/10.2118/214324-PA>
- Isah, A., Mahmoud, M., Kamal, M. S., Arif, M., & Jawad, M. Al. (2023a). Multiscale Wettability Characterization of Anhydrite-Rich Carbonate Rocks: Insights into Zeta Potential, Flotation, and Contact Angle Measurements. *SPE Reservoir Evaluation & Engineering*, 1–19.
<https://doi.org/10.2118/214324-PA>
- Isah, A., Mahmoud, M., Kamal, M. S., Arif, M., & Jawad, M. Al. (2023b). Multiscale Wettability Characterization of Anhydrite-Rich Carbonate Rocks: Insights into Zeta Potential, Flotation, and Contact Angle Measurements. *SPE Reservoir Evaluation & Engineering*, 1–19.
<https://doi.org/10.2118/214324-PA>
- Ivanova, A., Mitiurev, N., Cheremisin, A., Orekhov, A., Kamyshinsky, R., & Vasiliev, A. (2019). Characterization of Organic Layer in Oil Carbonate Reservoir Rocks and its Effect on Microscale Wetting Properties. *Scientific Reports 2019* 9:1, 9(1), 1–10.
<https://doi.org/10.1038/s41598-019-47139-y>
- Ji, J., Ge, Y., Balsam, W., Damuth, J. E., & Chen, J. (2009). Rapid identification of dolomite using a Fourier Transform Infrared Spectrophotometer (FTIR): A fast method for identifying Heinrich events in IODP Site U1308. *Marine Geology*, 258(1–4), 60–68.
<https://doi.org/10.1016/J.MARGEO.2008.11.007>
- Jian, G., Puerto, M. C., Wehowsky, A., Dong, P., Johnston, K. P., Hirasaki, G. J., & Biswal, S. L. (2016). Static Adsorption of an Ethoxylated Nonionic Surfactant on Carbonate Minerals. *Langmuir*, 32(40), 10244–10252. <https://doi.org/10.1021/acs.langmuir.6b01975>
- Jiang, T., Hirasaki, G. J., & Miller, C. A. (2010). Characterization of kaolinite ζ potential for

- interpretation of wettability alteration in diluted bitumen emulsion separation. *Energy and Fuels*, 24(4), 2350–2360. <https://doi.org/10.1021/ef900999h>
- Joekar-Niasar, V., Schreyer, L., Sedighi, M., Icardi, M., & Huyghe, J. (2019). Coupled Processes in Charged Porous Media: From Theory to Applications. *Transport in Porous Media*. <https://doi.org/10.1007/s11242-019-01257-3>
- Kadkhodaie, R., Sohrabi, A., & Jodeyri-Agahi, R. (2022). A syngenetic classification of anhydrite textures in carbonate reservoirs and its relationship with reservoir quality: a case study from the Permo-Triassic Dalan and Kangan formations. *Carbonates and Evaporites*, 37(3), 1–19. <https://doi.org/10.1007/S13146-022-00790-5/METRICS>
- Kafili Kasmaei, A., & Rao, D. N. (2015). Is Wettability Alteration the Main Cause for Enhanced Recovery in Low-Salinity Waterflooding? *SPE Reservoir Evaluation & Engineering*, 18(02), 228–235. <https://doi.org/10.2118/169120-PA>
- Kakati, A., Kumar, G., & Sangwai, J. S. (2020). Low Salinity Polymer Flooding: Effect on Polymer Rheology, Injectivity, Retention, and Oil Recovery Efficiency. *Energy and Fuels*, 34(5), 5715–5732. <https://doi.org/10.1021/acs.energyfuels.0c00393>
- Karimi, M., Al-Maamari, R. S., Ayatollahi, S., & Mehranbod, N. (2016). Wettability alteration and oil recovery by spontaneous imbibition of low salinity brine into carbonates: Impact of Mg^{2+} , SO_4^{2-} and cationic surfactant. *Journal of Petroleum Science and Engineering*, 147, 560–569. <https://doi.org/10.1016/J.PETROL.2016.09.015>
- Karoussi, O., & Hamouda, A. A. (2007). Imbibition of Sulfate and Magnesium Ions into Carbonate Rocks at Elevated Temperatures and Their Influence on Wettability Alteration and Oil Recovery. *Energy and Fuels*, 21(4), 2138–2146. <https://doi.org/10.1021/EF0605246>
- Karpiński, B., Science, M. S.-A. in M., & 2015, U. (2015). *Clay minerals—mineralogy and phenomenon of clay swelling in oil & gas industry*. <https://doi.org/10.1515/adms-2015-0006>
- Kasha, A., Sauerer, B., Al-Hashim, H., & Abdallah, W. (2021). Interplay Between Ca^{2+} , Mg^{2+} , and SO_4^{2-} Ions and Their Influence on the Zeta-Potential of Limestone during Controlled-Salinity Waterflooding. *Energy & Fuels*, acs.energyfuels.1c00940. <https://doi.org/10.1021/acs.energyfuels.1c00940>
- Katende, A., & Sagala, F. (2019). A critical review of low salinity water flooding: mechanism, laboratory and field application. *Journal of Molecular Liquids*, 278, 627–6. <https://www.sciencedirect.com/science/article/pii/S0167732218350761>
- Katiyar, A., Hassanzadeh, A., Patil, P., Hand, M., Perozo, A., Pecore, D., Kalaei, H., & Nguyen, Q. (2020). Successful Field Implementation of CO₂-Foam Injection for Conformance Enhancement in the EVGSAU Field in the Permian Basin. *Proceedings - SPE Symposium on Improved Oil Recovery*, 2020-August. <https://doi.org/10.2118/200327-MS>
- Kazempour, M., Gregersen, C. S., & Alvarado, V. (2013). Mitigation of anhydrite dissolution in alkaline floods through injection of conditioned water. *Fuel*, 107, 330–342. <https://doi.org/10.1016/J.FUEL.2012.10.003>
- Kelemen, P. B., Aines, R., Bennett, E., Benson, S. M., Carter, E., Coggon, J. A., De Obeso, J. C., Evans, O., Gadikota, G., Dipple, G. M., Godard, M., Harris, M., Higgins, J. A., Johnson, K. T.

- M., Kourim, F., Lafay, R., Lambart, S., Manning, C. E., Matter, J. M., ... Wilcox, J. (2018). In situ carbon mineralization in ultramafic rocks: Natural processes and possible engineered methods. *Energy Procedia*, 146, 92–102. <https://doi.org/10.1016/J.EGYPRO.2018.07.013>
- Kelemen, P., Benson, S. M., Pilorgé, H., Psarras, P., & Wilcox, J. (2019). An Overview of the Status and Challenges of CO₂ Storage in Minerals and Geological Formations. *Frontiers in Climate*, 1, 482595. <https://doi.org/10.3389/FCLIM.2019.00009/BIBTEX>
- Kelemen, Peter B., McQueen, N., Wilcox, J., Renforth, P., Dipple, G., & Vankeuren, A. P. (2020). Engineered carbon mineralization in ultramafic rocks for CO₂ removal from air: Review and new insights. *Chemical Geology*, 550, 119628. <https://doi.org/10.1016/J.CHEMGEO.2020.119628>
- Khan, H. J., Prodanović, M., & DiCarlo, D. A. (2019). The Effect of Vuggy Porosity on Straining in Porous Media. *SPE Journal*, 24(03), 1164–1178. <https://doi.org/10.2118/194201-PA>
- Khather, M., Saeedi, A., Myers, M. B., & Verrall, M. (2019). An experimental study for carbonate reservoirs on the impact of CO₂-EOR on petrophysics and oil recovery. *Fuel*, 235(March 2018), 1019–1038. <https://doi.org/10.1016/j.fuel.2018.08.094>
- Kim, M., Haroun, M., Rahman, M. M., & Al Kobaisi, M. (2020). Hybrid Nano Acid Fluid Pulsed with Electrokinetic to Stimulate Tight Carbonate Reservoirs: A Novel EOR/IOR Method. *Society of Petroleum Engineers - SPE/IATMI Asia Pacific Oil and Gas Conference and Exhibition 2019, APOG 2019*. <https://doi.org/10.2118/196317-MS>
- Kim, S., & Santamarina, J. C. (2014). CO₂ geological storage: Hydro-chemo-mechanical analyses and implications. *Greenhouse Gases: Science and Technology*, 4(4), 528–543. <https://doi.org/10.1002/GHG.1421>
- Koleini, M. M., Badizad, M. H., Mahani, H., Dastjerdi, A. M., Ayatollahi, S., & Ghazanfari, M. H. (2021). Atomistic insight into salinity dependent preferential binding of polar aromatics to calcite/brine interface: implications to low salinity waterflooding. *Scientific Reports*, 11(1), 1–17. <https://doi.org/10.1038/s41598-021-91402-0>
- Koleini, M. M., Mehraban, M. F., & Ayatollahi, S. (2018). Effects of low salinity water on calcite/brine interface: A molecular dynamics simulation study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 537(October 2017), 61–68. <https://doi.org/10.1016/j.colsurfa.2017.10.024>
- Kong, L., Ostadhassan, M., Hou, X., Mann, M., & Li, C. (2019). Microstructure characteristics and fractal analysis of 3D-printed sandstone using micro-CT and SEM-EDS. *Journal of Petroleum Science and Engineering*, 175, 1039–1048. <https://doi.org/10.1016/J.PETROL.2019.01.050>
- Kremieniewski, M., Wiśniowski, R., Stryczek, S., & Łopata, P. (2021). Comparison of Efficient Ways of Mud Cake Removal from Casing Surface with Traditional and New Agents. *Energies*, 14(12), 3653. <https://doi.org/10.3390/en14123653>
- Ku, M., Clauser, C., Back, M., & Peiffer, S. (2009). *Mineral Trapping of CO₂ in Operated Hydrogeothermal Reservoirs*. 545–552. <https://doi.org/10.1306/13171260ST593395>
- Kubicki, J. D., & Stolper, E. M. (1995). Structural roles of CO₂ and [CO₃]²⁻ in fully polymerized sodium aluminosilicate melts and glasses. *Geochimica et Cosmochimica Acta*, 59(4), 683–698. [https://doi.org/10.1016/0016-7037\(94\)00317-F](https://doi.org/10.1016/0016-7037(94)00317-F)

- Kulesza, S., & Bramowicz, M. (2014). A comparative study of correlation methods for determination of fractal parameters in surface characterization. *Applied Surface Science*, 293, 196–201. <https://doi.org/10.1016/J.APSUSC.2013.12.132>
- Kumar, Amit, & Mandal, A. (2018). Characterization of rock-fluid and fluid-fluid interactions in presence of a family of synthesized zwitterionic surfactants for application in enhanced oil recovery. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 549, 1–12. <https://doi.org/10.1016/J.COLSURFA.2018.04.001>
- Kumar, Ashish, Chaudhuri, P., Kumar, B., & Panja, S. S. (2016). Review on aggregation of asphaltene vis-a-vis spectroscopic studies. *Fuel*, 185, 541–554. <https://doi.org/10.1016/j.fuel.2016.08.031>
- Kumar, S., Naiya, T. K., & Kumar, T. (2018). Developments in oilfield scale handling towards green technology-A review. *Journal of Petroleum Science and Engineering*, 169, 428–444. <https://doi.org/10.1016/J.PETROL.2018.05.068>
- L'Orange Seigo, S., Dohle, S., & Siegrist, M. (2014). Public perception of carbon capture and storage (CCS): A review. *Renewable and Sustainable Energy Reviews*, 38, 848–863. <https://doi.org/10.1016/J.RSER.2014.07.017>
- Lai, J., Fan, Z., Zhou, Z., Chen, J., Wang, S., & Wang, G. (2018). Fractal analysis of tight shaly sandstones using nuclear magnetic resonance measurements. *AAPG Bulletin*, 102(2), 175–193. <https://doi.org/10.1306/0425171609817007>
- Lai, J., & Wang, G. (2015). Fractal analysis of tight gas sandstones using high-pressure mercury intrusion techniques. *Journal of Natural Gas Science and Engineering*, 24, 185–196. <https://doi.org/10.1016/J.JNGSE.2015.03.027>
- Lander, L. M., Siewierski, L. M., Britain, W. J., & Vogler, E. A. (2002). A systematic comparison of contact angle methods. *Langmuir*, 9(8), 2237–2239. <https://doi.org/10.1021/LA00032A055>
- Lara Orozco, R. A., Abeykoon, G. A., Okuno, R., & Lake, L. W. (2021). The impact of glycine on the zeta potential of calcite at different temperatures and brine compositions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 624(March), 126851. <https://doi.org/10.1016/j.colsurfa.2021.126851>
- Lee, M. gyu, Jang, Y. N., Ryu, K. won, Kim, W., & Bang, J. H. (2012). Mineral carbonation of flue gas desulfurization gypsum for CO₂ sequestration. *Energy*, 47(1), 370–377. <https://doi.org/10.1016/J.ENERGY.2012.09.009>
- Leontaritis, K. J. (1998). Challenges and solutions to asphaltene and wax deposition. In *Offshore* (Vol. 58, Issue 9, pp. 1–9).
- Li, D. (2004). *Electrokinetics in microfluidics*. https://books.google.com/books?hl=en&lr=&id=1QkpluJqQegC&oi=fnd&pg=PP1&dq=Li,+D.,+2004.+Electrokinetics+in+microfluidics.+Elsevier.&ots=7i6srGy5DC&sig=gS4ayJpY_stNovnC6gEMNXnpMIY
- Li, J., & Duan, Z. (2011). A thermodynamic model for the prediction of phase equilibria and speciation in the H₂O–CO₂–NaCl–CaCO₃–CaSO₄ system from 0 to 250 °C, 1 to 1000 bar with NaCl concentrations up to halite saturation. *Geochimica et Cosmochimica Acta*, 75(15), 4351–4376. <https://doi.org/10.1016/J.GCA.2011.05.019>

- Li, K. (2010). Analytical derivation of Brooks–Corey type capillary pressure models using fractal geometry and evaluation of rock heterogeneity. *Journal of Petroleum Science and Engineering*, 73(1–2), 20–26. <https://doi.org/10.1016/J.PETROL.2010.05.002>
- Li, S., Zhang, S., Xing, H., & Zou, Y. (2022). CO₂–brine–rock interactions altering the mineralogical, physical, and mechanical properties of carbonate-rich shale oil reservoirs. *Energy*, 256, 124608. <https://doi.org/10.1016/J.ENERGY.2022.124608>
- Li, X., Li, Q., Yang, S., & Yang, G. (2019). Swelling of clay minerals: dual characteristics of K⁺ ions and exploration of critical influencing factors. *Physical Chemistry Chemical Physics*, 21(4), 1963–1971. <https://doi.org/10.1039/C8CP07567K>
- LI, Y., WANG, R., ZHAO, Q., XUE, Z., & ZHOU, Y. (2023). A CO₂ storage potential evaluation method for saline aquifers in a petroliferous basin. *Petroleum Exploration and Development*, 50(2), 484–491. [https://doi.org/10.1016/S1876-3804\(23\)60403-3](https://doi.org/10.1016/S1876-3804(23)60403-3)
- Lim, S., Lee, H. S., & Kawashima, S. (2018). Pore structure refinement of cement paste incorporating nanosilica: Study with dual beam scanning electron microscopy/focused ion beam (SEM/FIB). *Materials Characterization*, 145(August), 323–328. <https://doi.org/10.1016/j.matchar.2018.08.045>
- LIN, M., HUA, Z., & LI, M. (2018). Surface wettability control of reservoir rocks by brine. *Petroleum Exploration and Development*, 45(1), 145–153. [https://doi.org/10.1016/S1876-3804\(18\)30014-4](https://doi.org/10.1016/S1876-3804(18)30014-4)
- Liu, F., & Wang, M. (2020). Review of low salinity waterflooding mechanisms: Wettability alteration and its impact on oil recovery. *Fuel*, 267, 117112. <https://doi.org/10.1016/J.FUEL.2020.117112>
- Liu, Jian, Wani, O. B., Alhassan, S. M., & Pantelides, S. T. (2018). Wettability Alteration and Enhanced Oil Recovery Induced by Proximal Adsorption of Na⁺, Cl⁻, Ca²⁺, Mg²⁺, and SO₄²⁻ Ions on Calcite. *Physical Review Applied*, 10(3), 1. <https://doi.org/10.1103/PhysRevApplied.10.034064>
- Liu, Jun, Yao, Y., Liu, D., Cai, Y., & Cai, J. (2018). COMPARISON OF PORE FRACTAL CHARACTERISTICS BETWEEN MARINE AND CONTINENTAL SHALES. <https://doi.org/10.1142/S0218348X18400169>, 26(2), 1840016. <https://doi.org/10.1142/S0218348X18400169>
- Liu, Q., Zhang, X., Jiang, B., Li, J., Li, T., Shao, X., Cai, W., Wang, H., & Zhang, Y. (2021). Molecular Dynamics Simulation of Ion Adsorption and Ligand Exchange on an Orthoclase Surface. *ACS Omega*, 6(23), 14952–14962. <https://doi.org/10.1021/acsomega.1c00826>
- Liu, T., Artacho, E., Gázquez, F., Walters, G., & Hodell, D. (2019). Prediction of equilibrium isotopic fractionation of the gypsum/bassanite/water system using first-principles calculations. *Geochimica et Cosmochimica Acta*, 244, 1–11. <https://doi.org/10.1016/j.gca.2018.08.045>
- Liu, X. (1994). *Modeling of formation damage due to particulate processes in two-phase flow systems* - ProQuest. <https://www.proquest.com/docview/304102666?pq-origsite=gscholar&fromopenview=true>
- Long, H., Nardi, C., Idowu, N., Carnerup, A., Øren, P. E., Knackstedt, M., Varslot, T., Sok, R. M., &

- Lithicon, A. S. (2013). Multi-scale imaging and modeling workflow to capture and characterize microporosity in sandstone. *International Symposium of the Society of Core Analysts*, 13.
- Lopez-Salinas, J. L., Hirasaki, G. J., & Miller, C. A. (2011). Determination of Anhydrite in Reservoirs for EOR. *Proceedings - SPE International Symposium on Oilfield Chemistry*, 2, 769–786. <https://doi.org/10.2118/141420-MS>
- Lu, Jingwen, Wang, Z., Su, S., Liu, H., Ma, Z., Ren, Q., Xu, K., Wang, Y., Hu, S., & Xiang, J. (2024). Single-step integrated CO₂ absorption and mineralization using fly ash coupled mixed amine solution: Mineralization performance and reaction kinetics. *Energy*, 286, 129615. <https://doi.org/10.1016/J.ENERGY.2023.129615>
- Lu, Jun, & Pope, G. A. (2017). Optimization of Gravity-Stable Surfactant Flooding. *SPE Journal*, 22(02), 480–493. <https://doi.org/10.2118/174033-PA>
- Lucia, F. J., & Ruppel, S. C. (1996). Characterization of Diagenetically Altered Carbonate Reservoirs, South Cowden Grayburg Reservoir, West Texas. *Society of Petroleum Engineers - SPE Annual Technical Conference and Exhibition*, 883–893. <https://doi.org/10.2118/36650-MS>
- Lv, W., Bazin, B., Ma, D., Liu, Q., Han, D., & Wu, K. (2011). Static and dynamic adsorption of anionic and amphoteric surfactants with and without the presence of alkali. *Journal of Petroleum Science and Engineering*, 77(2), 209–218. <https://doi.org/10.1016/j.petrol.2011.03.006>
- Ma, X., Guo, S., Shi, D., Zhou, Z., & Liu, G. (2019). Investigation of pore structure and fractal characteristics of marine-continental transitional shales from Longtan Formation using MICP, gas adsorption, and NMR (Guizhou, China). *Marine and Petroleum Geology*, 107, 555–571. <https://doi.org/10.1016/J.MARPETGEO.2019.05.018>
- Madadi Mogharrab, J., Ayatollahi, S., & Reza Pishvaie, M. (2022). *Experimental study and surface complexation modeling of non-monotonic wettability behavior due to change in brine salinity/composition: Insight into anhydrite impurity in carbonates*. <https://doi.org/10.1016/j.molliq.2022.120117>
- Madhav, D., Coppitters, T., Ji, Y., Thielemans, W., Desplentere, F., Moldenaers, P., & Vandeginste, V. (2023). Amino acid promoted single-step carbon dioxide capture and mineralization integrated with polymer-mediated crystallization of carbonates. *Journal of Cleaner Production*, 415, 137845. <https://doi.org/10.1016/J.JCLEPRO.2023.137845>
- Mady, M. F., Abdel-Azeim, S., & Kelland, M. A. (2021). Antiscaling Evaluation and Quantum Chemical Studies of Nitrogen-Free Organophosphorus Compounds for Oilfield Scale Management. *Industrial & Engineering Chemistry Research*, acs.iecr.1c02441. <https://doi.org/10.1021/acs.iecr.1c02441>
- Mahani, H., Menezes, R., Berg, S., Fadili, A., Nasralla, R., Voskov, D., & Joekar-Niasar, V. (2017). Insights into the Impact of Temperature on the Wettability Alteration by Low Salinity in Carbonate Rocks. *Energy and Fuels*, 31(8), 7839–7853. https://doi.org/10.1021/ACS.ENERGYFUELS.7B00776/SUPPL_FILE/EF7B00776_SI_001.PDF
- Mahani, Hassan, Keya, A. L., Berg, S., Bartels, W. B., Nasralla, R., & Rossen, W. R. (2015). Insights

- into the mechanism of wettability alteration by low-salinity flooding (LSF) in carbonates. *Energy and Fuels*, 29(3), 1352–1367.
https://doi.org/10.1021/EF5023847/SUPPL_FILE/EF5023847_SI_001.PDF
- Mahmoud, M. A. (2014). Evaluating the Damage Caused by Calcium Sulfate Scale Precipitation During Low- and High-Salinity-Water Injection. *Journal of Canadian Petroleum Technology*, 53(03), 141–150. <https://doi.org/10.2118/164634-PA>
- Mahmoud, M. A., & Abdelgawad, K. Z. (2015a). Chelating-Agent Enhanced Oil Recovery for Sandstone and Carbonate Reservoirs. *SPE Journal*, 20(03), 483–495.
<https://doi.org/10.2118/172183-PA>
- Mahmoud, M. A., & Abdelgawad, K. Z. (2015b). Chelating-Agent Enhanced Oil Recovery for Sandstone and Carbonate Reservoirs. *SPE Journal*, 20(03), 483–495.
<https://doi.org/10.2118/172183-PA>
- Mahmoud, M., Aljawad, M. S., Kamal, M. S., Ali, A., & Al-Nakhli, A. (2020). Two-Stage Stimulation of Gas Carbonate Reservoirs with High Anhydrite Content: Experimental and Modeling Study. *Energy & Fuels*, 34(8), 9978–9989.
<https://doi.org/10.1021/ACS.ENERGYFUELS.0C01778>
- Mahmoud, M., Attia, M., & Al-Hashim, H. (2017). EDTA chelating agent/seawater solution as enhanced oil recovery fluid for sandstone reservoirs. *Journal of Petroleum Science and Engineering*, 152, 275–283. <https://doi.org/10.1016/J.PETROL.2017.03.019>
- Mahmoud, M., Kamal, M. S., Aljawad, M. S., Ali, A., & Al-Nakhli, A. (2021a). Single-Stage Stimulation of Anhydrite-Rich Carbonate Rocks Using Chelating Agent: An Experimental and Modeling Investigation. *SPE Journal*, 26(03), 1144–1160.
<https://doi.org/10.2118/203840-PA>
- Mahmoud, M., Kamal, M. S., Aljawad, M. S., Ali, A., & Al-Nakhli, A. (2021b). Single-Stage Stimulation of Anhydrite-Rich Carbonate Rocks Using Chelating Agent: An Experimental and Modeling Investigation. *SPE Journal*, 26(03), 1144–1160.
<https://doi.org/10.2118/203840-PA>
- Maire, E., & Withers, P. J. (2014). Quantitative X-ray tomography. *International Materials Reviews*, 59(1), 1–43. <https://doi.org/10.1179/1743280413Y.0000000023>
- Manceau, J. C., Ma, J., Li, R., Audigane, P., Jiang, P. X., Xu, R. N., Tremosa, J., & Lerouge, C. (2015). Two-phase flow properties of a sandstone rock for the CO₂/water system: Core-flooding experiments, and focus on impacts of mineralogical changes. *Water Resources Research*, 51(4), 2885–2900. <https://doi.org/10.1002/2014WR015725>
- Mandelbrot, B. (1982). *The fractal geometry of nature*. Freeman, San Francisco, CA.
http://users.math.yale.edu/~bbm3/web_pdfs/encyclopediaBritannica.pdf
- Mannhardt, K., Novosad, J. J., & Jha, K. N. N. (1994). Adsorption of Foam-forming Surfactants In Berea Sandstone. *Journal of Canadian Petroleum Technology*, 33(02).
<https://doi.org/10.2118/94-02-04>
- Mannhardt, Karin, Schramm, L. L., & Novosad, J. J. (1993). Effect of rock type and brine composition on adsorption of two foam-forming surfactants. *SPE Advanced Technology Series*, 1(1), 212–218. <https://doi.org/10.2118/20463-pa>

- Marbler, H., Erickson, K. P., Schmidt, M., Lempp, C., & Pöllmann, H. (2013). Geomechanical and geochemical effects on sandstones caused by the reaction with supercritical CO₂: An experimental approach to in situ conditions in deep geological reservoirs. *Environmental Earth Sciences*, 69(6), 1981–1998. <https://doi.org/10.1007/S12665-012-2033-0/METRICS>
- Marmur, A., Volpe, C. Della, Siboni, S., Amirfazli, A., & Drelich, J. W. (2017). Contact angles and wettability: Towards common and accurate terminology. *Surface Innovations*, 5(1), 3–8. <https://doi.org/10.1680/JSUIN.17.00002/ASSET/IMAGES/SMALL/JSUIN5-0003-F6.GIF>
- Matter, J. M., Stute, M., Snæbjörnsdóttir, S., Oelkers, E. H., Gislason, S. R., Aradóttir, E. S., Sigfusson, B., Gunnarsson, I., Sigurdardóttir, H., Gunnlaugsson, E., Axelsson, G., Alfredsson, H. A., Wolff-Boenisch, D., Mesfin, K., Taya, D. F. D. L. R., Hall, J., Dideriksen, K., & Broecker, W. S. (2016a). Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science*, 352(6291), 1312–1314. https://doi.org/10.1126/SCIENCE.AAD8132/SUPPL_FILE/AAD8132-MATTER-SM.PDF
- Matter, J. M., Stute, M., Snæbjörnsdóttir, S., Oelkers, E. H., Gislason, S. R., Aradóttir, E. S., Sigfusson, B., Gunnarsson, I., Sigurdardóttir, H., Gunnlaugsson, E., Axelsson, G., Alfredsson, H. A., Wolff-Boenisch, D., Mesfin, K., Taya, D. F. D. L. R., Hall, J., Dideriksen, K., & Broecker, W. S. (2016b). Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science*, 352(6291), 1312–1314. https://doi.org/10.1126/SCIENCE.AAD8132/SUPPL_FILE/AAD8132-MATTER-SM.PDF
- Mcgrail, B. P., Schaef, H. T., Ho, A. M., Chien, Y.-J., Dooley, J. J., Davidson, C. L., Mcgrail, C. :, Schaef, H. T., Ho, A. M., Chien, Y.-J., Dooley, J. J., & Davidson, C. L. (2006). Potential for carbon dioxide sequestration in flood basalts. *Journal of Geophysical Research: Solid Earth*, 111(B12), 12201. <https://doi.org/10.1029/2005JB004169>
- Milton, D. I. (1967). *Geology of the Arabian Peninsula Powers, RW, LF Ramirez, CD Redmond, and EL Elberg. 1966. Geology of the Arabian Peninsula (United States Department of the Interior, Geological Survey).*
- Minde, M. W., Zimmermann, U., Madland, M. V., Korsnes, R. I., Schulz, B., & Gilbricht, S. (2020). Mineral replacement in long-term flooded porous carbonate rocks. *Geochimica et Cosmochimica Acta*, 268, 485–508. <https://doi.org/10.1016/J.GCA.2019.09.017>
- Miri, R., Haftani, M., & Nouri, A. (2021). A review of fines migration around Steam Assisted Gravity Drainage wellbores. *Journal of Petroleum Science and Engineering*, 205, 108868. <https://doi.org/10.1016/J.PETROL.2021.108868>
- Mishra, S., Bera, A., & Mandal, A. (2014). Effect of Polymer Adsorption on Permeability Reduction in Enhanced Oil Recovery. *Journal of Petroleum Engineering*, 2014, 1–9. <https://doi.org/10.1155/2014/395857>
- Mitchell, J., & Fordham, E. J. (2014). Contributed review: Nuclear magnetic resonance core analysis at 0.3 T. *Review of Scientific Instruments*, 85(11). <https://doi.org/10.1063/1.4902093/356469>
- Moffitt, P., Pecore, D., Trees, M., & Salts, G. (2015). East Vacuum Grayburg San Andres Unit, 30 Years of CO₂ Flooding: Accomplishments, Challenges and Opportunities. *Proceedings - SPE Annual Technical Conference and Exhibition, 2015-January*, 3844–3859. <https://doi.org/10.2118/175000-MS>

- Mogensen, K., & Masalmeh, S. (2020). A review of EOR techniques for carbonate reservoirs in challenging geological settings. *Journal of Petroleum Science and Engineering*, 195, 107889. <https://doi.org/10.1016/J.PETROL.2020.107889>
- Mogharab, J. M., Ayatollahi, S., & Pishvaie, M. R. (2022). Experimental study and surface complexation modeling of non-monotonic wettability behavior due to change in brine salinity/composition: Insight into anhydrite impurity in carbonates. *Journal of Molecular Liquids*, 365, 120117. <https://doi.org/10.1016/J.MOLLIQ.2022.120117>
- Mohamed, A., Elkatatny, S., & Al-Majed, A. (2020). Removal of Calcium Carbonate Water-Based Filter Cake Using a Green Biodegradable Acid. *Sustainability*, 12(3), 994. <https://doi.org/10.3390/su12030994>
- Mohammadi, S., Kord, S., Mohammadzadeh, O., & Moghadasi, J. (2021a). An experimental study into rock dissolution mechanism during diluted seawater injection in carbonate rocks. *Upstream Oil and Gas Technology*, 6, 100031. <https://doi.org/10.1016/J.UPSTRE.2021.100031>
- Mohammadi, S., Kord, S., Mohammadzadeh, O., & Moghadasi, J. (2021b). An experimental study into rock dissolution mechanism during diluted seawater injection in carbonate rocks. *Upstream Oil and Gas Technology*, 6, 100031. <https://doi.org/10.1016/J.UPSTRE.2021.100031>
- Mohammadian, E., Hadavimoghaddam, F., Kheirollahi, M., Jafari, M., Chenlu, X., & Liu, B. (2023). Probing Solubility and pH of CO₂ in aqueous solutions: Implications for CO₂ injection into oceans. *Journal of CO₂ Utilization*, 71, 102463. <https://doi.org/10.1016/J.JCOU.2023.102463>
- Mohammed-Sajed, O. K., & Glover, P. W. J. (2022). Influence of anhydritisation on the reservoir quality of the Butmah Formation in north-western Iraq. *Marine and Petroleum Geology*, 135, 105391. <https://doi.org/10.1016/J.MARPETGEO.2021.105391>
- Mohammed, I., Abdel-Azeim, S., Shehri, D. Al, Mahmoud, M., Kamal, M. S., Alade, O. S., & Patil, S. (2022). Calcite–Brine Interface and Its Implications in Oilfield Applications: Insights from Zeta Potential Experiments and Molecular Dynamics Simulations. *Energy & Fuels*. https://doi.org/10.1021/ACS.ENERGYFUELS.2C02425/ASSET/IMAGES/LARGE/EF2C02425_0006.JPEG
- Mohammed, I., Al Shehri, D. A., Mahmoud, M., Kamal, M. S., & Alade, O. (2021a). Surface Charge Investigation of Reservoir Rock Minerals. *Energy & Fuels*, 35(7), 6003–6021. <https://doi.org/10.1021/acs.energyfuels.1c00459>
- Mohammed, I., Al Shehri, D., Mahmoud, M., Kamal, M. S., Alade, O., Arif, M., & Patil, S. (2022). Effect of Native Reservoir State and Oilfield Operations on Clay Mineral Surface Chemistry. *Molecules*, 27(5), 1739. <https://doi.org/10.3390/molecules27051739>
- Mohammed, I., Al Shehri, D., Mahmoud, M., Kamal, M. S., & Alade, O. S. (2021b). A Surface Charge Approach to Investigating the Influence of Oil Contacting Clay Minerals on Wettability Alteration. *ACS Omega*. <https://doi.org/10.1021/acsomega.1c01221>
- Mohammed, I., Al Shehri, D., Mahmoud, M., Kamal, M. S., & Alade, O. S. (2021c). Impact of Iron Minerals in Promoting Wettability Alterations in Reservoir Formations. *ACS Omega*, 6(5),

4022–4033. <https://doi.org/10.1021/acsomega.0c05954>

Mohammed, I., Al Shehri, D., Mahmoud, M., Kamal, M. S., & Alade, O. S. (2022). Feature Ranking and Modeling of Mineral Effects on Reservoir Rock Surface Chemistry Using Smart Algorithms. *ACS Omega*, 7(5), 4194–4201. <https://doi.org/10.1021/acsomega.1c05820>

Mohammed, I., Al Shehri, D., Mahmoud, M., Kamal, M. S., Arif, M., Alade, O. S., & Patil, S. (2022). Investigation of Surface Charge at the Mineral/Brine Interface: Implications for Wettability Alteration. *Frontiers in Materials*, 9(April), 1–15. <https://doi.org/10.3389/fmats.2022.891455>

Mohammed, I., Isah, A., Al Shehri, D., Mahmoud, M., Arif, M., Kamal, M. S., Alade, O. S., & Patil, S. (2022a). Effect of Sulfate-Based Scales on Calcite Mineral Surface Chemistry: Insights from Zeta-Potential Experiments and Their Implications on Wettability. *ACS Omega*, 7(32), 28571–28587. https://doi.org/10.1021/ACSOMEGA.2C03403/ASSET/IMAGES/LARGE/AO2C03403_0011.JPEG

Mohammed, I., Isah, A., Al Shehri, D., Mahmoud, M., Arif, M., Kamal, M. S., Alade, O. S., & Patil, S. (2022b). Effect of Sulfate-Based Scales on Calcite Mineral Surface Chemistry: Insights from Zeta-Potential Experiments and Their Implications on Wettability. *ACS Omega*, 7(32), 28571–28587. https://doi.org/10.1021/ACSOMEGA.2C03403/ASSET/IMAGES/LARGE/AO2C03403_0011.JPEG

Mohammed, I., Isah, A., Al Shehri, D., Mahmoud, M., Arif, M., Kamal, M. S., Alade, O. S., & Patil, S. (2022c). Effect of Sulfate-Based Scales on Calcite Mineral Surface Chemistry: Insights from Zeta-Potential Experiments and Their Implications on Wettability. *ACS Omega*, 7(32), 28571–28587. https://doi.org/10.1021/ACSOMEGA.2C03403/ASSET/IMAGES/LARGE/AO2C03403_0011.JPEG

Mohammed, I., Mahmoud, M., Al Shehri, D., El-Husseiny, A., & Alade, O. (2021). Asphaltene precipitation and deposition: A critical review. *Journal of Petroleum Science and Engineering*, 197, 107956. <https://doi.org/10.1016/J.PETROL.2020.107956>

Mohammed, I., Mahmoud, M., Al Shehri, D., Kamal, M. S., & Alade, O. S. (2022). Effects of the Reservoir Environment and Oilfield Operations on the Iron Mineral Surface Charge Development: An Insight into Their Role in Wettability Alteration. *Energy & Fuels*, 36(3), 1676–1687. <https://doi.org/10.1021/acs.energyfuels.1c03909>

Mohammed, I., Mahmoud, M., El-Husseiny, A., Al Shehri, D., Al-Garadi, K., Kamal, M. S., & Alade, O. S. (2021). Impact of Asphaltene Precipitation and Deposition on Wettability and Permeability. *ACS Omega*, 6(31), 20091–20102. <https://doi.org/10.1021/acsomega.1c03198>

Mohammed, I., Yaseri, A., Al Shehri, D., & Mahmoud, M. (2024). Basalt mineral surface charge and the effect of mineralization on its colloidal stability: Implications of subsurface CO₂ storage. *Fuel*, 356, 129569. <https://doi.org/10.1016/J.FUEL.2023.129569>

Mohammed Sajed, O. K., & Glover, P. W. J. (2020). Dolomitisation, cementation and reservoir quality in three Jurassic and Cretaceous carbonate reservoirs in north-western Iraq. *Marine*

- and *Petroleum Geology*, 115, 104256. <https://doi.org/10.1016/J.MARPETGEO.2020.104256>
- Mohammed Sajed, O. K., Glover, P. W. J., & Collier, R. E. L. (2021). Reservoir quality estimation using a new ternary diagram approach applied to carbonate formations in north-western Iraq. *Journal of Petroleum Science and Engineering*, 196, 108024. <https://doi.org/10.1016/J.PETROL.2020.108024>
- Mohan, K., Gupta, R., & Mohanty, K. K. (2011). Wettability Altering Secondary Oil Recovery in Carbonate Rocks. *Energy & Fuels*, 25(9), 3966–3973. <https://doi.org/10.1021/ef200449y>
- Mohnot, S. M., Bae, J. H., & Foley, W. L. (1987). A Study of Mineral/Alkali Reactions. *SPE Reservoir Engineering*, 2(04), 653–663. <https://doi.org/10.2118/13032-PA>
- Mokhtari, R., Anabaraonye, B. U., Afrough, A., Mohammadkhani, S., & Feilberg, K. L. (2022). Experimental investigation of low salinity water-flooding in tight chalk oil reservoirs. *Journal of Petroleum Science and Engineering*, 208(PA), 109282. <https://doi.org/10.1016/j.petrol.2021.109282>
- Mora, C. I., & Valley, J. W. (1989). *Halogen-rich scapolite and biotite; implications for metamorphic fluid-rock interaction*. American Mineralogist | GeoScienceWorld. https://pubs.geoscienceworld.org/msa/ammin/article/74/7-8/721/42266/Halogen-rich-scapolite-and-biotite-implications?casa_token=wTGIVQPSeuoAAAAA:TW0YICdXjkm2uPwKc6YubPTt3rT1QegeW a9TV5RHjEE5mpTscnXNcQWonZaTDup8tYse0cizYg
- Morad, D., Nader, F. H., Gasparrini, M., Morad, S., Rossi, C., Marchionda, E., Al Darmaki, F., Martinez, M., & Hellevang, H. (2018). Comparison of the diagenetic and reservoir quality evolution between the anticline crest and flank of an Upper Jurassic carbonate gas reservoir, Abu Dhabi, United Arab Emirates. *Sedimentary Geology*, 367, 96–113. <https://doi.org/10.1016/J.SEDGEO.2018.02.008>
- Morad, S., Al-Aasm, I. S., Nader, F. H., Ceriani, A., Gasparrini, M., & Mansurbeg, H. (2012). Impact of diagenesis on the spatial and temporal distribution of reservoir quality in the Jurassic Arab D and C members, offshore Abu Dhabi oilfield, United Arab Emirates. *GeoArabia*, 17(3), 17–56. <https://doi.org/10.2113/geoarabia170317>
- Moradi, S., Isari, A. A., Bachari, Z., & Mahmoodi, H. (2019). Combination of a new natural surfactant and smart water injection for enhanced oil recovery in carbonate rock: Synergic impacts of active ions and natural surfactant concentration. *Journal of Petroleum Science and Engineering*, 176, 1–10. <https://doi.org/10.1016/J.PETROL.2019.01.043>
- Mormone, A., Piochi, M., Bellatreccia, F., De Astis, G., Moretti, R., Ventura, G. Della, Cavallo, A., & Mangiacapra, A. (2011). A CO₂-rich magma source beneath the Phlegraean Volcanic District (Southern Italy): Evidence from a melt inclusion study. *Chemical Geology*, 287(1–2), 66–80. <https://doi.org/10.1016/J.CHEMGEO.2011.05.019>
- Morrissey, L. J., & Tomkins, A. G. (2020). Evaporite-bearing orogenic belts produce ligand-rich and diverse metamorphic fluids. *Geochimica et Cosmochimica Acta*, 275, 163–187. <https://doi.org/10.1016/J.GCA.2020.02.017>
- Morrow, N., Buckley, J., & Morrow, N. R. (2011). Improved Oil Recovery by Low-Salinity Waterflooding. *Journal of Petroleum Technology*, 63(05), 106–112.

<https://doi.org/10.2118/129421-JPT>

- Mosallanezhad, A., & Kalantariasl, A. (2021). Geochemical simulation of Single-Phase Ion-Engineered water interactions with carbonate Rocks: Implications for enhanced oil recovery. *Journal of Molecular Liquids*, 341, 117395. <https://doi.org/10.1016/j.molliq.2021.117395>
- Mouallem, J., Fathy, A., Arif, M., & Mahmoud, M. (2023). CO₂ Mineral Trapping Potential of Carbonates: A Numerical Investigation. *SPE Middle East Oil and Gas Show and Conference, MEOS, Proceedings*. <https://doi.org/10.2118/213517-MS>
- Mroczkowska-Szerszeń, M., Nafta-Gaz, M. O.-, & 2018, U. (2018). Infrared spectroscopy methods in reservoir rocks analysis—semiquantitative approach for carbonate rocks. *Bibliotekanauki.PL M Mroczkowska-Szerszeń, M OrzechowskiNafta-Gaz, 2018•bibliotekanauki.PL*. <https://doi.org/10.18668/NG.2018.11.04>
- Muecke, T. W. (1979). Formation Fines and Factors Controlling Their Movement in Porous Media. *Journal of Petroleum Technology*, 31(02), 144–150. <https://doi.org/10.2118/7007-PA>
- Mwangi, P., Brady, P. V., Radonjic, M., & Thyne, G. (2018a). The effect of organic acids on wettability of sandstone and carbonate rocks. *Journal of Petroleum Science and Engineering*, 165, 428–435. <https://doi.org/10.1016/J.PETROL.2018.01.033>
- Mwangi, P., Brady, P. V., Radonjic, M., & Thyne, G. (2018b). The effect of organic acids on wettability of sandstone and carbonate rocks. *Journal of Petroleum Science and Engineering*, 165, 428–435. <https://doi.org/10.1016/J.PETROL.2018.01.033>
- Nader, F. H., De Boever, E., Gasparrini, M., Liberati, M., Dumont, C., Ceriani, A., Morad, S., Lerat, O., & Doligez, B. (2013). Quantification of diagenesis impact on the reservoir properties of the Jurassic Arab D and C members (Offshore, U.A.E.). *Geofluids*, 13(2), 204–220. <https://doi.org/10.1111/GFL.12022>
- Nafisi, F., & Tavakoli, V. (2023). The role of textural parameters of industrial core CT scan images in detecting the petrophysical characteristics of carbonate reservoirs, Permian Dalan Formation, the central Persian Gulf. *Geoenergy Science and Engineering*, 230, 212277. <https://doi.org/10.1016/J.GEOEN.2023.212277>
- Nasr-El-Din, H.A., & Al-Humaidan, A. Y. (2001, April). Iron Sulfide Scale: Formation, Removal and Prevention. *International Symposium on Oilfield Scale*. <https://doi.org/10.2118/68315-MS>
- Nasr-El-Din, Hisham A., Al-Otaibi, M. B., Al-Qahtani, A. A., & Samuel, M. (2007). An Effective Fluid Formulation to Remove Drilling-Fluid MudCake in Horizontal and Multilateral Wells. *SPE Drilling & Completion*, 22(01), 26–32. <https://doi.org/10.2118/87960-PA>
- Nasralla, R., Mahani, H., ... H. van der L.-J. of P., & 2018, U. (2018). Low salinity waterflooding for a carbonate reservoir: Experimental evaluation and numerical interpretation. *Elsevier*. <https://doi.org/https://doi.org/10.1016/j.petro.2018.01.028>
- Nelson, R. C., Lawson, J. B., Thigpen, D. R., & Stegemeier, G. L. (1984). Cosurfactant-Enhanced Alkaline Flooding. *Society of Petroleum Engineers of AIME, (Paper) SPE*, 1, 413–424. <https://doi.org/10.2523/12672-ms>

- Newton, R. C., & Goldsmith, J. R. (1975). Stability of the scapolite meionite ($3\text{CaAl}_2\text{Si}_2\text{O}_2 \cdot \text{CaCO}_3$) at high pressures and storage of CO_2 in the deep crust. *Contributions to Mineralogy and Petrology*, 49(1), 49–62. <https://doi.org/10.1007/BF00371078/METRICS>
- Nguyen, M. B., Le, G. H., Pham, T. T. T., Pham, G. T. T., Quan, T. T. T., Nguyen, T. D., & Vu, T. A. (2020). Novel Nano- Fe_2O_3 - Co_3O_4 Modified Dolomite and Its Use as Highly Efficient Catalyst in the Ozonation of Ammonium Solution. *Journal of Nanomaterials*, 2020. <https://doi.org/10.1155/2020/4593054>
- Nguyen, P., Fadaei, H., & Sinton, D. (2013). Microfluidics underground: A micro-core method for pore scale analysis of supercritical CO_2 reactive transport in saline aquifers. *Journal of Fluids Engineering, Transactions of the ASME*, 135(2), 1–7. <https://doi.org/10.1115/1.4023644>
- Nguyen, T. T., Janik, L. J., & Raupach, M. (1991). Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy in soil studies. *Soil Research*, 29(1), 49–67. <https://doi.org/10.1071/SR9910049>
- Ni, H., & Keppler, H. (2013). Carbon in Silicate Melts. *Reviews in Mineralogy and Geochemistry*, 75(1), 251–287. <https://doi.org/10.2138/RMG.2013.75.9>
- Nikbin, M., Khanehbad, M., Moussavi-Harami, R., Mahboubi, A., Khoddami, M., & Ghofrani, E. (2021). Porosity system analysis and its relation to the permeability of the reservoir zones in the Upper Dalan Member and Kangan Formation: A case study, one of the gas fields in the Zagros Coastal Fars, SW Iran. *Journal of Petroleum Science and Engineering*, 196, 107835. <https://doi.org/10.1016/J.PETROL.2020.107835>
- Nikoo, A. H., & Malayeri, M. R. (2021a). On the affinity of carbonate and sandstone reservoir rocks to scale formation – Impact of rock roughness. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 610, 125699. <https://doi.org/10.1016/J.COLSURFA.2020.125699>
- Nikoo, A. H., & Malayeri, M. R. (2021b). Interfacial interactions between scale-brine and various reservoir rocks. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 611, 125840. <https://doi.org/10.1016/J.COLSURFA.2020.125840>
- Noh, M., Lake, L. W., Bryant, S. L., & Araque-Martinez, A. (2007). Implications of Coupling Fractional Flow and Geochemistry for CO_2 Injection in Aquifers. *SPE Reservoir Evaluation & Engineering*, 10(04), 406–414. <https://doi.org/10.2118/89341-PA>
- Norrish, K. (1954). The swelling of montmorillonite. *Discussions of the Faraday Society*, 18(0), 120–134. <https://doi.org/10.1039/DF9541800120>
- Oelkers, E. H., Gislason, S. R., & Matter, J. (2008). Mineral Carbonation of CO_2 . *Elements*, 4(5), 333–337. <https://doi.org/10.2113/GSELEMENTS.4.5.333>
- Olajire, A. A. (2015). A review of oilfield scale management technology for oil and gas production. *Journal of Petroleum Science and Engineering*, 135, 723–737. <https://doi.org/10.1016/J.PETROL.2015.09.011>
- Olayiwola, S. O., & Dejam, M. (2019). A comprehensive review on interaction of nanoparticles with low salinity water and surfactant for enhanced oil recovery in sandstone and carbonate reservoirs. *Fuel*, 241, 1045–1057. <https://doi.org/10.1016/J.FUEL.2018.12.122>

- Oliveira, G. J. R., de Oliveira, P. C., Surmas, R., Ferreira, L. de P., Markötter, H., Kardjilov, N., Manke, I., Montoro, L. A., & Isaac, A. (2019). Probing the 3D molecular and mineralogical heterogeneity in oil reservoir rocks at the pore scale. *Scientific Reports* 2019 9:1, 9(1), 1–10. <https://doi.org/10.1038/s41598-019-44763-6>
- Omidpour, A., Rahimpour-Bonab, H., Moussavi-Harami, R., & Mahboubi, A. (2023). Anhydrite fabrics as an indicator for relative sea-level signatures in the sequence stratigraphic framework of a carbonate ramp. *Marine and Petroleum Geology*, 155, 106400. <https://doi.org/10.1016/J.MARPETGEO.2023.106400>
- Osinga, S., Zambrano-Narvaez, G., & Chalaturnyk, R. J. (2015). *Study of Geomechanical Properties Of 3D Printed Sandstone Analogue*. OnePetro.
- Ostovari, H., Müller, L., Mayer, F., & Bardow, A. (2022). A climate-optimal supply chain for CO₂ capture, utilization, and storage by mineralization. *Journal of Cleaner Production*, 360, 131750. <https://doi.org/10.1016/J.JCLEPRO.2022.131750>
- Ouyang, M., & Cao, Y. (2023). Utilizations of reaction exothermic heat to compensate the cost of the permanent CO₂ sequestration through the geological mineral CO₂ carbonation. *Energy*, 284, 128626. <https://doi.org/10.1016/J.ENERGY.2023.128626>
- Ouyang, Z., Liu, D., Cai, Y., & Yao, Y. (2016). Fractal Analysis on Heterogeneity of Pore-Fractures in Middle-High Rank Coals with NMR. *Energy and Fuels*, 30(7), 5449–5458. https://doi.org/10.1021/ACS.ENERGYFUELS.6B00563/ASSET/IMAGES/LARGE/EF-2016-005637_0011.JPEG
- Pan, F., McPherson, B. J., Esser, R., Xiao, T., Appold, M. S., Jia, W., & Moodie, N. (2016). Forecasting evolution of formation water chemistry and long-term mineral alteration for GCS in a typical clastic reservoir of the Southwestern United States. *International Journal of Greenhouse Gas Control*, 54, 524–537. <https://doi.org/10.1016/J.IJGGC.2016.07.035>
- Pang, X., Wang, G., Kuang, L., Li, H., Zhao, Y., Li, D., Zhao, X., Wu, S., Feng, Z., & Lai, J. (2022). Insights into the pore structure and oil mobility in fine-grained sedimentary rocks: The Lucaogou Formation in Jimusar Sag, Junggar Basin, China. *Marine and Petroleum Geology*, 137, 105492. <https://doi.org/10.1016/J.MARPETGEO.2021.105492>
- Parkinson, D. (2018a). Carbon Mineralization. *Methods of Soil Analysis, Part 2: Microbiological and Biochemical Properties*, 835–863. <https://doi.org/10.2136/SSSABOOKSER5.2.C38>
- Parkinson, D. (2018b). Carbon Mineralization. *Methods of Soil Analysis, Part 2: Microbiological and Biochemical Properties*, 835–863. <https://doi.org/10.2136/SSSABOOKSER5.2.C38>
- Pawar, R. J., Bromhal, G. S., Carey, J. W., Foxall, W., Korre, A., Ringrose, P. S., Tucker, O., Watson, M. N., & White, J. A. (2015). Recent advances in risk assessment and risk management of geologic CO₂ storage. *International Journal of Greenhouse Gas Control*, 40, 292–311. <https://doi.org/10.1016/J.IJGGC.2015.06.014>
- Peng, S., Marone, F., & Dultz, S. (2014). Resolution effect in X-ray microcomputed tomography imaging and small pore's contribution to permeability for a Berea sandstone. *Journal of Hydrology*, 510, 403–411. <https://doi.org/10.1016/j.jhydrol.2013.12.028>
- Perras, M. A., & Vogler, D. (2019). Compressive and Tensile Behavior of 3D-Printed and Natural Sandstones. *Transport in Porous Media*, 129(2), 559–581. <https://doi.org/10.1007/S11242->

- Pfeifer, P., & Avnir, D. (1983). Chemistry in noninteger dimensions between two and three. I. Fractal theory of heterogeneous surfaces. *The Journal of Chemical Physics*, 79(7), 3558–3565. <https://doi.org/10.1063/1.446210>
- Pierre, A., Lamarche, J. M., Merciei, R., Foissy, A., & Persello, J. (1990). Calcium as potential determining ion in aqueous calcite suspensions. *Journal of Dispersion Science and Technology*, 11(6), 611–635. <https://doi.org/10.1080/01932699008943286>
- Pokrovsky, O. S., Golubev, S. V., Schott, J., & Castillo, A. (2009). Calcite, dolomite and magnesite dissolution kinetics in aqueous solutions at acid to circumneutral pH, 25 to 150 °C and 1 to 55 atm pCO₂: New constraints on CO₂ sequestration in sedimentary basins. *Chemical Geology*, 265(1–2), 20–32. <https://doi.org/10.1016/J.CHEMGEO.2009.01.013>
- Power, I. M., Harrison, A. L., Dipple, G. M., Wilson, S. A., Kelemen, P. B., Hitch, M., & Southam, G. (2013a). Carbon Mineralization: From Natural Analogues to Engineered Systems. *Reviews in Mineralogy and Geochemistry*, 77(1), 305–360. <https://doi.org/10.2138/RMG.2013.77.9>
- Power, I. M., Harrison, A. L., Dipple, G. M., Wilson, S. A., Kelemen, P. B., Hitch, M., & Southam, G. (2013b). Carbon Mineralization: From Natural Analogues to Engineered Systems. *Reviews in Mineralogy and Geochemistry*, 77(1), 305–360. <https://doi.org/10.2138/RMG.2013.77.9>
- Powers, R. W., Ramirez, L. F., Redmond, C. D., & Jr., E. L. E. (1966). Geology of the Arabian Peninsula: Sedimentary geology of Saudi Arabia. *Professional Paper*. <https://doi.org/10.3133/PP560D>
- Prabhakar, S., & Melnik, R. (2017). Wettability alteration of calcite oil wells: Influence of smart water ions. *Scientific Reports*, 7(1), 17365. <https://doi.org/10.1038/s41598-017-17547-z>
- Prakash, R., Kana Nguene, P., Seers, T. D., Noshadravan, A., & Abedi, S. (2019). *Chemo-mechanical investigation of CO₂ -fluid-rock interaction in CO₂ storage and CO₂ -EOR processes in unconventional reservoirs*.
- Pu, H., Xie, X., Yin, P., & Morrow, N. R. (2010). Low Salinity Waterflooding and Mineral Dissolution. *Proceedings - SPE Annual Technical Conference and Exhibition*, 2, 1574–1590. <https://doi.org/10.2118/134042-MS>
- Pudlo, D., Henkel, S., Enzmann, F., Heister, K., Werner, L., Ganzer, L., Reitenbach, V., Albrecht, D., & Gaupp, R. (2014). The Relevance of Mineral Mobilization and -Dissolution on the Reservoir Quality of Sandstones in CO₂ Storage Sites. *Energy Procedia*, 59, 390–396. <https://doi.org/10.1016/J.EGYPRO.2014.10.393>
- Purswani, P., Tawfik, M. S., & Karpyn, Z. T. (2017). Factors and Mechanisms Governing Wettability Alteration by Chemically Tuned Waterflooding: A Review. *Energy and Fuels*, 31(8), 7734–7745. <https://doi.org/10.1021/ACS.ENERGYFUELS.7B01067>
- Puthiya Veetil, S. K., Rebane, K., Yörük, C. R., Lopp, M., Trikkel, A., & Hitch, M. (2021). Aqueous mineral carbonation of oil shale mine waste (limestone): A feasibility study to develop a CO₂ capture sorbent. *Energy*, 221, 119895. <https://doi.org/10.1016/J.ENERGY.2021.119895>
- Putnis, A. (2002). Mineral replacement reactions: from macroscopic observations to microscopic

- mechanisms. *Mineralogical Magazine*, 66(5), 689–708.
<https://doi.org/10.1180/0026461026650056>
- Qiao, C., Johns, R., & Li, L. (2016). Modeling Low-Salinity Waterflooding in Chalk and Limestone Reservoirs. *Energy and Fuels*, 30(2), 884–895.
https://doi.org/10.1021/ACS.ENERGYFUELS.5B02456/ASSET/IMAGES/LARGE/EF-2015-02456B_0010.JPEG
- Rao, Y., Guo, Q., Zhang, S., & Liao, L. (2023). Comparative Study on Gemmological Characteristics and Luminescence of Colorless and Yellow Scapolites. *Crystals*, 13(3), 462.
<https://doi.org/10.3390/CRYST13030462/S1>
- Rashid, F., Glover, P. W. J., Lorinczi, P., Hussein, D., & Lawrence, J. A. (2017). Microstructural controls on reservoir quality in tight oil carbonate reservoir rocks. *Journal of Petroleum Science and Engineering*, 156, 814–826. <https://doi.org/10.1016/J.PETROL.2017.06.056>
- Rathnaweera, T. D., Ranjith, P. G., Perera, M. S. A., Haque, A., Lashin, A., Al Arifi, N., Chandrasekharam, D., Yang, S. Q., Xu, T., Wang, S. H., & Yasar, E. (2015). CO₂-induced mechanical behaviour of Hawkesbury sandstone in the Gosford basin: An experimental study. *Materials Science and Engineering: A*, 641, 123–137.
<https://doi.org/10.1016/J.MSEA.2015.05.029>
- Raza, A., Glatz, G., Gholami, R., Mahmoud, M., & Alafnan, S. (2022). Carbon mineralization and geological storage of CO₂ in basalt: Mechanisms and technical challenges. *Earth-Science Reviews*, 229, 104036. <https://doi.org/10.1016/J.EARSCIREV.2022.104036>
- Raza, W., Raza, N., Agbe, H., Kumar, R. V., Kim, K. H., & Yang, J. (2018). Multistep sequestration and storage of CO₂ to form valuable products using forsterite. *Energy*, 155, 865–873.
<https://doi.org/10.1016/J.ENERGY.2018.05.077>
- Reedy, C. L., Anderson, J., Reedy, T. J., & Liu, Y. (2014). Image Analysis in Quantitative Particle Studies of Archaeological Ceramic Thin Sections. *Advances in Archaeological Practice*, 2(4), 252–268. <https://doi.org/10.7183/2326-3768.2.4.252>
- Rezaeidoust, A., Puntervold, T., Strand, S., & Austad, T. (2009). Smart Water as Wettability Modifier in Carbonate and Sandstone: A Discussion of Similarities/Differences in the Chemical Mechanisms. *Energy and Fuels*, 23(9), 4479–4485.
<https://doi.org/10.1021/EF900185Q>
- Riazi, M. (2018). Influences of Asphaltene Deposition on Formation Damage and Gas Coning. *Biomedical Journal of Scientific & Technical Research*, 3(5), 3561–3565.
<https://doi.org/10.26717/BJSTR.2018.03.000960>
- Ricci, J. L., Weiner, M. J., Mamidwar, S., & Alexander, H. (2008). Calcium sulfate. *Bioceramics and Their Clinical Applications*, 302–325. <https://doi.org/10.1533/9781845694227.2.302>
- Ricci, M., Spijker, P., Stellacci, F., Molinari, J. F., & Voitchovsky, K. (2013). Direct visualization of single ions in the Stern layer of calcite. *Langmuir*, 29(7), 2207–2216.
<https://doi.org/10.1021/la3044736>
- Rice-Birchall, E., Faulkner, D. R., & Bedford, J. D. (2021). The manufacture, mechanical properties, and microstructural analysis of synthetic quartz-cemented sandstones. *International Journal of Rock Mechanics and Mining Sciences*, 146, 104869.

<https://doi.org/10.1016/J.IJRMMS.2021.104869>

- Riffaldi, R., Saviozzi, A., & Levi-Minzi, R. (1996). Carbon mineralization kinetics as influenced by soil properties. *Biology and Fertility of Soils*, 22(4), 293–298. <https://doi.org/10.1007/BF00334572/METRICS>
- Rochelle, C. A., Czernichowski-Lauriol, I., & Milodowski, A. E. (2004). The impact of chemical reactions on CO₂ storage in geological formations: A brief review. *Geological Society Special Publication*, 233, 87–106. <https://doi.org/10.1144/GSL.SP.2004.233.01.07>
- Rodrigues, R., Levant, M., & Klimenko, A. (2022). Relevance of zeta potential as a tool for predicting the response of controlled salinity waterflooding in oil–water–carbonate systems. *Fuel*, 324(PB), 124629. <https://doi.org/10.1016/j.fuel.2022.124629>
- Rodriguez, F., Rousseau, D., Bekri, S., Djabourov, M., & Bejarano, C. (2014). *Polymer Flooding for Extra-Heavy Oil : New Insights on the Key Polymer*.
- Romanov, V., Soong, Y., Carney, C., Rush, G. E., Nielsen, B., & O'Connor, W. (2015). Mineralization of Carbon Dioxide: A Literature Review. *ChemBioEng Reviews*, 2(4), 231–256. <https://doi.org/10.1002/CBEN.201500002>
- Romero-Flores, M., García-Cuellar, A. J., Montesinos-Castellanos, A., & Lopez-Salinas, J. L. (2018). Modeling surfactant adsorption/retention and transport through porous media. *Chemical Engineering Science*, 183, 190–199. <https://doi.org/10.1016/J.CES.2018.02.048>
- Roncal-Herrero, T., Astilleros, J. M., Bots, P., Rodríguez-Blanco, J. D., Prieto, M., Benning, L. G., & Fernández-Díaz, L. (2017). Reaction pathways and textural aspects of the replacement of anhydrite by calcite at 25 °C. *American Mineralogist*, 102(6), 1270–1278. <https://doi.org/10.2138/AM-2017-5963CCBY>
- Rosenbauer, R. J., Koksalan, T., & Palandri, J. L. (2005). Experimental investigation of CO₂–brine–rock interactions at elevated temperature and pressure: Implications for CO₂ sequestration in deep-saline aquifers. *Fuel Processing Technology*, 86(14–15), 1581–1597. <https://doi.org/10.1016/J.FUPROC.2005.01.011>
- Rücker, M., Bartels, W. B., Bultreys, T., Boone, M., Singh, K., Garfi, G., Scanziani, A., Spurin, C., Yesufu-Rufai, S., Krevor, S., Blunt, M. J., Wilson, O., Mahani, H., Cnudde, V., Luckham, P. F., Georgiadis, A., & Berg, S. (2020). Workflow for Upscaling Wettability from the Nanoscale to Core Scale. *Petrophysics - The SPWLA Journal of Formation Evaluation and Reservoir Description*, 61(02), 189–205. <https://doi.org/10.30632/PJV61N2-2020A5>
- Ruiz-Agudo, C., Álvarez-Lloret, P., Lorenzo, F. Di, Gebauer, D., & Putnis, C. V. (2019). Baryte cohesive layers formed on a (010) gypsum surface by a pseudomorphic replacement. *European Journal of Mineralogy*, 31(2), 289–299. <https://doi.org/10.1127/EJM/2019/0031-2847>
- Ruiz-Agudo, E., Putnis, C. V., Hövelmann, J., Álvarez-Lloret, P., Ibáñez-Velasco, A., & Putnis, A. (2015). Experimental study of the replacement of calcite by calcium sulphates. *Geochimica et Cosmochimica Acta*, 156, 75–93. <https://doi.org/10.1016/J.GCA.2015.02.012>
- Ruppel, S., & Bebout, D. (1996). *Effects of stratal architecture and diagenesis on reservoir development in the Grayburg formation: SSouth Cowden field, Ector County, Texas. Annual report, 1 October 1994--30 September 1995*. <https://doi.org/10.2172/207042>

- Sadeghi, M., Hashemi, R., & Shahverdi, H. (2022). A contribution to flotation technique as a reliable wettability alteration measurement method for carbonate minerals in separation processes involving hydrocarbons, low salinity water and nanofluids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 633, 127912. <https://doi.org/10.1016/J.COLSURFA.2021.127912>
- Sadeqi-Moqadam, M., Riahi, S., & Bahramian, A. (2016). An investigation into the electrical behavior of oil/water/reservoir rock interfaces: The implication for improvement in wettability prediction. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 490, 268–282. <https://doi.org/10.1016/J.COLSURFA.2015.11.040>
- Sakuma, H., Andersson, M. P., Bechgaard, K., & Stipp, S. L. S. (2014). Surface tension alteration on calcite, induced by ion substitution. *Journal of Physical Chemistry C*, 118(6), 3078–3087. <https://doi.org/10.1021/jp411151u>
- Sanaei, A., Tavassoli, S., & Sepehrnoori, K. (2018). Investigation of Modified Water Chemistry for Improved Oil Recovery: Application of DLVO Theory and Surface Complexation Model. *SPE Western Regional Meeting*, 574, 131–145. <https://doi.org/10.2118/190017-MS>
- Sanni, O., Charpentier, T., Kapur, N., & Neville, A. (2015). *Study of Surface Deposition and Bulk Scaling Kinetics in Oilfield Conditions Using an In-Situ Flow Rig | NACE CORROSION | OnePetro*. <https://onepetro.org/NACECORR/proceedings-abstract/CORR15/All-CORR15/NACE-2015-5916/65917>
- Sarg, J. F. (2001). The sequence stratigraphy, sedimentology, and economic importance of evaporite–carbonate transitions: a review. *Sedimentary Geology*, 140(1–2), 9–34. [https://doi.org/10.1016/S0037-0738\(00\)00170-6](https://doi.org/10.1016/S0037-0738(00)00170-6)
- Sari, A., Al Maskari, N. S., Saeedi, A., & Xie, Q. (2020). Impact of surface roughness on wettability of oil-brine-calcite system at sub-pore scale. *Journal of Molecular Liquids*, 299, 112107. <https://doi.org/10.1016/J.MOLLIQ.2019.112107>
- Satish-Kumar, M., Hermann, J., Tsunogae, T., & Osanai, Y. (2006). Carbonation of Cl-rich scapolite boudins in Skallen, East Antarctica: evidence for changing fluid condition in the continental crust. *Journal of Metamorphic Geology*, 24(3), 241–261. <https://doi.org/10.1111/J.1525-1314.2006.00635.X>
- Saxena, N., Goswami, A., Dhodapkar, P. K., Nihalani, M. C., & Mandal, A. (2019). Bio-based surfactant for enhanced oil recovery: Interfacial properties, emulsification and rock-fluid interactions. *Journal of Petroleum Science and Engineering*, 176(November 2018), 299–311. <https://doi.org/10.1016/j.petrol.2019.01.052>
- Schanofski, M., Koch, L., & Schmidt, B. C. (2023). CO₂ quantification in silicate glasses using μ -ATR FTIR spectroscopy. *American Mineralogist*, 108(7), 1346–1356. <https://doi.org/10.2138/AM-2022-8477>
- Schlueter, E. M., Zimmerman, R. W., Witherspoon, P. A., & Cook, N. G. W. (1997). The fractal dimension of pores in sedimentary rocks and its influence on permeability. *Engineering Geology*, 48(3–4), 199–215. [https://doi.org/10.1016/S0013-7952\(97\)00043-4](https://doi.org/10.1016/S0013-7952(97)00043-4)
- Schmatz, J., Urai, J. L., Berg, S., & Ott, H. (2015). Nanoscale imaging of pore-scale fluid-fluid-solid contacts in sandstone. *Geophysical Research Letters*, 42(7), 2189–2195.

<https://doi.org/10.1002/2015GL063354>

- Serafeimidis, K., & Anagnostou, G. (2015). The Solubilities and Thermodynamic Equilibrium of Anhydrite and Gypsum. *Rock Mechanics and Rock Engineering*, 48(1), 15–31. <https://doi.org/10.1007/S00603-014-0557-1/FIGURES/8>
- Serafeimidis, K., Anagnostou, G., & Vrakas, A. (2015). Scale effects in relation to swelling pressure in anhydritic claystones. *Geomechanics from Micro to Macro*, 2, 795–800. <https://doi.org/10.1201/B17395-142>
- Setta, F. A., & Neville, A. (2011). Efficiency assessment of inhibitors on CaCO₃ precipitation kinetics in the bulk and deposition on a stainless steel surface (316 L). *Desalination*, 281(1), 340–347. <https://doi.org/10.1016/J.DESAL.2011.08.021>
- Shafiq, M. U., Ben Mahmud, H. K., & Arif, M. (2018). Mineralogy and pore topology analysis during matrix acidizing of tight sandstone and dolomite formations using chelating agents. *Journal of Petroleum Science and Engineering*, 167, 869–876. <https://doi.org/10.1016/J.PETROL.2018.02.057>
- Shahsavari, M. H., & Shakiba, M. (2022). An experimental insight into the influence of sand grain size distribution on the petrophysical and geomechanical properties of artificially made sandstones. *Journal of Petroleum Science and Engineering*, 215, 110632. <https://doi.org/10.1016/J.PETROL.2022.110632>
- Shao, Xinhe, Pang, X., Li, H., & Zhang, X. (2017). Fractal Analysis of Pore Network in Tight Gas Sandstones Using NMR Method: A Case Study from the Ordos Basin, China. *Energy and Fuels*, 31(10), 10358–10368. https://doi.org/10.1021/ACS.ENERGYFUELS.7B01007/ASSET/IMAGES/LARGE/EF-2017-010076_0011.JPEG
- Shao, Xu, Qin, B., Shi, Q., Yang, Y., Ma, Z., Li, Y., Jiang, Z., & Jiang, W. (2024). The impacts of CO₂ mineralization reaction on the physicochemical characteristics of fly ash: A study under different reaction conditions of the water-to-solid ratio and the pressure of CO₂. *Energy*, 287, 129676. <https://doi.org/10.1016/J.ENERGY.2023.129676>
- Sharma, H., Dufour, S., Arachchilage, G. W. P. P., Weerasooriya, U., Pope, G. A., & Mohanty, K. (2015). Alternative alkalis for ASP flooding in anhydrite containing oil reservoirs. *Fuel*, 140, 407–420. <https://doi.org/10.1016/J.FUEL.2014.09.082>
- Sharma, H., & Mohanty, K. K. (2018a). An experimental and modeling study to investigate brine-rock interactions during low salinity water flooding in carbonates. *Journal of Petroleum Science and Engineering*, 165, 1021–1039. <https://doi.org/10.1016/j.petrol.2017.11.052>
- Sharma, H., & Mohanty, K. K. (2018b). An experimental and modeling study to investigate brine-rock interactions during low salinity water flooding in carbonates. *Journal of Petroleum Science and Engineering*, 165, 1021–1039. <https://doi.org/10.1016/J.PETROL.2017.11.052>
- Sharma, H., & Mohanty, K. K. (2022). Modeling of low salinity waterflooding in carbonates: Effect of rock wettability and organic acid distribution. *Journal of Petroleum Science and Engineering*, 208, 109624. <https://doi.org/10.1016/J.PETROL.2021.109624>
- Shen, Y. J., Zhang, Y. L., Gao, F., Yang, G. S., & Lai, X. P. (2018). Influence of Temperature on the Microstructure Deterioration of Sandstone. *Energies* 2018, Vol. 11, Page 1753, 11(7), 1753.

<https://doi.org/10.3390/EN11071753>

- Shojai Kaveh, N., Rudolph, E. S. J., Van Hemert, P., Rossen, W. R., & Wolf, K. H. (2014). Wettability evaluation of a CO₂/water/bentheimer sandstone system: Contact angle, dissolution, and bubble size. *Energy and Fuels*, 28(6), 4002–4020. https://doi.org/10.1021/EF500034J/SUPPL_FILE/EF500034J_SI_001.PDF
- Siddig, O., Mahmoud, A. A., & Elkatatny, S. (2022). A review of the various treatments of oil-based drilling fluids filter cakes. *Journal of Petroleum Exploration and Production Technology*, 12(2), 365–381. <https://doi.org/10.1007/s13202-021-01427-4>
- Snosy, M. F., Abu El Ela, M., El-Banbi, A., & Sayyoub, H. (2021). Comprehensive investigation of low salinity waterflooding in carbonate reservoirs. *Journal of Petroleum Exploration and Production Technology*, 0123456789. <https://doi.org/10.1007/s13202-021-01330-y>
- Sohal, M. A., Thyne, G., & Sogaard, E. G. (2017). Effect of the Temperature on Wettability and Optimum Wetting Conditions for Maximum Oil Recovery in a Carbonate Reservoir System. *Energy and Fuels*, 31(4), 3557–3566. https://doi.org/10.1021/ACS.ENERGYFUELS.6B02612/ASSET/IMAGES/LARGE/EF-2016-02612H_0008.JPEG
- Sokolova, E., & Hawthorne, F. C. (2008). THE CRYSTAL CHEMISTRY OF THE SCAPOLITE-GROUP MINERALS. I. CRYSTAL STRUCTURE AND LONG-RANGE ORDER. *The Canadian Mineralogist*, 46(6), 1527–1554. <https://doi.org/10.3749/CANMIN.46.6.1527>
- Song, J., Wang, Q., Shaik, I., Puerto, M., Bikkina, P., Aichele, C., Biswal, S. L., & Hirasaki, G. J. (2020). Effect of salinity, Mg²⁺ and SO₄²⁻ on “smart water”-induced carbonate wettability alteration in a model oil system. *Journal of Colloid and Interface Science*, 563, 145–155. <https://doi.org/10.1016/j.jcis.2019.12.040>
- Song, W., & Kovscek, A. R. (2015). Functionalization of micromodels with kaolinite for investigation of low salinity oil-recovery processes. *Lab on a Chip*, 15(16), 3314–3325. <https://doi.org/10.1039/c5lc00544b>
- Song, Yao, Zou, Q., Su, E., Zhang, Y., & Sun, Y. (2020). Changes in the microstructure of low-rank coal after supercritical CO₂ and water treatment. *Fuel*, 279, 118493. <https://doi.org/10.1016/J.FUEL.2020.118493>
- Song, Youngsoo, Jun, S., Na, Y., Kim, K., Jang, Y., & Wang, J. (2023). Geomechanical challenges during geological CO₂ storage: A review. *Chemical Engineering Journal*, 456, 140968. <https://doi.org/10.1016/J.CEJ.2022.140968>
- Souayah, M., Al-Maamari, R. S., Karimi, M., & Aoudia, M. (2021). Wettability alteration and oil recovery by surfactant assisted low salinity water in carbonate rock: The impact of nonionic/anionic surfactants. *Journal of Petroleum Science and Engineering*, 197, 108108. <https://doi.org/10.1016/J.PETROL.2020.108108>
- Soulgani, B. S., Reisi, F., & Norouzi, F. (2020). Investigation into mechanisms and kinetics of asphaltene aggregation in toluene/n-hexane mixtures. *Petroleum Science*, 17(2), 457–466. <https://doi.org/10.1007/s12182-019-00383-3>
- Speelman, H. P., & Schwarcz, E. L. (1965). Determination of sulfur and carbon coordination in scapolite by infra-red absorption spectrophotometry | *American Mineralogist* |

- GeoScienceWorld*. https://pubs.geoscienceworld.org/msa/ammin/article/50/5-6/656/540090/Determination-of-sulfur-and-carbon-coordination-in?casa_token=_3eXrlXYbMIAAAAAA: xu5G4z3BjLoHWAMaYWOrFiCu2cK-dKGEnqBkjPZmW50abhClrWMPwWjm4eufnXcsXldqNSPhmA
- Stalker, R., Collins, I. R., & Graham, G. M. (2003). The Impact of Chemical Incompatibilities in Commingled Fluids on the Efficiency of a Produced Water Reinjection System: A North Sea Example. *SPE International Symposium on Oilfield Chemistry*, 441–453. <https://doi.org/10.2118/80257-MS>
- Strand, S., Høgnesen, E. J., & Austad, T. (2006). Wettability alteration of carbonates - Effects of potential determining ions (Ca²⁺ and SO₄²⁻) and temperature. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 275(1–3), 1–10. <https://doi.org/10.1016/j.colsurfa.2005.10.061>
- Swayze, G. A., & Clark, R. N. (1990). Infrared spectra and crystal chemistry of scapolites: Implications for Martian mineralogy. *Journal of Geophysical Research: Solid Earth*, 95(B9), 14481–14495. <https://doi.org/10.1029/JB095IB09P14481>
- Taheriotagsara, M., Eftekhari, A. A., & Nick, H. M. (2020). Adsorption- and Diffusion-Controlled Wettability Change in Modified Salinity Water Flooding. *Energy & Fuels*, 34(11), 13767–13781. <https://doi.org/10.1021/acs.energyfuels.0c02493>
- Tang, Y., Hou, C., He, Y., Wang, Y., Chen, Y., & Rui, Z. (2021). Review on Pore Structure Characterization and Microscopic Flow Mechanism of CO₂ Flooding in Porous Media. *Energy Technology*, 9(1), 1–21. <https://doi.org/10.1002/ente.202000787>
- Tang, Y., Hu, S., He, Y., Wang, Y., Wan, X., Cui, S., & Long, K. (2021). Experiment on CO₂-brine-rock interaction during CO₂ injection and storage in gas reservoirs with aquifer. *Chemical Engineering Journal*, 413, 127567. <https://doi.org/10.1016/J.CEJ.2020.127567>
- Teertstra, D. K., Schindler, M., Sherriff, B. L., & Hawthorne, F. C. (1999). Silicalite, a new sulfate-dominant member of the scapolite group with an Al-Si composition near the 14/ m – P 4 2 / n phase transition . *Mineralogical Magazine*, 63(3), 321–329. <https://doi.org/10.1180/002646199548547>
- Teertstra, David K., & Sherriff, B. L. (1996). Scapolite cell-parameter trends along the solid-solution series. *American Mineralogist*, 81(1–2), 169–180. <https://doi.org/10.2138/AM-1996-1-221>
- Tetteh, J. T., Barimah, R., & Korsah, P. K. (2022). Ionic Interactions at the Crude Oil–Brine–Rock Interfaces Using Different Surface Complexation Models and DLVO Theory: Application to Carbonate Wettability. *ACS Omega*, 7(8), 7199–7212. <https://doi.org/10.1021/acsomega.1c06954>
- Tetteh, J. T., Brady, P. V., & Barati Ghahfarokhi, R. (2020). Review of low salinity waterflooding in carbonate rocks: mechanisms, investigation techniques, and future directions. *Advances in Colloid and Interface Science*, 284, 102253. <https://doi.org/10.1016/J.CIS.2020.102253>
- Thomas, N. C., Ghosh, B., Alameri, W. S., & Kilybay, A. (2016). Alkali and Hybrid-Alkali Flooding as a Tertiary Oil Recovery Mode: Prospects and Challenges. *International Journal of Petroleum and Petrochemical Engineering*, 2(2), 22–31. <https://doi.org/10.20431/2454-7980.0202005>

- Tirjoo, A., Bayati, B., Rezaei, H., & Rahmati, M. (2019). Molecular dynamics simulations of asphaltene aggregation under different conditions. *Journal of Petroleum Science and Engineering*, 177(November 2018), 392–402. <https://doi.org/10.1016/j.petrol.2019.02.041>
- Todd, S. H., & Peter, M. B. (2005). Direct measurements of pH and dissolved CO₂ in H₂O-CO₂ brine mixtures to supercritical conditions. *Greenhouse Gas Control Technologies*, 2169–2173. <https://doi.org/10.1016/B978-008044704-9/50294-9>
- Tooseh, E. K., Jafari, A., & TEYMOURI, A. (2018). Gas-water-rock interactions and factors affecting gas storage capacity during natural gas storage in a low permeability aquifer. *Petroleum Exploration and Development*, 45(6), 1123–1128. [https://doi.org/10.1016/S1876-3804\(18\)30115-0](https://doi.org/10.1016/S1876-3804(18)30115-0)
- Torró, L., Martin, R. F., Schumann, D., Cox, J., Medina, S. G., Carles, J., & Draper, M. (2018). The incipient flash melting of scapolite and plagioclase megacrysts in alkali basalts of the Olot suite, Catalunya, Spain, and at Chuquet Genestoux, Puy-de-Dôme, France. *European Journal of Mineralogy*, 30(1), 45–59. <https://doi.org/10.1127/EJM/2017/0029-2682>
- Totland, C., Lewis, R. T., & Nerdal, W. (2011). 1H NMR relaxation of water: A probe for surfactant adsorption on kaolin. *Journal of Colloid and Interface Science*, 363(1), 362–370. <https://doi.org/10.1016/J.JCIS.2011.07.064>
- Uetani, T., Kaido, H., & Yonebayashi, H. (2019). Investigation of Anhydrite Dissolution as a Potential Low Salinity Waterflooding Mechanism Using Carbonate Reservoir Rocks. *International Petroleum Technology Conference 2019, IPTC 2019*. <https://doi.org/10.2523/IPTC-19133-MS>
- Usman, M., Siddiqui, N. A., Mathew, M., Zhang, S., El-Ghali, M. A. K., Ramkumar, M., Jamil, M., & Zhang, Y. (2020). Linking the influence of diagenetic properties and clay texture on reservoir quality in sandstones from NW Borneo. *Marine and Petroleum Geology*, 120, 104509. <https://doi.org/10.1016/J.MARPETGEO.2020.104509>
- Vanko, D. A., & Bishop, F. C. (1982). Occurrence and origin of marialitic scapolite in the Humboldt lopolith, N.W. Nevada. *Contributions to Mineralogy and Petrology*, 81(4), 277–289. <https://doi.org/10.1007/BF00371682/METRICS>
- Vega, B., Dutta, A., & Kovscek, A. R. (2014). CT Imaging of Low-Permeability, Dual-Porosity Systems Using High X-ray Contrast Gas. *Transport in Porous Media*, 101(1), 81–97. <https://doi.org/10.1007/s11242-013-0232-0>
- Verri, G., Sorbie, K. S., & Silva, D. (2017). A rigorous general workflow for accurate prediction of carbonate and sulphide scaling profiles in oil and gas wells. *Journal of Petroleum Science and Engineering*, 156, 673–681. <https://doi.org/10.1016/J.PETROL.2017.06.037>
- Vivanco, D. C., & Alberto, C. (2017). *SURFACTANT AND POLYMER RETENTION IN CHEMICAL ENHANCED OIL RECOVERY*.
- Volokitin, Y. E., Koltsov, I. N., Evseeva, M. Y., Nurieva, O. A., Akhatov, I. S., Kovaleva, L. A., Zinnatullin, R. R., Mavletov, M. V., & Kudasheva, F. H. (2014). Experimental studies of surfactant adsorption under conditions of ASP flooding at West Salym field. *Society of Petroleum Engineers - SPE Russian Oil and Gas Exploration and Production Technical Conference and Exhibition 2014, RO and G 2014 - Sustaining and Optimising Production:*

- Challenging the Limits with Technology*, 1, 694–706. <https://doi.org/10.2118/171223-ms>
- Wang, B., Pan, Z., Cheng, H., Zhang, Z., & Cheng, F. (2021). A review of carbon dioxide sequestration by mineral carbonation of industrial byproduct gypsum. *Journal of Cleaner Production*, 302, 126930. <https://doi.org/10.1016/J.JCLEPRO.2021.126930>
- Wang, B., Pan, Z., Du, Z., Cheng, H., & Cheng, F. (2019). Effect of impure components in flue gas desulfurization (FGD) gypsum on the generation of polymorph CaCO_3 during carbonation reaction. *Journal of Hazardous Materials*, 369, 236–243. <https://doi.org/10.1016/J.JHAZMAT.2019.02.002>
- Wang, F., Lian, P., Jiao, L., Liu, Z., Zhao, J., & Gao, J. (2018). Fractal analysis of microscale and nanoscale pore structures in carbonates using high-pressure mercury intrusion. *Geofluids*, 2018. <https://doi.org/10.1155/2018/4023150>
- Wang, Hanxun, Zhang, B., Wang, L., Yu, X., Shi, L., & Fu, D. (2020). Experimental investigation on the long-term interactions of anhydrite rock, crude oil, and water in a mine-out space for crude-oil storage. *Engineering Geology*, 265, 105414. <https://doi.org/10.1016/J.ENGGEOL.2019.105414>
- Wang, Heming, Liu, Y., Song, Y., Zhao, Y., Zhao, J., & Wang, D. (2012). Fractal analysis and its impact factors on pore structure of artificial cores based on the images obtained using magnetic resonance imaging. *Journal of Applied Geophysics*, 86, 70–81. <https://doi.org/10.1016/J.JAPPGEO.2012.07.015>
- Wang, Heng, Alvarado, V., McLaughlin, J. F., Bagdonas, D. A., Kaszuba, J. P., Campbell, E., & Grana, D. (2018). Low-Field Nuclear Magnetic Resonance Characterization of Carbonate and Sandstone Reservoirs From Rock Spring Uplift of Wyoming. *Journal of Geophysical Research: Solid Earth*, 123(9), 7444–7460. <https://doi.org/10.1029/2018JB015779>
- Wang, Heng, Kou, Z., Ji, Z., Wang, S., Li, Y., Jiao, Z., Johnson, M., & McLaughlin, J. F. (2023). Investigation of enhanced CO_2 storage in deep saline aquifers by WAG and brine extraction in the Minnelusa sandstone, Wyoming. *Energy*, 265, 126379. <https://doi.org/10.1016/J.ENERGY.2022.126379>
- Wang, J., Han, M., Fuseni, A. B., & Cao, D. (2015). Surfactant adsorption in Surfactant-Polymer flooding for carbonate reservoirs. *SPE Middle East Oil and Gas Show and Conference, MEOS, Proceedings, 2015-Janua*, 1736–1746. <https://doi.org/10.2118/172700-ms>
- Wang, K., Taylor, K. G., & Ma, L. (2021). Advancing the application of atomic force microscopy (AFM) to the characterization and quantification of geological material properties. *International Journal of Coal Geology*, 247, 103852. <https://doi.org/10.1016/J.COAL.2021.103852>
- Wang, M., Pande, G. N., Kong, L. W., & Feng, Y. T. (2017). Comparison of Pore-Size Distribution of Soils Obtained by Different Methods. *International Journal of Geomechanics*, 17(1), 06016012. [https://doi.org/10.1061/\(ASCE\)GM.1943-5622.0000696/ASSET/C5350347-F92A-4CF4-A240-C89E5CDF052B/ASSETS/IMAGES/LARGE/FIGURE8.JPG](https://doi.org/10.1061/(ASCE)GM.1943-5622.0000696/ASSET/C5350347-F92A-4CF4-A240-C89E5CDF052B/ASSETS/IMAGES/LARGE/FIGURE8.JPG)
- Wang, Xiaolei, Geng, J., Zhang, D., Xiao, W., Chen, Y., & Zhang, H. (2022). Influence of sub-supercritical CO_2 on pore structure and fractal characteristics of anthracite: An experimental study. *Energy*, 261, 125115. <https://doi.org/10.1016/J.ENERGY.2022.125115>

- Wang, Xiuyu, Alvarado, V., Swoboda-Colberg, N., & Kaszuba, J. P. (2013). Reactivity of dolomite in water-saturated supercritical carbon dioxide: Significance for carbon capture and storage and for enhanced oil and gas recovery. *Energy Conversion and Management*, 65, 564–573. <https://doi.org/10.1016/J.ENCONMAN.2012.07.024>
- Warren, J. K. (2010). Evaporites through time: Tectonic, climatic and eustatic controls in marine and nonmarine deposits. *Earth-Science Reviews*, 98(3–4), 217–268. <https://doi.org/10.1016/J.EARSCIREV.2009.11.004>
- Washburn, E. W. (1921). The Dynamics of Capillary Flow. *Physical Review*, 17(3), 273. <https://doi.org/10.1103/PhysRev.17.273>
- Webler, G. D., Zapata, M. J. M., Maciel, G. S., Patra, A., Hickmann, J. M., & Alencar, M. A. R. C. (2014). Influence of impurities on the luminescence of Er³⁺ doped BaTiO₃ nanophosphors. *Journal of Nanomaterials*, 2014. <https://doi.org/10.1155/2014/708719>
- Wei, B., Wu, R., Lu, L., Ning, X., Xu, X., Wood, C., & Yang, Y. (2017). Influence of Individual Ions on Oil/Brine/Rock Interfacial Interactions and Oil-Water Flow Behaviors in Porous Media. *Energy and Fuels*, 31(11), 12035–12045. https://doi.org/10.1021/ACS.ENERGYFUELS.7B02458/SUPPL_FILE/EF7B02458_SI_001.PDF
- Westphal, H., Surholt, I., Kiesel, C., Thern, H. F., & Kruspe, T. (2005). NMR measurements in carbonate rocks: Problems and an approach to a solution. *Pure and Applied Geophysics*, 162(3), 549–570. <https://doi.org/10.1007/S00024-004-2621-3/METRICS>
- Wilson, A. O. (1986). Depositional and diagenetic facies in the Jurassic Arab-C and D reservoirs, Qatif field, Saudi Arabia. *Carbonate Petroleum Reservoirs*, 319–340. https://doi.org/10.1007/978-1-4612-5040-1_21/COVER
- Worden, R. H., & Smalley, P. C. (1996). H₂S-producing reactions in deep carbonate gas reservoirs: Khuff Formation, Abu Dhabi. *Chemical Geology*, 133(1–4), 157–171. [https://doi.org/10.1016/S0009-2541\(96\)00074-5](https://doi.org/10.1016/S0009-2541(96)00074-5)
- Xu, C., Kang, Y., You, Z., & Chen, M. (2016). Review on formation damage mechanisms and processes in shale gas reservoir: Known and to be known. *Journal of Natural Gas Science and Engineering*, 36, 1208–1219. <https://doi.org/10.1016/J.JNGSE.2016.03.096>
- Xu, L., Li, Q., Myers, M., Chen, Q., & Li, X. (2019). Application of nuclear magnetic resonance technology to carbon capture, utilization and storage: A review. *Journal of Rock Mechanics and Geotechnical Engineering*, 11(4), 892–908. <https://doi.org/10.1016/J.JRMGE.2019.01.003>
- Xu, P. (2015). A DISCUSSION ON FRACTAL MODELS FOR TRANSPORT PHYSICS OF POROUS MEDIA. <https://doi.org/10.1142/S0218348X15300019>, 23(3). <https://doi.org/10.1142/S0218348X15300019>
- Xue, H., Wang, C., Jiang, L., Wang, H., Lv, Z., Huang, J., & Xiao, W. (2022). Asphaltene precipitation trend and controlling its deposition mechanism. *Natural Gas Industry B*, 9(1), 84–95. <https://doi.org/10.1016/j.ngib.2021.12.001>
- Yan, M., Deng, J., Tian, D., Yu, B., Chen, Z., & Xiao, Q. (2021). Preparation of Synthetic Sandstones With Weak to Moderate Strength for Sand Production Experiments. *OnePetro*.

- Yang, F., Ning, Z., & Liu, H. (2014). Fractal characteristics of shales from a shale gas reservoir in the Sichuan Basin, China. *Fuel*, 115, 378–384. <https://doi.org/10.1016/J.FUEL.2013.07.040>
- Yang, R., He, S., Yi, J., & Hu, Q. (2016). Nano-scale pore structure and fractal dimension of organic-rich Wufeng-Longmaxi shale from Jiaoshiba area, Sichuan Basin: Investigations using FE-SEM, gas adsorption and helium pycnometry. *Marine and Petroleum Geology*, 70, 27–45. <https://doi.org/10.1016/J.MARPETGEO.2015.11.019>
- Yang, W., Brownlow, J. W., Walker, D. L., & Lu, J. (2021). Effect of Surfactant-Assisted Wettability Alteration on Immiscible Displacement: A Microfluidic Study. *Water Resources Research*, 57(8), e2020WR029522. <https://doi.org/10.1029/2020WR029522>
- Yang, Y., Li, Y., Yao, J., Iglauder, S., Luquot, L., Zhang, K., Sun, H., Zhang, L., Song, W., & Wang, Z. (2020). Dynamic Pore-Scale Dissolution by CO₂-Saturated Brine in Carbonates: Impact of Homogeneous Versus Fractured Versus Vuggy Pore Structure. *Water Resources Research*, 56(4), 0–2. <https://doi.org/10.1029/2019WR026112>
- Yao, Y., Liu, D., Che, Y., Tang, D., Tang, S., & Huang, W. (2010). Petrophysical characterization of coals by low-field nuclear magnetic resonance (NMR). *Fuel*, 89(7), 1371–1380. <https://doi.org/10.1016/J.FUEL.2009.11.005>
- Yao, Y., Liu, D., Tang, D., Tang, S., & Huang, W. (2008). Fractal characterization of adsorption-pores of coals from North China: An investigation on CH₄ adsorption capacity of coals. *International Journal of Coal Geology*, 73(1), 27–42. <https://doi.org/10.1016/J.COAL.2007.07.003>
- Yi-gang, Z. (1981). Cool Shallow Origin of Petroleum—Microbial Genesis and Subsequent Degradation. *Journal of Petroleum Geology*, 3(4), 427–444. <https://doi.org/10.1111/J.1747-5457.1981.TB00940.X>
- Yin, S., & Xie, R. (2019). Experimental analysis of dynamic and static mechanical properties of deep thick anhydrite cap rocks under high-stress conditions. *Carbonates and Evaporites*, 34(3), 807–823. <https://doi.org/10.1007/S13146-018-0450-1/TABLES/5>
- Yousef, A. A., Al-Saleh, S., & Al-Jawfi, M. (2012a). Improved/enhanced oil recovery from carbonate reservoirs by tuning injection water salinity and ionic content. *Proceedings - SPE Symposium on Improved Oil Recovery*, 1, 819–836. <https://doi.org/10.2118/154076-ms>
- Yousef, A. A., Al-Saleh, S., & Al-Jawfi, M. (2012b). Improved/Enhanced Oil Recovery from Carbonate Reservoirs by Tuning Injection Water Salinity and Ionic Content. *Proceedings - SPE Symposium on Improved Oil Recovery*, 1(5), 819–836. <https://doi.org/10.2118/154076-MS>
- Youssef, S., Han, M., Bauer, D., Rosenberg, E., Bekri, S., Fleury, M., & Vizika, O. (2008). High resolution μ -CT combined to numerical models to assess electrical properties of bimodal carbonates. *Int. Symp. Soc. Core Analysts*, 2(January), 1–12.
- Yu, B., & Cheng, P. (2002). A fractal permeability model for bi-dispersed porous media. *International Journal of Heat and Mass Transfer*, 45(14), 2983–2993. [https://doi.org/10.1016/S0017-9310\(02\)00014-5](https://doi.org/10.1016/S0017-9310(02)00014-5)
- Yu, B., & Li, J. (2011). SOME FRACTAL CHARACTERS OF POROUS MEDIA. <https://doi.org/10.1142/S0218348X01000804>, 9(3), 365–372.

<https://doi.org/10.1142/S0218348X01000804>

- Yu, L., Daniels, L. M., Mulders, J. J. P. A., Saldi, G. D., Harrison, A. L., Liu, L., & Oelkers, E. H. (2019). An experimental study of gypsum dissolution coupled to CaCO₃ precipitation and its application to carbon storage. *Chemical Geology*, 525, 447–461. <https://doi.org/10.1016/J.CHEMGEO.2019.08.005>
- Yuan, P., Zhao, Y., Xu, B., & Shen, J. (2022). A Study on the Mineralogy and Volatile Fraction of Scapolite from Mogok, Myanmar. *Crystals* 2022, Vol. 12, Page 1779, 12(12), 1779. <https://doi.org/10.3390/CRYST12121779>
- Yuan, S., Ma, D., Li, J., Zhou, T., Ji, Z., & Han, H. (2022). Progress and prospects of carbon dioxide capture, EOR-utilization and storage industrialization. *Petroleum Exploration and Development*, 49(4), 955–962. [https://doi.org/10.1016/S1876-3804\(22\)60324-0](https://doi.org/10.1016/S1876-3804(22)60324-0)
- Yutkin, M. P., Mishra, H., Patzek, T. W., Lee, J., & Radke, C. J. (2018). Bulk and Surface Aqueous Speciation of Calcite: Implications for Low-Salinity Waterflooding of Carbonate Reservoirs. *SPE Journal*, 23(01), 84–101. <https://doi.org/10.2118/182829-PA>
- Zachariah, Z., Espinosa-Marzal, R. M., Spencer, N. D., & Heuberger, M. P. (2016). Stepwise collapse of highly overlapping electrical double layers. *Physical Chemistry Chemical Physics*, 18(35), 24417–24427. <https://doi.org/10.1039/C6CP04222H>
- Zajacz, Z., & Tsay, A. (2019). An accurate model to predict sulfur concentration at anhydrite saturation in silicate melts. *Geochimica et Cosmochimica Acta*, 261, 288–304. <https://doi.org/10.1016/J.GCA.2019.07.007>
- Zallaghi, M., & Khaz'ali, A. R. (2021). Experimental and modeling study of enhanced oil recovery from carbonate reservoirs with smart water and surfactant injection. *Fuel*, 304(April), 121516. <https://doi.org/10.1016/j.fuel.2021.121516>
- Zarrouk, S. J., & McLean, K. (2019). Operation and management of geothermal wells. In *Geothermal Well Test Analysis*. <https://doi.org/10.1016/b978-0-12-814946-1.00009-8>
- Zekri, A., Nantongo, H., & Boukadi, F. (2021). The effect of carbonate rock wettability on the performance of low salinity waterflooding: an experimental approach. *Journal of Petroleum Exploration and Production Technology*, 11(12), 4325–4338. <https://doi.org/10.1007/s13202-021-01309-9>
- Zevenhoven, R., Slotte, M., Åbacka, J., & Highfield, J. (2016). A comparison of CO₂ mineral sequestration processes involving a dry or wet carbonation step. *Energy*, 117, 604–611. <https://doi.org/10.1016/J.ENERGY.2016.05.066>
- Zhang, G. Q., Huang, C. C., & Hirasaki, G. J. (2000). Interpretation of wettability in sandstones with NMR analysis. *Log Analyst*, 41(3), 223–233.
- Zhang, G., & Seright, R. S. (2014). Effect of concentration on HPAM retention in porous media. *SPE Journal*, 19(3), 373–380. <https://doi.org/10.2118/166265-PA>
- Zhang, G., & Seright, R. S. (2015). Hydrodynamic Retention and Rheology of EOR Polymers in Porous Media. *Proceedings - SPE International Symposium on Oilfield Chemistry*, 1, 266–280. <https://doi.org/10.2118/173728-MS>

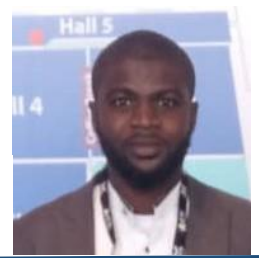
- Zhang, Jian, Deng, H., Deng, J., & Gao, R. (2019). Fractal Analysis of Pore Structure Development of Sandstone: A Nuclear Magnetic Resonance Investigation. *IEEE Access*, 7, 47282–47293. <https://doi.org/10.1109/ACCESS.2019.2909782>
- Zhang, Jin, Wang, D., & Olatunji, K. (2016). Surfactant adsorption investigation in ultra-lower permeable rocks. *Society of Petroleum Engineers - SPE Low Perm Symposium, May*, 5–6. <https://doi.org/10.2118/180214-ms>
- Zhang, Junjian, Wei, C., Ju, W., Yan, G., Lu, G., Hou, X., & Kai, Z. (2019). Stress sensitivity characterization and heterogeneous variation of the pore-fracture system in middle-high rank coals reservoir based on NMR experiments. *Fuel*, 238, 331–344. <https://doi.org/10.1016/J.FUEL.2018.10.127>
- Zhang, K., Lai, J., Bai, G., Pang, X., Ma, X., Qin, Z., Zhang, X., & Fan, X. (2020). Comparison of fractal models using NMR and CT analysis in low permeability sandstones. *Marine and Petroleum Geology*, 112, 104069. <https://doi.org/10.1016/J.MARPETGEO.2019.104069>
- Zhang, N., Wang, S., Xun, X., Wang, H., Sun, X., & He, M. (2023). Pore Structure and Fractal Characteristics of Coal-Measure Sedimentary Rocks Using Nuclear Magnetic Resonance (NMR) and Mercury Intrusion Porosimetry (MIP). *Energies* 2023, Vol. 16, Page 3812, 16(9), 3812. <https://doi.org/10.3390/EN16093812>
- Zhang, P., & Austad, T. (2005). Waterflooding in chalk: Relationship between oil recovery, new wettability index, brine composition and cationic wettability modifier. *67th European Association of Geoscientists and Engineers, EAGE Conference and Exhibition, Incorporating SPE EUROPE2005 - Extended Abstracts, 67th Europ*, 925–931. <https://doi.org/10.2523/94209-ms>
- Zhang, Peimao, & Austad, T. (2006). Wettability and oil recovery from carbonates: Effects of temperature and potential determining ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 279(1–3), 179–187. <https://doi.org/10.1016/j.colsurfa.2006.01.009>
- Zhang, Peimao, Tweheyo, M. T., & Austad, T. (2006). Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate. *Energy and Fuels*, 20(5), 2056–2062. <https://doi.org/10.1021/ef0600816>
- Zhang, Peimao, Tweheyo, M. T., & Austad, T. (2007). Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca²⁺, Mg²⁺, and SO₄²⁻. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 301(1–3), 199–208. <https://doi.org/10.1016/j.colsurfa.2006.12.058>
- Zhang, Ronghua, Hu, S., Zhang, X., & Yu, W. (2007). Dissolution kinetics of dolomite in water at elevated temperatures. *Aquatic Geochemistry*, 13(4), 309–338. <https://doi.org/10.1007/S10498-007-9022-Z/METRICS>
- Zhang, Rui, & Somasundaran, P. (2006). Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. *Advances in Colloid and Interface Science*, 123–126(SPEC. ISS.), 213–229. <https://doi.org/10.1016/j.cis.2006.07.004>
- Zhang, Y., Jackson, C., & Krevor, S. (2022). An Estimate of the Amount of Geological CO₂ Storage over the Period of 1996–2020. *Environmental Science and Technology Letters*, 9(8), 693–698. https://doi.org/10.1021/ACS.ESTLETT.2C00296/SUPPL_FILE/EZ2C00296_SI_002.XLSX

- Zhang, Z., & Weller, A. (2014). Fractal dimension of pore-space geometry of an Eocene sandstone formation. *https://doi.org/10.1190/Geo2014-0143.1*, 79(6), D377–D387. <https://doi.org/10.1190/GEO2014-0143.1>
- Zhang, Z. Z., & Low, P. F. (1989). Relation between the heat of immersion and the initial water content of Li-, Na-, and K-montmorillonite. *Journal of Colloid and Interface Science*, 133(2), 461–472. [https://doi.org/10.1016/S0021-9797\(89\)80057-8](https://doi.org/10.1016/S0021-9797(89)80057-8)
- Zhao, Yixin, Zhu, G., Dong, Y., Danesh, N. N., Chen, Z., & Zhang, T. (2017). Comparison of low-field NMR and microfocus X-ray computed tomography in fractal characterization of pores in artificial cores. *Fuel*, 210, 217–226. <https://doi.org/10.1016/J.FUEL.2017.08.068>
- Zhao, Yu, Wang, C., Ning, L., Zhao, H., & Bi, J. (2022). Pore and fracture development in coal under stress conditions based on nuclear magnetic resonance and fractal theory. *Fuel*, 309, 122112. <https://doi.org/10.1016/J.FUEL.2021.122112>
- Zheng, S., Yao, Y., Liu, D., Cai, Y., & Liu, Y. (2018). Characterizations of full-scale pore size distribution, porosity and permeability of coals: A novel methodology by nuclear magnetic resonance and fractal analysis theory. *International Journal of Coal Geology*, 196, 148–158. <https://doi.org/10.1016/J.COAL.2018.07.008>
- Zhong, Z., Chen, Y., Fu, M., Li, M., Yang, K., Zeng, L., Liang, J., Ma, R., & Xie, Q. (2023). Role of CO₂ geological storage in China's pledge to carbon peak by 2030 and carbon neutrality by 2060. *Energy*, 272, 127165. <https://doi.org/10.1016/J.ENERGY.2023.127165>
- Zhou, H. ; , Zhong, J. ; , Xue, D. ; , Wang, C. ; , Liu, Z. A., Hamidi, H., Ren, W., Zhou, H., Zhong, J., Xue, D., Wang, C., & Liu, Z. (2022). A Multi-Scale Fractal Approach for Coal Permeability Estimation via MIP and NMR Methods. *Energies 2022, Vol. 15, Page 2807*, 15(8), 2807. <https://doi.org/10.3390/EN15082807>
- Zhu, G., Wei, Z., Li, W., Yang, X., Cao, S., Wu, X., & Li, Y. (2023). Interface dissolution kinetics and porosity formation of calcite and dolomite (1 1 0) and (1 0 4) planes: An implication to the stability of geologic carbon sequestration. *Journal of Colloid and Interface Science*, 650, 1003–1012. <https://doi.org/10.1016/J.JCIS.2023.07.035>
- Zimmermann, U., Madland, M. V., Nermoen, A., Hildebrand-Habel, T., Bertolino, S. A. R., Hiorth, A., Korsnes, R. I., Audinot, J. N., & Grysan, P. (2015). Evaluation of the compositional changes during flooding of reactive fluids using scanning electron microscopy, nano-secondary ion mass spectrometry, x-ray diffraction, and whole-rock geochemistry. *AAPG Bulletin*, 99(5), 791–805. <https://doi.org/10.1306/12221412196>
- Zivar, D., Kumar, S., & Foroozesh, J. (2021). Underground hydrogen storage: A comprehensive review. *International Journal of Hydrogen Energy*, 46(45), 23436–23462. <https://doi.org/10.1016/J.IJHYDENE.2020.08.138>

Abubakar ISAH

Petroleum Engineering

+234-7038080307;
Zaria, Kaduna State, PO Box, 511, Nigeria



Goal-driven and enthusiastic Petroleum Engineer with a strong passion for fluids-rock interactions for CCUS and EOR applications. Possesses extensive knowledge across various aspects of petroleum and gas engineering. I have a strong background in subsurface CO₂-brine-rock interactions in the presence and absence of chemical additives, as well as an extensive experience in experimental petrophysics, HPHT core flooding, and rock-fluid interactions in porous media using both commercial and in-house designed static and batch reactors. I have experience in rock-fluids interactions quantification techniques such as micro-CT, NMR, SEM-EDX and FTIR, and through geochemical analysis of reaction effluents. Actively seeking opportunities in the Energy, Oil, and Gas sectors. Intending to apply academic experience, strong technical writing skills, research and development skills, as well as cross-functional team building to effectively contribute to the desired role. With a commitment to hard work and excellence, I can be relied upon to support your team in achieving its objectives.

Contact Details:

 **Email:** abuibnisah@yahoo.com; g201802900@kfupm.edu.sa

 **LinkedIn:** <https://www.linkedin.com/in/abubakar-isah-98726a173/>

Education:

King Fahd University of Petroleum and Minerals, Saudi Arabia.

Program: Doctor of Philosophy, Ph.D. **Petroleum Engineering**

May 2024

Academic Standing: Distinction (3.66 out of 4.00) [Transcript](#)

Thesis Topic: ***Systematic investigation of Rock/Fluids Interactions in Reservoirs at Nano-to-Millimeter Scale: Implications for Enhanced Oil Recovery and CO₂ Storage***

King Fahd University of Petroleum and Minerals, Saudi Arabia.

Program: Master of Science, **Petroleum Engineering**

May 2020

Academic Standing: Distinction (3.57 out of 4.00) [Transcript](#)

Thesis Topic: ***Characterization of Fluid Drainage Mechanism at Core and Pore Scales***

Abubakar Tafawa Balewa University, Nigeria

Program: Bachelor of Engineering, **Petroleum Engineering**

February 2014

Academic Standing: Second class upper (4.38 out of 5.00) [Transcript](#)

Thesis Topic: ***Water Coning Control in Horizontal Wells Using Multiple Completions***

Achievements/Awards:

- First place award in the Society of Petrophysicists Well Log Analysts (SPWLA) 2024 International Student Paper Contest (ISPC) in the Ph.D. category, as part of SPWLA 65th Annual Symposium, Rio de Janeiro, Brazil (**2024**).
- Second place award in the SPE Middle East and North Africa (MENA) Regional Student Paper Contest 2024, in the Ph.D. division, held at the Oman Petroleum and Energy Show (OPES) in Muscat (**2024**).
- Won a merit-based Ph.D. scholarship award in the King Fahd University of Petroleum & Minerals for MS in Petroleum Engineering (**2020**).
- Won a merit-based Masters scholarship award in the King Fahd University of Petroleum & Minerals for MS in Petroleum Engineering (**2018**).
- Won the Nigerian Society of Engineers (NSE) merit award for Excellence academic performance in Engineering (**2013**). [Award](#)
- Won the A.Y.M Shafa merit award for the best graduating student in Petroleum Engineering 2012/2013 academic session (**2013**). [Award](#)

- Won the National Center for Petroleum Research and Development (NCPRD) merit award for the best graduating student in Petroleum Engineering 2012/2013 academic session (**2013**). [Award](#)
- Certificates of training [Certificates](#)

Work Experience:

Graduate Teaching Assistance, [Petroleum Engineering Department, KFUPM](#)

Aug 2018 to date

- Conducted research in the field of petroleum engineering and gas storage.
- Assisted in teaching, coordinating exams, proctoring, and grading exams and assignments for undergraduate and graduate students.
- Mentored and assisted undergraduate and graduate students in research design and development.

Graduate student intern, [Halliburton, Dhahran Techno valley, Saudi Arabia.](#)

Sep 2023

- Participated in a Halliburton-Aramco project which involved conducting research and experiments using core flooding for fluid/rock, fluid/fluid interactions and compatibility study related to IOR applications.
- High pressure-high temperature (HPHT) coreflooding design and execution.

Process Engineer, [Dangote Oil Refining Company, Lagos Nigeria.](#)

May 2017 – Sep 2018

- Worked on refinery processes and operations in the RFCC unit and participated in various refinery units, including field and panel operations.
- Attained courses on oil refining from Oil experts through workshops organized by continuous learning department.

Student intern, [Kaduna Refinery- \(KRPC-PPMC\), Nigeria](#)

Jun 2012 – Dec 2012

- Development Team to deliver on their objectives, works closely with the technical team in daily Tankfarm operations, gained health safety and environmental control on oil and gas operations, undertook a range of refinery operations.
- Perform routine check and documentation of oil gauge, temperature, pump and control valves in the tank, perform other related terminal duties such as draining water from storage tanks.

Student intern, [Hydroflow Nigeria Limited.](#)

Sep 2010 – Nov 2010

- Worked as borehole drilling team, carried out water borehole drilling, completion and wellhead installation and maintenance.

Skills Highlights:

- Strong research and analytical skills
- Strong experimental skills
- Programming languages:

MS Packages

OriginPro

Matlab

- Grasp new concepts quickly and efficiently.
- Teamwork and leadership skills
- Industry related software:

CMG

Winprop

Techlog

Abaqus

Membership / Volunteering:

[Memberships:](#)

- Council for the Regulation of Engineering in Nigeria (COREN), (2021 to date)
- Society of petroleum engineers (SPE), (2009 to date)
- Nigerian Society of Engineers (NSE), (2020 to date)

Volunteering:

- National Youth service corps, Nigeria (2014)
- Chemistry instructor, Jama'atu health technology, Zaria, Nigeria (2015 to 2016)

- Mathematics and chemistry teacher, Demonstration school, Zaria (2014 to 2015)

Research Projects / Publications:

🔗 **Google scholar:** <https://scholar.google.com/citations?user=bJJmv2cAAAAJ&hl=en&oi=ao>

- **Isah, A.**, Mahmoud, M., Kamal, M. S., Arif, M., & Jawad, M. A. (2023). Multiscale Wettability Characterization of Anhydrite-Rich Carbonate Rocks: Insights into Zeta Potential, Flotation, and Contact Angle Measurements. *SPE Reservoir Evaluation & Engineering*, 1-19. <https://doi.org/10.2118/214324-PA>
- **Isah, A.**, Arif, M., Hassan, A., Mahmoud, M., & Iglauer, S. (2022). Fluid-rock interactions and its implications on EOR: Critical analysis, experimental techniques and knowledge gaps. *Energy Reports*, 8, 6355-6395. <https://doi.org/10.1016/j.egy.2022.04.071>
- **Isah, A.**, Arif, M., Hassan, A., Mahmoud, M., & Iglauer, S. (2022). A systematic review of Anhydrite-Bearing Reservoirs: EOR Perspective, CO₂-Geo-storage and future research. *Fuel*, 320, 123942. <https://doi.org/10.1016/j.fuel.2022.123942>
- **Isah, A.**, Adebayo, A. R., Mahmoud, M., Babalola, L. O., & El-Husseiny, A. (2020). Drainage Mechanisms in Gas Reservoirs with Bimodal Pores—A Core and Pore Scale Study. *Journal of Natural Gas Science and Engineering*, 103652. <https://doi.org/10.1016/j.jngse.2020.103652>
- **Isah, A.**, Mahmoud, M., Arif, M., Aljawad, M. S., & Kamal, M. S. (2023). Influence of Surface Cleaning on the Wettability of Quartz/Oil/Brine Systems. *Energy & Fuels*, 37(17), 12744-12761. <https://doi.org/10.1021/acs.energyfuels.3c01579>
- **Isah, A.**, Mahmoud, M., Arif, M., Al Jawad, M., & Amao, A. O. (2023). Influence of surface cleaning on the wettability of calcite/oil/brine systems. *Fuel*, 351, 128908. <https://doi.org/10.1016/j.fuel.2023.128908>
- **Isah, A.**, Arif, M., Mahmoud, M., & Kamal, M. S. (2023). Influence of rock permeability and surface conditioning on carbonate wettability: A link between contact angle and Amott-index. *Geoenergy Science and Engineering*, 227, 211892. <https://doi.org/10.1016/j.geoen.2023.211892>
- **Isah, A.**, Hiba, M., Al-Azani, K., Aljawad, M. S., & Mahmoud, M. (2021). A Comprehensive Review of Proppant Transport in Fractured Reservoirs: Experimental, Numerical, and Field Aspects. *Journal of Natural Gas Science and Engineering*, 103832. <https://doi.org/10.1016/j.jngse.2021.103832>
- **Isah, A.**, Mahmoud, M., Aljawad, M. S., Arif, M., & Kamal, M. S. (2023, October). Relationship Between Geomechanical Properties and Rock Wetting Behavior. In *ARMA/DGS/SEG International Geomechanics Symposium* (pp. ARMA-IGS). ARMA. <https://doi.org/10.56952/IGS-2023-0447>
- **Isah, A.**, Adebayo, A. R., Mahmoud, M., Babalola, L. O., & El-Husseiny, A. (2021). Characterization of Fluid Drainage Mechanism at Core and Pore Scales: An NMR Capillary Pressure-Based Saturation Exponent Prediction. *SPE-205176-MS* <https://doi.org/10.2118/205176-MS>
- Elsayed, M., **Isah, A.**, Hiba, M., Hassan, A., Al-Garadi, K., Mahmoud, M., ... & Radwan, A. E. (2022). A review on the applications of nuclear magnetic resonance (NMR) in the oil and gas industry: laboratory and field-scale measurements. *Journal of Petroleum Exploration and Production Technology*, 1-38. <https://doi.org/10.1007/s13202-022-01476-3>
- Afagwu, C., **Abubakar, I.**, Kalam, S., Al-Afnan, S. F., & Awotunde, A. A. (2020). Pressure-Transient Analysis in Shale Gas Reservoirs: A Review. *Journal of Natural Gas Science and Engineering*, 103319. Doi: <https://doi.org/10.1016/j.jngse.2020.103319>
- Adebayo A. R., A., **Isah, A.**, Mahmoud, M., & Al-Shehri, D. (2020). Effects of Foam Microbubbles on Electrical Resistivity and Capillary Pressure of Partially Saturated Porous Media. *Molecules*, 25(15), 3385. Doi: <https://doi.org/10.3390/molecules25153385>

- Mohammed, I., **Isah, A.**, Al Shehri, D., Mahmoud, M., Arif, M., Kamal, M. S., ... & Patil, S. (2022). Effect of Sulfate-Based Scales on Calcite Mineral Surface Chemistry: Insights from Zeta-Potential Experiments and Their Implications on Wettability. *ACS omega*, 7(32), 28571-28587. <https://doi.org/10.1021/acsomega.2c03403>
- Alameedy, U., Alhaleem, A. A., **Isah, A.**, Al-Yaseri, A., Mahmoud, M., & Salih, I. S. (2022). Effect of acid treatment on the geomechanical properties of rocks: an experimental investigation in Ahdeb oil field. *Journal of Petroleum Exploration and Production Technology*, 12(12), 3425-3441. <https://doi.org/10.1007/s13202-022-01533-x>
- Abdelgawad, K. Z., Adebayo, A. R., **Isah, A.**, & Muhammed, N. S. (2022). A literature review of the strength and stability of foam and their relationship with the absolute permeability of porous media. *Journal of Petroleum Science and Engineering*, 211, 110195. <https://doi.org/10.1016/j.petrol.2022.110195>
- Abbasi, G. R., Arif, M., **Isah, A.**, Ali, M., Mahmoud, M., Hoteit, H., ... & Iglauer, S. (2022). Gas hydrate characterization in sediments via x-ray microcomputed tomography. *Earth-Science Reviews*, 104233. <https://doi.org/10.1016/j.earscirev.2022.104233>
- Alameedy, U., Alhaleem, A. A., **Isah, A.**, Al-Yaseri, A., El-Husseiny, A., & Mahmoud, M. (2022). Predicting dynamic shear wave slowness from well logs using machine learning methods in the Mishrif Reservoir, Iraq. *Journal of Applied Geophysics*, 205, 104760. <https://doi.org/10.1016/j.jappgeo.2022.104760>
- Als Salman, M., Raza, A., Mahmoud, M., Murtaza, M., Arif, M., **Isah, A.**, ... & Shahzad Kamal, M. (2024, April). Experimental Assessment of Time Dependent Wettability Alteration in CO₂-Brine-Rock System. In SPE Conference at Oman Petroleum & Energy Show. OnePetro. <https://doi.org/10.2118/218815-MS>
- Mouallem, J., Arif, M., **Isah, A.**, Raza, A., Rahman, M. M., Mahmoud, M., & Kamal, M. S. (2024). Effect of formation brine on interfacial interaction: Implications for CO₂ storage. *Fuel*, 371, 131986. <https://doi.org/10.1016/j.fuel.2024.131986>
- **Isah, A.**, Mahmoud, Aljawad, M. S., M., Arif, Hussani S.R., M., Amoa A., A. Raza., & Kamal, M. S. (*Under Review*). Enforced CO₂ Mineralization in Anhydrite-Rich Rocks. Elsevier *Energy*.
- **Isah, A.**, Mahmoud, A. Raza., M. Murtaza., M., Arif, M., & Kamal, M. S. (*Under Review*). CO₂-Brine Interactions in Anhydrite-Rich Rock: Implications for Carbon Mineralization and Geo-storage. *Int. Journal of Greenhouse gas Control*

References:

Referees will be provided upon request