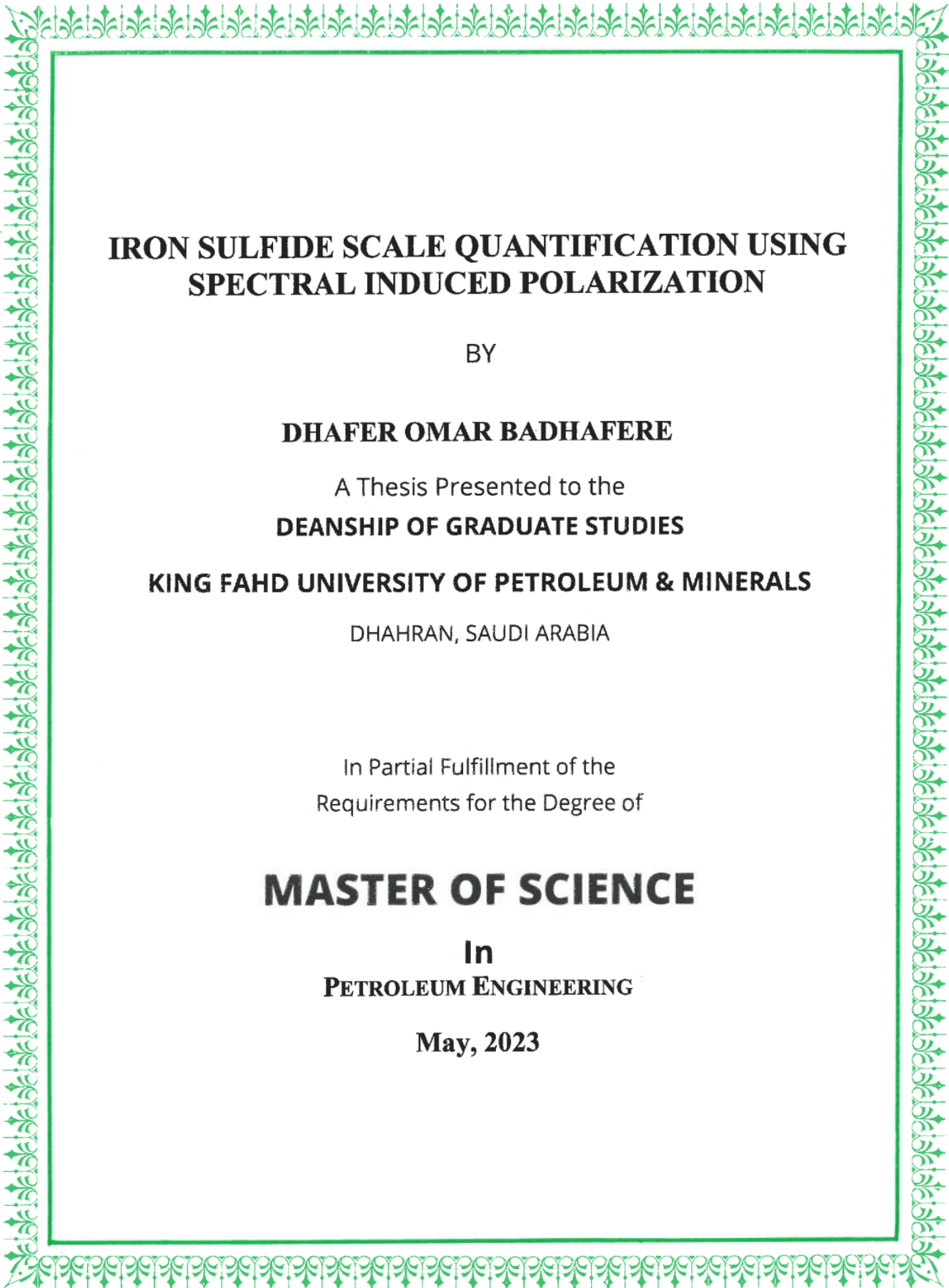




IRON SULFIDE SCALE QUANTIFICATION USING SPECTRAL INDUCED POLARIZATION

BY

DHAHER OMAR BADHAHERE

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

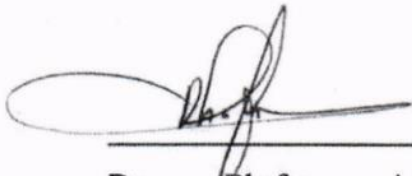
MASTER OF SCIENCE

**In
PETROLEUM ENGINEERING**

May, 2023

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

This thesis, written by **DHAFER OMAR BADHAFERE** under the direction of his thesis advisor 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 **MASTER OF SCIENCE IN PETROLEUM ENGINEERING.**

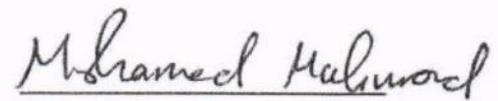


Dr. Dhafer A. Al-Shehri
Department Chairman



Dr. Suliman Saleh Al-Homidan
Dean of Graduate Studies

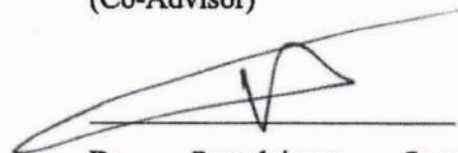
Date



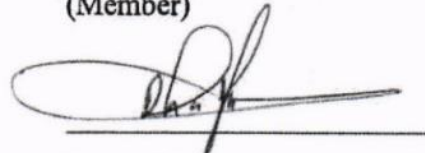
Dr. Mohammed A. Mahmoud
(Advisor)



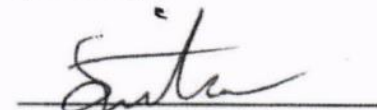
Dr. Ammar El-Husseiny
(Co-Advisor)



Dr. Panteleimon Souplos
(Member)



Dr. Dhafer A. Al-Shehri
(Member)



Dr. Sulaiman A. Alarifi
(Member)



My beloved father, and my caring mother, this is for you.

ACKNOWLEDGMENTS

First and foremost, this would never have been done without the mercy and blessing of Allah, so thank Allah in the beginning and in the end.

Second, the care and support of my advisor Prof. Mohamed Mahmoud and my co-advisor Dr. Ammar El-Husseiny was enormous to an extent I cannot describe. New gazes of knowledge, wisdom and academic insights have been opened to my eyes by being under their supervision and mentoring. I cannot express my gratitude enough for all the help and support Prof. Mohamed and Dr. Ammar offered to me through my graduate studies and research.

I would like to express my gratitude to Prof. Pantelis Sopiou, my committee member, for his support and mentoring throughout my thesis work. His mentoring and support are highly reflecting in the success of this work. Also, the success of this work is attributed to Dr. Dhafer Al-Shehri and Dr. Sulaiman Alarifi, my committee members, for their constructive review and mentoring, sharp vision and excellent notes and advice during my thesis work.

During the laboratory work, I shared many times with my colleagues in the college to whom I give my thanks and gratitude for their support. Thanks to my lab mate Ali Oshaish for his support in the experimental and research work, Dr. Panos for operating and handling the SIP tool and being a part of the research group, Dr. Jaber al-Jaberi for his companionship, support, and kind treatment, and Mohamed Hanfy, my teammate and office neighbor for his advising and kind brotherhood.

This work and degree, after Allah's mercy, would have been much difficult without the support of my friends and close companions: Mohamed Alsakkaf, Faisal, Rakan, Ahmed, Haidar and Mohamed Albaiti. Also, it was a blessing having Dr. Bader Bagari, Alaa Aldugail and Dr. Salem Basfar by my side throughout, their support and care was unlimited.

Finally, to my family, who patiently went through the hustle of my departure many times and covered me with their love, care, and prayers. My mother, the soul of my father, and my brothers and sister, thank you for always being there for me and supporting me through thick and thin. You have always been my rock, and I cannot thank you enough for all the sacrifices you have made for me. The greatest thanks go to you.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
Table of Contents.....	VII
List of Tables	X
List of figures	III
LIST OF ABBREVIATIONS.....	III
ABSTRACT	IV
Chapter 1 INTRODUCTION TO ELECTRICAL EXPLORATION METHODS AND SPECTRAL INDUCED POLARIZATION	1
1.1. Background.....	1
1.1.1 Electrical properties	1
1.1.2 Electrical Surveying Methods.....	2
1.1.3 Induced polarization (IP) and spectral IP (SIP)	3
1.2. SIP Measurement Instrument and Mechanism.....	23
1.2.1 PSIP Tool and Mechanism.....	23
1.2.2 Tool Calibration	24
1.3. Thesis organization	25
Chapter 2 IRON SULFIDE SCALES CONTENT ASSESSMENT AND EARLY DETECTION BY SPECTRAL INDUCED POLARIZATION	27

2.1.	Introduction	27
2.2.	Statement of Problem.....	29
2.3.	Objectives	29
2.4.	Literature Review.....	30
2.4.1.	Scales	30
2.5.	Methodology	35
2.5.1.	Sample preparation and sample characterization	35
2.5.2.	Testing Concept.....	37
2.5.3.	Tool preparation and test setup.....	38
2.6.	Results and Discussion.	39
2.6.1.	SIP Phase Shift	39
2.6.2.	SIP Imaginary Conductivity	40
2.6.3.	SIP Real Conductivity	41
2.6.4.	SIP Impedance	42
2.6.5.	Overall Results Discussion	43
2.7.	Conclusion.....	44
 Chapter 3 WEIGHTING MATERIAL CONCENTRATION ASSESSMENT AND SAG EARLY DETECTION		46
3.1.	Introduction	46
3.2.	Statement of Problem.....	49

3.3.	Objectives	49
3.4.	Literature Review	49
3.4.1.	Drilling fluids and weighting materials.....	49
3.4.2.	Weighting material sag.....	51
3.4.3.	SAG identification methods	51
3.5.	Methodology	52
3.5.1.	Drilling fluid preparation and components.....	52
3.5.2.	Approach and Method.....	55
3.5.3.	Experimental procedure and test parameters.....	55
3.6.	Results and Discussion.	58
3.6.1.	SIP for monitoring changes in calcium carbonate concentration	60
3.6.2.	SIP for monitoring and early detect weighting material sag	67
	Chapter 4 CONCLUSION	83
	References	87
	Vitae	107

LIST OF TABLES

Table 1a: Common SIP models (modified from [19]).....	20
Table 1b: Common SIP models (modified from [19]).....	21
Table 1c: Common SIP models (modified from [19]).....	22
Table 2: KCl buffer solutions at different concentrations	25
Table 3: Common scale types (modified from [71])	32
Table 4: the effect of iron sulfide on permeability (modified from [91]).....	33
Table 5: XRF test results for pyrite sample	36
Table 6: Percentage volumes and mass of the tested mixtures	37
Table 7: SIP test configuration	39
Table 8: Drilling fluid with different mixing ratios	53
Table 9: Barite drilling fluid formula.....	54
Table 10: Calcite drilling fluid formula	55
Table 11: Calcium carbonate concentration SIP test configuration.....	56
Table 12: Barite SIP test specifications	58
Table 13: Calcite SIP test specifications.....	58
Table 14: Density evaluation with time done in the drilling fluid lab utilizing the conventional mass difference method to measure sag in room temperature and atmospheric pressure.....	68

LIST OF FIGURES

Figure 1: A schematic illustration of the polarization phenomena a) in minerals surface and b) in a mineralized vein [23].....	5
Figure 2: Induced polarization in the time domain [21]	5
Figure 3: The electrical double layer and the conductivity of the stern and diffusive layers [46].....	8
Figure 4: A particle before and after applying an electrical field and undergoing stern layer polarization [47].	8
Figure 5: A pore throat before and after applying an electrical field and undergoing membrane polarization.....	9
Figure 6: The effect of existence of electron-conducting particles on SIP conductivity readings [50].....	10
Figure 7: Energy band levels in different types of solids.	12
Figure 8: Real and imaginary conductivities vs FeS precipitation [53].....	13
Figure 9: Phase shift and complex conductivity plots from [54].....	16
Figure 10: KFUPM PSIP Field/Lab unit	23
Figure 11: Scale deposition in pipelines [84]	31
Figure 12: Photos of FeS scale samples by [79]	34
Figure 13: filled SIP test columns (left) and test schematic (right)	39
Figure 14: Phase shift readings over a frequency range [0.01-10000] Hz of pyrite-calcium carbonate mixtures of different concentrations.	40

Figure 15: Imaginary conductivity readings over a frequency range [0.01-10000] Hz of pyrite-calcium carbonate mixtures of different concentrations.	41
Figure 16: Real conductivity readings over a frequency range [0.01-10000] Hz of pyrite-calcium carbonate mixtures of different concentrations.	42
Figure 17: Impedance readings over a frequency range [0.01-10000] Hz of pyrite- calcium carbonate mixtures of different concentrations.	43
Figure 18: Calcium Carbonate scale in pipelines [110].	46
Figure 19: Drilling fluid mixer	54
Figure 20: Horizontally oriented SIP column and channels distribution.	56
Figure 21: SIP test column schematic (modified by Siddiq et al. 2020)	57
Figure 22: Density vs CaCO ₃ concentration.	59
Figure 23: Conductivity vs CaCO ₃ concentration.	59
Figure 24: Phase shift measurements over a broad frequency range (0.1 – 10,000 Hz) for the different concentrations of calcite	61
Figure 25: Real conductivity over a broad frequency range (0.1 – 10,000 Hz) for the different concentrations of calcite fluids.	63
Figure 26: Imaginary conductivity measurements over a broad frequency range (0.1 – 10,000 Hz) for the different concentrations of calcite fluids.	64
Figure 27: Overall comparison of SIP measurements vs CaCO ₃ concentration at channel 3.	65
Figure 28: SIP measurements (phase shift, imaginary conductivity, real conductivity, and impedance) over a broad frequency range (0.1 – 10,000 Hz) for barite drilling fluid.	67

Figure 29: SIP measurements (phase shift, imaginary conductivity, real conductivity, and impedance) over a broad frequency range (0.1 – 10,000 Hz) for calcite drilling fluid.....	68
Figure 30: A time-lapse of barite drilling fluid SIP signals measurements (phase shift, imaginary conductivity, real conductivity, and impedance) at 10K Hz	70
Figure 31: A time-lapse of calcite drilling fluid SIP signals measurements (phase shift, imaginary conductivity, real conductivity, and impedance) at 10K Hz.....	72
Figure 32: Phase shift measurements over a broad frequency range (0.1 – 10,000 Hz) for barite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).	73
Figure 33: Imaginary conductivity measurements over a broad frequency range (0.1 – 10,000 Hz) for barite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).	74
Figure 34: Real conductivity measurements over a broad frequency range (0.1 – 10,000 Hz) for barite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).	75
Figure 35: Impedance measurements over a broad frequency range (0.1 – 10,000 Hz) for barite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).	76
Figure 36: Phase shift measurements over a broad frequency range (0.1 – 10,000 Hz) for calcite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).	77

Figure 37: Imaginary conductivity measurements over a broad frequency range (0.1 – 10,000 Hz) for calcite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).	78
Figure 38: Real conductivity measurements over a broad frequency range (0.1 – 10,000 Hz) for calcite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).	79
Figure 39: Impedance measurements over a broad frequency range (0.1 – 10,000 Hz) for calcite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).	80

LIST OF ABBREVIATIONS

IP	:	Induced Polarization
SIP	:	Spectral Induced Polarization
XRD	:	X-ray diffraction
XRF	:	X-ray fluorescence
FeS	:	Iron sulfide
SP	:	Self potential
KCL	:	Potassium chloride
H₂S	:	Hydrogen sulfide
SRB	:	Sulfide reducing bacteria
O&G	:	Oil and gas

ABSTRACT

Full Name : Dhafer Omar Farag Badhafere

Thesis Title : Iron Sulfide Scales Quantification Using Spectral Induced Polarization

Major Field : Petroleum Engineering

Date of Degree : May 2023

Spectral Induced Polarization (SIP), a branch of Induced polarization (IP) surveying, is an electrical geophysical surveying tool and technique that is used for subsurface exploration. In this thesis work, the SIP method is used to solve two major problems in the oil and gas industry: iron sulfides scale content in limestone formations and drilling fluids weighting materials concentration monitoring and sag detection.

In the first part of this thesis work, the SIP method was utilized to characterize pyrite concentration in limestone formations. Seven different samples of Indiana limestone with different pyrite content were tested starting from 0.25% per bulk volume of pyrite. The SIP method has been applied successfully in characterizing the early presence of pyrite as low as 0.25% per bulk volume of a 17 cc sample chamber. The concentration of pyrite in limestone was also assessed by the SIP phase shift and imaginary conductivity signals where they are found to be directly proportional to the pyrite content in the limestone body.

In the second part of this thesis work, calcium carbonate concentration in water-based bentonite drilling fluid was evaluated using the SIP method. Then, the second objective was to monitor drilling fluid weighting materials i.e., barite and calcite sag. 6 samples of different calcium carbonate content in 4% per weight bentonite drilling fluid were put

under test for concentration evaluation. Calcium carbonate concentration was successfully characterized using the real part of the SIP complex conductivity signal where the presence of calcium carbonate was characterized by a sharp decrease in real conductivity followed by a gradual increase with the increase of calcium carbonate concentration. Also, barite and calcite weighting materials sag was early detected and assessed by the SIP method where in the span of 3 hours, sag effect was noticed in SIP real conductivity and impedance signals by a decrease in impedance and increase in real conductivity signals with time. The SIP timelapse tests were successful in making a new method to detect weighing materials sag in a short time period in static, atmospheric conditions.

The output of this work proves the reliability of the SIP technique in iron sulfide scale detection in limestone formations and drilling fluid integrity monitoring. This work is setting the basis for upcoming work and development to enlarge the range of applications of the SIP method in both domains, iron sulfide characterization and drilling fluid components monitoring.

ملخص الرسالة

الاسم الكامل: ظافر عمر فرج باظفاري

عنوان الرسالة: الكشف عن تركيز كبريتيد الحديد في الصخور الجيرية باستخدام تقنية الاستقطاب الطيفي المحفز

التخصص: الهندسة البترولية

تاريخ الدرجة العلمية: مايو / 2023

يعد الاستقطاب الطيفي المحفز (SIP - Spectral Induced Polarization)، وهو فرع من فروع المسح الاستقطابي المحفز (IP - Induced Polarization)، أداة وتقنية جيوفيزيائية كهربائية تستخدم لاستكشاف الطبقات الجوفية والكشف عن المعادن. في هذا العمل العلمي، تم استخدام تقنية الاستقطاب الطيفي المحفز لحل مشكلتين رئيسيتين في مجال النفط والغاز: الكشف عن محتوى مركبات كبريتيد الحديد في تكوينات الحجر الجيري ومراقبة تركيز مواد اكساب الكثافة والكشف عن ترسبها في سوائل الحفر.

في الجزء الأول من هذا العمل العلمي، تم استخدام طريقة الاستقطاب الطيفي المحفز لتوصيف تركيز البايराيت في تكوينات الحجر الجيري. وتم اختبار سبع عينات مختلفة من الحجر الجيري بتركيزات مختلفة من البايرايت في الحجم الكلي للعينة. لقد تم تطبيق طريقة الاستقطاب الطيفي المحفز بنجاح في توصيف وجود البايرايت في مراحل وجوده المبكرة بتركيز قليل يصل إلى 0.25% من الحجم الكلي لغرفة الفحص التي تسع سبعة عشر سائلي متر مكعب. ايضاً، تم تقييم تركيز البايرايت في عينات الحجر الجيري بواسطة إشارات الفرق بين الطور (phase shift) والتوصيلية الخيالية (imaginary conductivity) حيث تم العثور على أنها تتناسب طردياً مع محتوى البايرايت في الجسم الحجري الجيري.

في الجزء الثاني من هذا العمل العلمي، تم تقييم تركيز كربونات الكالسيوم، كمادة اكساب كثافة، في سائل حفر الآبار المائي القائم على البنتونايت باستخدام طريقة الاستقطاب الطيفي المحفز. ثم تمت مراقبة مواد حفر الآبار والكشف عن

ترسب مواد اكساب الكثافة المتمثلة بالبارايت (كبريتات الباريوم) والكالسيت (كربونات الكالسيوم) في سوائل الحفر. أولاً، تم اختبار ست عينات بتركيزات مختلفة من كربونات الكالسيوم في سائل الحفر القائم على البنتونايت بنسبة أربعة بالمائة من الوزن لتقييم التركيز. تم تمييز تركيز كربونات الكالسيوم بنجاح باستخدام الجزء الحقيقي من إشارة توصيل الاستقطاب الطيفي المحفز المعقدة، حيث تم تمييز وجود كربونات الكالسيوم بانخفاض حاد في التوصيل الحقيقي يتبعه زيادة تدريجية مع زيادة تركيز كربونات الكالسيوم. كما تم الكشف المبكر عن ترسب مواد التحميل البارايت والكالسيت باستخدام طريقة الاستقطاب الطيفي المحفز، حيث تم ملاحظة تأثير ترسب مواد اكساب الكثافة في سوائل الحفر في إشارات توصيل الاستقطاب الطيفي المحفز الحقيقية والمقاومة الكهربائية خلال وقت اقصاه خمس ساعات، وذلك من خلال انخفاض في والمقاومة الكهربائية وزيادة في إشارات التوصيل الحقيقية مع الوقت. تمت المراقبة باستخدام اختبارات تجري باستمرار مع الوقت وأسفر ذلك عن النجاح في تطوير طريقة جديدة للكشف عن ترسب مواد اكساب الكثافة في فترة زمنية قصيرة في ظروف ثابتة.

ختاماً، تبين أن تقنية الاستقطاب الطيفي المحفز فعالة وموثوقة لتوصيف محتوى رواسب كبريتيد الحديد في تكوينات الحجر الجيري ومراقبة تركيز مكونات مواد اكساب الكثافة في سوائل الحفر. اضافة الى القدرة على كشف وتقييم ترسب مواد اكساب الكثافة في فترة زمنية قصيرة في ظروف ثابتة بطريقة جيدة وفعالة. بشكل عام، يضع هذا العمل الأسس للأبحاث والتطوير المستقبلي لتوسيع نطاق تطبيقات تقنية الاستقطاب الطيفي المحفز في مجال انتاج وتنقيب النفط والغاز.

CHAPTER 1

INTRODUCTION TO ELECTRICAL EXPLORATION METHODS AND SPECTRAL INDUCED POLARIZATION

1.1. Background

Using electric surveys as measures of the subsurface structure has been a common geophysical approach since the twentieth century. The use of electrical methods started in the 1800s when the natural potential was used in exploring ore depositions in Cornwall. Later on, electrical surveys started emerging, and new surveys such as electrode resistivity, polarization, magnetic effects, and many other surveys were incorporated in the prospecting of subsurface composition [1]. Nowadays, electrical surveys are playing a very important and invaluable role in petroleum and geophysical explorations both before and while drilling wells. Electrical surveys are used either in terms of geophysical surveying or well logs to provide a complete picture that helps in a major way towards providing a full picture of the earth components, petrophysical properties, fluid types and saturations, and other important features of the petroleum and subsurface system [2], [3].

1.1.1 Electrical properties

The electrical properties of minerals are related to the response of their reaction to electric potential. Likewise, minerals' responses to electric current are related to their nature of composition. Many factors influence the electrical properties of materials such as porosity

and water content, the distribution of grain size, mineralogy, temperature, fabric...etc. [2]. The three main minerals' electrical properties are conduction, the ability of minerals to conduct electricity, pyroelectricity, the ability to create electrical charges responding to variations in temperature, and piezoelectricity, the ability to develop electrical charges when exposed to stress [4]. Most electrical surveys are dependent on measuring the conductivity or resistivity property of minerals by having a sender and receiver for electrical current, while there exist methods that measure the electrical properties of the area of interest without sending any currents. Other properties such as electrical polarization, the rearrangement of charges in a certain body in response to electric potential, are also being considered in electrical surveys of minerals [5].

1.1.2 Electrical Surveying Methods

In mineral prospection, electrical methods are one of the most used techniques. There are many field logs and surveys that rely on the electrical properties of minerals. One of the major methods is self-potential (SP). SP method is one of the oldest electrical surveying methods that rely on measuring the distribution of the electrical potential of minerals and mapping it to describe the surveyed area [6]. What makes SP unique is that it is passive, meaning that it does not need the application of current into the tested area. In short, the method is based on descriptively mapping the potential difference of the tested area using two types of electrodes: a reference electrode and a testing electrode at the location of interest. When used in petroleum wellbore logging, SP signals are highly affected by the difference in salinity between reservoir water and drilling fluid, and also by the clay content. As a result, SP logs are referred to usually when investigating the salinity of the

formation water, to estimate the clay content of beds and formation layers, or for permeable beds detection [7].

Another major approach is direct current resistivity methods. In this method, minerals' variations in resistivity are observed by passing a DC through them. Minerals with different compositions have different resistivity values to electrical currents that are mapped to identify different ground lithologies. Minerals with Ferro structure have higher electrical conductivity than others and resistivity logs are a good indicator of their depositions. In addition, resistivity surveys can be used to identify water, salt, and hydrocarbon depositions [8], [9].

Polarization is another major electrical property that has been extensively applied in minerals prospecting where an electrical potential is passed in the ground or certain bodies and polarization effect in terms of phase and complex electrical conductivity is read to yield chargeability of minerals and areas under investigation [10].

1.1.3 Induced polarization (IP) and spectral IP (SIP)

Spectral induced polarization (SIP) is one of the promising techniques in mineral characterizing and prospection. It is a method derived from its main phenomenal branch, induced polarization (IP). Recently, IP and SIP have drawn attention due to their proven capability in capturing mineral polarization characteristics with high sensitivity [11]–[18]. Although resistivity methods are used in subsurface lithology characterization, they mainly rely on the ionic conduction of the fluids in the pore spaces which limits their ability since in some cases two minerals might have the same resistivity readings, and this is where IP efficiency comes in handy [19]. Moreover, there are some cases of misread resistivity logs where clay and saline formation water could both have conductive natures that would

reflect similarly in the logs. IP can be used effectively in such cases to distinguish between ground water and soil particles [20]. The information acquired by IP provides insight into the lithological composition and chemistry of the grain surface of the desired investigated area [21]. This can be done by matching stock (pure) materials signals with acquired data similar to other material characterization techniques that are based on signal history matching. In this section, SIP and IP are going to be discussed thoroughly to reveal the state-of-science of their applications in mineral prospection.

A. Theory and concept of the induced polarization (IP) phenomena

The induced polarization phenomenon (IP) is the ability of a material to polarize in response to a passing electrical potential, such that the ions form densities of opposite charges that could be seen as two opposite electrical poles. As a result, polarized materials have the ability to store electrical potential even after the imposed electrical field vanishes [10]. Although an explanation of the phenomenon is complicated and not very clear, researchers have explained that IP is directly connected to the complex resistivity of minerals and, in parallel with DC resistivity, is occurring because of the disturbance in the low-frequency resistive and capacitive properties of the minerals [21].

Theoretically, when an electrical current pass through a polarizable element, the negative and positive charged ions in the body are rearranged with the direction of the electric field. hence, the body is seemed to have two oppositely charged poles as shown in Figure 1. After the electrical current is switched off, the polarization effect allows the body to store electrical potential for finite periods in what is called the *chargeability* property that then discharges, making the body function in a similar way to a capacitor [10], [22]

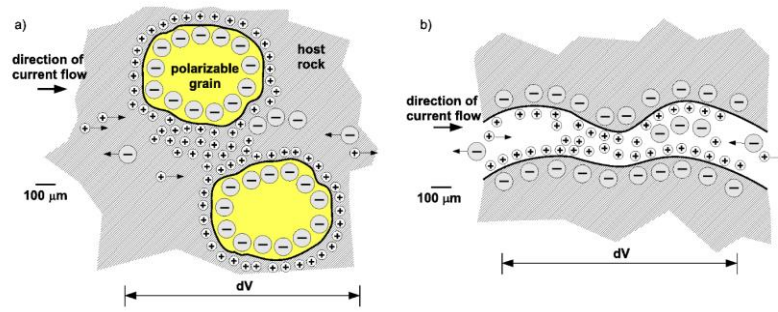


Figure 1: A schematic illustration of the polarization phenomena a) in minerals surface and b) in a mineralized vein [23]

As shown in Figure 2, the voltage is presented versus time. After the imposed electrical potential is released at time = 0.5 s, the voltage is not fully and spontaneously vanishing, rather, it takes a finite amount of time to vanish which illustrates the chargeability property brought by the polarization effect. This effect is explained in various ways throughout the literature and many proposed mechanisms are available and will be discussed.

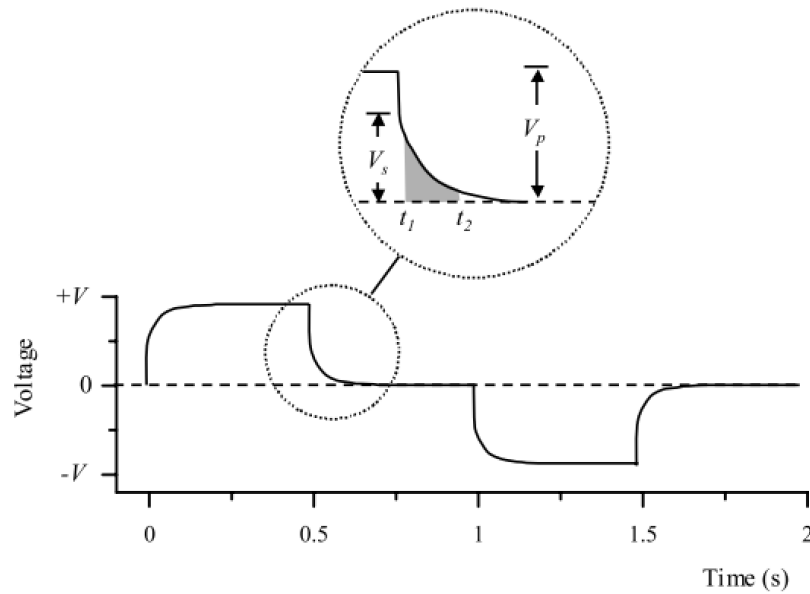


Figure 2: Induced polarization in the time domain [21]

B. Mechanisms of IP

The mechanisms that explain the polarization and induced polarization phenomena are widely available in literature and researched from many points of view. Mainly, the mechanisms are divided into two main genres: [1] polarization in porous media with the absence of electron conducting minerals such as clays and non-metallic grains, and [2] polarization in porous media containing electron conducting minerals i.e., conducting, and semiconducting materials [24]. In general, frequency-dependent polarization of porous media can be divided into three main zones depending on the frequency intensity: from 10^{-3} to 10^3 Hz, the polarization mechanism is dominated by the electrical double layer (EDL) polarization. At higher frequencies i.e., 10^2 to 10^8 Hz, the Maxwell-Wagner polarization arises. Finally, at 10^8 Hz and above, the polarization of porous media is dominated by water polarization due to the dipolar behavior of water molecules [25]. However, for the water dipolar polarization to be effectively taking over, low water salinity is required [26]. However, in the existence of electron conducting particles, a phenomenon called electrode polarization dominates the EDL polarization region [27], [28]

The Maxwell-Wagner (MW) theory is applicable to dielectric materials and the polarization associated with it is explained by bound-charge displacement. It takes place in a frequency range of 10^2 Hz to 10^6 Hz [29], [30]. The driving phenomenon for MW polarization is the bulk electrical properties of the material and it does not relate to the complex surface conductivity of the grains. In a general form, free charge densities form surrounding the interface between the grains and the fluid surrounding them responding to the passing electrical field. However, high frequencies are causing some errors due to

electrode effects, hence, it is hard to be sufficiently accurate whether the effect of MW polarization is existing or not [31]–[34].

The EDL polarization mechanisms are the main mechanisms concerned with non-metallic ion distribution in induced polarization of porous media. [6], [28], [30], [35], [36]. The EDL is composed of two layers: the stern layer (the inner part), and the diffusive layer (the outer part). The stern layer is composed of two parts, a part that bears closely and strongly attracted ions to the surface of the grain (of opposite charge to the particle's surface charge) and a part of weakly attached ions [25], [37]. Whereas the diffusive layer is filled with excess charges that electrically balance the grain body. Ions of the diffusive charge cannot pass through the stern layer because they are hydrated where the stern layer's ions are not hydrated [38], [39]. The EDL polarization is by far the main mechanism under the spotlight when explaining the IP effect within the typical spectral IP range where their effect is nearly discussed in many of the low-frequency SIP related publications in the literature [11], [40]–[44]. It is suggested by [25] that the stern layer possesses most of the charges and ions that are highly contributing to the particles' electric responses, see Figure 3 which shows the excess conductivity in both layers. Both layers of the EDL are provoking a polarization effect when an electric field is passing through a porous medium that is considerably acting in the absence of metallic minerals. The stern layer polarization is explained as an extraneous movement of the stern layer counterions to form a density of similar ions of different charges to the mineral surface. On the other side, ions of opposite charges accumulate to form a different charge density in the other direction, see Figure 4. On the other hand, membrane polarization is taking place in pores spaces and pore throats. It is explained as the accumulation of charges due to the blockage of ions passaging in the

pore throat, see Figure 5. in other words, membrane polarization is when the pore throat acts as a charge-selective membrane due to ions accumulation which differences in mobility between cations and anions [42], [45]. This event produces an opposite net charge system where the end of the pore through will have a deficit in blocked charge.

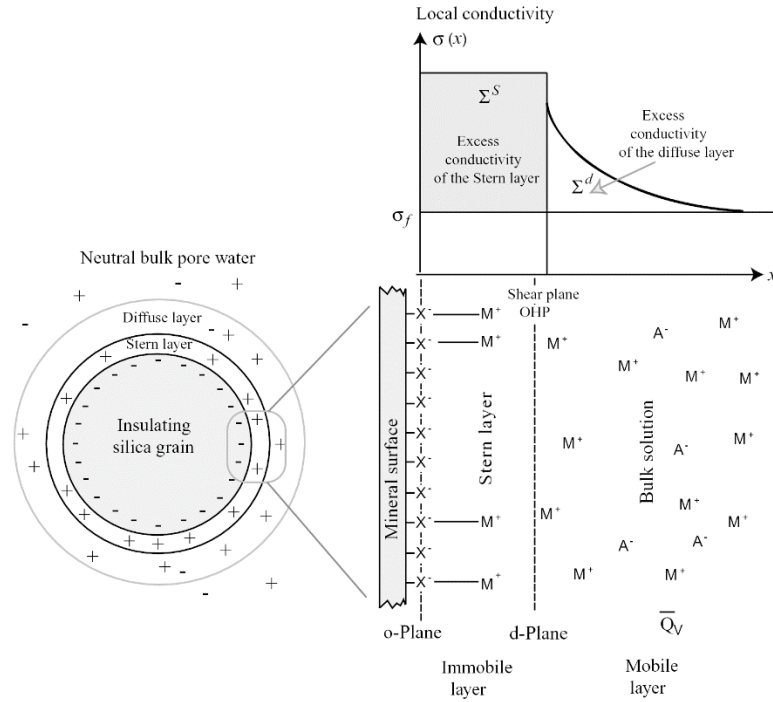


Figure 3: The electrical double layer and the conductivity of the stern and diffusive layers [46]

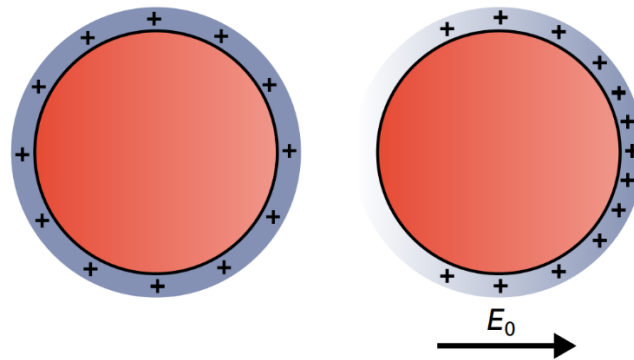


Figure 4: A particle before and after applying an electrical field and undergoing stern layer polarization [47].

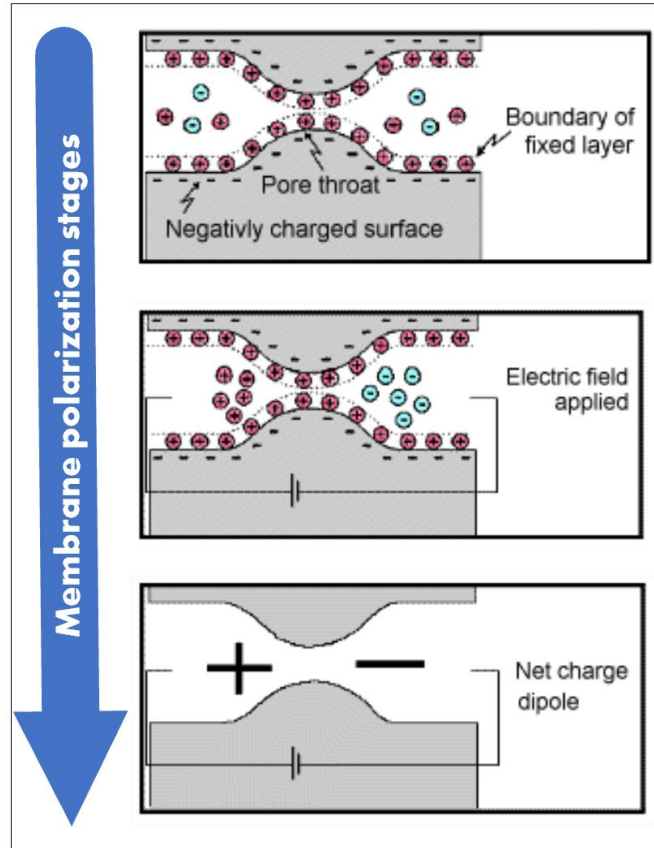


Figure 5: A pore throat before and after applying an electrical field and undergoing membrane polarization.

It is argued that the stern layer polarization is the dominant mechanism in IP in porous media [48] except when the salinity of the medium is very high where at such conditions, the polarization is mostly because of membrane polarization since the ions in the pore water is highly dense than the stern layer and the conductivity of the water is vastly larger than it is of the EDL [37], [49]. Moreover, the stern layer is believed to dominate the polarization processes in particles of porous media, while the diffusive layer is dominating in the electrical conduction of the particles.

The presence of electron conducting materials, such as conductors and semi-conductors, provokes another polarization mechanism to take place i.e., electrode polarization. Electrode polarization is the process in which the electron-conducting grains act like electrodes in porous media. This mechanism is explained as a joint mechanism of the EDL in the mineral-fluid interface and electrolytic conduction of an Archie-type. Both mechanisms are used to explain electrode polarization from an electrochemical point of view. The electrode polarization is causing an effect that is dramatically larger than the EDL polarization alone and that can be seen in Figure 6 where the same material was tested with and without the addition of electron-conducting minerals.

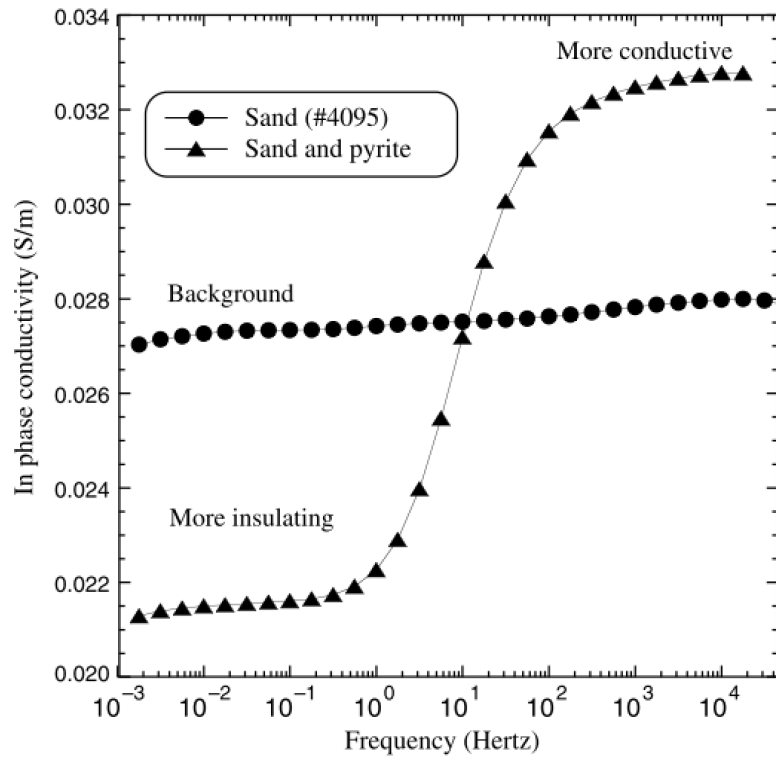


Figure 6: The effect of existence of electron-conducting particles on SIP conductivity readings [50]

Electrode polarization is more complicated than EDL since it is explained by ion movements inside the particle, and around the particle in the surrounding medium. The first mechanism in electrode polarization is the internal conduction in the particles where in the case of conductors, the charge is carried by the free electrons, and in the case of semi-conductors, the charge is carried by electrons and holes (positive charge carriers). The second mechanism involved in electrode polarization is ionic conduction where the electrolyte's ions act as charge carriers in the surrounding medium. When an external electric field passes by, the ions in the electrolyte are separated from the ions in the particle by an interface created by the polarization that took place responding to that exerted field [22], [31], [51], [52]. This mechanism explains thoroughly the polarization effect taking place in porous media with disseminated metallic particles saturated by a conducting (electrolytic) fluid.

C. Complex conductivity in IP

Electrical conductivity is a term describing the ability of a material to pass current. In general, the ability of a material to pass current is dependent on its chemical nature and chemical structure. The main driving mechanism in electrical conductivity is electrons passing through the material in the direction of the electrical field. Materials are divided based on their electrical conductivity into three main categories: conductors, semiconductors, and insulators. In theory, the ability to conduct electrical current is related to the external energy required to excite electrons enough to migrate from the valance energy band, a lower energy band, to the conducting energy band, a higher energy band, in which the material is now able to conduct electrical current. In the case of insulators and semiconductors, there is a gap between the valance band and conducting band that needs a

certain amount of external energy to be crossed by electrons. In insulators, the gap is much larger and requires an amount of energy that could reach 6 eV. However, semiconductors are having energy gaps starting at 1 eV. Whereas conductors are having an overlap between the valance and conducting band which results in high conductivity, see Figure 7.

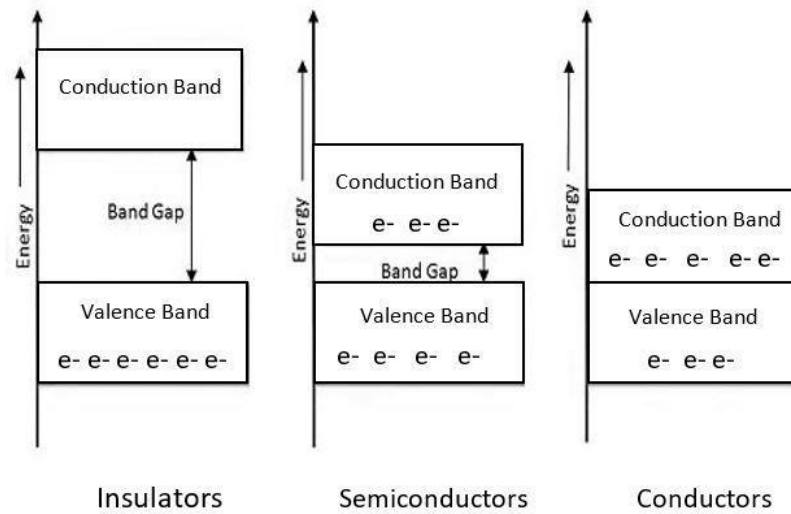


Figure 7: Energy band levels in different types of solids.

The general representation of electrical conductivity often comes in relation to conduction or electromigration through the material. Some materials and porous media usually have more information that could not be conveniently captured by general electrical conductivity and its driving mechanisms. Rather, the complex conductivity term is used where it provides more insight into such materials. As an example, Figure 8 [53] shows the effect of increasing FeS precipitation on the real and imaginary conductivities. As shown in the figure, the imaginary part shows a clear dependence on the amount of precipitated solid materials while the real part shows an almost constant response with very slight changes. Here, the imaginary part was able to capture the growing FeS solid particles while, on the

other hand, the real part was not provoked by the small amount and no clear distinction was captured.

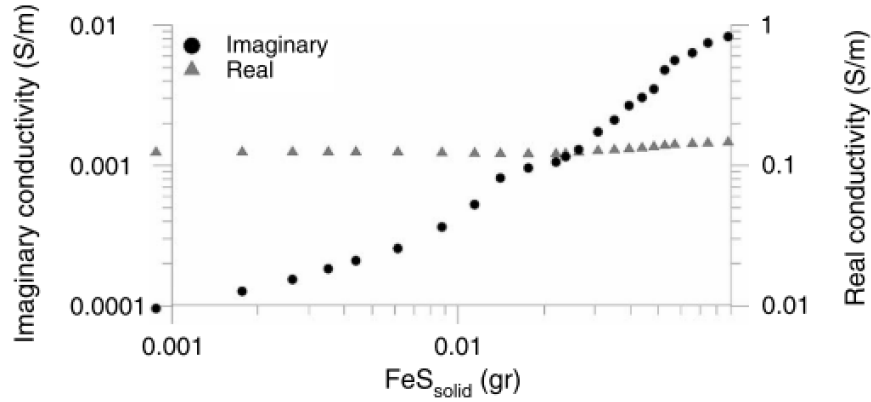


Figure 8: Real and imaginary conductivities vs FeS precipitation [53]

The term complex conductivity stands for the complex number that represents the real and imaginary components of conductivity, with the introduction of the imaginary number i which equals to the square root of -1.

In principle, minerals' capacitive and conductive properties such as surface charge density and area, pore fluid chemistry, water content, metallic minerals' concentration, and clay content are responsible for the IP effect of the tested body [10], [21]. Thus, induced polarization is related to and described in terms of complex conductivity σ^* . The complex conductivity in IP and SIP tests is computed from the values of the measured impedance and phase shift under the influence of low frequency. These measured properties are the core parameters in the study of low-frequency complex conductivity and induced polarization. Furthermore, complex conductivity is composed of two main parts a real part σ' and an imaginary part σ'' . Both parts are represented as the total complex conductivity and can be deduced from the phase shift ϕ as shown in equations 1 and 2 by [20]:

$$\sigma_{\text{surf}}^*(\omega) = \sigma'_{\text{surf}}(\omega) + i\sigma''_{\text{surf}}(\omega) \quad 1$$

$$\tan(\varphi) = \frac{\sigma''}{\sigma'} \quad 2$$

The real conductivity part is related to the ohmic conduction of the mineral, and it is influenced by the migration of ions in the interfacial surface between the stern and the diffusive layers of the EDL. On the other hand, the imaginary part is related to the capacitive nature of the mineral and influenced by the charge storage ability of the mineral or as known as the polarization strength [26]. Moreover, [20] showed that the imaginary conductivity of rocks is related to the electrochemical surface conductivity while the real conductivity is more dependent on the surface conductivity and bulk conductivity, see equations 3 and 4 by [20].

$$\sigma''_{\text{rock}}(\omega) = \sigma''_{\text{surf}}(\omega) \quad 3$$

$$\sigma'_{\text{rock}}(\omega) = \sigma'_{\text{bulk}}(\omega) + \sigma'_{\text{surf}}(\omega) \quad 4$$

Often, complex conductivity is studied at low frequencies i.e., below 1000 kHz where the effect of frequency is shown clearly. However, at high frequencies conductivity becomes a pure function of the physical interaction of the mineral. Many studies have shown that the complex resistivity is dependent on the surface area of the mineral, charge density, and ionic mobility [49], [54]–[56]. Nevertheless, their influence on complex conductivity changes when metallic minerals are present where they constitute a strong influential factor of the complex conductivity, both the real and imaginary parts since the real part will be influenced by the interfacial conduction between metallic minerals that possess good electron conducting nature, and the imaginary part by the strong EDL chargeability of metallic minerals. Additionally, in the presence of electrolytic media, the real part is mostly influenced by the fluid nature and electrical conduction while the imaginary part will be

mostly a function of the mineral nature. According to [27], the following relations show each part of the complex conductivity as a function of frequency and the parameters that they are influenced by:

$$\sigma'(\omega) = F(\sigma_f, \sigma_{en}, \sigma'_{surf}) \quad 5$$

$$\sigma''(\omega) = F(W_d, \sigma''_{sur}) \quad 6$$

where σ_f is the pore fluid conductivity, σ_{en} is the metallic mineral's electronic conductivity and W_d is the diffusion impedance [27], [54], [57]–[59].

D. Spectral Induced Polarization (SIP) and its applications

Spectral induced polarization (SIP) in basic terms is the representation of IP data in the frequency domain. The main concern in SIP incorporation in geophysical approaches is measuring the polarization strength of minerals via the acquisition of the surface complex conductivity at a broad range of frequencies. SIP was used primarily as a minerals and ore exploration tool and developed with time to become a strong geophysical exploration tool to distinguish minerals, metallic depositions, and many other environmental and hydrogeological applications [53], [54], [60], [61].

SIP has been utilized as an effective exploration tool in many studies such as monitoring chargeability variation due to CO₂ injection [62], studying abiotic FeS precipitations [53], monitoring stimulated uranium bioremediation [60], assessed in studying the effect of solute concentration on calcite precipitation [38], environmental monitoring and subsurface lithological discrimination [44], [63]–[65]. Such studies have utilized and proven that SIP is capable of providing strong information that is discriminative and sensitive to the presence of desired minerals and features under study.

In most cases, SIP data is given as complex conductivity readings (real and imaginary parts, separately) that are deduced from the phase shift and impedance raw data versus frequency as shown in Figure 9. SIP tests can be conducted in the laboratory as well to test samples in small chambers either in liquid or solid phases. More into the nature and components of the test is presented in the coming sections.

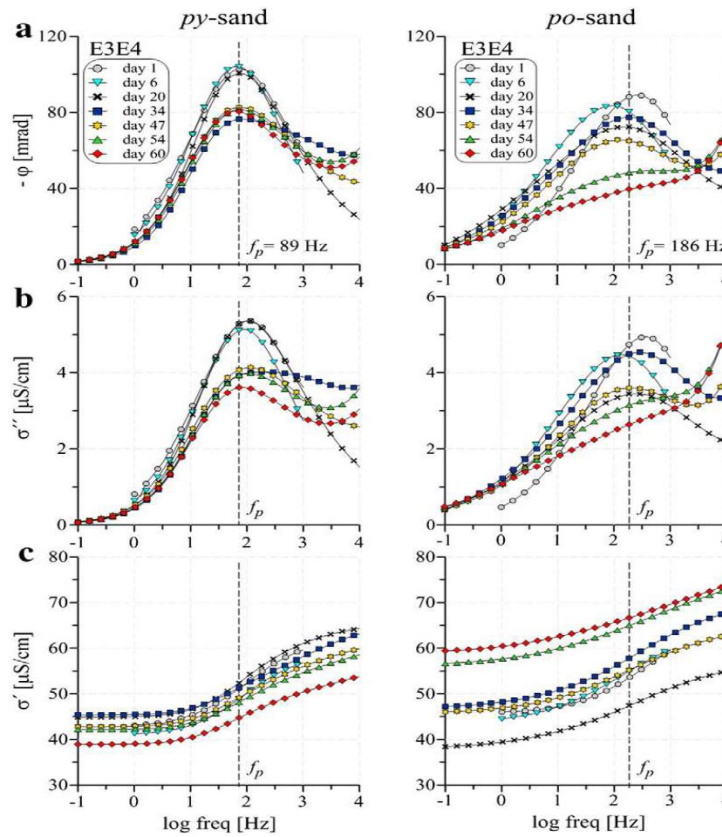


Figure 9: Phase shift and complex conductivity plots from [54]

From such plots, changes in the phase shift, real, and imaginary conductivity values are tracked. Minerals behave differently under the influence of an exerted electric field which

reflects differently in their SIP readings. When investigating minerals, the imaginary component is primarily under consideration since it is the component responsible for the mineral polarization while the real component is often slightly affected by the mineral state, rather, it reflects a higher response to the condition of the fluid-grain conductivity and majority of its influence is coming from the salinity and nature of the pore fluids [38].

E. SIP data modeling

Modeling SIP data has been under research and development since the early 1900s. Cole and Cole came up with an empirical model to describe the IP phenomena. The model was modified from the Debye model suggested in 1927. In the Debye model, the complex dielectric conductivity ε^* is given by:

$$\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + i\omega\tau_{CC_0})} \quad 7$$

Where $\varepsilon_0, \varepsilon_\infty$ are ε^* high and low limits, ω, τ_{CC_0} are angular frequency and relaxation time respectively. Debye model described SIP data for identical grain sizes. Later in 1941, Cole and Cole developed the Cole-Cole model in fitting SIP data by modifying Debye's model by adding the term $(\alpha-1)$, C in other representation, which stands for the Cole-Cole exponent as shown in the following equation:

$$\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (i\omega\tau_{CC_0})^{(1-\alpha)}]} \quad 8$$

The Cole-Cole equation can be represented in terms of complex conductivity as:

$$\sigma^* = \sigma_\infty + \frac{\sigma_0 - \sigma_\infty}{1 + (i\omega\tau_{CC})^c} \quad 9$$

Or in terms of chargeability as:

$$\sigma^* = \sigma_0 \left\{ 1 + \frac{M}{1-M} \left(1 - \frac{1}{1 + (i\omega\tau_{CC})^c} \right) \right\} \quad 10$$

Where M is:

$$M = \frac{(\sigma_{\infty} - \sigma_0)}{\sigma_{\infty}} \quad 11$$

Also, the equation of Cole-Cole can as well be represented in terms of complex resistivity ρ^* as proposed by Pelton in 1978 as:

$$\rho^* = \rho_{\infty} + \frac{\rho_0 - \rho_{\infty}}{1 + (i\omega\tau_{PM})^c} \quad 12$$

Where τ_{PM} stands for the relaxation time of the Pelton Model. Similarly, the model can be expressed with the inclusion of chargeability M as:

$$\rho^* = \rho_0 \left\{ 1 - M \left(1 - \frac{1}{(1 + (i\omega\tau_0)^c)} \right) \right\} \quad 13$$

And

$$M = \frac{(\rho_0 - \rho_{\infty})}{\rho_0} \quad 14$$

In 1951, the Cole-Cole model was modified when failed at dispersions at low and high frequencies. The modification was done by Davidson and Cole and was able to fit the SIP behavior at those ends. Pelton in 1983 proposed another modification in what is called the generalized Cole-Cole model (GCC) given as:

$$\rho_{(\omega)}^* = \rho_0 \left[1 - M \left(1 - \frac{1}{(1 + (i\omega\tau_{PM_{GCC}})^c)^a} \right) \right] \quad 15$$

Here, the Cole-Cole model can be obtained when $a = 1$, and the Debye model can be obtained as well when $c = 1$.

Many attempts were recorded without considering the dispersion term as a single term, rather, it was taken as multiple terms. One approach was recorded by Pelton in 1978 where

he considered the relaxation term to be a multiple of relaxation terms at lower and higher frequencies as shown [66]:

$$Z(\omega) = R_0 \left\{ 1 - \frac{1}{1 + (i\omega\tau_{PM_1})^{c_1}} \right\} \left\{ \frac{1}{1 + (i\omega\tau_{PM_2})^{c_2}} \right\} \quad 16$$

Where $Z(\omega)$ is the impedance, R_0 is the DC electrical resistivity, τ_{PM_1} and c_1 and τ_{PM_2} and c_2 are relaxation time constants and Cole-Cole exponents for the higher and lower frequency ends.

Another approach was suggested by Kemna in 2000 where they modified the Cole-Cole model to take the complex resistivity as a function of multiple, if desired, Cole-Cole relaxation terms, each with its different chargeability M_l , relaxation exponent τ_{PM_l} and Cole-Cole exponent c_l as given in the following equation [67]:

$$\rho_{(\omega)}^* = \rho_0 \left[1 - \sum_{l=1}^L M_l \left(1 - \frac{1}{1 + (i\omega\tau_{PM_l})^{c_l}} \right) \right] \quad 17$$

Further modifications came up such as the suggestion of a model that can fit dispersion at high frequencies by Kruschwitz in 2010 as given in the equation [68]:

$$\sigma_{(\omega)}^* = \frac{\sigma_0}{1 - m \left(1 - \left(\frac{1}{(1 + i\omega(\tau_{PM_{GCC}})^C)^a} \right) \right)} + i\omega\epsilon_\infty \quad 18$$

Nordsiek and Waller suggested a modification to the Debye model in 2008 called the Debye Decomposition model [69]. The approach takes the superposition of a different number of Debye spectra. Where each spectrum has its specific chargeability M_k and time relaxation τ_{PM_k} as:

$$Z(\omega) = R_0 \left(1 - \sum_{k=1}^n M_k \left(1 - \frac{1}{1 + i\omega\tau_{PM_k}} \right) \right) \quad 19$$

Many other methods have been suggested with time to account for different changes or specific conditions. Some are shown in Table 1 summarized by [19]. SIP modeling work is absent in this thesis work due to complexity and time cost.

Table 1a: Common SIP models (modified from [19])

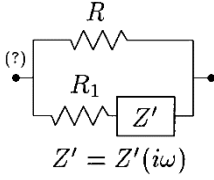
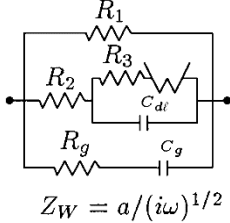
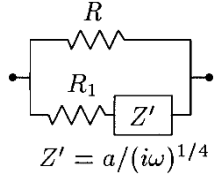
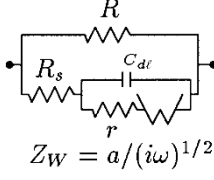
Item	Model and Reference	Circuit Diagram	Complex resistivity
1	Wait (1959)	 $Z' = Z'(i\omega)$	$\rho = \rho_s \left(1 - \frac{A}{1 + 2A/3} \right)$ A = average polarizability per unit volume of an infinite heterogeneous medium ρ_s = resistivity of the host medium
2	Ward and Fraser (1967)	 $Z_W = a/(i\omega)^{1/2}$	$\rho = \rho_D \left[1 - \frac{1}{1 + (\rho g + \gamma/t\omega)/\rho_D} \right]$ ρ_D = resistivity function associated with Dias model
3	Madden and Cantwell (1967)	 $Z' = a/(i\omega)^{1/4}$	$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{1 + (t_K)^{1/4}} \right) \right]$ $m = (\rho_0 - \rho_\infty)/\rho_0 = \frac{R}{R + R_1}$ $\tau = ((R + R_1)/a)^4$
4	Dias (1968, 1972)	 $Z_W = a/(i\omega)^{1/2}$	$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{1 + \text{mor}_r^r(1 + \mu^{-1})} \right) \right]$ $m = (\rho_0 - \rho_\infty)/\rho_0 = \frac{R}{R + R_s}$ $\mu = i\omega\tau + (i\omega\tau'')^{\frac{1}{2}}$ $\tau = rC_{dl}; \tau' = (R + R_s)C_{dl}$ $\tau'' = (aC_{dl})^2$

Table 1b: Common SIP models (modified from [19])

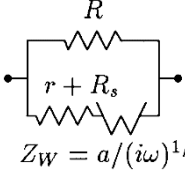
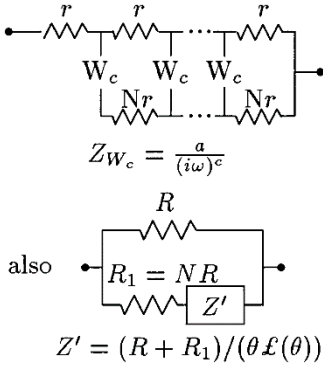
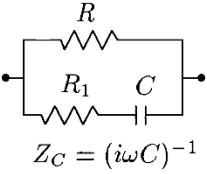
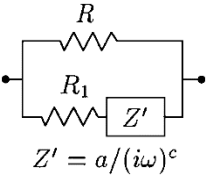
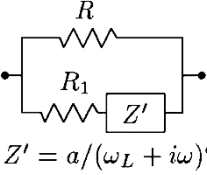
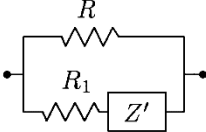
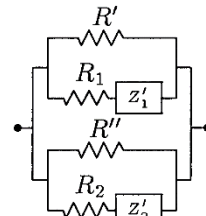
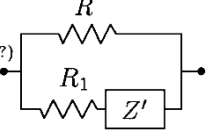
5	Warburg Dias (1968, 1972) Pelton (1977)	 $Z_W = a/(i\omega)^{1/2}$	$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{1 + (\omega\omega\tau)^{1/2}} \right) \right]$ $m = (\rho_0 - \rho_\infty)/\rho_0 = \frac{R}{(r + R_s) + R}$ $\tau = \left(\frac{r + R_s + R}{a} \right)^2$
6	Zonge (1972) Pelton (1977)	 $Z_{Wc} = \frac{a}{(i\omega)^c}$ also $Z' = (R + R_1)/(\theta \mathcal{L}(\theta))$	$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{1 + \theta \mathcal{L}(\theta)} \right) \right]$ $\theta = (i\omega\tau)^{c/2}$ $\mathcal{L}(\theta) = \coth \theta - \frac{1}{\theta}$ $m = (\rho_0 - \rho_\infty)/\rho_0 = \frac{R}{R + R_1}$ $\tau = \left(\frac{R + R_1}{a} \right)^{1/c}; 0 \leq c \leq 1$ $0 < N \leq 1$
7	Debye Pelton (1977)	 $Z_C = (i\omega C)^{-1}$	$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{1 + i\omega\tau} \right) \right]$ $m = (\rho_0 - \rho_\infty)/\rho_0 = \frac{R}{R + R_1}$ $\tau = C(R + R_1)$
8	Cole-Cole Pelton (1977)	 $Z' = a/(i\omega)^c$	$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{1 + (i\omega\tau)^c} \right) \right]$ $m = \frac{R}{R + R_1}; 0 \leq c \leq 1$ $\tau = \left(\frac{R + R_1}{a} \right)^{1/c}$
9	Davidson- Cole Pelton (1977)	 $Z' = a/(\omega_L + i\omega)^c$ with $(R + R_1)/(a/\omega_L^c) \gg 1$	$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{[1 + (i\omega\tau)^c]^k} \right) \right]$ $m = \frac{R}{R + R_1} \frac{a/\omega_L^{ck}}{R_1 + a/\omega_L^{ck}}$ $0 \leq (c; k) \leq 1$ $\tau = 1/\omega_L$

Table 1c: Common SIP models (modified from [19])

10 Generalized Cole-Cole Pelton (1977)	 $Z' = a/(\omega_L^c + (i\omega)^c)^k$ with $(R + R_1)/(a/\omega_L^{ck}) \gg 1$	$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{[1 + (i\omega\tau)^c]^k} \right) \right]$ $m = \frac{R}{R + R_1} \frac{a/\omega_L^{ck}}{R_1 + a/\omega_L^{ck}}$ $0 \leq (c; k) \leq 1$ $\tau = 1/\omega_L$
11 Multi-Cole- Cole Pelton et al. (1978)	 $Z'_j = a_j/(i\omega)^{c_j}; j=1,2$ at least one of the following conditions satisfied: 1) $R_1 \gg R' \gg R''$ 2) $R_2 \gg R'' \gg R'$ 3) $R_1 \gg R'; R_2 \gg R''$	$\rho = \rho_0 \left[1 - m_1 \left(1 - \frac{1}{1 + (i\omega\tau_1)^{c_1}} \right) \right]$ $\left[1 - m_2 \left(1 - \frac{1}{1 + (i\omega\tau_2)^{c_2}} \right) \right]$ $m_1 = \frac{R'}{R_1 + R'}; 0 \leq (c_1; c_2) \leq 1$ $\tau_1 = \left(\frac{R_1 + R'}{a_1} \right)^{1/c_1}$ $m_2 = \frac{R''}{R_2 + R''}$ $\tau_2 = \left(\frac{R_2 + R''}{a_2} \right)^{1/c_2}$
12 Wong (1979)	 $Z' = Z'(i\omega)$	$\rho = \rho_s \left(1 - \frac{3 \sum_j N_j f_j}{1 + 2 \sum_j N_j f_j} \right)$ N_j = number of spherical particles j per unit volume f_j = reflection coefficient at the interface between a homogeneous infinite ionic solution and the medium ρ_s = resistivity of the homogeneous solution

1.2.SIP Measurement Instrument and Mechanism

1.2.1 PSIP Tool and Mechanism

The PSIP is multi-channel optimized for SIP measurements. In this work, a full multi-channel PSIP unit with 4 stimuli and 24 voltage sense pairs shown in Figure 10 that is obtained from Ontash & Ermac® was used. Each stimulus channel can be used independently, which allows for surveying different samples simultaneously with each sample being linked to a separate stimulus. The required sample is put into a testing column connected to the instrument by the required number of potential electrodes, where every pair of voltage sensing electrodes represents a testing segment.

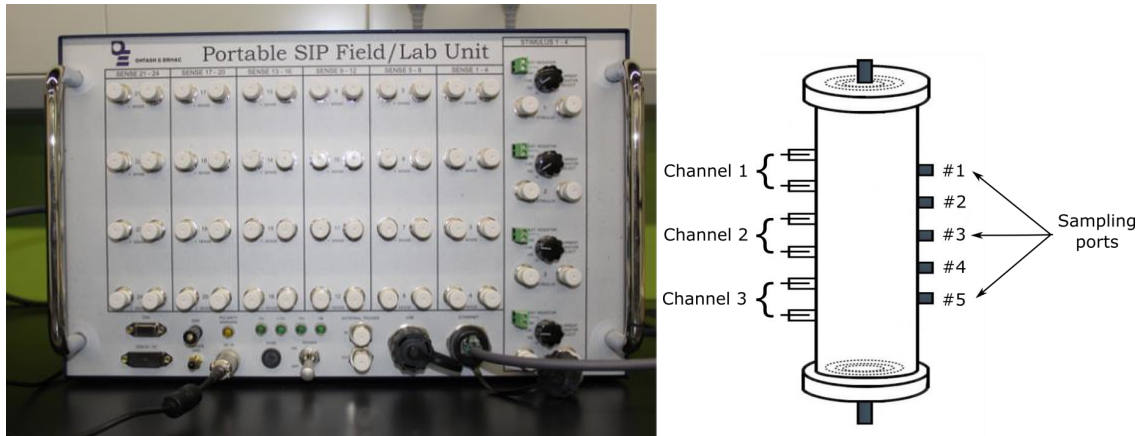


Figure 10: KFUPM PSIP Field/Lab unit

The SIP technique measures the phase shift ϕ , and the complex conductivity magnitude $|\sigma|$ (impedance) of an injected current, typically across a wide frequency range (the base configuration is 0.01 Hz – 20 kHz) to estimate the real σ' and imaginary σ'' component of complex conductivity σ^* . The resistance amplitude is deduced from the magnitude times the value of the selected shunt resistor. The PSIP offers the possibility to choose the most appropriate value (10 Ω , 100 Ω , 1000 Ω , and 10000 Ω) depending on the resistance of the sample along with a port for an external reference resistor. In addition, PSIP can also

perform self-potential (SP) and time domain induced polarization (TDIP) measurements with the use of a stimulus switch unit.

The SIP tests vary from liquids to solids depending on the nature of the experiment. But the general concept and workflow remain the same in all tests. To conduct an SIP test, the tested sample is prepared by fixing its properties i.e., mass, density, concentration, grain size ...etc. fixing such parameters ensures repeatability and correct measurement. The sample is then put into the suitable testing column or cell while making sure no spaces, discontinuities, or contaminations are present that may differ the passage of electric current through the system. The column is linked to the PSIP unit through the current injecting electrodes at the top and the bottom, and through several potential measuring electrodes on the side of the testing column to measure the IP properties of the tested sample. When the test starts, the unit injects an electric current that passes through the sample while continuous measuring of potential is carried through the potential measuring electrodes. The unit records the signals in terms of phase shift and complex conductivity magnitude signals versus frequency. Later, the recorded signals are used to deduce the complex conductivity parts using mathematical equations.

1.2.2 Tool Calibration

The preparation of the tool starts with calibrating the unit. In the calibration process, a buffer with known conductivity, such as potassium chloride (KCl) as illustrated in Table 2. Three different concentrations of KCl solution are tested and the SIP instrument is calibrated based on their readings. Also, a geometric factor representing the volume between the sensing electrode is measured. This factor is used in the conversion of resistance to resistivity values that are later used in the calculation of the imaginary and

real parts of the complex conductivity, whereas if these coefficients are not utilized, the measurements are not accurate.

Table 2: KCl buffer solutions at different concentrations

Sample	Conductivity
KCl Buffer 1	70 $\mu\text{S}/\text{cm}$
KCl Buffer 2	300 $\mu\text{S}/\text{cm}$
KCl Buffer 3	900 mS/cm

Each pair of potential electrodes has its certain geometric factor, and all pair combinations are tested, and their geometric factors are recorded. To measure the error of the instrument in measuring conductivity, buffer solutions are used as reference solutions. The conductivities of buffer solutions are measured using a conductivity meter then the SIP tool and the error in the SIP is recorded by plotting the reading from the SIP tool versus the conductivity meter and the slope of the plot is taken as the geometric factor for each pair.

Another procedure to be executed before the start of the SIP tests is the depolarization of the Ag electrodes. Chlorine is used to make the pure silver electrodes non-polarized by immersing the electrode in it. Thus, any additional electrode polarization is removed in later tests.

1.3. Thesis organization

This thesis work is studying the ability of the SIP method as a part of the formation evaluation process by using it to detect and assess pyrite content, one of the most common types of iron sulfide scales in petroleum formations. In addition to a case application of the

method in other petroleum aspects i.e., characterizing drilling fluids and weighting materials.

In chapter 2, the SIP method is applied to characterize and early detect pyrite content in limestone formations. A thorough review is given on scales and iron sulfide scales with the most used method to detect and mitigate the problem in petroleum reservoirs and facilities. Then, experimental work is presented to illustrate the methodology of iron sulfide scale detection and characterization in formation rocks.

In chapter 3, the SIP method is applied to characterize and monitor drilling fluids in two main stages. In stage 1, the concentration of calcium carbonate, a common weighting material, is monitored and characterized for concentration evaluation in bentonite drilling fluids. Whereas in stage 2, barite and calcium carbonate sag are monitored and characterized over short periods of time i.e., 3 hours. This research case study shows the robustness and sensitivity of the SIP method in drilling fluid. A review of the current case of drilling fluid monitoring and sag characterization. Then, the method is proposed with supporting experimental work.

Chapter 4 puts the conclusion of both chapters, 1 and 2, into a summarized form. It gives the outcomes of the work and comments on the achieved results.

CHAPTER 2

IRON SULFIDE SCALES CONTENT ASSESSMENT AND EARLY DETECTION BY SPECTRAL INDUCED POLARIZATION

2.1. Introduction

Hydrocarbon production is one of the most crucial stages in the petroleum industry and its well-being is an important nerve in the complete process' success. Formation damage problems are very common in hydrocarbon flow systems and require clear attention in order to guarantee an economically profitable flow of hydrocarbons to the wellbore. One of the major types of formation damage problems is the formation and deposition of scales in the formation rocks and on the inner region of pipelines. Scales are organic or inorganic materials that form in the wellbore and rock formations due to chemical reactions (i.e., iron sulfides) or physical phenomena (i.e., hydrates) [70], [71]. Scales inhabitation and removal have been under investigation over the last decade due to the importance of properly understanding their nature and coming up with ways to dissolve and prevent their presence [72]–[77]. One of the most common types of scales present in the wellbore is iron sulfides, specifically iron sulfide (FeS) and iron disulfide (FeS₂).

Iron sulfide scales form in sour environments due to the presence of hydrogen sulfide (H₂S) in the reservoir and due to their low solubility, they deposit in the near formation pores and on the walls of the production tubing causing reductions in flow ability and losses in the production potential and other tubing corrosion issues [78], [79]. Thus, early investigation

of iron sulfide products is crucial to maintain a safe and profitable production environment where fresh iron sulfide scales are easier to remove via acidizing while relatively old, formed iron sulfide scales require additional mechanical ways to remove (e.g. mechanical jetting) [79]. As a result, methods are developed to investigate the presence of iron sulfides in a wellbore such as induced polarization (IP) [53]. IP is a branch of electrical resistivity investigation tools that utilizes the measurement of materials' ability to charge and discharge electrical current. Such phenomenon takes place at lower frequencies than what regular resistivity tools can measure. IP signals can both be measured with respect to time or frequency as its domain [22]. Theoretically, SIP is related to the capacitive and conductive nature of the material where it provides readings in a combination of both a real and an imaginary component. [10], [53]. Also, SIP reading depends on the surface area and the capacity of cation exchange of the material [10], [80]. As a result, every certain mineral possesses a defined chargeability value that makes it differentiable from other minerals [64]; and the SIP method is considered to be a strong detecting tool in mineral detection especially iron sulfides where they give unique readings for such minerals [81]. Moreover, Research has shown that the concentration of minerals in solutions is related to the SIP readings [53]

Sulfur is a known insulator, but when coupled with other metals, it possesses interesting electric properties similar to semiconductors and dielectric materials. Pyrite (FeS_2), a form of iron sulfides, is a well-known semiconductor and dielectric material. It has high electrical charge storage ability and a high dielectric constant at low frequencies. Indication of storage charge ability can be made by relating to the imaginary part of the measured

complex conductivity of the material. Thus, SIP can be used to spot iron sulfide accumulations since it utilizes low frequency complex conductivity surveys.

In this chapter, the incorporation of SIP readings in the detection and characterization of FeS_2 as scales within a mixed-mineral environment is evaluated and the effect of variations of concentration of scales to other materials is studied utilizing primarily the imaginary component of the complex conductivity reading of the system. This work will provide a valuable assessment to the detection of iron sulfide scales in rock formation and will enhance the scale detection capability in wellbores.

2.2. Statement of Problem

The in-situ indication of iron sulfide scales in formation and production pipes is crucial. Scale presence is often not in pure form, rather, it is in a form of complex mixtures of scale and other minerals that make the formation rock, mainly limestone. A key to preventing iron sulfide accumulations is to early detect its presence in formation rock and take necessary actions to prevent and inhibit its formation and deposition in wellbore tubular and facilities. While lab investigation methods are available, the urge is present for robust and efficient ways with adequate sensitivity to scale presence and features to detect iron sulfide in formation rock in situ and in the laboratory.

2.3. Objectives

With SIP as an effective tool of mineral characterization and detection tool, the urge for more applications of the tool in the oil and gas domain is thriving. Usually, scales are not

found in pure form, which makes it harder for investigation tools to detect their existence as other minerals' signals might interfere with the scale's signals. In this work, the SIP tool is going to be utilized and tested in FeS₂ detection in calcium carbonate matrices with variations in the concentration of iron sulfide. This work will shed light on the potential and sensitivity of SIP in scale detection and quantification and will set a basis for real-life use in well pipes and equipment for scale early detection and characterization. Utilization of the SIP method would assess stimulation jobs, near wellbore rock properties, and flow assurance where it will provide a good characterization of the scale condition.

2.4. Literature Review

2.4.1. Scales

A. Scales in the subsurface

Subsurface formation damage is any disturbance in the physical or chemical nature of the formation that may lead to losses in its production quality. Scales, a very common type of formation damage, is a name called on materials that exist naturally or inducibly in a subsurface flow system. Such materials deposit and lead to either reducing the inner area of the flow path or, in extreme cases, blocking and seizing the production flow and causing financial losses that can reach millions of dollars every year see Figure 11 [82]. Accumulations of scales can occur anywhere in the flow system, including in pipelines, casing, bottom hole equipment, or even in the formation itself. These accumulations pose a threat to the production process by potentially causing full blockages of the flow system,

leading to pressure buildup in the pipes [83]. The primary cause of scale formation is the presence of water, which can react with certain minerals in the formation [71].

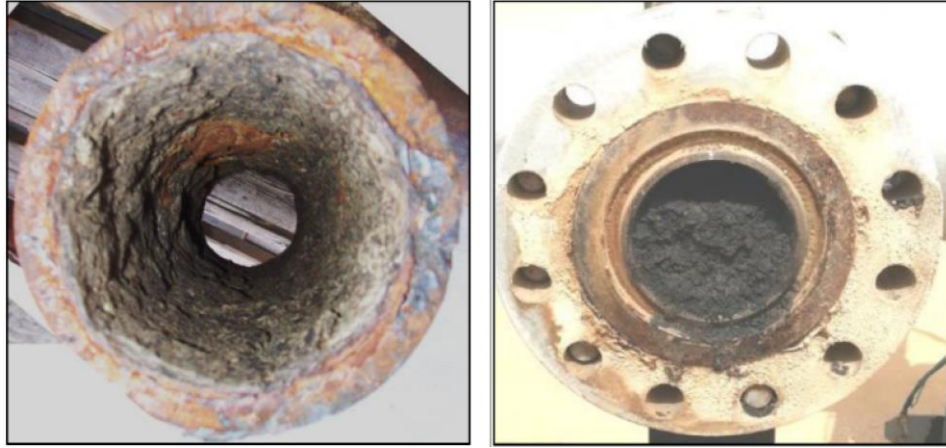


Figure 11: Scale deposition in pipelines [84]

B. Types of scales

Due to the variety of minerals in the subsurface, scales that occur in production systems can take many forms (e.g., solid-like, and solid) [82] and types (organic and inorganic) [85] Scales can range from fine particles that flow and accumulate to wax-like (asphaltene) and frozen (hydrates) types. Common types of scales can be classified as sulfides, oxides, sulfates, and carbonates. Table 3 shows other common scale types [71], [86].

Table 3: Common scale types (modified from [71])

Sulfates		Sulfides	
gypsum	CaSO ₄ .2H ₂ O	Pyrrhotite	Fe ₇ S ₈
Anhydrate	CaSO ₄	Troilite	FeS
Barite	BaSO ₄	Mackinawite	Fe ₉ S ₈
Hemihydrate	CaSO ₄ .2H ₂ O	Pyrite	FeS ₂
Celestite	SrSO ₄	Marcasite	FeS ₂
Iron scales		Greigite	Fe ₃ S ₄
Ferrous Hydroxide	Fe(OH) ₂	Sphalerite	ZnS
Ferrous Hydroxide	Fe(OH) ₂	Galena	PbS
Hematite	Fe ₂ O ₃	Carbonates	
Magnetite	Fe ₃ O ₄	Calcite	CaCO ₃
Akageneite	α-FeOOH	Vaterite	CaCO ₃
Goethite	β-FeOOH	Aragonite	CaCO ₃
Lepidocrocite	γ-FeOOH	Siderite	FeCO ₃
Hibbingite	Fe ₃ (OH) ₃ Cl	Dolomite	CaMg(CO ₃) ₂

C. Iron sulfide scales

Iron sulfide scales are one of the most common types of scales [79]. The formation of iron sulfides is common in sour formations and is usually linked to the presence of hydrogen sulfide (H₂S). H₂S is a naturally occurring gas in the wellbore and subsurface due to many reasons. It is reported that the presence of H₂S is a product of the reaction of sulfate-reducing bacteria (SRB) with naturally present sulfate in the formation [87]. As a result, iron reacts with H₂S and produces iron sulfides of many forms that precipitate in the formation and production system [88], [89]. The chemical reaction of iron sulfides is shown as follows:



Depending on the iron-to-sulfur ratio in the compound, electric and magnetic properties, and morphology, many types of iron sulfides are present. Some familiar types are the mono-sulfides such as iron sulfide-I (FeS) or as known as mackinawite, and disulfides such as pyrite (FeS₂) [90]. Figure 12: Photos of FeS scale samples by [79] shows some FeS samples gathered from pipelines. Iron sulfides are among the most troublesome types of scales to occur in the reservoir and pipelines since they deposit on the walls of the pipe and cause corruptions that shorten the life of pipelines in addition to minimizing the productivity of the performance of wells. As shown in Table 4 [91], the permeability of limestone was drastically affected by iron sulfide presence in the pores where they initiated it by core flooding where core NF-1 lost about 68% of its initial permeability and core NI-1 lost 15% of its initial permeability.

Table 4: The effect of iron sulfide on permeability (modified from [91])

Core number	Initial rock permeability, mD	FeS-contaminated permeability, mD	Loss %
NF – 1	9	2.9	68%
NI – 1	12.5	10.6	15%

Eliminating iron sulfide scales is not easy since they require complicated and quick removal procedures where if iron sulfide scales are deposited for extended periods, more effort in the removal action is required [79].

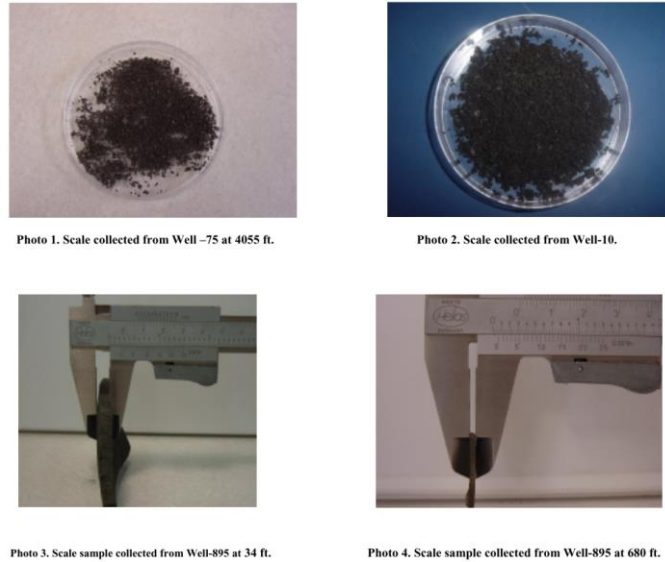


Figure 12: Photos of FeS scale samples by [79]

D. Iron sulfide scales investigation

It is essential to remove scale whenever present in the wellbore, and many efforts have been done in the research field and industry to spot, prevent and remove such scales from water and hydrocarbon production systems. [76], [92]–[94]. To contain iron sulfide scales, the roots of its formation need to be eliminated. As mentioned, two main elements in iron scales formation are elemental iron (Fe) and hydrogen sulfide (H_2S); and to prevent iron sulfide formation, their presence needs to be constrained. However, their presence, especially H_2S gas, cannot be prevented due to their high concentrations in hydrocarbon wells especially in sour formations such as Khuff formation in Saudi Arabia which has high H_2S content. Therefore, scale inhabitation is assessed as a secondary line of defense [95].

In production tubulars, iron sulfides cause pipeline corruptions if their formation reaction took place on the inner surface of the pipe where H_2S gas reacts with the pipe inner material

causing accumulations of iron sulfide scales in some places and pitting in other places of the pipe that leads to metals losses and weakens the collapse and tension stresses of the pipe. The detection of iron sulfide scales is possible through either testing the stream via chemical or material characterization means, or the use of corrosion detection tools such as mechanical caliper fingers. Usually, high H_2S combined with iron concentrations, and even the presence of SRB, are signs of possible iron sulfide scales formation. Hereby, bulk sample testing of the fluid stream is required for iron sulfide scale testing. Some common test methodologies are the stirred vessel, filter blockage, iron sulfide stress test, and static bottle tests. However, another approach is via potential surveys either electrical or magnetic [95], [96]. Some forms of surveys are Magnetic Flux Leakage MFL and its other forms such as circumferential and tri axial MFL, and ultrasonic tools that detect metal losses in pipes that might be attributed to iron sulfide corrosion [97].

2.5. Methodology

2.5.1. Sample preparation and sample characterization

Pyrite was acquired from an international supplier and ground to particle size between 250 and 600 μm . Indiana limestone was acquired and ground to a similar particle size to pyrite. X-Ray Fluorescence (XRF) result is shown in Table 5. Ottawa sand is used as buffer layers at the top and bottom of the column. The column preparation is composed of 3 sections: a top and bottom section of Ottawa sand and a 4 cm section in the middle filled with the tested sample.

Table 5: XRF test results for pyrite sample

Element	Weight %
Aluminum (Al)	4.63
Silicon (Si)	0.64
Sulfur(S)	70.64
Calcium (Ca)	0.04
Chromium (Cr)	0.01
Iron (Fe)	23.83
Cobalt (Co)	0.08
Copper (Cu)	0.08
Zink (Zn)	0.02
Arsenic (As)	0.02

In the XRF results, the sample shows that the sample is more than 96% pure iron sulfide. The deposition of pyrite can sometimes be associated with other minerals such as carbonates, quartz, and aluminum as shown in the sample used in this study.

A 17 cc SIP testing column was used to characterize the pyrite-limestone mixtures. For preparing the mixtures, the conning and quartering method is used to ensure decent distribution of pyrite particles within the mixture. 7 different samples of different concentrations of pyrite (0%, 0.25%, 0.5%, 1%, 30%, 70%, and 100%) are prepared by mixing them with limestone grains.

While filling the columns with the mixtures, the apparent porosity was calculated by dividing the zero-porosity mass by the measured mass after filling the column. For pyrite, the apparent density was 2.48 g/cc when tested in a graduated cylinder, while for limestone, the apparent density was 1.37 g/cc. These values are to help reach a similar compaction level each time while filling the samples in the columns. The samples were calculated by

a bulk volume of 4 cm or 16.62 cc. Table 6 shows the combinations of pyrite-limestone used in the testing period.

Each mixture is filled in the middle of the SIP testing column with two layers of Ottawa sandstone as buffers in the top and bottom of the column. Sandstone was used due to the limitation of the sample available. While filling the samples, no confining pressure or compaction was used.

Table 6: Percentage volumes and mass of the tested mixtures

Pyrite							
wt. %	0.00%	0.25%	0.50%	1%	30%	70%	100%
Volume (cc)	0.00	0.04	0.09	0.17	5.10	11.90	17.00
Mass (g)	0.00	0.21	0.43	0.42	12.64	29.49	42.36
Limestone							
wt. %	100.00%	99.75%	99.5%	99%	70%	30%	0%
Volume (cc)	17.00	16.96	16.92	16.83	11.90	5.10	0.00
Mass (g)	46.07	45.95	45.84	23.11	16.34	7.00	0.00

2.5.2. Testing Concept

Pyrite has nearly 53% per weight sulfide in its chemical structure. Knowing that sulfur is highly detectable in IP readings following the previous findings, the ability to utilize SIP signals to detect iron sulfide in formations is believed to be promising. Embedded pyrite particles are assumed to cause a sharp and visible change in the signals of SIP especially the signals responsible for the polarization effect i.e., imaginary conductivity. Increasing the volume percentage of iron sulfide is believed to cause even more increases in the signals.

2.5.3. Tool preparation and test setup

After placing the samples in the SIP columns, the columns are pumped with a saline solution (KCl) of known electric conductivity (295 uS/cm) to ensure proper electric current passage through the testing column. After full saturation is achieved, the columns are connected in the configuration shown in Figure 13 to stimuli in the SIP unit. SIP tests were run over frequency ranges of 0.01 - 10000 Hz to monitor changes in peaks and behavior of the spectrum vs concentration. Test input configurations are shown in Table 7. Every sample was tested twice using SIP to validate the repeatability of the method.

Complex conductivity (σ^*) of a certain matter can be described as shown in equation 20, where σ' and σ'' are the real and imaginary conductivity, respectively [98].

$$\sigma^* = \sigma' + i\sigma'' \quad 20$$

Similarly, σ' and σ'' can be obtained as a function of the phase shift (ϕ) and the magnitude of the complex conductivity recorded from the SIP tool as shown in equations 21, 22, and 23 [98].

$$\phi = \tan^{-1} \left(\frac{\sigma''}{\sigma'} \right) \quad 21$$

$$\sigma' = |\sigma| \cos \phi \quad 22$$

$$\sigma'' = |\sigma| \sin \phi \quad 23$$

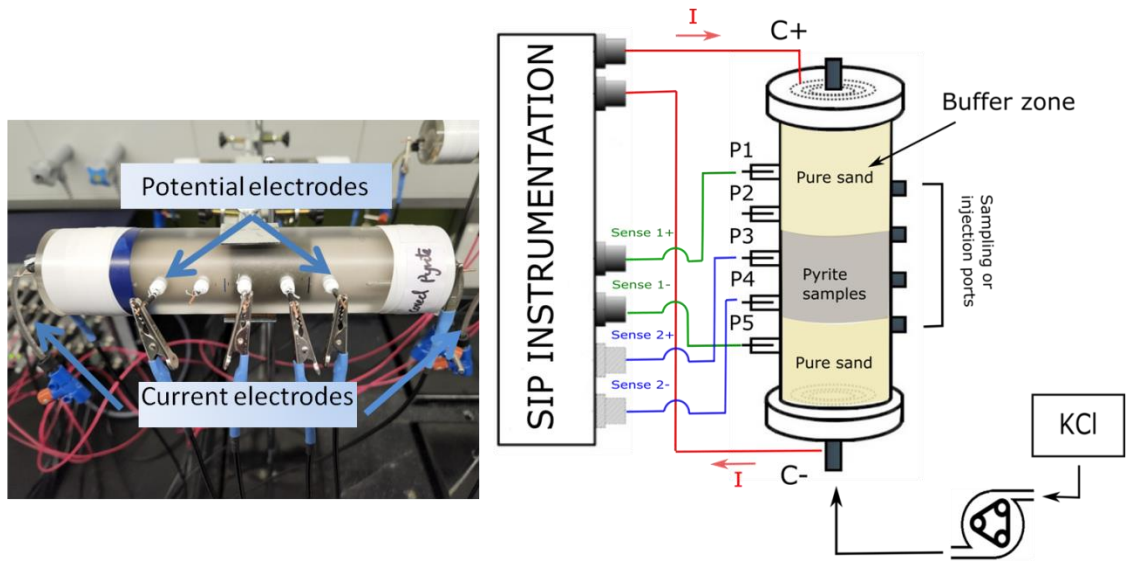


Figure 13: filled SIP test columns (left) and test schematic (right)

Table 7: SIP test configuration

Freq. (Hz)	Sampling steps	Amplitude (V)	Current Resistor (Ohms)
0.01-10,000	41	5	100

2.6. Results and Discussion.

2.6.1. SIP Phase Shift

Phase shift readings for all samples are acquired and plotted in Figure 14 against frequency. As shown, there is a dependency between phase shift and frequency where it increases with an increase in frequency until it reaches a peak at a frequency of 316 Hz. This constant peak value indicates the uniformity of the particle size for the sample used. A study showed that the peak frequency and magnitude are controlled by the grain size where finer grains give larger peak frequencies and higher magnitudes than coarse ones. This comes in agreement with the hypothesis by Slater and Martin [43], [99] that related larger values of

specific surface area to higher phase signals and peaks where the latter increase the polarization effect. Small concentrations are showing a clear distinction as well where they provide a peaking behavior in the peaking frequency for pyrite i.e., 316 Hz, see the zoomed section in Figure 14. Phase shift is a strong indicator of concentration where it shows an increase in the peaking frequency uniformly with the increase in concentration.

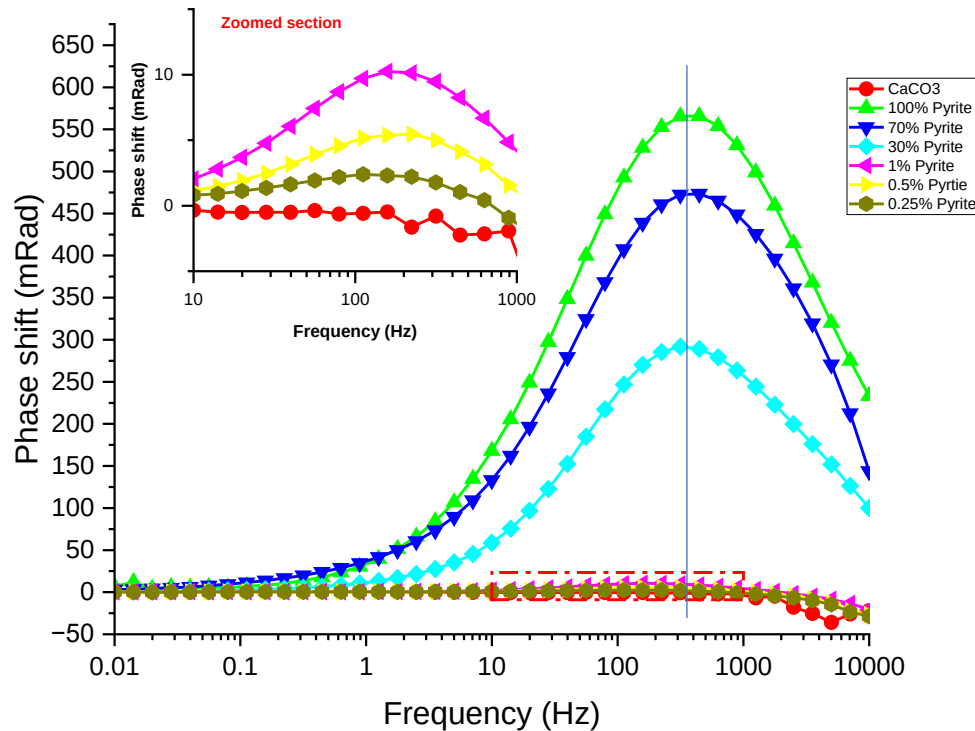


Figure 14: Phase shift readings over a frequency range [0.01-10000] Hz of pyrite-calcium carbonate mixtures of different concentrations.

2.6.2. SIP Imaginary Conductivity

Imaginary conductivity is related to the ability of the material to store charges, known as the polarization effect. Figure 4 shows the relation between the concentration of pyrite and imaginary conductivity. The peak frequency is around the 1000 Hz mark for all samples due to conformity in particle size. The zoomed-in section in Figure 15 shows the spectrums

of low concentrations of pyrite. Clearly, SIP can efficiently detect low concentrations of pyrite in complex limestone matrices.

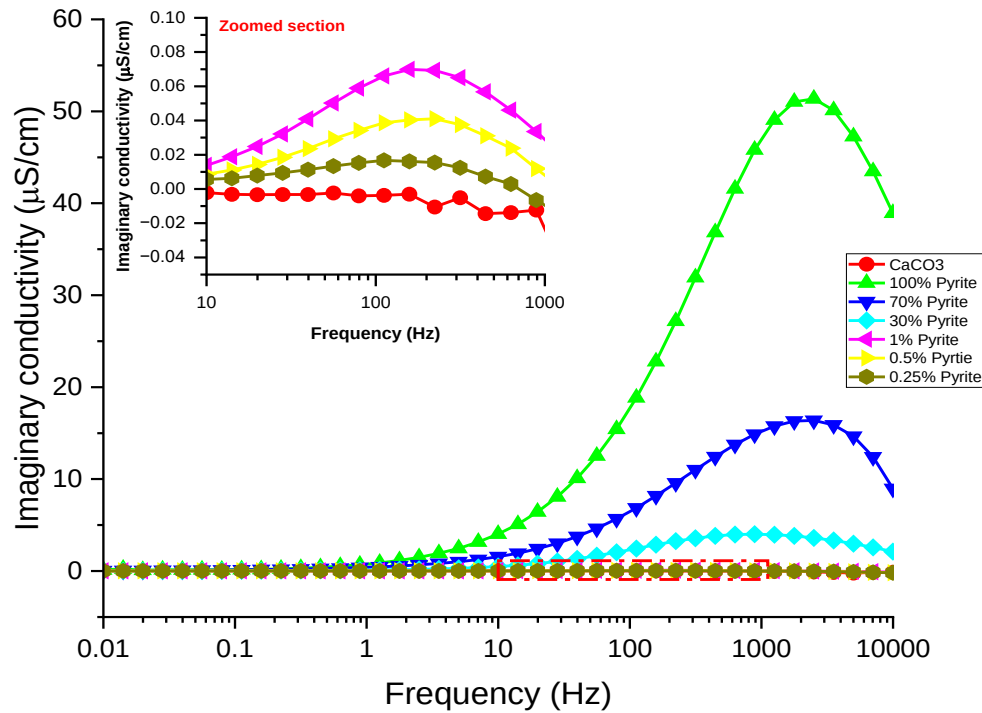


Figure 15: Imaginary conductivity readings over a frequency range [0.01-10000] Hz of pyrite-calcium carbonate mixtures of different concentrations.

From the figures above, imaginary conductivity can be used effectively as a measure of particle size approximation and intensity or concentration of pyrite in the carbonate sediment body.

2.6.3. SIP Real Conductivity

Real conductivity is a measure of ohmic conductivity. As shown in Figure 16, signals of real conductivity of the pyrite mixtures are undergoing a constant behavior of low real

conductivity values of below 25 $\mu\text{S}/\text{cm}$. after reaching frequencies of 100 Hz the spectrums started to increase nearly linearly with time with a slope of increasing that sharpens in higher concentrations. The increase in real conductivity with frequency decreases in low pyrite concentrations as observed in the figures. At low frequencies, the trend is missing but a clear distinction between clean and contaminated calcium carbonate is observed.

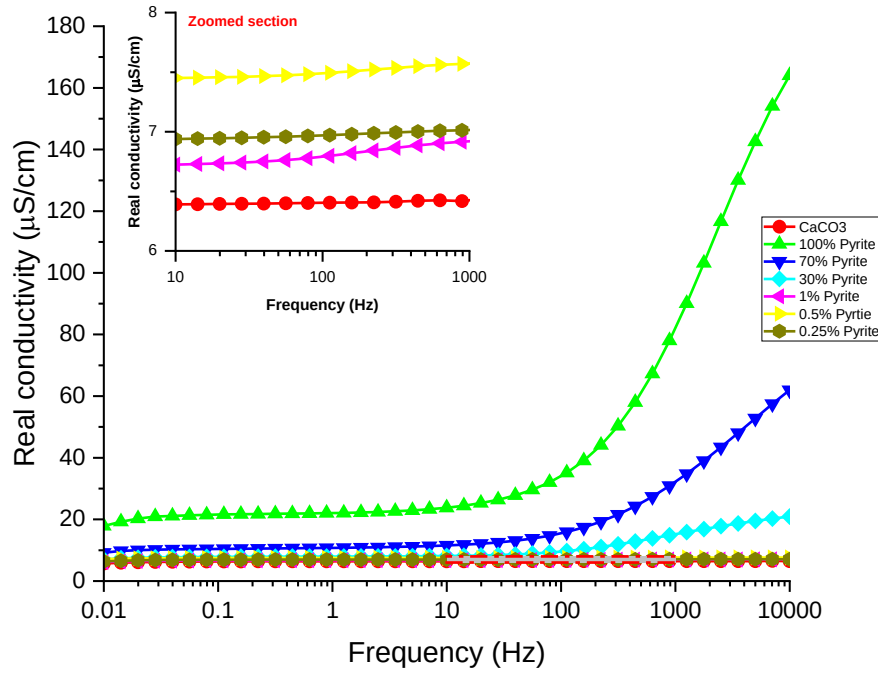


Figure 16: Real conductivity readings over a frequency range [0.01-10000] Hz of pyrite-calcium carbonate mixtures of different concentrations.

2.6.4. SIP Impedance

Impedance is a direct measurement of the resistance of the sample. As seen in Figure 17, the impedance decreases as the concentration of pyrite increases. This can be explained by the higher conductivity of the mixtures containing more metallic components. In the figure, it is clear that the presence of pyrite introduces a clear distinguishable effect that distanced the pyrite mixtures by more than 500 ohms for only 1% of pyrite. The same behavior as

real conductivity is shown at lower concentrations (i.e., 0.25%, 0.5%, and 1%) where an unordered trend is shown. However, early detection is qualitatively effective where the distinction between clean and contaminated calcite is more than 500 ohms.

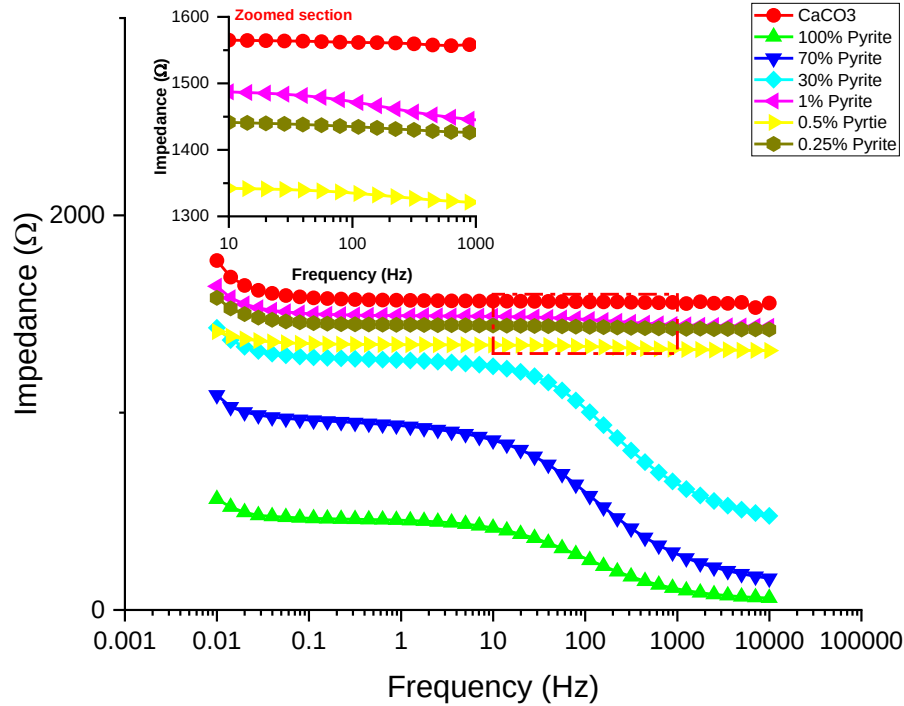


Figure 17: Impedance readings over a frequency range [0.01-10000] Hz of pyrite-calcium carbonate mixtures of different concentrations.

2.6.5. Overall Results Discussion

In the previous results, it is clear that the SIP scale detection method is working efficiently in the detection of iron sulfide scales. The four signals are working complementarily to each other by providing descriptive signals that indicate the presence and particle size in the phase shift and imaginary conductivity, and early detection and qualitative concentration detection in the real conductivity and impedance. All signals perform as a

system of decision making as the early detection can be made by analyzing the total system conductivity and impedance, and the peaking effect in the phase shift and imaginary conductivity, then looking for more details such as a rough estimation of the particle size by analyzing the phase shift and imaginary conductivity of the tested region, however, the latter was not discussed in this work. Apparently, Low concentrations don't highly activate the polarization effect for metallic particles, which is translated as the magnitude of the peak in phase shift, which causes some disturbance in the signals. This comes in agreement with the results reported by [100] when they related the polarization effect to concentrations of pyrite. However, this is also dependent on the particle size as the critical frequency (frequency at which the spectrum has a maximum) is inversely proportional to the particle size [99], [100]. The further from the critical frequency, the less polarization effect reflected as phase or imaginary conductivity is shown in the spectrum which allows other components' signals that are out of the survey scope to show.

All in all, the SIP method can be sequentially employed to investigate the early presence of iron sulfide scales in carbonate formations. By looking at different signals of the test, a conclusive decision can be made about the presence of iron sulfide scales and severity, and quick mitigation can be performed to limit the effect of iron sulfide scale formation in the petroleum production system.

2.7. Conclusion

SIP tests were conducted on different samples of iron sulfide scales impeded into limestone unconsolidated matrices. 7 Pyrite-carbonate mixtures with varying concentrations (0%, 0.25%, 0.5%, 1%, 30%, 70%, 100%) per bulk volume were prepared to simulate inorganic iron sulfide scales in oil and gas systems and all samples were tested to prove the SIP

method ability to early detect, qualitatively identify and assess concentrations of iron sulfide scales. Successful early detection and qualitative concentration identification were achieved by analyzing the samples using the four different signals of the SIP test. With phase shift and imaginary conductivity being the main signals that provide a qualitative assessment of the grain size and concentration of pyrite in the system, and real conductivity and impedance being complementary signals that qualitatively indicate the early presence of pyrite, a systematic process is acquired and can be used efficiently to monitor iron sulfide scales presence in oil and gas production systems in concentrations less than 1% per volume. Another important function of this method is to evaluate the formation rock based on its pyrite content. Knowing the pyrite content can assist the future plans of reservoir productivity and start iron sulfide scale inhabiting before the problem endangers the production system. This method delivers a robust and reliable solution to iron sulfide early detection in formations and pipeline complex scale matrices.

CHAPTER 3

WEIGHTING MATERIAL CONCENTRATION

ASSESSMENT AND SAG EARLY DETECTION

3.1. Introduction

Calcium Carbonate (CaCO_3), better known in the industry as calcite, is one of the most common minerals in the oil and gas drilling industry. It can exist naturally as a part of the formation matrix or induced by the reaction of carbon dioxide with carbonates or calcium ions with bicarbonate ions in the well [101]–[105]. Nevertheless, calcium carbonate is a well-known inorganic scale type that precipitates in the wellbore and on drilling tubes (Figure 18) which hinders fluids flow and, in severe cases, leads to a complete closure of the production tube and well shutdown, resulting in millions of dollars in losses [101], [102], [106]–[109]. Thus, it is important to keep an eye on calcium carbonate presence in the well outflow to detect and resolve any unplanned increase in its presence early.



Figure 18: Calcium Carbonate scale in pipelines [110]

In designing drilling fluid for drilling and workover operations, calcium carbonate is used as an add-on material to achieve roles such as sealing fluid loss zones [111], [112] and weighting material in the drilling fluid [113]–[116]. Weighting materials are one of the main additives in drilling fluids and they play a crucial role in maintaining the density of the drilling fluid and controlling the drilling process. Calcium Carbonate (CaCO_3) is one of the most common weighting materials used in the industry second to Barite (BaSO_4) for its low cost and good efficiency in controlling the density of the drilling fluid [113], [116], [117]. However, it is critical to carefully design the drilling fluid and mind its physical and rheological properties, where failure to do so may lead to weighting material SAG.

Weighting material sag is a process where separation between the solids and liquids in the drilling fluid takes place in which the weighting materials separate from the drilling fluid and settle in the bottom of the wellbore or drilling compartment. Such a process hinders the balance and design of the drilling fluid since the weighting materials are the main component that gives the drilling fluid its density, which makes it possible to maintain the drilling operation safe against formation pressure and fluid fluxes.

Most of the conventional existing methods nowadays are relying on traditional mass over volume techniques where the density of the fluid is the main parameter to be tested to confirm the existence of weighting material sag. These methods are taking time and cost where mostly they are done either in traditional tools such as the march funnel, or in more sophisticated tools such as rheometers and high-pressure high-temperature (HPHT) facilities where wellbore conditions are met.

In this chapter, the difference in concentration of weighting materials i.e., calcium carbonate is detected by utilizing spectral induced polarization. Also, barite and calcium

carbonate sag, as weighting materials, has been evaluated using SIP. The SIP method has been demonstrated in previous work to be of significant value for subsurface investigations such as the detection of inorganic and organic contaminants and the prediction of hydraulic properties. SIP has been used to monitor the effect of microbial-induced calcite precipitation, and bioremediation (including hydrocarbons) monitoring. SIP can be used to reduce ambiguity in the interpretation of the subsurface compared to conventional resistivity surveys. SIP utilizes the electric-conductivity properties of the drilling fluid to identify calcite concentrations to very small ratios. Identifying differences in calcium carbonate concentrations is used to assess drilling fluid well-being and stability. Also, sag could be evaluated, and detected at a very early stage by utilizing this method which can replace conventional density measurements.

In the concentration change detection process, multiple samples of spud drilling fluid with different concentrations of calcium carbonate were tested using SIP to detect variations in their signals based on their concentrations. A wide range of calcium carbonate concentrations is used to assure the detectability of the method to very small and large amounts of drilling fluid weighting materials.

In the second part of the chapter, barite and calcium carbonate have been used to mix a drilling fluid in formulations similar to the ones used in the industry. Both drilling fluids were tested for several hours to evaluate the sensitivity and reliability of the SIP method to detect weighting material sag.

The work done in this chapter will shed light on using the SIP tool as a new reliable tool for a robust evaluation of drilling fluid and as a monitoring tool for wellbore streams before and while drilling.

3.2. Statement of Problem

Drilling fluids are a major compartment of the drilling operation. Failure to maintain their structure throughout the drilling operation is dangerous because it could lead to catastrophic events in the case of major losses of solids. Current tools available for concentration and sag detection are mainly based on the density of the tested sample. Extraction of the sample and applying density measurements and conventional sag tests are time-consuming and cost additional expenses. The urge for a robust and in situ solution is rising to achieve a characterization process that is operating side by side with the ongoing operations and costs less time to characterize density and sag events.

3.3. Objectives

Calcium carbonate and barite characterization in the drilling fluids are mostly done within density testing procedure. For more accuracy, the content assessment of calcium carbonate and barite is suggested to be done by specifically looking for their existence in the drilling fluids. In this work, two main objectives are under investigation by SIP. The first objective is to characterize the content of calcium carbonate in drilling fluids where this will work as an indication of its contribution as a weighting material and as a possible scaling agent in the stream. The second objective is to monitor the weighting material content (barite and calcium carbonate) in the drilling fluid and characterize their sag in static conditions.

3.4. Literature Review

3.4.1. Drilling fluids and weighting materials

Drilling fluids are liquid-based or gas-based mixtures that are used in the wellbore during drilling operations. The main rule of the drilling fluids is to control the well against any

reflexes that might threaten the safety of the drilling operation. The main components of a drilling fluid are the base fluid, the viscosifier, and weighting materials in addition to stabilizers and thickening agents that enhance the efficiency of the drilling fluid. The base fluid can be either water, oil, or in some cases gas, with oil and water as the main common base fluids. The viscosifier are materials that give the drilling fluid the required viscosity to gain enough rheological properties to suspend the solids and cuttings in the drilling fluid during the drilling operations. One famous viscosifier is sodium montmorillonite, as known as sodium bentonite. Weighting materials are solid materials that give the drilling fluid the required density to create a hydrostatic column of pressure enough to overbalance the reservoir pressure and prevent any collapses or incoming fluid fluxes from the reservoir to the wellbore which can cause drastic events to the drilling site. Two of the main drilling fluid weighting materials are barium sulfate which is better known as barite (BaSO_4) and calcium carbonate or as known as calcite (CaCO_3). These two weighting materials have the ability to increase the density of the drilling fluid by mixing them in desired ratios to achieve the required outcomes. Barite and calcite have very minimal to no solubility in water, which requires them to be suspended in the drilling fluid in order to do their role in controlling the density and eventually the hydrostatic pressure. The suspension of these materials in a colloidal system required good gel strength in the drilling fluid since failure in designing the drilling fluid in a way that ensures the suspension of these solids leads to weighting material settlement in the bottom of the wellbore which causes density variation in the drilling fluid column in what is called weighing material sag. Stabilizers and other components of drilling fluid enhance the rheological properties of the drilling fluids such as XC polymer and corn starch.

3.4.2. Weighting material sag

Weighting material sag is known as the separation of weighting materials for the liquid phase of the drilling fluid and settling down, plugging the pipes, or in extreme cases making a bed of sediment which leads to pipe sticking [114], [118], [119]. Mohamed et al. elaborated that the issue in sag is that the separated particles are not playing a role in forming the density of the drilling fluid, which results in ununiform pressure distribution. Using this difference in calcium carbonate concentration in the drilling system sag can be assessed and monitored.

Weighting materials sag is paid attention to in the industry since the early 1980s when research was conducted to solve the problem. Earlier studies investigated static sag in inclined pipes and related sag to the rheological properties of the fluid [120]. Ofei et al. stated that the number of particles i.e., particle number density is also a major factor that affects weighting material sagging where a smaller number of particles lead to severe sedimentation [121].

3.4.3. SAG identification methods

Many techniques are utilized to measure and detect calcium carbonate density and sag for laboratory or industry use. For laboratory operations, the most common method is manually measuring the density of the upper and lower segments of a static drilling fluid left for some time and then calculating the sag factor as shown in equation 24. A sag factor of 0.5 indicates non-sagging mud, whereas anything above 0.52 suggests a sagging drilling fluid. This method is known as the static cell test [121].

$$SAG\ Factor = \frac{density_{top}}{density_{bottom} + density_{top}} \quad 24$$

However, the method is not feasible for industrial use because it lacks accurate reproducibility and not being time-effective [120]. Also, a small fraction of density changes in calcium carbonate could not be easily captured by conventional mass-over-volume methods. In field applications, many tests are used to monitor sag such as monitoring downhole density, rate of penetration, and changes in pump rate and drill string rotational speed [103]. Other techniques stated in the literature are the standard viscometer test [122], flow loops [123], rheological methods [111], [115], [117], High Angle Sag Test (HAST) [120], [124] and Ultrasonic and direct weight measurements [120], [125], [126].

Most of the aforementioned techniques either lack reproducibility such as weighting methods, require sophisticated large setups such as flow loops, or require more time such as extended static tests [122]. Moreover, small changes in density are not investigated where they could indicate early detection of weighting material sag. In addition, the need for an in-situ dynamic method to monitor calcium carbonate concentration as a weighting material in drilling fluid is urging to accelerate the sag detection process.

3.5. Methodology

3.5.1. Drilling fluid preparation and components

A. Drilling Fluid preparation for concentration testing

Spud drilling fluid is prepared using 4% per weight bentonite mixed with deionized water in mud mixers for 15 minutes. Afterward, extra pure calcite at 50 μm grain size is added to the mixers in different concentrations as shown in Table 8, and mixed for extra 15 minutes until the fluid is homogeneous. The density of each mixture is measured directly after the

mixing is finished using a graduated cylinder of fixed calibrated volume and a digital balance. The density values were confirmed using the mud balance for further validation. At the end of the preparation, 6 samples of 4% per weight bentonite and different concentrations of calcite ranging from 0% to 20% per weight were prepared and ready for SIP measurements.

The concentrations of calcite were chosen based on the existing concentrations found in petroleum wells. Although the concentrations could go up to higher concentrations, 20% was used as the upper limit.

Table 8: Drilling fluid with different mixing ratios

Calcium carbonate concentration (wt. %)	Water content (wt. %)	Bentonite content (wt. %)
0	96	4
0.1	95.9	4
2	94	4
5	91	4
10	86	4
20	76	4



Figure 19: Drilling fluid mixer

B. Drilling Fluid preparation for weighting material sag testing

Water-based drilling fluids were prepared using barite and calcite using specified formulas in Table 9 and Table 10, following standard mixing steps for drilling fluids preparation. Deionized water eliminates any unwanted signals related to water salinity or components since SIP is highly sensitive to minor contaminations. Samples were tested afterward for density.

Table 9: Barite drilling fluid formula

Component	Weight %	Mixing time
XC Polymer	0.19	20 minutes
Starch	0.76	10 minutes
Barite	53.00	10 minutes
Water	46.04	-

Table 10: Calcite drilling fluid formula

Component	Weight %	Mixing time
Bentonite	4	10 minutes
Calcite	5	10 minutes
Water	91	-

3.5.2. Approach and Method

Water-based drilling fluid properties are expected to encounter many changes, unlike oil-based ones. The SIP method is very sensitive to material contents especially when any increase or change is expected to take place. Drilling fluids are composed of many components with different properties. Some like bentonite, which has higher electrical conductivity than calcium carbonates, another component of drilling fluids, for instance. In the concentration monitoring tests, the change in the amount of calcium carbonate particles is expected to be visible in the SIP readings. In the sag monitoring part, different segments of the drilling fluid body are monitored. It is expected that the concentration of the weighting material is going to decrease in the top sections of the drilling fluid column. However, the change is also expected to happen to the entire body where the weighting material particles are expected to settle in the bottom of the column.

3.5.3. Experimental procedure and test parameters

A. Test Setup for concentration testing

Before conducting SIP tests, the electric conductivity values of the samples were acquired using a Hanna multi-range conductivity meter. In running the SIP tests for concentration

measurement, a fixed volume of the drilling fluids is filled into the test columns while assuring the columns are air-tight and no air bubbles are inside the test columns. For concentration monitoring, the SIP test is run in a horizontal orientation (Figure 20). The reason for the horizontal orientation is to keep the sample homogenous and minimize any potential sagging of the weighting material.

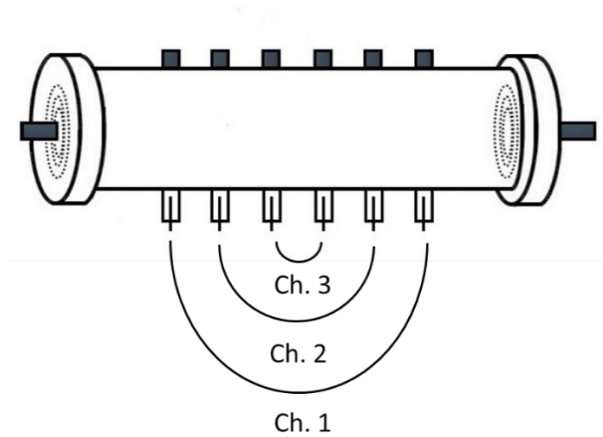


Figure 20: Horizontally oriented SIP column and channels distribution

For the sake of validation, every sample was run multiple times to assure reproducibility. SIP signal output settings were as shown in Table 11. SIP tests are nondestructive, which allows the reusability of the sample in other tests i.e., rheological properties testing.

Table 11: Calcium carbonate concentration SIP test configuration

Freq. (Hz)	Sampling steps	Amplitude (V)	Current Resistor (Ohms)
0.1-10,000	36	5	100

B. Test Setup for weighting material sag testing

The sag test and validation are composed of two major steps: SIP tests and density validation. A setup of a 340 ml test columns is used for SIP tests and its schematic is shown

in Figure 21. The potential electrodes in the SIP columns were divided into 3 testing channels based on the elevation where channels 1 and 3 are used as testing segments. The distance between the center of each channel is 5 cm, and between the top and bottom channels (1 and 3 respectively) is 12.5 cm on the other side of the column, fluid sampling channels are existing in the middle opposite side of each testing channel. Fluid samples are taken exactly from the corresponding channel to measure density for validation.

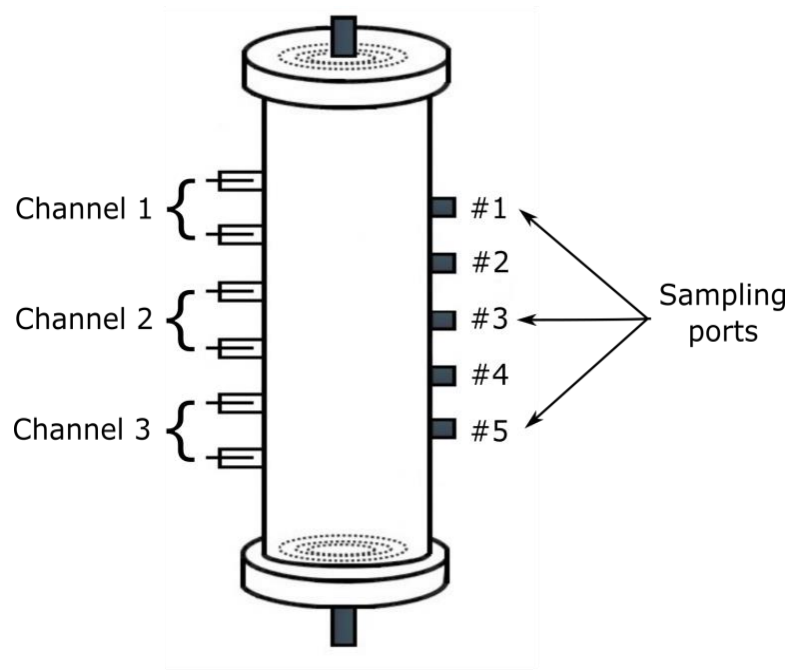


Figure 21: SIP test column schematic (modified by Siddiq et al. 2020)

For SIP surveys, tests were performed over 5.5 hours for barite and 3 hours for calcite, where each fluid has its unique time periods due to differences in densities. Tests were conducted in loops for specified frequency points shown in Table 12 and Table 13.

Table 12: Barite SIP test specifications

Frequency (Hz)	Sampling steps	Amplitude (V)	Shunt Current Resistor (Ohms)	Loop time (sec)	Number of loops
0.1-10,000	6 logarithmic steps	5	100	117	178

Table 13: Calcite SIP test specifications

Frequency (Hz)	Sampling steps	Amplitude (V)	Shunt Current Resistor (Ohms)	Loop time (sec)	Number of loops
100-10,000	3 logarithmic steps	5	100	28	300

3.6. Results and Discussion.

Before SIP testing, samples' densities were measured and recorded. As predicted, the densities followed an increasing trend with increasing calcium carbonate concentration. However, due to the small density of calcium carbonate, the overall density is increased in small fractions that are observed in the second and third decimal figures (Figure 22).

Similarly, electric conductivity is a very important variable to keep track of since the SIP test is based on low-frequency electrical injection of current. The electric conductivity was measured using a conventional conductivity meter to yield an increasing trend with the increase in calcium carbonate concentration (Figure 23).

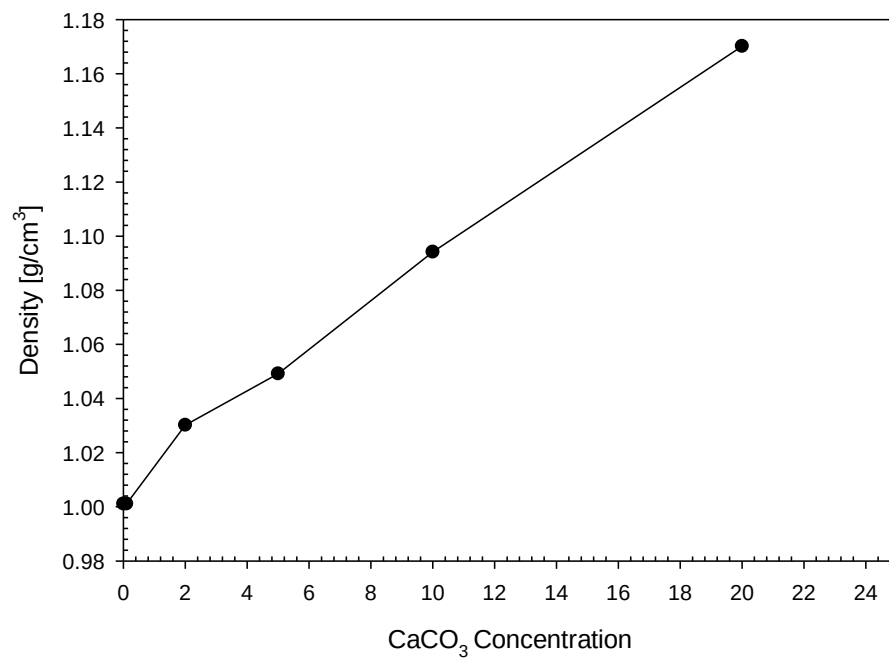


Figure 22: Density vs CaCO₃ concentration.

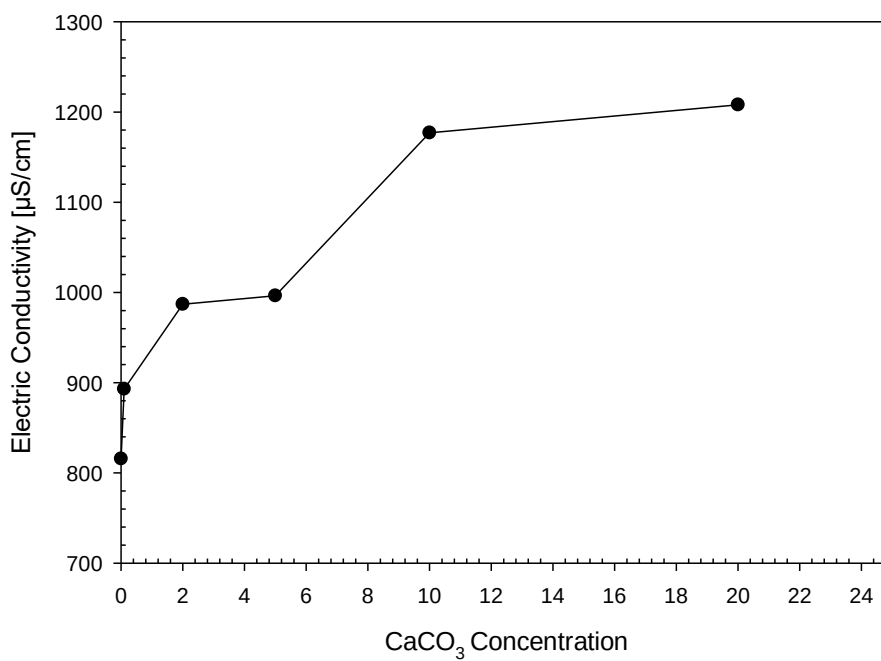


Figure 23: Conductivity vs CaCO₃ concentration.

Even though calcite has very low solubility in the water and does not disassociate easily, it still promotes the electrical current flow because calcite is a polar compound and has been suspended by bentonite to form a colloidal system.

3.6.1. SIP for monitoring changes in calcium carbonate concentration

The SIP measurements were utilized in studying the changes in calcium carbonate concentration. Each parameter is studied separately in the following subsections.

A. Phase Shift

Phase shift is one of the basic outputs of the SIP instrument. It can be considered as a measure of the polarizability relative to ohmic conduction, with measured accuracy of 0.1 mRad.

In the studied cases, phase shift responses increase with increasing frequency. However, this increase with frequency appears to be irresponsive at low frequencies and sharpens starting around 20 Hz. Phase shift is mainly influenced by the polarization of the material. However, the signals captured for different calcium carbonate concentrations do not reflect a conclusive correlation with the CaCO_3 concentration changes (Figure 24). Nonetheless, it is important to consider this signal as its role comes into play while calculating the real and imaginary parts of SIP complex conductivity.

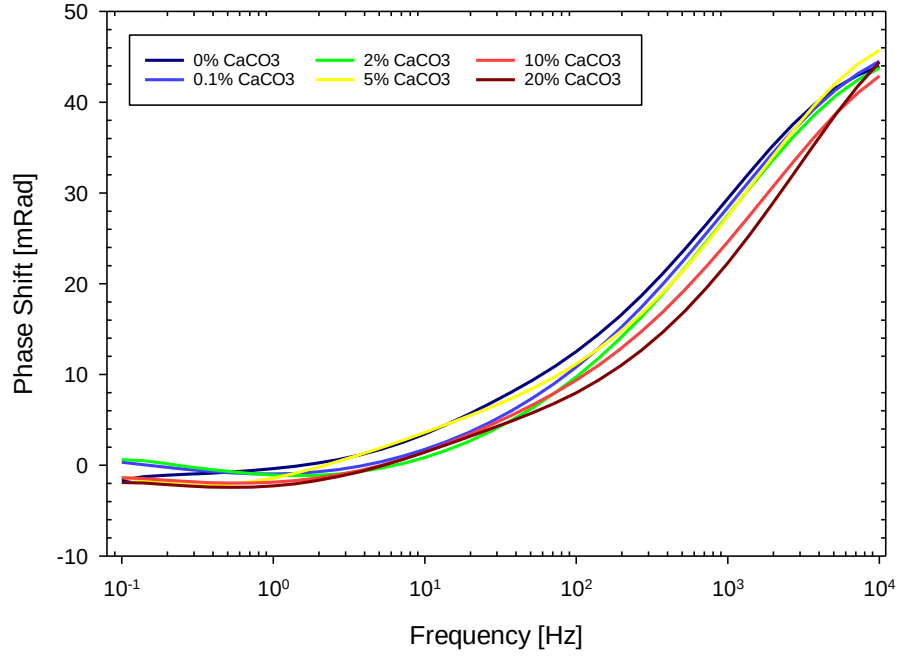


Figure 24: Phase shift measurements over a broad frequency range (0.1 – 10,000 Hz) for the different concentrations of calcite fluids.

B. Real Conductivity

The real conductivity component, σ' , represents the ohmic conduction (energy loss). The magnitude of the complex conductivity at a certain frequency, $|\sigma^*|$, can be calculated from the impedance, Z , and the phase shift, φ , measurements while including the resistance value of an embedded resistor in the SIP instrumentation. The measurement accuracy is within 0.5 $\mu\text{S}/\text{cm}$. The real part of conductivity, σ' , can be obtained by equation 22 in Chapter 2.

Real conductivity measurements positively correlated with changing calcite concentration under the range investigated. Noteworthy, SIP real conductivity measurements displayed an excellent performance in detecting small concentrations of CaCO_3 . The control sample (with 4% bentonite and 0% calcite) showed distinctively high real conductivity values.

This might be attributed to the higher electric conductivity of bentonite with respect to calcite. However, this real conductivity drops drastically with the introduction of only 0.1 wt.% of calcite to the solution due to the fact that calcite electric conductivity is minimal where this might affect the conductivity of the entire system. This indicates excellent efficiency in detecting the presence of small values of calcite concentrations. Real conductivity values improve consistently with increasing the calcite concentration. This is attributed to the increase in calcite particles which lead to an increase in the surface area since calcite is at 50 μm particle size. This enhanced the ohmic electrical conductivity by enhancing the colloidal system efficiency with more polar calcite particles that in water, made a medium for electrical conductivity. Nevertheless, the control sample still showed relatively higher values of real conductivity than the values of the sample with the maximum CaCO_3 concentration used in the study. The real conductivity measurement showed a minimum difference of 24.6% between the control sample and the sample with 20 wt. % calcite concentration, see Figure 25. Furthermore, the separation between the real conductivity curves of different CaCO_3 concentrations appears to be almost constant through the frequency range leading to parallel curves.

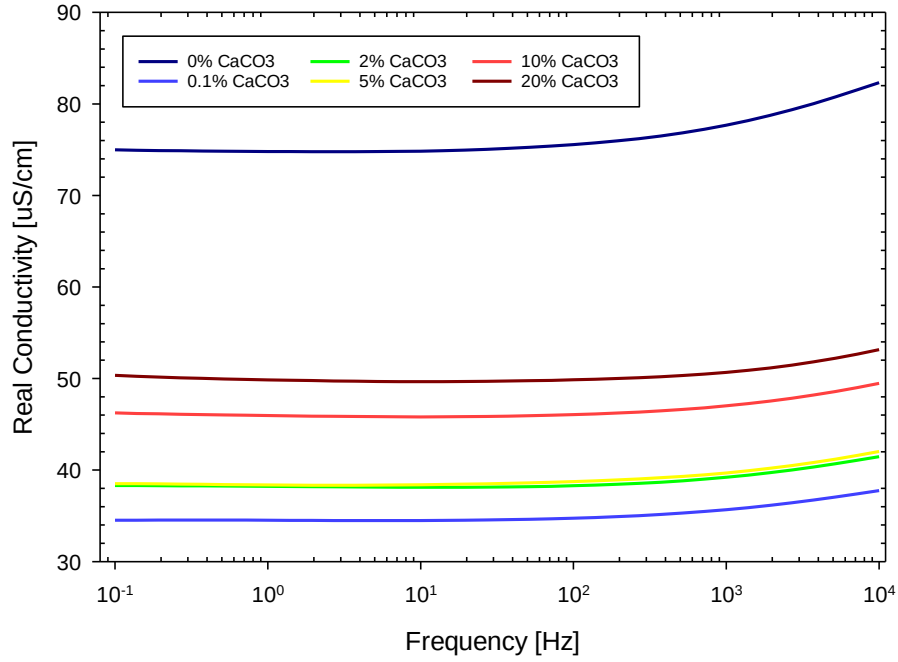


Figure 25: Real conductivity over a broad frequency range (0.1 – 10,000 Hz) for the different concentrations of calcite fluids.

C. SIP Imaginary Conductivity

The imaginary conductivity represents the rate of polarization (energy storage) term which at low frequencies can be expressed as a function of the grain–fluid interface’s physicochemical properties [20], [49], [56], [127]. The imaginary conductivity, σ'' , can be obtained with an accuracy level of 0.5 $\mu\text{S}/\text{cm}$ by equation 23 in Chapter 2.

As Figure 26 illustrates, imaginary conductivity increases with the increase in frequency. However, this increase with frequency appears to be intense at a very low frequency, and then it slows down starting from approximately 5 Hz.

Similar to the real conductivity measurements, a sharp drop in the imaginary conductivity is observed once a very small amount of calcite (0.1 wt. %) is added to the solution, especially at frequencies higher than 5 Hz. On the other hand, the imaginary conductivity increases with the increment of CaCO_3 concentration reflecting the same trend as one of

the real measurements. However, even though the imaginary conductivity increases with adding more calcite, it remains at a maximum of around 24.6 % less than the values of the control sample, which indicates good detectability of calcite.

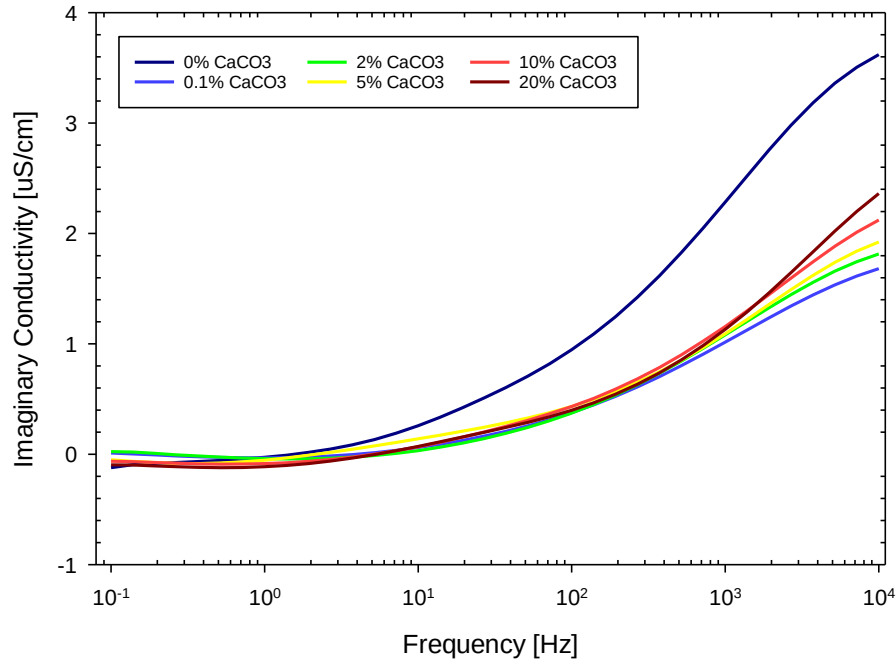


Figure 26: Imaginary conductivity measurements over a broad frequency range (0.1 – 10,000 Hz) for the different concentrations of calcite fluids.

D. Discussion and Comparison:

All four SIP signals were plotted as a function of CaCO_3 concentration at different frequencies along with a plot of the solution measured density to best explain and interpret the acquired signals. As shown in Figure 27, real conductivity represents the most responsive measurement to concentration changes among all SIP signals. Under all the frequencies, the real conductivity increased with increasing calcite concentration in the drilling fluid. On the other hand, the phase shift and imaginary conductivity showed

inconsistent small variations in their values to CaCO_3 concentration which cannot yield a conclusive relationship with concentration. Therefore, SIP real conductivity is the most reliable measure to evaluate CaCO_3 concentration. Moreover, since CaCO_3 concentration has almost a straight-line relationship with density, we can relate all the aforementioned SIP responses to the fluid density of the CaCO_3 and bentonite mixtures which form several types of drilling fluids.

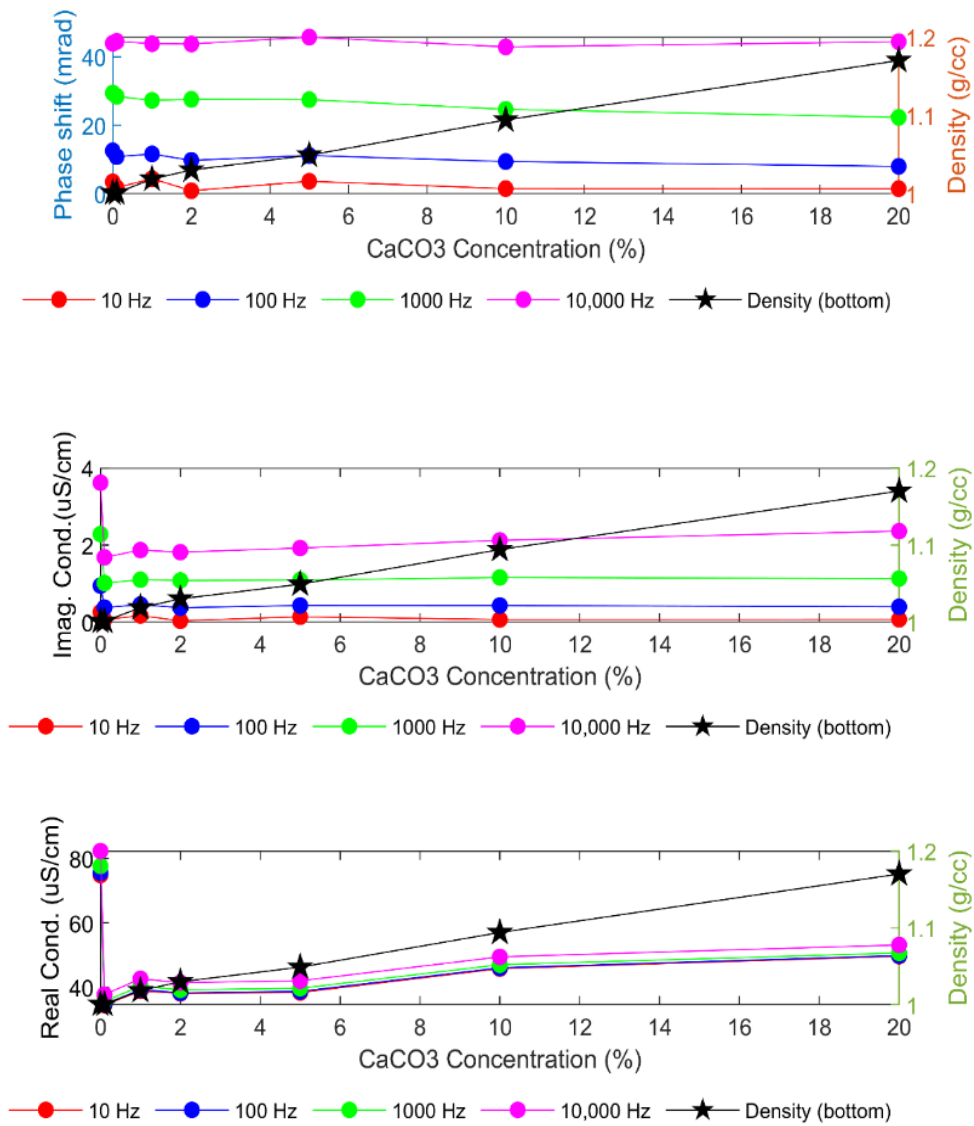


Figure 27: Overall comparison of SIP measurements vs CaCO_3 concentration at channel 3.

E. Conclusion

The results in this part have illustrated the use of the SIP technique as a robust and very sensitive method to measure calcium carbonate concentration in spud drilling fluids. Calcium carbonate concentration was assessed successfully to very minor fractions of 0.1% per weight of drilling fluid. Seven samples with different concentrations starting at 0.1% and reaching 20% of calcium carbonate per weight of drilling fluid were tested, and the presence and increase of calcium carbonate content were detected in every sample via SIP. The major parameter that assessed calcium carbonate concentration is the real component of the SIP complex conductivity. In which, calcium carbonate was detected at first presence at 0.1% per weight by a sharp decline in the SIP real conductivity curve followed by a gradual increase with the increase of calcium carbonate concentration. SIP phase shift and imaginary conductivity are also detecting changes with changing calcium carbonate content, but their use is limited to qualitative assessment since they do not offer vast and clear indications that could be reliable for quantitative evaluations.

It is concluded that the concentration of calcium carbonate is inversely proportional to SIP phase shift and directly proportional to the complex conductivity minding the sharp shift downwards in the curve responding to calcite first presence, which is relayed on as the early detection mechanism.

This work sheds light on the importance of SIP as a density and concentration detector. Its application can be broadened to include more drilling fluid types, cement, and other related fluids that construct the drilling and production industry.

3.6.2. SIP for monitoring and early detect weighting material sag

A. Preliminary sag and SIP sample testing

Before testing, full-spectrum SIP tests were conducted on barite and calcite to understand their behavior and to define the optimum frequency range and the acquisition time based on the selected frequencies. As seen in the plots in Figure 28 and Figure 29, barite and calcite possess different SIP responses in all signals. SIP responses correspond to the characteristics of the tested materials and how they respond to electrical currents. Due to the different chemical and electrical properties of barium sulfate and calcium carbonate, they show different magnitude in all four signals, where barite show lower phase shift and imaginary conductivity and higher real conductivity and impedance than calcite which represents a higher electrical conductivity in barite.

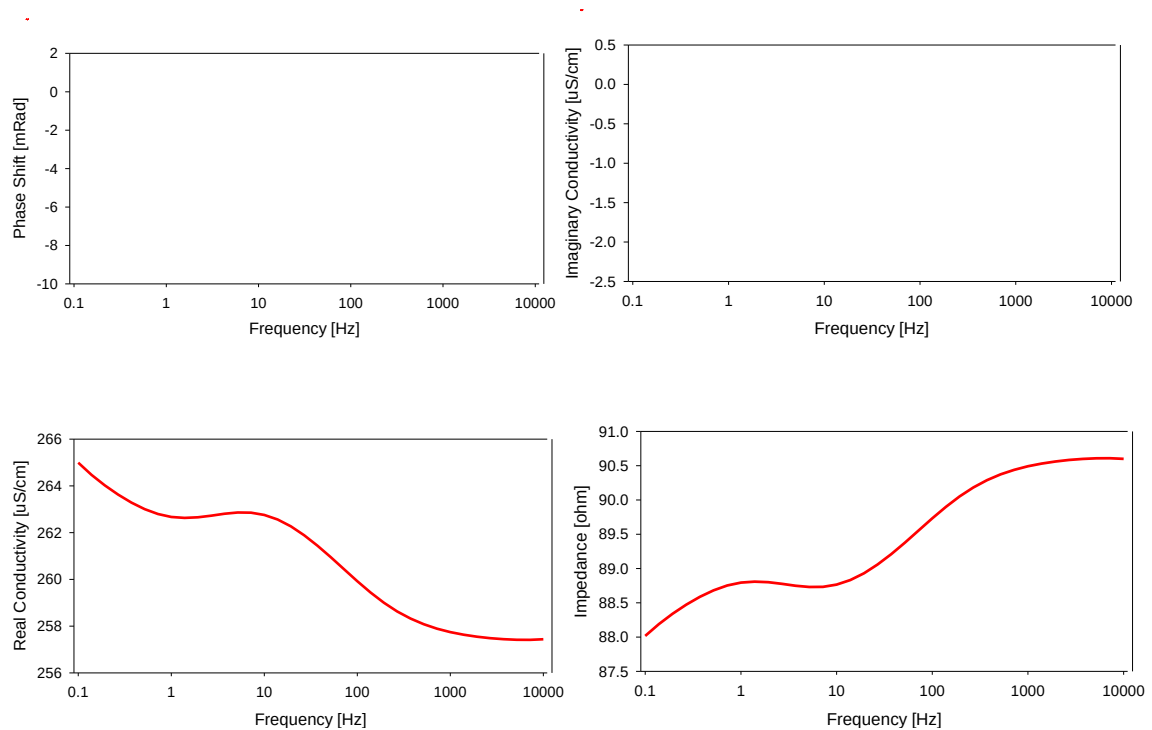


Figure 28: SIP measurements (phase shift, imaginary conductivity, real conductivity, and impedance) over a broad frequency range (0.1 – 10,000 Hz) for barite drilling fluid.

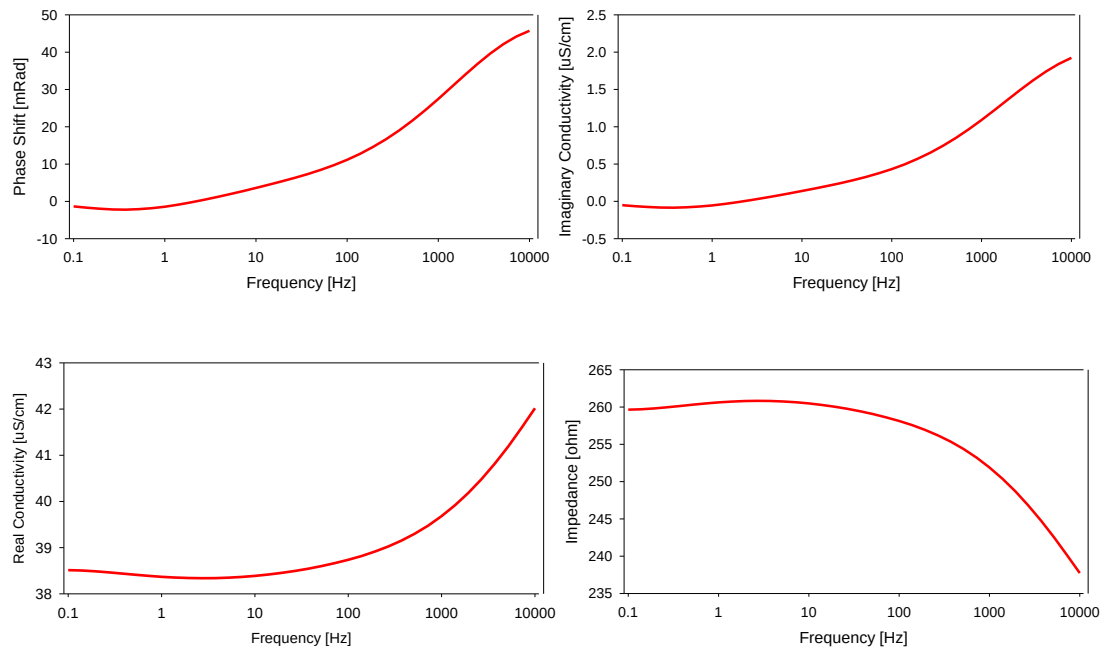


Figure 29: SIP measurements (phase shift, imaginary conductivity, real conductivity, and impedance) over a broad frequency range (0.1 – 10,000 Hz) for calcite drilling fluid.

Drilling fluid concentration was estimated in the channels initially and after the test is conducted to evaluate the change in density related to sag. Both samples showed differences in density between channels 1 and 3, as shown in Table 14 where density is decreasing in both channels due to solid particles settlement in the bottom of the column, which indicates weighting material sag in both barite and calcite drilling fluids. The effect of this concentration difference is shown in coming subsections in SIP signals that change with time.

Table 14: Density evaluation with time done in the drilling fluid lab utilizing the conventional mass difference method to measure sag in room temperature and atmospheric pressure.

Barite drilling fluid		
Time	Density channel 1 (g/cc)	Density channel 3 (g/cc)
0	1.6804	1.6804
180	1.6357	1.6605
Difference	0.0447	0.0199

Calcite drilling fluid		
Time	Density channel 1 (g/cc)	Density channel 3 (g/cc)
0	1.0492	1.0492
180	1.0072	1.0197
Difference	0.042	0.0295

B. SIP signals time lapse at 10 kHz

Based on the preliminary results presented above, SIP signals show peaks at high frequencies (in the 1000-10,000 Hz range) for both fluids. To better visualize the temporal behavior of SIP parameters, we focused on the 10 kHz frequency, as the higher average difference with time was also observed, but other frequencies showed similar trends. SIP tests of 178 loops of 117 seconds each for barite drilling fluid and 300 loops of 28 sec for calcite drilling fluid were conducted to monitor weighting material settlement. The tests were conducted on two channels, an upper channel (channel 1) and a lower channel (channel 3). All tests show shifting in plots between channel 1 and channel 3. This is due to small differences in the particles' concentration between the two channels during the testing time. SIP signals are very sensitive to the sample components, and minor changes can lead to visible changes in the behavior.

As shown in Figure 30, phase shift and imaginary conductivity decrease (going towards 0) slightly with time, especially in both channels. Phase shift is directly proportional to conductivity, and a lower concentration of solids corresponds to a lower phase shift due to the loss of solids that makes up the fluid conductivity. With deionized water as the base fluid, the conductivity is expected to decrease, corresponding to the loss of barite particles.

Nonetheless, the changes in both measures are not representative enough of the ongoing settlement event since they are more related to highly chargeable materials.

However, real conductivity and impedance are the most responsive measures that show evidence of particle loss that could be tracked with time. It is evident in Figure 30 that the behavior is undergoing fast changes in real conductivity and impedance with time in the first 2 hours. Afterward, the difference in signal slowed down as the particles' migration is believed to decrease. A total change in signal of 11.5 $\mu\text{S}/\text{cm}$ and 4.9 ohms in real conductivity and impedance, respectively is observed, with most happening in the first 2 hours. Real conductivity and impedance have opposite responses to changes in concentration, where impedance will increase due to loss in conductivity, and real conductivity will undergo the opposite due to its direct relation to electric conductivity.

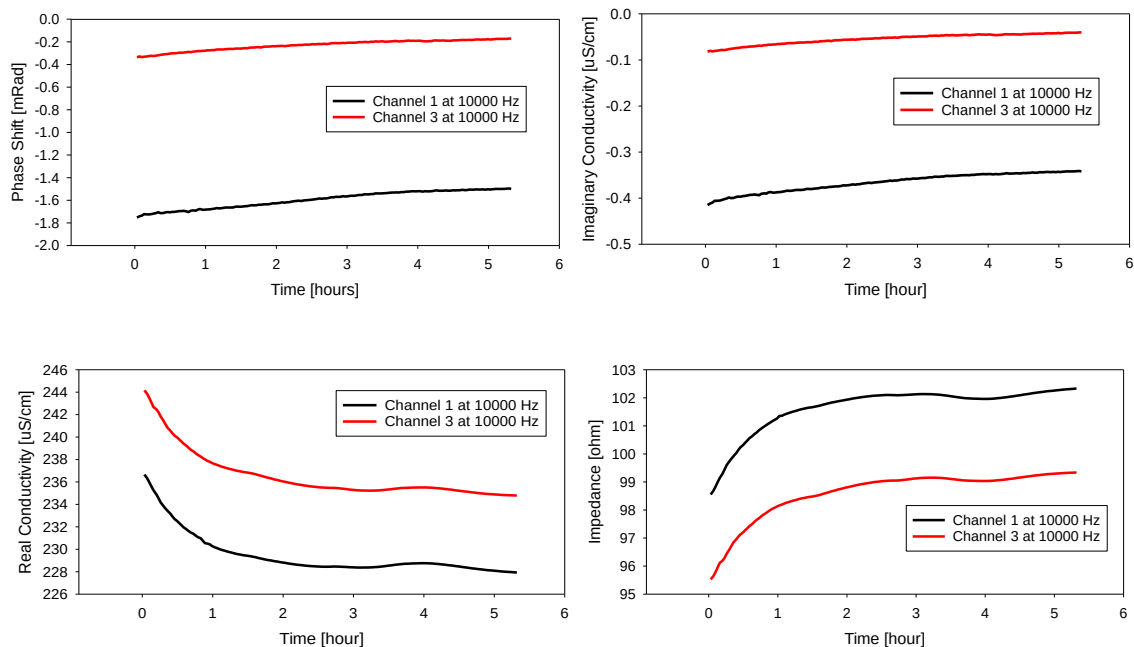


Figure 30: A time-lapse of barite drilling fluid SIP signals measurements (phase shift, imaginary conductivity, real conductivity, and impedance) at 10K Hz

Calcite possesses similar behavior with a decrease in conductivity due to solids loss. Like barite behavior, phase shift and imaginary conductivity responses decrease with time because conductivity decreases see Figure 31. Moreover, calcite experiences a higher sag probability than barite, which is shown in the high dispersion between the two channels due to the concentration difference. But again, such measures do not offer conclusive measures of the ongoing events. More distinctive insight is shown clearly in the real conductivity and impedance plots where the plot flattens earlier than the barite drilling fluid.

Real conductivity and impedance show higher dispersion and more conclusive signals where the change in signals is visible and linked to concentration change. The average observed change is 3.9uS/cm and 9.5 ohms in the real conductivity and impedance, respectively. This change clearly shows the particle loss that leads to a decrease in concentration and conductivity that could be traced along the real conductivity and impedance plots. The effect also decelerates near the 2 hours mark, indicating a slowing in particle migration toward the bottom of the testing column.

Calcite drilling fluid's real conductivity and impedance change with time come were less than the barite drilling fluid since calcite is less conductive than barite. Hence, the decrease in real conductivity is lower because the amount of particle loss in the channel contributed less to the total conductivity. Yet, impedance change is high where the fluid gets more resistive to current flow due to the decrease in the amount of solids that makes the colloidal conductive system.

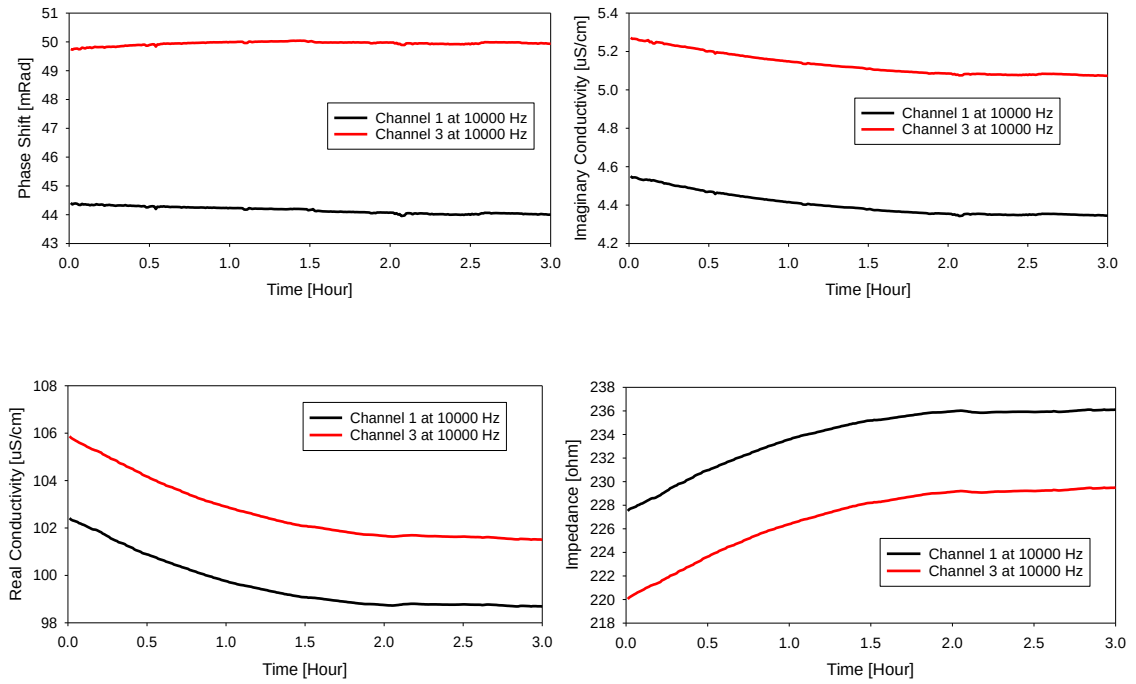


Figure 31: A time-lapse of calcite drilling fluid SIP signals measurements (phase shift, imaginary conductivity, real conductivity, and impedance) at 10K Hz

C. SIP signals behavior with time

The full spectrums for each testing time are plotted, to see the full behavior changes with time. Six selected frequencies were acquired in the barite drilling fluid and 3 in the calcite drilling fluid. The assigned testing times were 0.03, 0.16, 0.3, 0.5, 1.02, 2.02, 3.01 and 5.02 hours for barite drilling fluid. And 0.01, 0.16, 0.3, 0.5, 1, 2, 3 hours for calcite drilling fluid.

i Barite drilling fluid SIP Phase shift and imaginary conductivity

In barite drilling fluid, phase shift and imaginary conductivities show small dispersion between testing times (Figure 32 and Figure 33). This small variation is due to the nature of the samples. It is not expected that phase shift, and imaginary conductivity values show a sharp increase or decrease since they are showing more in metallic materials and represent the energy storage ability of such materials. Moreover, the phase shift and imaginary conductivity are more related to the concentration of the polarizable materials and their

contribution to the current passing and storing system. Since barite and calcite are believed to have low energy storage properties, it is expected to see minor changes in phase shift and imaginary conductivities that are not believed to give a strong indication of particle settlement.

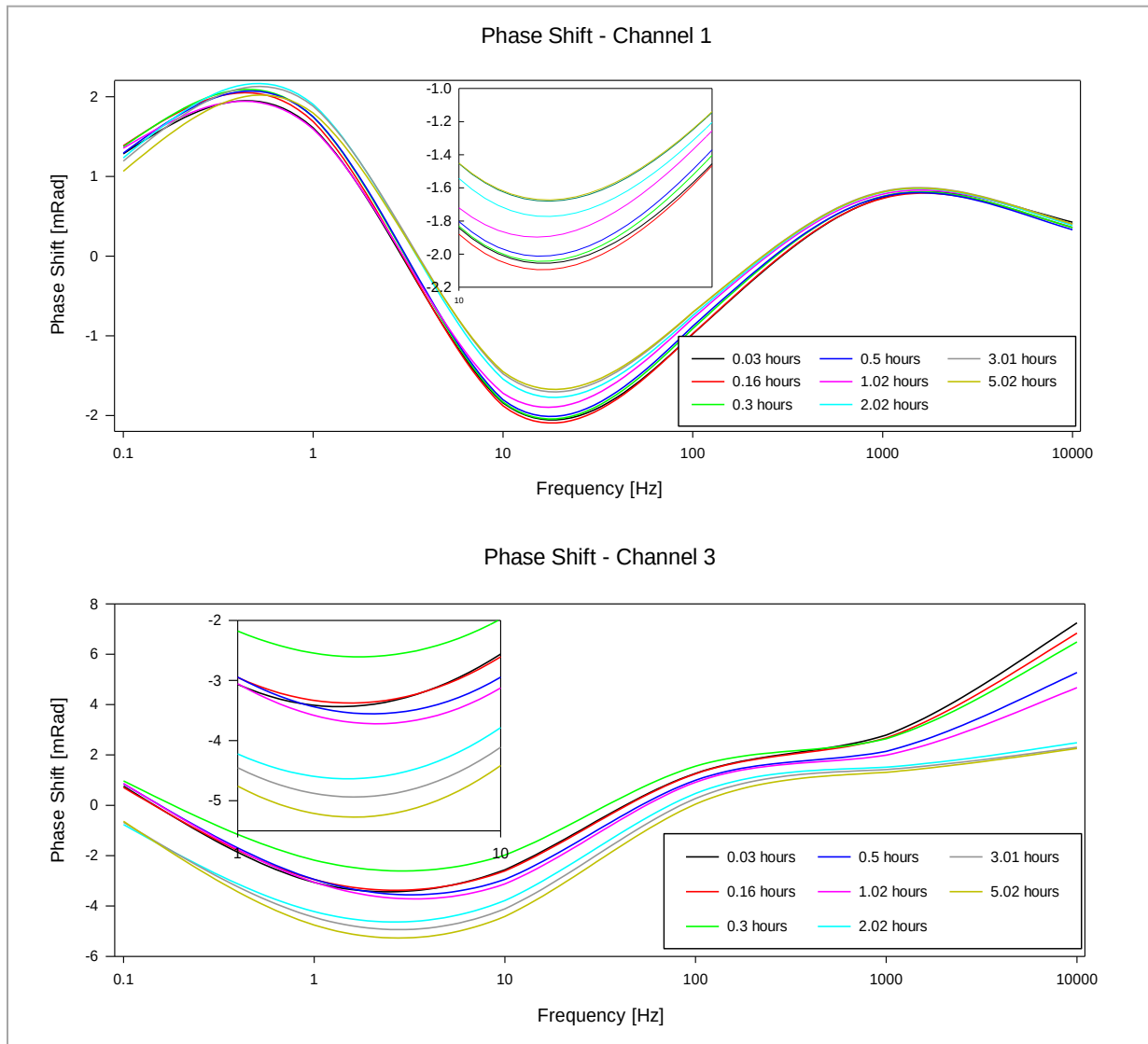


Figure 32: Phase shift measurements for barite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).

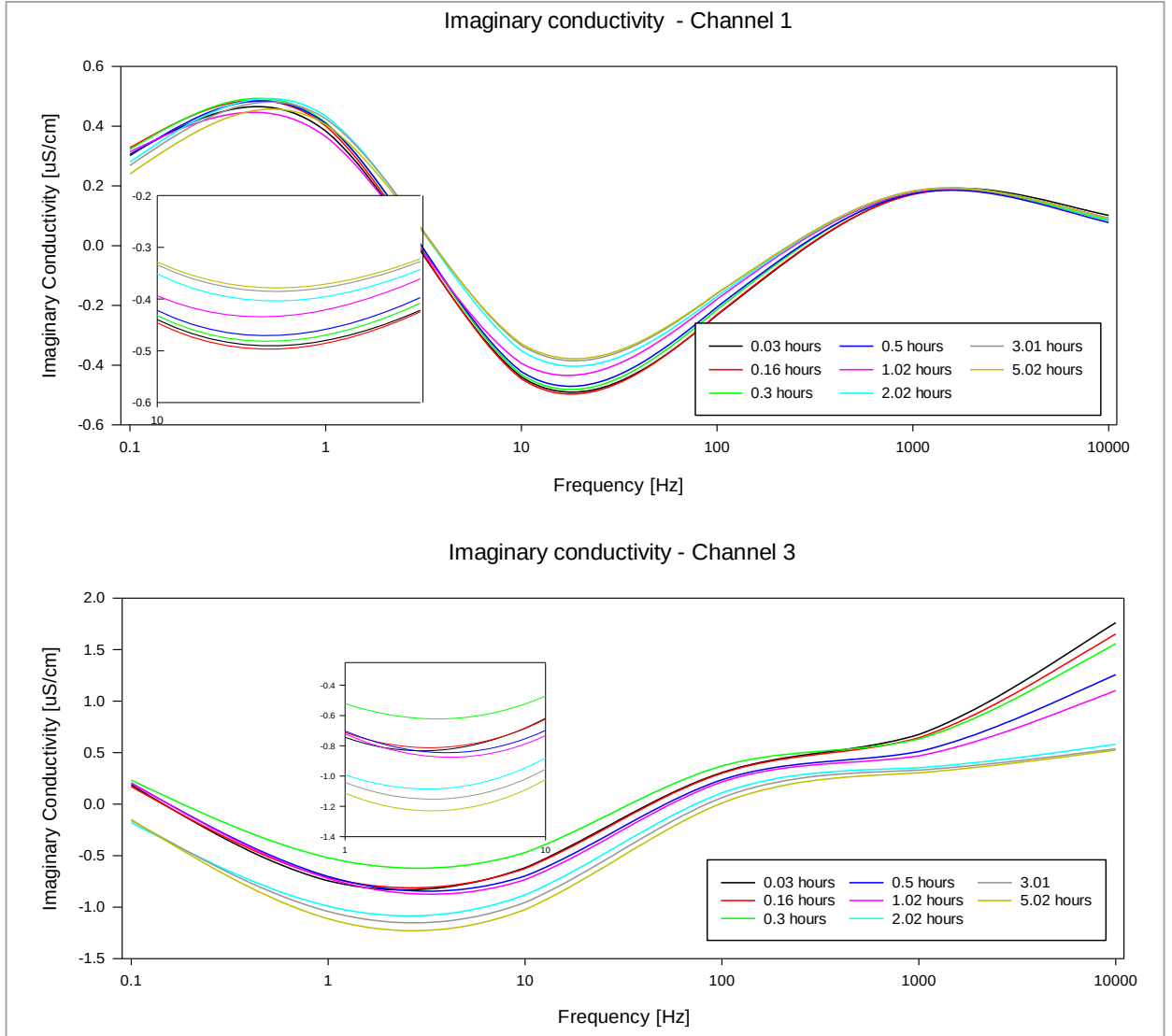


Figure 33: Imaginary conductivity measurements for barite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).

ii Barite drilling fluid SIP real conductivity and Impedance

Real conductivity and impedance spectrums were the highest in terms of shifting with respect to elapsed time periods (Figure 34 and Figure 35). In fluids, the real conductivity and impedance are the highest to react to changes in concentration since they are more related to the properties of fluids. With time, the concentration in the fluid's segments

corresponding to channels 1 and 3 decreases due to particles settlement. This behavior is clear in Figure 34 and Figure 35 in the real conductivity and impedance plots, where the average change is a 9.5 $\mu\text{S}/\text{cm}$ drop in real conductivity and a 3.9 Ω increase in impedance. Such changes in signals can be used primarily to track drilling fluids' weighting material sag.

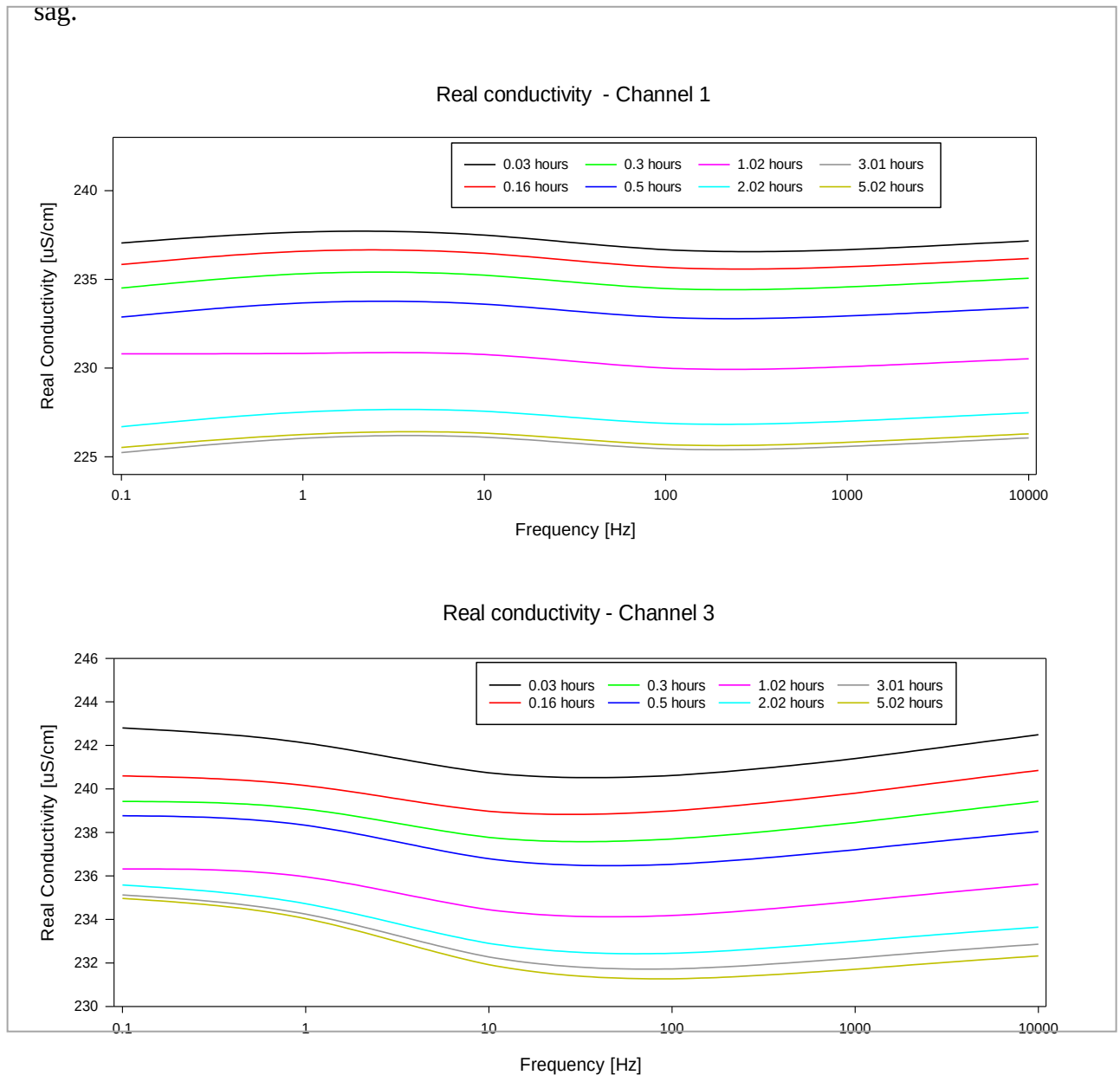


Figure 34: Real conductivity measurements for barite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).

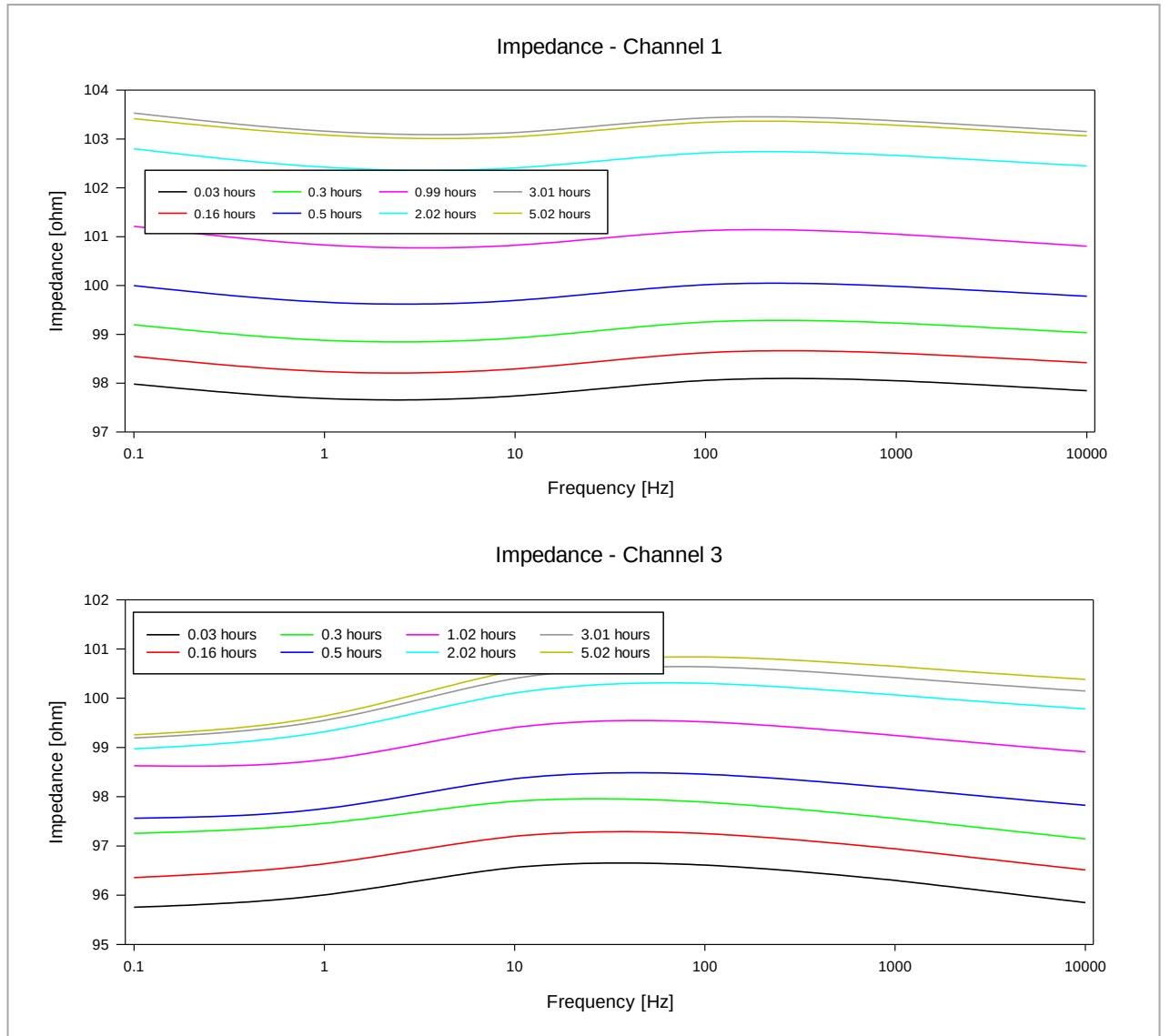


Figure 35: Impedance measurements for barite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).

iii Calcite drilling fluid SIP Phase shift and imaginary conductivity

Due to calcite's low electric conductivity and charge storage ability, it is difficult to see vast changes in phase shift and imaginary conductivity over time. However, the change in these two parameters is relative to the tested material (Figure 36 and Figure 37). As the total amount of solids in the sample is not changing broadly and their nature is not highly

electric conductive, it is expected that the change in both phase shift and imaginary conductivity will be minor in terms of magnitude.

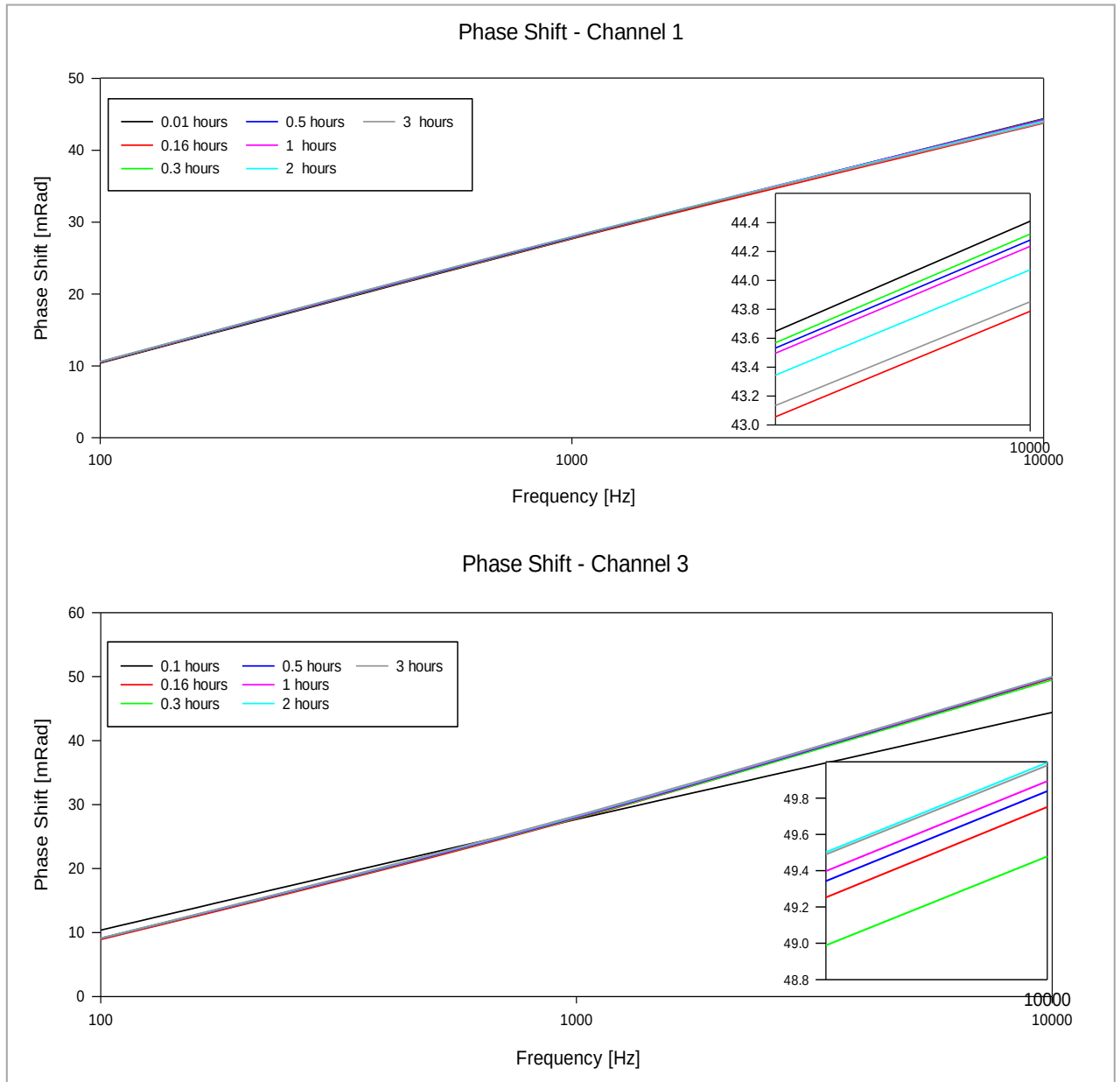


Figure 36: Phase shift measurements for calcite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).

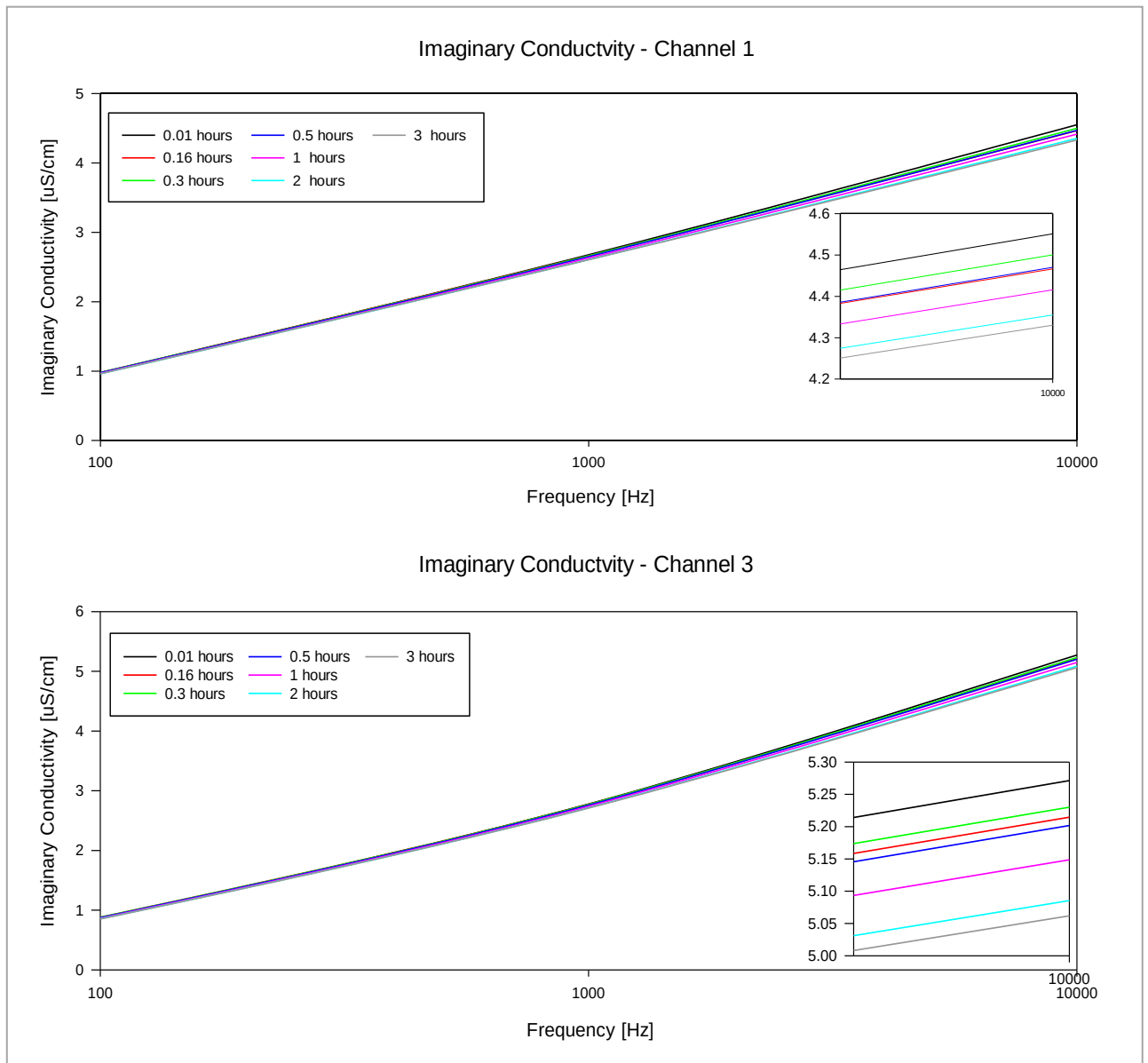


Figure 37: Imaginary conductivity measurements for calcite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).

iv Calcite drilling fluid SIP real conductivity and impedance

A clear trend of increasing impedance and decreasing real conductivity is shown in Figure 38 and Figure 39 that show the behavior shift with time. The higher the time period, the lower the concentration in the channels due to settlement which stimulates the behavior mentioned above in both signals. The change mentioned in the time-lapse study is shown

clearly here at every frequency anchor. As in the barite drilling fluid, SIP real conductivity and impedance are the two main signals to track in assessing drilling fluids' weighting material sag.

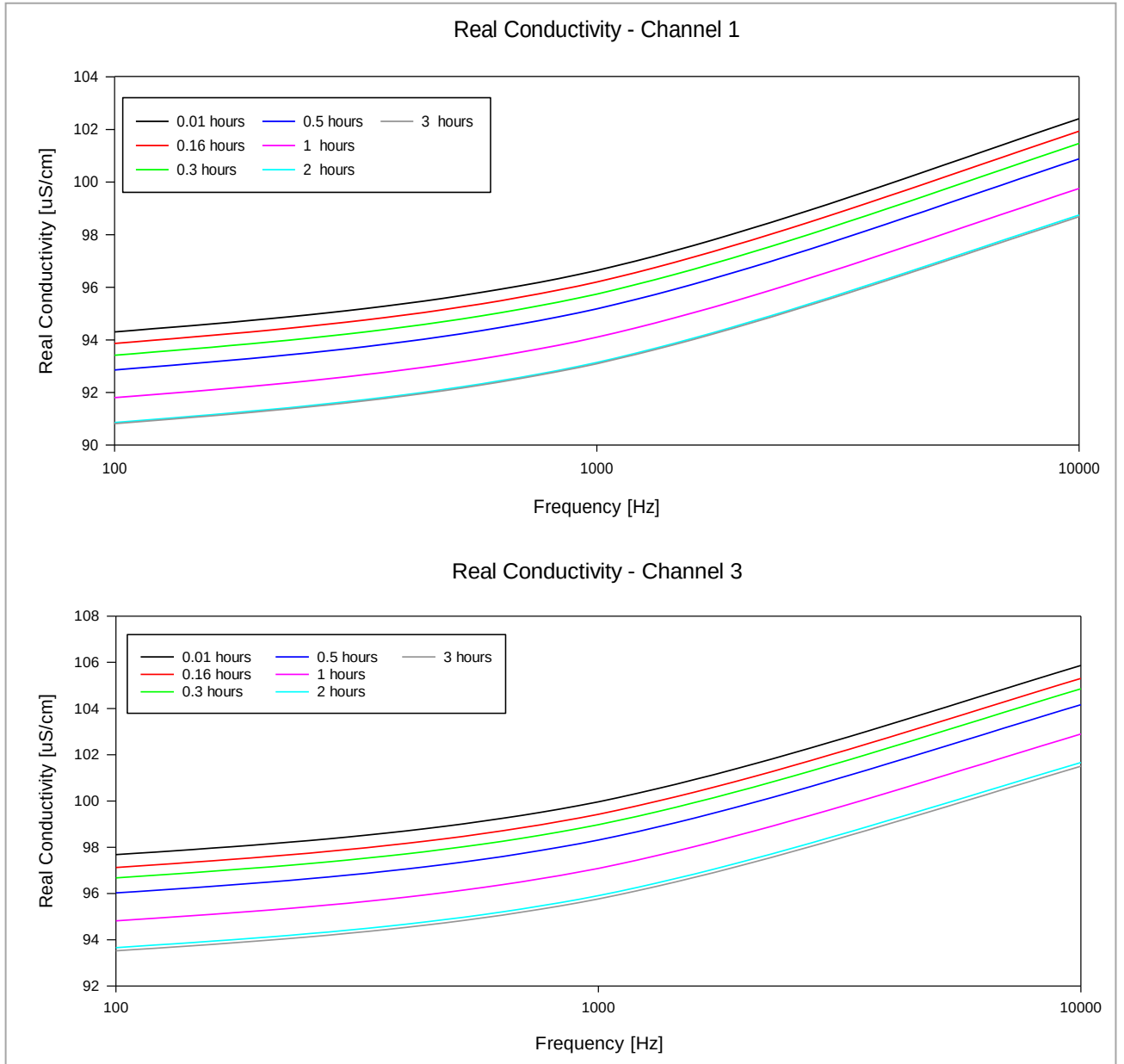


Figure 38: Real conductivity for calcite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).

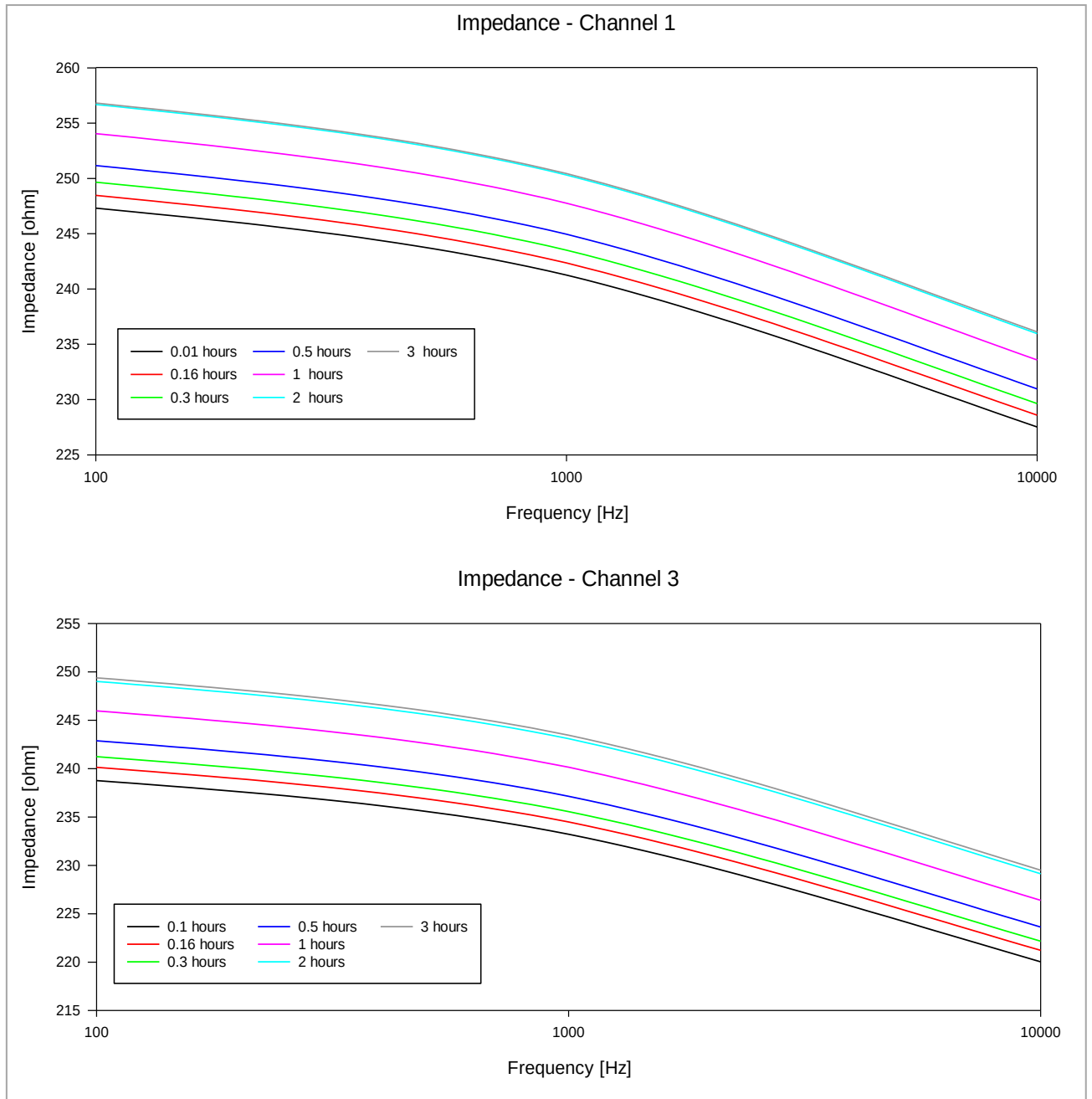


Figure 39: Impedance measurements calcite drilling fluid at 6 time periods for upper channel 1 (top) and lower channel 3 (bottom).

D. Discussion

Based on the previous results, SIP real conductivity and impedance are the most conclusive and distinctive signals when assessing weighting material sag in water-based drilling

fluids. The signal change with time agrees with the concentration change in the fluid column. Real conductivity measures the fluids' total electrical conductivity system and reflects the fluids' and solids' readings. As the base fluid is deionized water, the conductivity is mainly related to the drilling components' solids additives; hence, once the solids concentration drops due to settlement, a clear response is shown in the real conductivity signals. Impedance is a measure of the fluid resistance to current flow, meaning that it should be opposite to real conductivity in terms of behavior. Whenever real conductivity presents a fast increase, the impedance will decrease in the same way.

There is a vast difference between barite and calcite drilling fluids signals. This change is related to the nature of barite being more conductive than calcite. Also, the components in both fluids are different which makes comparing both fluids' signals difficult in this case. In barite drilling fluid, real conductivity has a larger change than impedance, indicating that barite particles are migrating downwards and out of the testing channel. With barite being more conductive than other components, its loss from the system causes a higher effect than calcite which is less conductive. On the other side, the increase in impedance in barite is less than in calcite since the system is still conductive even after barite leaves the testing channel due to other components in the drilling fluid. Whereas in calcite, impedance shows a higher increase due to the lack of conductive materials in the drilling fluid and because calcite, by nature, tends to settle severely in the absence of drilling fluid stabilizers.

Other SIP parameters, such as phase shift and imaginary conductivity, are studied but not found to be as efficient as real conductivity and impedance. This is because the later signals are related more to solids' charge storage ability. Unlike metallic materials, drilling fluids weighing materials are non-metallic solids that cannot highly store and/or accumulate

electrical charges. Thus, real conductivity and impedance are more relied on to be used in this study to monitor drilling fluid sag.

E. Conclusion

Barite and calcite sag were monitored as drilling fluids weighting materials by the SIP method in various time frames. SIP signals proved high accuracy in tracking weighting materials sag in a period of 2 hours where signals flattened after that, showing settlement deceleration. The two main conclusive signals are the real conductivity and impedance due to the loss of conductivity in the system because of particle migration. With the latter signals being highly related to electrical conductivity, they showed a superior effect to phase shift and imaginary conductivity that are mostly related to electric chargeability.

Changes in real and impedance set rules for detecting drilling fluids sag in early stages in ambient temperatures. For example, where minor particles settlement of nearly 1% and 2.6% in the bottom and top segment of the fluid, respectively for barite and 2.8% and 4% in the bottom and top segment of the fluid, respectively for calcite could be visibly tracked by real conductivity and impedance signals with an 11.5 uS/cm drop, and 4.9 ohms increase respectively for barite drilling fluid, and 3.9 uS/cm drop and 9.5 ohms increase, respectively for calcite drilling fluid. This novel approach sets the SIP method as a reliable and robust method in drilling fluid weighting material sag detection. Such an early detection method is advantageous in the Oil and Gas industry and can be implemented downhole to provide a real-time sag tracking system that could spot drilling fluid settlement at early stages.

CHAPTER 4

CONCLUSION

In this thesis work, the SIP method was utilized to characterize two main subjects in the oil and gas industry. The first subject is the quantification and early detection of iron sulfide content in limestone formations, a formation evaluation petrophysical issue that is arising and urging for solutions. Iron sulfide presence is reported to cause many issues in the oil and gas exploration and production processes. It hinders the permeability and quality of formation rocks and precipitates in the bottomhole assembly of the production system and causes catastrophic losses either in production rates or in piping and metallic pipes.

The SIP method was used to detect the presence of pyrite, a common iron sulfide type, in limestone unconsolidated matrices. The main two objectives were to early detect the presence of pyrite in limestone matrices, and qualitatively assess the presence and severity of the iron sulfide bodies within limestone formations.

Early detection of pyrite presence was successfully achieved where ultimately small concentrations of pyrite up to 0.25% in bulk volume were successfully detected in the SIP tool via utilizing the SIP phase shift and imaginary part of the complex electric conductivity. The main mechanism behind this is the big difference between iron sulfide and calcium carbonate polarization and charge storage properties. It is believed that iron sulfide particles undergo a different and stronger mechanism of polarization which is electrode polarization, whereas calcium carbonate particles are only expected to undergo clay (EDL) polarization as reported in many literature works.

Moreover, the characterization of iron sulfide presence is also feasible through the SIP technique via imaginary conductivity part and phase shift where it has been found that the phase shift and imaginary conductivity both are directly proportional to the concentration of pyrite in the matrix. Also, the real part of the complex conductivity and impedance can be used as a qualitative measure for iron sulfide concentration, but they cannot be used as early detection measures. The real conductivity is directly influenced by the ohmic electric conductivity and the electron exchange. In small concentrations, pyrite particles are believed to be isolated by the surrounding non-conductive calcite particles that might have disturbed the accuracy of the signals unlike phase shift and imaginary conductivity where they are related to charge storage property of the particles.

The second subject addressed in this thesis work is drilling fluid calcium carbonate content monitoring and weighting material sag early detection and characterization. Drilling fluid is the main well control barrier that must be monitored for integrity and well-being. In this work, calcium carbonate content in water-based sodium bentonite drilling fluid was assessed. In addition, weighting materials sag for both barite and calcite weighting materials was early detected and monitored.

In the first part, six samples of water-based sodium bentonite drilling fluid with different calcite concentrations in them were tested using SIP to assess their concentrations and monitor the increase of calcium carbonate in the system. Detection of calcium carbonate in the system was successfully achieved as low as 0.1% per weight of the total fluid sample. A sharp decrease in the real conductivity reading was detected as soon as 0.1% calcium carbonate was added to the system which indicated the high sensitivity of the SIP tool. The

phase shift and imaginary conductivity were also used but their contribution is inconclusive and might only be used qualitatively.

In the second part of the drilling fluid characterization, weighting material sag was assessed. 2 samples of barite and calcite water-based mud were prepared and tested for weighting material settlement through 2 testing channels with different elevations on the side of the testing SIP column. The test was done at room temperature and atmospheric pressure, unlike conventional sag tests that require high pressure and high temperature. Sag early detection was reached where samples showed a clear distinction between new and settled samples after being tested for 3 and 5 hours for calcite and barite respectively. Barite is more conductive and has sulfur that is favorable in SIP tests where it could be detected easily for its high polarizability. In the results, both samples showed good results that could conclude and detect weighting material sag in less than 5 hours. Impedance and real conductivity were the most sensitive parameters to the content change in the drilling fluid body since the change is mostly due to the loss of solid particles in the system. Both channels experienced loss in solids where the accumulation of solid particles took place in the bottom of the testing column, however, the top channel is showing more signals of solid loss reflected by higher impedance and lower real conductivity. The change was quantified to be an 11.5 uS/cm drop in real conductivity, and 4.9 ohms increase in impedance for barite drilling fluid, and a 3.9 uS/cm drop in real conductivity, and 9.5 ohms increase in impedance for calcite drilling fluid with high sensitivities of 0.5 uS/cm and 0.25% for real conductivity and impedance, respectively. The vast differences in the SIP signals are coming in agreement with the density tests where density in both channels of both fluids

reduced slightly. The results show the reliability and robustness of the SIP tool as a drilling fluid monitoring tool.

All in all, this work has provided a proof of concept for the utilization of the SIP method in the characterization of iron sulfide scales in limestone formations. Also, the utilization of the SIP method has been extended in this work to cover weighting materials concentration assessment and sag detection. The results in this work shed light on the ability of the SIP method to be considered in O&G domains and paved the way for upcoming research work and innovations to the method for wider usage in solving O&G problems.

REFERENCES

- [1] W. M. Rust, “A historical review of electrical prospecting methods,” *Geophysics*, vol. 3, no. 1, pp. 1–6, Jan. 1938, doi: 10.1190/1.1439461.
- [2] A. Binley and L. Slater, “Introduction,” in *Resistivity and Induced Polarization*, Cambridge University Press, 2020, pp. 1–17. doi: 10.1017/9781108685955.002.
- [3] F. A. Assaad and P. E. LaMoreaux, “Field Methods for Geologists and Hydrogeologists,” 2004. doi: 10.1007/978-3-662-05438-3.
- [4] C. K. Wong and F. G. Shin, “Effect of electrical conductivity on poling and the dielectric, pyroelectric and piezoelectric properties of ferroelectric 0-3 composites,” *J Mater Sci*, vol. 41, no. 1, pp. 229–249, 2006, doi: 10.1007/s10853-005-7243-3.
- [5] K. Rabe, Ch. H. Ahn, and J.-M. Triscone, *Physics of Ferroelectrics: A Modern Perspective*, vol. 103, no. 2. Springer Verlag, 2007. doi: 10.1179/096797804225012891.
- [6] A. Revil, M. Karaoulis, T. Johnson, and A. Kemna, “Review: Some low-frequency electrical methods for subsurface characterization and monitoring in hydrogeology,” *Hydrogeol J*, vol. 20, no. 4, pp. 617–658, 2012, doi: 10.1007/s10040-011-0819-x.
- [7] H. G. Doll, “The S.P. Log: Theoretical Analysis and Principles of Interpretation,” 1948, [Online]. Available: <http://onepetro.org/TRANS/article-pdf/179/01/146/2179030/spe-949146-g.pdf/1>
- [8] C. A. Moreira, M. F. S. Casagrande, and K. Borssatto, “Analysis of the potential application of geophysical survey (induced polarization and DC resistivity) to a

- long-term mine planning in a sulfide deposit,” *undefined*, vol. 13, no. 20, Oct. 2020, doi: 10.1007/S12517-020-06096-X.
- [9] A. Binley and A. Kemna, “DC Resistivity and Induced Polarization Methods,” *Hydrogeophysics*, pp. 129–156, Aug. 2005, doi: 10.1007/1-4020-3102-5_5.
- [10] L. D. Slater and D. Lesmes, “the Induced Polarization Method,” *Presented at the First International Conference on the Application of Geophysical Methodologies and NDT to Transportation Facilities and Infrastructure, St. Louis, Mo*, pp. 1–8, 2000, [Online]. Available: <https://hendragrandis.files.wordpress.com/2008/03/the-ip-method.pdf>
- [11] O. M. Siddiq, B. S. Tawabini, P. Soupios, and D. Ntarlagiannis, “Removal of arsenic from contaminated groundwater using biochar: a technical review,” *International Journal of Environmental Science and Technology*. 2021. doi: 10.1007/s13762-020-03116-x.
- [12] M. O. Siddiq, B. Tawabini, P. Kirmizakis, D. Kalderis, D. Ntarlagiannis, and P. Soupios, “Combining geophysics and material science for environmental remediation: Real-time monitoring of Fe-biochar arsenic wastewater treatment,” *Chemosphere*, vol. 284, p. 131390, Dec. 2021, doi: 10.1016/j.chemosphere.2021.131390.
- [13] P. Soupios and D. Ntarlagiannis, “Characterization and monitoring of solid waste disposal sites using geophysical methods: Current applications and novel trends,” in *Modelling Trends in Solid and Hazardous Waste Management*, Springer Singapore, 2017, pp. 75–103. doi: 10.1007/978-981-10-2410-8_5.

- [14] D. Ntarlagiannis, D. Kalderis, and P. Soupios, “Geophysical Methods for Contaminant Management: the Case for Biochar,” *Fast TIMES*, vol. 25, no. 2, pp. 80–90, 2020.
- [15] D. Ntarlagiannis, J. Robinson, P. Soupios, and L. Slater, “Field-scale electrical geophysics over an olive oil mill waste deposition site: Evaluating the information content of resistivity versus induced polarization (IP) images for delineating the spatial extent of organic contamination,” *J Appl Geophy*, vol. 135, pp. 418–426, Dec. 2016, doi: 10.1016/j.jappgeo.2016.01.017.
- [16] D. Ntarlagiannis, P. Kirmizakis, D. Kalderis, and P. Soupios, “Using the spectral induced polarization method to assess biochar performance as a remediation agent,” in *AGU Fall Meeting 2016*, 2016. [Online]. Available: [https://pure.qub.ac.uk/en/publications/using-the-spectral-induced-polarization-method-to-assess-biochar-performance-as-a-remediation-agent\(1c75a2f7-e1fd-40f2-bfe9-69d00ebd560f\).html](https://pure.qub.ac.uk/en/publications/using-the-spectral-induced-polarization-method-to-assess-biochar-performance-as-a-remediation-agent(1c75a2f7-e1fd-40f2-bfe9-69d00ebd560f).html)
- [17] K. Gerodimou, P. Kirmizakis, P. Soupios, and A. Vafidis, “Preliminary results from lab experiments on the use and sensitivity of spectral induced polarization (SIP) method,” *8th Congress of the Balkan Geophysical Society, BGS 2015*, no. November, 2015, doi: 10.3997/2214-4609.201414148.
- [18] P. Kirmizakis, B. Tawabini, O. M. Siddiq, D. Kalderis, D. Ntarlagiannis, and P. Soupios, “Adsorption of Arsenic on Fe-Modified Biochar and Monitoring Using Spectral Induced Polarization,” *Water (Switzerland)*, vol. 14, no. 4, pp. 1–16, 2022, doi: 10.3390/w14040563.

- [19] S. Joseph, “The Application of Spectral Induced Polarization to Determination of Hydraulic Conductivity,” *Thesis*, 2016.
- [20] L. D. Slater and D. Lesmes, “IP interpretation in environmental investigations,” *Geophysics*, vol. 67, no. 1, pp. 77–88, 2002, doi: 10.1190/1.1451353.
- [21] A. Binley and A. Kemna, *DC Resistivity and Induced Polarization Methods*, no. January. 2005. doi: 10.1007/1-4020-3102-5_5.
- [22] D. J. Marshall and T. R. Madden, “INDUCED POLARIZATION, A STUDY OF ITS CAUSES,” *GEOPHYSICS*, vol. 24, no. 4, pp. 790–816, 1959, doi: 10.1190/1.1438659.
- [23] C. R. Phillips, “Experimental Study of the Induced Polarization Effect Using Cole-Cole and Gemtip Models,” *Thesis*, no. December, 2010.
- [24] A. Revil, A. Binley, L. Mejus, and P. Kessouri, “Predicting permeability from the characteristic relaxation time and intrinsic formation factor of complex conductivity spectra,” *Water Resour Res*, vol. 51, no. 8, pp. 6672–6700, 2015, doi: 10.1002/2015WR017074.
- [25] A. Revil, “On charge accumulation in heterogeneous porous rocks under the influence of an external electric field,” *Geophysics*, vol. 78, no. 4, 2013, doi: 10.1190/GEO2012-0503.1.
- [26] A. Binley and L. Slater, *Resistivity and Induced Polarization*. 2020. doi: 10.1017/9781108685955.

- [27] J. Wong, “An electrochemical model of the induced-polarization phenomenon in disseminated sulfide ores.,” *Geophysics*, vol. 44, no. 7, pp. 1245–1265, 1979, doi: 10.1190/1.1441005.
- [28] A. Kemna *et al.*, “An overview of the spectral induced polarization method for near-surface applications,” *Near Surface Geophysics*, vol. 10, no. 6, pp. 453–468, 2012, doi: 10.3997/1873-0604.2012027.
- [29] S. Izumoto, “Spectral induced polarization of calcite precipitation in porous media,” 2021.
- [30] O. A. L. De Lima and M. M. Sharma, “A generalized Maxwell-Wagner theory for membrane polarization in shaly sands,” *Geophysics*, vol. 57, no. 3, pp. 431–440, Mar. 1992, doi: 10.1190/1.1443257.
- [31] M. Samet, V. Levchenko, G. Boiteux, G. Seytre, A. Kallel, and A. Serghei, “Electrode polarization vs. Maxwell-Wagner-Sillars interfacial polarization in dielectric spectra of materials: Characteristic frequencies and scaling laws,” *Journal of Chemical Physics*, vol. 142, no. 19, 2015, doi: 10.1063/1.4919877.
- [32] M. Samet, A. Kallel, and A. Serghei, “Maxwell-Wagner-Sillars interfacial polarization in dielectric spectra of composite materials: Scaling laws and applications,” *J Compos Mater*, vol. 56, no. 20, pp. 3197–3217, 2022, doi: 10.1177/00219983221090629.
- [33] D. Jougnot, A. Ghorbani, A. Revil, P. Leroy, and P. Cosenza, “Spectral induced polarization of partially saturated clay-rocks: A mechanistic approach,” *Geophys J Int*, vol. 180, no. 1, pp. 210–224, 2010, doi: 10.1111/j.1365-246X.2009.04426.x.

- [34] G. V. Gurin, Y. T. Ilyin, and K. V. Titov, “Induced Polarization of Anisotropic Models with Metallic Particles,” *undefined*, pp. 243–252, 2019, doi: 10.3997/2214-4609.201901712.
- [35] Y. Chen and D. Or, “Geometrical factors and interfacial processes affecting complex dielectric permittivity of partially saturated porous media,” *Water Resour Res*, vol. 42, no. 6, p. 6423, Jun. 2006, doi: 10.1029/2005WR004744.
- [36] K. Titov, V. Komarov, V. Tarasov, and A. Levitski, “Theoretical and experimental study of time domain-induced polarization in water-saturated sands,” *J Appl Geophy*, vol. 50, no. 4, pp. 417–433, Jul. 2002, doi: 10.1016/S0926-9851(02)00168-4.
- [37] A. Revil, “Spectral induced polarization of shaly sands: Influence of the electrical double layer,” *Water Resour Res*, vol. 48, no. 2, pp. 1–23, 2012, doi: 10.1029/2011WR011260.
- [38] S. Izumoto, J. A. Huisman, Y. Wu, and H. Vereecken, “Effect of solute concentration on the spectral induced polarization response of calcite precipitation,” *Geophys J Int*, vol. 220, no. 2, pp. 1187–1196, 2020, doi: 10.1093/gji/ggz515.
- [39] P. Leroy, N. Devau, A. Revil, and M. Bizi, “Influence of surface conductivity on the apparent zeta potential of amorphous silica nanoparticles,” *J Colloid Interface Sci*, vol. 410, pp. 81–93, 2013, doi: 10.1016/j.jcis.2013.08.012.
- [40] P. Vaudelet, A. Revil, M. Schmutz, M. Franceschi, and P. Bégassat, “Induced polarization signatures of cations exhibiting differential sorption behaviors in

- saturated sands,” *Water Resour Res*, vol. 47, no. 2, pp. 1–21, 2011, doi: 10.1029/2010WR009310.
- [41] Q. Niu and A. Revil, “Connecting complex conductivity spectra to mercury porosimetry of sedimentary rocks,” *Geophysics*, vol. 81, no. 1, pp. E17–E32, 2016, doi: 10.1190/GEO2015-0072.1.
- [42] M. Bucker and A. Hördt, “Analytical modelling of membrane polarization with explicit parametrization of pore radii and the electrical double layer,” *Geophys J Int*, vol. 194, no. 2, pp. 804–813, 2013, doi: 10.1093/gji/ggt136.
- [43] L. Slater, D. Ntarlagiannis, and D. Wishart, “On the relationship between induced polarization and surface area in metal-sand and clay-sand mixtures,” vol. 71, no. 2, pp. 1–5, 2006.
- [44] M. Attwa and T. Gunther, “Spectral induced polarization measurements for environmental purposes and predicting the hydraulic conductivity in sandy aquifers,” *Hydrology and Earth System Sciences Discussions*, vol. 10, no. 4, pp. 5315–5354, 2013, doi: 10.5194/hessd-10-5315-2013.
- [45] N. Rezaii; A. Hördt, “Numerical Study of Membrane Polarization for a Network of Connected Pores,” vol. 24, no. 4, p. 2018, 2018, [Online]. Available: <https://www.comsol.com/paper/numerical-study-of-membrane-polarization-for-a-network-of-connected-pores-64581>
- [46] A. Revil and A. Jardani, “The self-potential method: Theory and applications in environmental geosciences,” *The Self-Potential Method: Theory and Applications*

- in *Environmental Geosciences*, vol. 9781107019. pp. 1–386, 2010. doi: 10.1017/CBO9781139094252.
- [47] G. Pesch and M. Sc, “On the dielectrophoretic particle retention in porous media On the dielectrophoretic particle retention in porous media zur Erlangung des Grades,” no. January, 2019.
- [48] A. Revil and N. Florsch, “Determination of permeability from spectral induced polarization in granular media,” *Geophys J Int*, vol. 181, no. 3, pp. 1480–1498, 2010, doi: 10.1111/j.1365-246X.2010.04573.x.
- [49] H. J. Vinegar and M. H. Waxman, “Induced polarization of shaly sands,” *Geophysics*, vol. 49, no. 8, pp. 1267–1287, Aug. 1984, doi: 10.1190/1.1441755.
- [50] D. Mao, A. Revil, and J. Hinton, “Induced polarization response of porous media with metallic particles - Part 4: Detection of metallic and nonmetallic targets in time-domain-induced polarization tomography,” *Geophysics*, vol. 81, no. 4, pp. D359–D375, 2016, doi: 10.1190/GEO2015-0480.1.
- [51] R. Jairath and P. Patel, “Chapter 10: Electrode polarization,” *ELECTROCHEMICAL SCIENCE AND TECHNOLOGY Fundamentals and Applications*, pp. 1–5, 2012.
- [52] P. Ben Ishai, M. S. Talary, A. Caduff, E. Levy, and Y. Feldman, “Electrode polarization in dielectric measurements: A review,” *Meas Sci Technol*, vol. 24, no. 10, 2013, doi: 10.1088/0957-0233/24/10/102001.

- [53] D. Ntarlagiannis, R. Doherty, and K. H. Williams, “Spectral induced polarization signatures of abiotic FeS precipitation,” *Geophysics*, vol. 75, no. 4, 2010, doi: 10.1190/1.3467759.
- [54] E. Placencia-Gómez, L. Slater, D. Ntarlagiannis, and A. Binley, “Laboratory SIP signatures associated with oxidation of disseminated metal sulfides,” *J Contam Hydrol*, vol. 148, pp. 25–38, 2013, doi: 10.1016/j.jconhyd.2013.02.007.
- [55] A. Revil and P. W. J. Glover, “Nature of surface electrical conductivity in natural sands, sandstones, and clays,” *Geophys Res Lett*, vol. 25, no. 5, pp. 691–694, Mar. 1998, doi: 10.1029/98GL00296.
- [56] D. P. Lesmes and K. M. Frye, “Influence of pore fluid chemistry on the complex conductivity and induced polarization responses of Berea sandstone,” *J Geophys Res Solid Earth*, vol. 106, no. B3, pp. 4079–4090, Mar. 2001, doi: 10.1029/2000JB900392.
- [57] R. Kirsch, “Groundwater geophysics: a tool for hydrogeology,” 2006. doi: 10.5860/choice.44-1535.
- [58] A. Revil *et al.*, “Complex conductivity of soils,” *Water Resour Res*, vol. 53, no. 8, pp. 7121–7147, Aug. 2017, doi: 10.1002/2017WR020655.
- [59] F. Börner, “EFFECT OF POROSITY CHANGES ON COMPLEX ELECTRICAL CONDUCTIVITY IN SHALY SANDS.”

- [60] A. F. Orozco, K. H. Williams, and A. Kemna, “Time-lapse spectral induced polarization imaging of stimulated uranium bioremediation,” *Near Surface Geophysics*, vol. 11, no. 5, pp. 531–544, 2013, doi: 10.3997/1873-0604.2013020.
- [61] P. Leroy and A. Revil, “A mechanistic model for the spectral induced polarization of clay materials,” *J Geophys Res Solid Earth*, vol. 114, no. B10, p. 10202, Oct. 2009, doi: 10.1029/2008JB006114.
- [62] J. Doetsch, G. Fiandaca, E. Auken, A. V. Christiansen, A. G. Cahill, and R. Jakobsen, “Field-scale time-domain spectral induced polarization monitoring of geochemical changes induced by injected CO₂ in a shallow aquifer,” *Geophysics*, vol. 80, no. 2, pp. WA113–WA126, 2015, doi: 10.1190/GEO2014-0315.1.
- [63] A. Weller and F. D. Brner, “Measurements of spectral induced polarization for environmental purposes,” *Environmental Geology*, vol. 4, no. 27, pp. 329–334, 1996, Accessed: Dec. 11, 2021. [Online]. Available: <https://www.infona.pl/resource/bwmeta1.element.springer-306c0db1-3a5c-3ca4-9fac-d9dd96fa14d5>
- [64] A. Kemna, A. Binley, and L. Slater, “Crosshole IP imaging for engineering and environmental applications,” *Geophysics*, vol. 69, no. 1, pp. 97–107, 2004, doi: 10.1190/1.1649379.
- [65] P. Kirmizakis, D. Kalderis, D. Ntarlagiannis, and P. Soupios, “Preliminary assessment on the application of biochar and spectral-induced polarization for wastewater treatment,” *Near Surface Geophysics*, vol. 18, no. 2, pp. 109–122, 2020, doi: 10.1002/nsg.12076.

- [66] W. H. Pelton, S. H. Ward, P. G. Hallof, W. R. Sill, and P. H. Nelson, “Mineral discrimination and removal of inductive coupling with multifrequency IP,” *Geophysics*, vol. 43, no. 3, pp. 588–609, Apr. 1978, doi: 10.1190/1.1440839.
- [67] A. Kemna, “Tomographic inversion of complex resistivity,” 2000. [Online]. Available: http://www2.geo.uni-bonn.de/members/kemna/Kemna_2000_PhD_thesis.pdf
- [68] S. Kruschwitz, A. Binley, D. Lesmes, and A. Elshenawy, “Textural controls on low-frequency electrical spectra of porous media,” *Geophysics*, vol. 75, no. 4, 2010, doi: 10.1190/1.3479835.
- [69] S. Nordsiek and A. Weller, “A new approach to fitting induced-polarization spectra,” *Geophysics*, vol. 73, no. 6, pp. F235–F245, Nov. 2008, doi: 10.1190/1.2987412.
- [70] M. B. Tomson, A. T. Kan, G. Fu, M. Al-Thubaiti, D. Shen, and H. J. Shipley, “Scale Formation and Prevention in the Presence of Hydrate Inhibitors,” *SPE Journal*, vol. 11, no. 02, pp. 248–258, Jun. 2006, doi: 10.2118/80255-PA.
- [71] M. S. Kamal, I. Hussein, M. Mahmoud, A. S. Sultan, and M. A. S. Saad, “Oilfield scale formation and chemical removal: A review,” *J Pet Sci Eng*, vol. 171, pp. 127–139, Dec. 2018, doi: 10.1016/J.PETROL.2018.07.037.
- [72] A. M. Siefers and A. M. Siefers, “A novel and cost-effective hydrogen sulfide removal technology using tire derived rubber particles,” 2010.

- [73] J. Lee and R. Kumar, "Laboratory study of hydrogen sulfide removal in slug flows in a high pressure crude oil loop," 2013, doi: 10.1016/j.petrol.2013.01.009.
- [74] A. Hamza, I. A. Hussein, R. Jalab, M. Saad, and M. Mahmoud, "Review of Iron Sulfide Scale Removal and Inhibition in Oil and Gas Wells: Current Status and Perspectives," *Energy and Fuels*, vol. 35, no. 18, pp. 14401–14421, 2021, doi: 10.1021/acs.energyfuels.1c02177.
- [75] M. A. Mahmoud, M. Kamal, B. S. Bageri, and I. Hussein, "Removal of pyrite and different types of iron sulfide scales in oil and gas wells without H₂S generation," *International Petroleum Technology Conference, IPTC 2015*, vol. 2015-Janua, 2015, doi: 10.2523/IPTC-18279-MS.
- [76] Y. Chen *et al.*, "Modification, application and reaction mechanisms of nano-sized iron sulfide particles for pollutant removal from soil and water: A review," *Chemical Engineering Journal*, vol. 362, pp. 144–159, Apr. 2019, doi: 10.1016/J.CEJ.2018.12.175.
- [77] N. A. Al-baghli, S. A. Pruess, V. F. Yesavage, and M. S. Selim, "A rate-based model for the design of gas absorbers for the removal of CO₂ and H₂S using aqueous solutions of MEA and DEA," vol. 185, pp. 31–43, 2001.
- [78] W. Li *et al.*, "Development of Novel Iron Sulfide Scale Control Chemicals," *Society of Petroleum Engineers - SPE International Oilfield Scale Conference and Exhibition 2018*, Jun. 2018, doi: 10.2118/190755-MS.
- [79] H. A. Nasr-El-Din and A. Y. Al-Humaidan, "Iron Sulfide Scale: Formation, Removal and Prevention," 2001, doi: 10.2118/68315-ms.

- [80] Y. R. Personna, D. Ntarlagiannis, L. Slater, N. Yee, M. O'Brien, and S. Hubbard, "Spectral induced polarization and electrodic potential monitoring of microbially mediated iron sulfide transformations," *J Geophys Res Biogeosci*, vol. 113, no. 2, pp. 1–13, 2008, doi: 10.1029/2007JG000614.
- [81] E. Placencia-Gómez, L. Slater, D. Ntarlagiannis, and A. Binley, "Laboratory SIP signatures associated with oxidation of disseminated metal sulfides," *J Contam Hydrol*, vol. 148, pp. 25–38, 2013, doi: 10.1016/J.JCONHYD.2013.02.007.
- [82] M. Crabtree, D. Eslinger, P. Fletcher, M. Miller, J. Ashley, and G. King, "Fighting Scale-Removal and Prevention," 1999.
- [83] M. El-Said, M. Ramzi, and T. Abdel-Moghny, "Analysis of oilfield waters by ion chromatography to determine the composition of scale deposition," *Desalination*, vol. 249, no. 2, pp. 748–756, Dec. 2009, doi: 10.1016/J.DESAL.2008.12.061.
- [84] A. Behrangi *et al.*, "Scale Build-Up Prediction of FeS and FeCO₃ in Gas Production Pipes," *J Phys Conf Ser*, vol. 877, no. 1, p. 012029, Jul. 2017, doi: 10.1088/1742-6596/877/1/012029.
- [85] M. Buali *et al.*, "Extreme Challenges in FeS Scale Cleanout Operation Overcome using Temporary Isolation, High Pressure Coiled Tubing, and Tailored Fluid Systems," May 2014, doi: 10.2118/SPE-169759-MS.
- [86] M. A. Kelland, "History of the development of low dosage hydrate inhibitors," *Energy and Fuels*, vol. 20, no. 3, pp. 825–847, May 2006. doi: 10.1021/ef050427x.

- [87] D. A. Lytle, T. L. Gerke, and J. B. Maynard, "Effect of bacterial sulfate reduction on iron-corrosion scales," *J Am Water Works Assoc*, vol. 97, no. 10, pp. 109–120, Oct. 2005, doi: 10.1002/J.1551-8833.2005.TB07500.X.
- [88] C. J. Seto and D. A. Beliveau, "Reservoir souring in the Caroline field," *Society of Petroleum Engineers - SPE/CERI Gas Technology Symposium 2000, GTS 2000*, pp. 1–9, 2000, doi: 10.2523/59778-ms.
- [89] M. L. Walker, W. R. Dill, M. R. Besler, D. G. Mcfatridge, and H. Services, "Iron Control in West Texas Sour-Gas Wells Provides Sustained Production Increases," 1991, Accessed: Dec. 15, 2021. [Online]. Available: <http://onepetro.org/JPT/article-pdf/43/05/603/2222095/spe-20122-pa.pdf/1>
- [90] T. Chen, Q. Wang, F. F. Chang, and Y. T. Al-Janabi, "New developments in iron sulfide scale dissolvers," in *NACE - International Corrosion Conference Series*, 2016, pp. 1168–1180.
- [91] N. Gasimli, M. Mahmoud, A. Hassan, M. Shahzad Kamal, S. Patil, and R. Al-Abdrabalnabi, "Iron Sulfide Scale Inhibition Through Adsorption of Chelating Agents," 2022. doi: 10.2118/210275-ms.
- [92] T. Almubarak, J. H. Ng, and H. Nasr-El-Din, "Oilfield scale removal by chelating agents: An aminopolycarboxylic acids review," *SPE Western Regional Meeting Proceedings*, vol. 2017-April, no. Iii, pp. 1053–1065, 2017, doi: 10.2118/185636-ms.

- [93] Q. Wang *et al.*, “Iron sulfide and removal in scale formation sour gas wells,” *Society of Petroleum Engineers - SPE International Oilfield Scale Conference and Exhibition*, 2016, doi: 10.2118/179869-ms.
- [94] P. Zhang, Y. Liu, S. C. Kuok, A. T. Kan, and M. B. Tomson, “Development of modeling approaches to describe mineral scale deposition kinetics in porous medium and pipe flow system,” *J Pet Sci Eng*, vol. 178, no. March, pp. 594–601, Jul. 2019, doi: 10.1016/j.petrol.2019.03.070.
- [95] C. Okocha *et al.*, “Review of Iron Sulfide Scale: The Facts & Developments and Relation to Oil and Gas Production,” *Society of Petroleum Engineers - SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition 2018, SATS 2018*, pp. 23–26, Apr. 2018, doi: 10.2118/192207-MS.
- [96] E. S. Ameh, S. C. Ikpeseni, and L. S. Lawal, “A Review of Field Corrosion Control and Monitoring Techniques of the Upstream Oil and Gas Pipelines,” *Nigerian Journal of Technological Development*, vol. 14, no. 2, p. 67, Jan. 2018, doi: 10.4314/NJTD.V14I2.5.
- [97] H. R. Vanaei, A. Eslami, and A. Egbewande, “A review on pipeline corrosion, in-line inspection (ILI), and corrosion growth rate models,” *International Journal of Pressure Vessels and Piping*, vol. 149, pp. 43–54, Jan. 2017, doi: 10.1016/J.IJPVP.2016.11.007.
- [98] C. Kimak *et al.*, “Geophysical Monitoring of Hydrocarbon Biodegradation in Highly Conductive Environments,” *J Geophys Res Biogeosci*, vol. 124, no. 2, pp. 353–366, 2019, doi: 10.1029/2018JG004561.

- [99] T. Martin, “Laboratory SIP-investigation on unconsolidated mineral-sand-mixtures,” in *3rd International Workshop on Induced Polarization*, 2014.
- [100] S. Hupfer *et al.*, “Polarization effects of unconsolidated sulphide-sand-mixtures,” *undefined*, vol. 135, pp. 456–465, Dec. 2016, doi: 10.1016/J.JAPPGEO.2015.12.003.
- [101] A. Khormali and D. G. Petrakov, “Laboratory investigation of a new scale inhibitor for preventing calcium carbonate precipitation in oil reservoirs and production equipment,” *Pet Sci*, vol. 13, no. 2, pp. 320–327, May 2016, doi: 10.1007/s12182-016-0085-6.
- [102] M. Amiri and J. Moghadasi, “The effect of temperature on calcium carbonate scale formation in iranian oil reservoirs using oli scalechem software,” *Pet Sci Technol*, vol. 30, no. 5, pp. 453–466, 2012, doi: 10.1080/10916461003735145.
- [103] P. A. Bern, M. Zamora, A. T. Hemphill, D. Marshall, T. H. Omland, and E. K. Morton, “Field Monitoring of Weight-Material Sag,” *the 2010 AADE Fluids Conference and Exhibition*, 2010.
- [104] T. Kumar, S. Vishwanatham, and S. S. Kundu, “A laboratory study on pteroyl-l-glutamic acid as a scale prevention inhibitor of calcium carbonate in aqueous solution of synthetic produced water,” *J Pet Sci Eng*, vol. 71, no. 1–2, pp. 1–7, 2010, doi: 10.1016/j.petrol.2009.11.014.
- [105] J. Moghadasi, H. Müller-Steinhagen, M. Jamialahmadi, and A. Sharif, “Model study on the kinetics of oil field formation damage due to salt precipitation from

- injection,” *J Pet Sci Eng*, vol. 43, no. 3–4, pp. 201–217, 2004, doi: 10.1016/j.petrol.2004.02.014.
- [106] M. Wangen, J. Sagen, T. Bjørnstad, H. Johansen, and A. Souche, “Models for Calcium Carbonate Precipitation in the Near-Well Zone by Degassing of CO₂,” *The Open Petroleum Engineering Journal*, vol. 9, pp. 178–194, 2016, doi: 10.2174/1874834101609160178.
- [107] E. Granados, “Calcium carbonate deposition in geothermal wellbores Miravalles Geothermal Field, Costa Rica,” *M.S. Thesis*, no. June, p. 154, 1983.
- [108] T. Larsen, P. Randhol, M. Lioliou, L. O. Jøsang, and T. Østvold, “Kinetics of CaCO₃ scale formation during core flooding,” in *Society of Petroleum Engineers - 9th International Conference on Oilfield Scale 2008 - “Managing Scale Through the Field Lifetime,”* 2008, pp. 162–173. doi: 10.2118/114045-ms.
- [109] M. Ikbw, A. N. Bin, and A. B. Nasir, “The study of effect of calcium carbonate scale precipitation to the core sample permeability,” 2011.
- [110] X. Bu *et al.*, “Analysis of calcium carbonate scaling and antiscaling field experiment,” *Geothermics*, vol. 104, p. 102433, Sep. 2022, doi: 10.1016/J.GEOTHERMICS.2022.102433.
- [111] F. Dehghani, A. Kalantariasl, R. Saboori, S. Sabbaghi, and K. Peyvandi, “Performance of carbonate calcium nanoparticles as filtration loss control agent of water-based drilling fluid,” *SN Appl Sci*, vol. 1, no. 11, pp. 1–8, 2019, doi: 10.1007/s42452-019-1446-8.

- [112] Justin ; Dru ; Andrew ; Sai ; Danielle, and Fortin, “The mitigation of deep depth wellbore leakage using microbially induced carbonate precipitation (MICP),” *Geoconvention*, 2019.
- [113] K. A. Fattah and A. Lashin, “Investigation of mud density and weighting materials effect on drilling fluid filter cake properties and formation damage,” *Journal of African Earth Sciences*, vol. 117, pp. 345–357, 2016, doi: 10.1016/j.jafrearsci.2016.02.003.
- [114] T. Nguyen, C. Silva, A. Dare, A. Saasen, and E. Al-, “Optimization of Calcium Carbonate Particles and pH in Oil Based Drilling Fluids to Minimize Barite Sag,” 2016.
- [115] V. Wagle, S. Maghrabi, and D. Kulkarni, “Formulating sag-resistant, low-gravity solids-free invert emulsion fluids,” *SPE Middle East Oil and Gas Show and Conference, MEOS, Proceedings*, vol. 1, pp. 508–519, 2013, doi: 10.2118/164200-ms.
- [116] A. Odabaşı, “An Experimental Study of Particle Size and Concentration Effects of Calcium Carbonate on Rheological and Filtration Properties of Drill-in Fluids,” Middle East Technical University, 2015.
- [117] A. Mohamed, S. Basfar, S. Elkatatny, and A. Al-Majed, “Prevention of Barite Sag in oil-based drilling fluids using a mixture of barite and ilmenite as weighting material,” *Sustainability (Switzerland)*, vol. 11, no. 20, p. 5617, Oct. 2019, doi: 10.3390/su11205617.

- [118] A. Mohamed, S. Al-Afnan, S. Elkatatny, and I. Hussein, "Prevention of barite sag in water-based drilling fluids by a urea-based additive for drilling deep formations," *Sustainability (Switzerland)*, vol. 12, no. 7, p. 2719, Mar. 2020, doi: 10.3390/su12072719.
- [119] J. J. Miller, N. Braley, D. R. Siems, D. E. Jamison, and P. Baker, "Drilling Fluids Having Reduced SAG Potential and Related Methods." 2013.
- [120] T. H. Omland, A. Saasen, C. v.d. Zwaag, and P. A. Amundsen, "The effect of weighting material sag on drilling operation efficiency," *SPE - Asia Pacific Oil and Gas Conference*, vol. 2, pp. 1013–1017, 2007, doi: 10.2523/110537-ms.
- [121] T. N. Ofei, B. Lund, and A. Saasen, "Effect of particle number density on rheological properties and barite sag in oil-based drilling fluids," *J Pet Sci Eng*, vol. 206, no. January, 2021, doi: 10.1016/j.petrol.2021.108908.
- [122] T. H. Omland, *Particle Settling in non-Newtonian Drilling Fluids*. 2009. [Online]. Available: <http://brage.bibsys.no/xmlui/bitstream/id/179394/Omland>,
- [123] R. Murphy, D. Jamison, T. Hemphill, S. Bell, and C. Albrecht, "Measuring and predicting dynamic sag," *SPE Drilling and Completion*, vol. 23, no. 2, pp. 142–149, 2008, doi: 10.2118/103088-pa.
- [124] D. E. Jamison and R. J. Murphy Jr, "Apparatus and method for analyzing well fluid sag," no. 19. 2003.

- [125] J. A. Fort, J. A. Bamberger, J. M. Bates, C. W. Enderlin, and M. R. Elmore, “1/12-scale physical modeling experiments in support of tank 241-SY- 101 hydrogen mitigation.,” 1993.
- [126] C. Shen and U. Lemmin, “Ultrasonic measurements of suspended sediments: A concentration profiling system with attenuation compensation,” *Meas Sci Technol*, vol. 7, no. 9, pp. 1191–1194, 1996, doi: 10.1088/0957-0233/7/9/001.
- [127] F. D. Börner, J. R. Schopper, and A. Weller, “Evaluation of transport and storage properties in the soil and groundwater zone from induced polarization measurements,” *Geophys Prospect*, vol. 44, no. 4, pp. 583–601, 1996, doi: 10.1111/j.1365-2478.1996.tb00167.x.

VITAE

Name : Dhafer Omar Farag Badhafere

Nationality : Yemeni

Date of Birth : 10/4/1996

Email : Dhafer.ob@gmail.com

Address : Khobar, 34448, Kingdom of Saudi Arabia

Academic Background : B.Sc. in Petroleum Engineering with a minor in Mathematics from King Fahd University of Petroleum and Minerals (Dhahran, Saudi Arabia)

M.Sc. in Petroleum Engineering from King Fahd University of Petroleum and Minerals (Dhahran, Saudi Arabia)

Published Papers:

1. Hassan, A., Mohammed, E., Oshaish, A., **Badhafere, D.**, Ayranci, K., Dong, T., ... Mahmoud, M. (2023). Prediction of Total Organic Carbon in Organic-Rich Shale Rocks Using Thermal Neutron Parameters. ACS Omega. <https://doi.org/10.1021/acsomega.2c06918>.

Conference Posters:

1. **Badhafere, D.**, Oshaish, A., Kirmizakis, P., El-Husseiny, A., Soupios, P., & Mahmoud, M. Geophysical Monitoring of Iron Sulfide Scales. Poster presented at the American Association of Petroleum Geologists (AAPG) Integrated Emerging Exploration Concepts; 2022 Dec 07-09; Khobar, Saudi Arabia.

Submitted Papers:

1. **Badhafere, D.**, Kirmizakis, P., Oshaish, A., El-Husseiny, A., Mahmoud, M., Ntarlagiannis, D., & Soupios, P.. Detection of Iron Sulfide Materials in Geological Porous Media Using Spectral Induced Polarization Method.