

**Calcium carbonate scale inhibition by non
chemical methods**

BY

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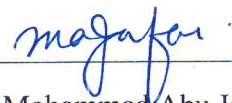
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Dedication

I dedicate my dissertation work to the soul of my father, may Allah forgive him and rest his soul in Jannat Al-Firdaus. A special feeling of gratitude to my mother whose words of encouragement and push for tenacity ring in my ears.

I dedicate this work to my future wife for her support during my Master studies.

I also dedicate this dissertation to my English language teacher, Mr. Hussein Meshref who has supported me throughout my High school studies.

I dedicate this work and give special thanks to my best friend Said Sayed for his support and helping me during hard times. |

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LIST OF ABBREVIATIONS

ATMP	Amino tris (methylenephosphonic acid)
MSF	Multi-stage flash
RO	Reversible osmosis
UV	Ultra violet
EDTA	Ethylene diamine tetra acetic acid
CCI	Calcium carbonate inhibition
SEM	Scanning electron microscope
XRD	X-ray diffraction

ABSTRACT

Full Name : **[Mokhtar Sayed Mohamed Nooreldeen Hafez]**
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Formation of mineral scale in calcareous deposits is persistent in nature. Removal of these scales is an expensive problem in the major chemical and water treatment industries. Scaling on the metallic surfaces may create technical problems including impedance of heat transfer, increase of energy consumption and unscheduled equipment shutdown. The prevention of this mineral deposit costs billions of dollars to the worldwide economy. Acid solutions were used to prevent any additional residual alkalinity depositing from CaCO_3 scale, however, acid-induced corrosion and sludge were the major problems associated with this treatment.

To overcome these problems, antiscalants have been developed for scale inhibition in boiler industry. The use of antiscalants is widespread and effective for controlling scale formation. Modification of crystal involves distortion of the formed particle, resulting in an irregularly shaped, less adherent crystal that cannot continue to grow, preventing crystal growth at calcite surfaces. However, these chemicals also pose danger on human health and environment with accidental spills, or accumulated chemical residues over a long period of time. Hence, nowadays there is an increasing need for a new approach that is environmentally friendly and economically feasible. In our work, we have investigated the effect of UV radiation, ultrasound, and electric field on calcium carbonate scale formation in water. Using UV light; the calcium carbonate crystal growth rate decreased

by about 85%, compared to 43% after the addition of 3 ppm of amino tris (methylenephosphonic acid) antiscalant, producing mostly calcite crystals, that are less dense, less adherent, and easily removed than other types of calcium carbonate phases; increasing the life time of the desalination membrane.

Application of ultrasound increased the CCI % to 94% after 60 minutes compared to 63% in case of the control experiment, without affecting the morphology of the formed crystals. Meanwhile, applying electric field enhanced the precipitation of calcium carbonate, independent of the degree of supersaturation of solution. |

ملخص الرسالة

الاسم الكامل: مختار سيد محمد نور الدين حافظ رشوان

عنوان الرسالة: تقليل ترسيب كربونات الكالسيوم باستخدام طرق غير كيميائية

التخصص: الكيمياء

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يعتبر تكون الأملاح في صورة رواسب جيرية مشكلة دائمة في الطبيعة, و لكن إزالة هذه الرواسب مكلفة للغاية في شركات الكيماويات و محطات معالجة المياه. إن ترسيب هذه الأملاح على أسطح المعادن يؤدي إلى مشاكل تقنية مثل إعاقة انتقال الحرارة بالشكل المطلوب, زيادة مقدار الطاقة المستخدمة, و أعطال فنية غير متوقعة. إن منع ترسيب هذه الأملاح يكبد الاقتصاد العالمي بلايين الدولارات. قديماً كان يتم معالجة المياه بإضافة محاليل حمضية لمنع ترسيب كربونات الكالسيوم, و لكن إضافة الأحماض تتسبب في صدأ و تآكل المواسير والمعدات المستخدمة في معالجة المياه.

ولكى يتم تجنب هذه المشكلة, تم تطوير مثبطات كيميائية لتثبيط ترسيب كربونات الكالسيوم. إن استخدام تلك المثبطات أصبح شائعاً و فعال للتحكم في تكوين تلك الأملاح. تعتمد طريقة عمل تلك المثبطات على تشويه الجسيمات المتكونة مانعة ترسيب مزيد من البلورات, و بالتالى تؤدي إلى تثبيط ترسيب كربونات الكالسيوم.

رغم كفاءة استخدام تلك المثبطات إلا أنها تشكل خطراً على الصحة و البيئة في حالة انسكابها أو تراكمها لفترة زمنية طويلة. و من ثم, يعمل الباحثون في هذه الأيام على تطوير أساليب جديدة صديقة للبيئة و مقبولة اقتصادياً.

لقد قمنا في هذا البحث بدراسة تأثير الأشعة فوق البنفسجية, الموجات فوق الصوتية, و المجال الكهربى على تكوين كربونات الكالسيوم في الماء. لقد قلل استخدام الأشعة فوق البنفسجية معدل نمو كربونات الكالسيوم بنسبة 85% مقارنة ب 43% في حالة إضافة 3 جزء من المليون من Amino tris (methylenephosphonic acid), بالإضافة إلى تكوين بلورات كالسيت فقط والتي تعتبر أقل التصاق و أقل كثافة من أشكال كربونات الكالسيوم الأخرى; مما يؤدي إلى زيادة فترة عمر الغشاء المستخدم في محطات معالجة المياه.

أما بالنسبة لتطبيق الموجات فوق الصوتية فقد أدى إلى زيادة معدل تثبيط تريب كربونات الكالسيوم إلى 94% مقارنة ب 63% فى حالة عدم استخدام الموجات فوق الصوتية, بدون تغيير الشكل المورفولوجى للبلورات المترسبة. بينما أدى تطبيق المجال الكهربى إلى زيادة ترسيب كربونات الكالسيوم بدون تغيير شكل البلورات المتكونة.

CHAPTER 1

INTRODUCTION

Potable water scarcity, which occurs not only in arid regions, may be characterized as a mismatch between water supply and water demand. The Kingdom of Saudi Arabia occupies the highest rank among all the states of the world in the production of potable water from the sea. This is achieved by desalination process, which meets 70% of the Kingdom's drinking water requirement. The volume of production capacity of the desalination stations in 2006 had reached 743,640,000 gallons per day. Most of these stations employ membrane based technology; however the presence of mineral ions in water causes major concern in the operation and maintenance of membrane based desalination plants. A key constraint to further application of membrane technology in water treatment is the deposition of these mineral ions on their surface (Gary Amy 2008). Inorganic ions such as calcium, potassium, sulphate in the water not only cause the hardness of water thus making it unsuitable for drinking purpose, but also cause process challenges to the industry. They cause undesirable hard, adherent deposit that usually precipitates from solution and grows on surfaces (e.g. membrane, metal etc.) thus decreasing the efficiency of the system (Koo et al 2005). Such deposits are very hard to remove from the membrane surface.

The formation of such deposits is generally termed as chemical scale; potential for scale deposition is present whenever a flow surface is exposed to a supersaturated solution.

Excessive scale create problems like lowering of heat transfer efficiency in heat exchangers by coating the heat transfer surfaces and increased pressure drop across pipe thus resulting in increased energy consumption and unscheduled equipment shutdown (Chen et al).

It is widely reported that the presence of calcium ions in water is primarily responsible for the chemical deposits on the surface.

Traditional method to prevent such mineral deposits employs use of chemicals, but such methods are not reliable for environmental reasons. The use of commercially available cleaners runs the risk of damaging membranes thereby, limiting membrane lifetime.

Recent environmental awareness in many countries around the world encourages the societies to have less dependence on chemicals and device methods or processes, which are environment friendly. Negative influences may not only damage the environment, but can also result in financial penalties if toxicity standards are not met.

Hence there is a considerable interest to find methods that effectively prevent the formation of this adherent deposit. In order to prevent the potential problems caused by such chemical deposits, understanding the mechanism of its precipitation and deposition is of major interest.

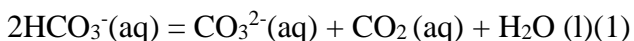
New innovative methods need to be explored to meet the objectives thereby meeting environmental challenges. The present work proposes non-chemical techniques that attempt to replace the use of chemical additives in desalination plants. Three techniques proposed are use of ultrasound, UV light, and electric field to remove calcium carbonate from water. These techniques could be applied as pre-treatment for membrane process,

reducing the membrane damage in long run. In addition, a synchronized effect of all the three techniques can be applied which has never been reported in the scientific literature.

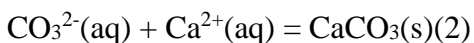
CHAPTER 2

LITERATURE REVIEW

Arid countries that lack sources of potable water and have a coastline usually revert to sea water desalination to secure their daily demands.[1]Desalination involves thermal (e.g., multi-stage flash, MSF) and membrane (e.g., reverse osmosis) processes triggering the decomposition of HCO_3^- according to the overall reaction



leading to the precipitation of CaCO_3 once its solubility limit is reached



Calcium carbonate can be found as an amorphous solid and in three different crystalline forms, calcite, aragonite, and vaterite. At high temperatures ($T > 70^\circ\text{C}$), aragonite is favored, while calcite is favored at low temperature ($T < 30^\circ\text{C}$). At any temperature, all polymorphs eventually recrystallize to the thermodynamically favored calcite. [2]

Scale formation is a serious and expensive problem in various oil, gas, and water plants. [3]

CaCO_3 precipitation starts when Ca^{2+} and CO_3^{2-} agglomerate as a cluster, forming colloidal nuclei that grow and give a stable crystal. Generally speaking, precipitation involves three main stages; nucleation, dehydration and crystalline growth.

Nucleation may be either homogeneous or heterogeneous, depending on the medium where precipitation occurs. If the nuclei are formed in the bulk solution, resulting in a non-adherent precipitate, the precipitation is considered homogenous; whereas, if the nuclei are developed on a support, leading to an adherent precipitate, the precipitation is considered heterogeneous. The deposit is called scale if the support is metallic or plastic pipe. [4]

The degree of supersaturation of solution is an important factor controlling both the onset time and type of nucleation. While weak supersaturation renders long starting nucleation time and heterogeneous precipitation, strong supersaturation leads to short onset nucleation time and homogenous precipitation. [5]

The formation of mineral scale, in particular calcareous deposits, is a persistent and expensive problem in industries ranging from oil and gas to desalination. Scaling on metallic or insulating walls in contact with water supersaturated with respect to calcium carbonate may create technical problems including impedance of heat transfer, increase of energy consumption and unscheduled equipment shutdown. [6]

The experimental induction period of precipitation is defined as the time which elapses between the creation of supersaturation and the first observable change in some physical property of the precipitating system, e.g. the appearance of crystals or turbidity, change of solution conductivity, change in solution composition, etc. [7]

The driving force for scale formation is supersaturation ratio (S) of the scale formation solution which affects the induction time, growth, morphology of crystals and rate of scale formation. [8]

The supersaturation index is $SI = \text{Log } S$

$$S = (a_{\text{Ca}^{2+}})(a_{\text{CO}_3^{2-}}) / K_{\text{sp}} \quad (3)$$

Where a_i is the activity of a given ion and K_{sp} is the solubility product of the scale forming mineral

There are 3 possibilities in terms of scale formation

- (1) $S < 1$: the solution is undersaturated and scale formation is not thermodynamically feasible
- (2) $S = 1$: the solution is saturated. The scale formation and dissolution rate in the solution is the same and no scale is formed in the solution
- (3) $S > 1$: the solution is supersaturated and scale formation is thermodynamically possible

[9]

High supersaturation scale formation solutions tend to promote precipitation in the bulk solution and scale formed on the metal surface. [10]

Calcium carbonate can be found as an amorphous solid and in three different crystalline forms, calcite, aragonite, and vaterite. Aragonite is favored at high temperatures, while calcite is favored at low temperatures. At any temperature, all polymorphs eventually recrystallize to the thermodynamically favored calcite.

Mineral scale formation is an expensive problem in oil, gas, and desalination plants. Scale formation on membrane surfaces in contact with water supersaturated with calcium carbonate creates technical problems including heat transfer hindrance, more energy consumption, and equipment shutdown [11-13]. Nucleation is homogeneous when the nuclei develop only in the liquid phase and are not influenced by impurities in the surrounding system. On the other hand, classical nucleation theory predicts that heterogeneous nucleation on surfaces is energetically more favorable than homogeneous nucleation due to lowering of the surface energy of the nucleus and the substrate upon interfacial contact [14].

To control scaling in desalination plants, several methods have been adopted. From the early stages of reverse osmosis desalination, acidification of water was one of the approaches considered to affect the decomposition of HCO_3^- ,



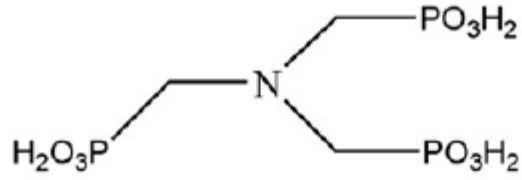
However, acid treatment results in the corrosion of metallic surfaces of the of multi stage flash units. [15]

Afterwards, water was treated with ion exchange resins replacing calcium ions by sodium ions, or adding complex-forming agents such as EDTA, sequestering the calcium ion from solution. [16]

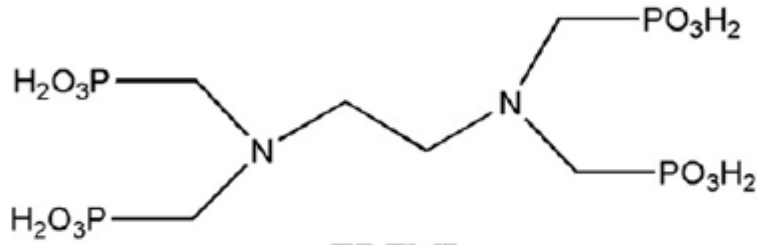
2.1. Antiscalants

Antiscalants have been developed to reduce the problem of scale formation, including polyacrylic acid (PAA), polyacrylamide, hydrolyzed polymaleic anhydride (HPMA), 1-hydroxyethane-1,1-diphosphonic acid (HEDP) and polyphosphates.[17-23].

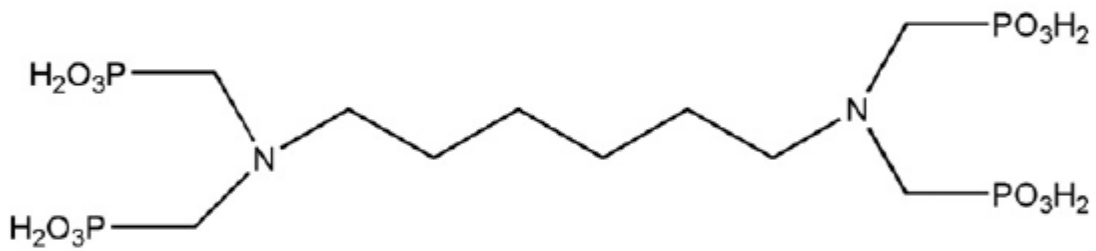
The mechanism of some antiscalants involve chelating the ions forming scales, keeping it in solution. [24]. On the other hand, some mitigate the scale formation by interaction with the formed nuclei, disrupting the crystal growth process, keep the crystal particles dispersed in solution. [25]. Meanwhile, some antiscalants can retard both nucleation and crystal growth processes by distorting the crystal lattice of the scaling material, weakening its cohesive bonds and its adherence to the flow surface. The adsorbed layer may also exert a dispersive effect by an electric charge which stabilizes colloidal suspensions and repels particles from the deposition surface. [26]



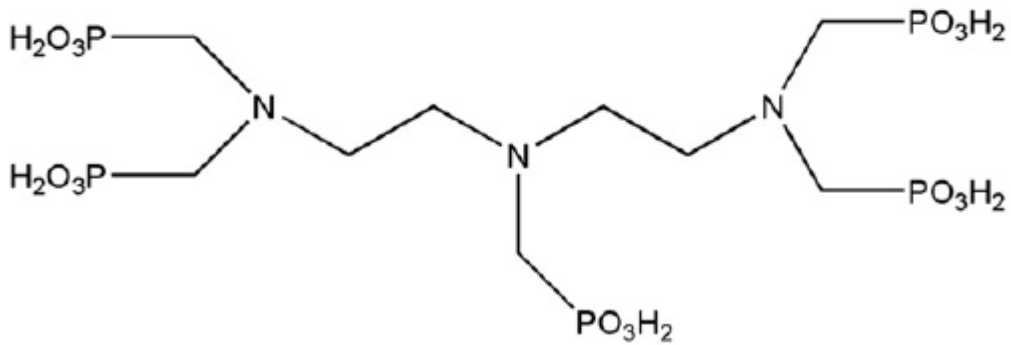
ATMP



EDTMP



HDTMP



DTPMP

Fig.2.1. Chemical structure of commonly used antiscalants [27]

Antiscalants commonly used in the industry include phosphates and polyphosphates, phosphate esters, organic phosphonates, polyacrylates, and various other polymers and copolymers of phosphonates, carboxylates, and sulfonates. The choice of inhibitors depends on the particular solution composition, compatibility, stability and temperature. The appropriate inhibitor to use and its effective concentration still remain empirical often requiring extensive testing for each individual case. [28]

Using antiscalants poses many drawbacks because they are environmental unfriendly due to their chemical effect on the treated water, and the surrounding environment over a long period of time; beside the high cost of chemicals.

Thus, there is an increasing need for a new approach which is safe and economical from both environmental and cost points of view in cleaning desalination membranes. Physical water treatment is a non-chemical method to mitigate mineral fouling with the use of electromagnetic fields, ultrasounds, or UV light.

2.2. Physical water treatment

2.2.1. UV light

The crystal growth rate of sparingly soluble salts, as calcium carbonate, growing by a parabolic or an exponential rate law is explained by assuming that the rate determining step consists of two simultaneous phenomena: (a) the dehydration of the growth units, and (b) the

surface diffusion of the dehydrated growth unit into the lattice from the adsorption site. Exposure of UV light may alter the physio-chemical properties of calcium carbonate crystals. The attraction of the growth unit to a water molecule depends on the radius of the growth unit and the electronic structure. The UV radiation possibly changes the electronic structure of the growth unit, resulting in excited growth unit differences in dehydration energy from the ground state, retarding the dehydration of the growth units. On the other hand, carboxylic acids exhibit a decrease in acidity in the first excited singlet state relative to the ground state, affecting the diffusion step of the growth units into the lattice via changes of the surface properties of calcium carbonate at atomic level. The potential determining ions of calcite are Ca^{2+} and CO_3^{2-} ions. It is apparent that at high P^{H} values, CO_3^{2-} and HCO_3^- species are predominant, yielding a more negative charge, while at low P^{H} , Ca^{2+} and CaHCO_3^+ species are in excess, yielding a more positive charge. Changes in acidity of the carboxylic groups on the calcite surface due to UV radiation possibly result in changes of the calcite surface charge which in turn affects the diffusion of the dehydrated growth unit into the lattice. [29]

2.2.2. Ultrasound

Ultrasound is an acoustic signal of frequencies between 20 kHz to 10 MHz. Ultrasonic irradiation imposes an oscillating pressure on fluid that leads to two types of effects in solution; the physical effect (fluid particle displacement, acceleration, physical mixing) and chemical effect (radiation pressure, cavitation, interfacial instabilities, acoustic streaming) (Suslick, 1989 and Suslick, 1994).

The chemical effect of acoustic cavitation (the formation, growth, and implosive collapse of bubbles in a liquid) is important since it appears to be particularly effective as a means of inducing nucleation (Graham Rucroft et al).

Cavitation occurs when a new surface is created in the body of the liquid in the presence of sound (Neppiras E A). As a result of ultrasound application the cavitation bubbles are produced during the negative period of the sound, these bubbles grow rapidly and create a vacuum, which can cause gases dissolved in the liquid to start to diffuse into them. As the sound wave passes, the negative pressure is reduced and the bubble starts to shrink under surface tension and implodes. The growing cavity, can eventually reach a critical size where it will most efficiently absorb energy from the ultrasound; this depends on the frequency and intensity of the ultrasonic wave (Suslick, 1989; Earnshaw). At lower frequencies, the bubble grows bigger by a slower process called rectified diffusion and when they collapse, greater energies are produced which establishes an unusual environment for chemical reaction; this increases the precipitation rate and makes more clusters cross the size barrier and then become crystal nuclei, which finally grow. Under this effect, the induction period of precipitation is shortened (Aijun et al., 2006; Gua et al., 2006).

The short burst of ultrasound at intensity would induce nucleation of crystallization at low supersaturation levels than those required where no ultrasound application is applied (McCausland & Cains). The solubility of the solute in the solvent is sharply reduced and the solution immediately reaches its maximum supersaturation so that primary nucleation and crystal growth is implanted rapidly (Li Hong et al.). Thompson & Doraiswamy concluded that ultrasound increased the driving force for mass transfer coefficient and the interfacial

area. Prior removal of minerals from the mineral rich process-water is one of the ways to prevent scaling at undesirable locations. One of the ways for prior removal of minerals is using an equipment in which precipitation rate of scale is accelerated and the resulting precipitant can be easily removed. Ultrasound is one of the techniques that can be used for this purpose. (Nishida, 2004) carried out experiments using ultrasonic irradiation to observe the precipitation of calcium carbonate and it was concluded that the precipitation rate was proportional to the ultrasonic intensity and diameter of horn tip. He also concluded that the physical effect of mixing, which largely depends on the horn immersion depth, intensity and diameter of horn tip, affects the precipitation rate of calcium carbonate; whereas the effects of cavitation did not result in any improvements. Hence, precipitation of calcium carbonate was mostly affected by the physical effect of ultrasonic irradiation, especially macrostreaming rather than the chemical effects or microstreaming. [30] The ultrasonic irradiation affects neither the morphology nor the size of the calcium carbonate crystals formed. [31]

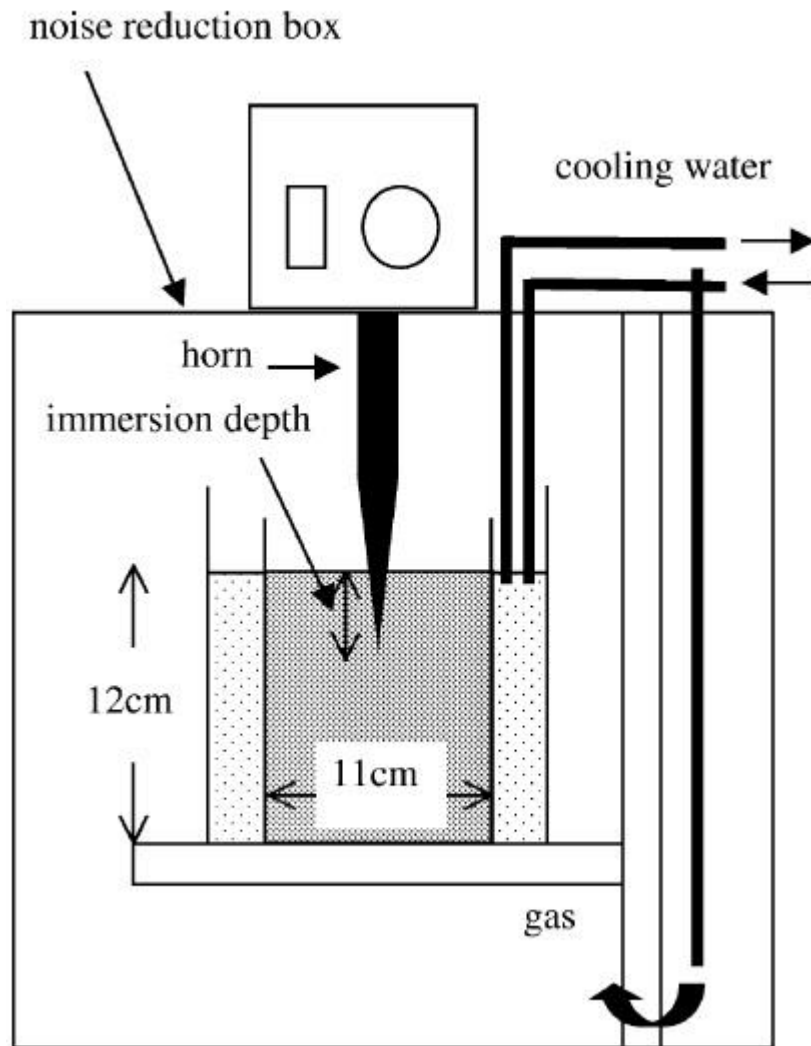


Fig.2.2. Schematic illustration of the ultrasound setup [30]

2.2.3. Electric field

Electric field is one of the nonchemical techniques used for prior removal of minerals from the mineral rich process-water, preventing scaling at undesirable locations.(Yong Yangetal.,

2011), used pulsed spark discharge to assist the precipitation of dissolved calcium ions in cooling towers, decreasing the water hardness by 20-26%. He reported that the reduction of water hardness is due in part to electrolysis. Furthermore, the chemistry behind calcium carbonate precipitation is as follows:

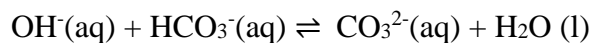
The combination and crystallization rates of calcium and carbonate ions are controlled by three reactions:-

- (a) The dissociation of bicarbonate ions into the hydroxyl ions OH^- and carbon dioxide



(5)

- (b) The hydroxyl ions further react with the existing bicarbonate ions, producing carbonate ions and water



(6)

- (c) The reaction between calcium and carbonate ions, resulting in the precipitation and crystallization of calcium carbonate particles



The dissociation of bicarbonate ions needs a certain amount of energy that can be provided by the applied pulsed spark discharge. The effect of electric field could also be explained by the disruption of the electric double layer of hydrated calcium and bicarbonate ions that do not react at room temperature as both ions are surrounded by water molecules forming electric double layers. According to Dhanasekaran and Ramasamy, the free energy for nucleation decreases as the strength of electric field increases at certain angles, leading to a higher nucleation rate. [32]

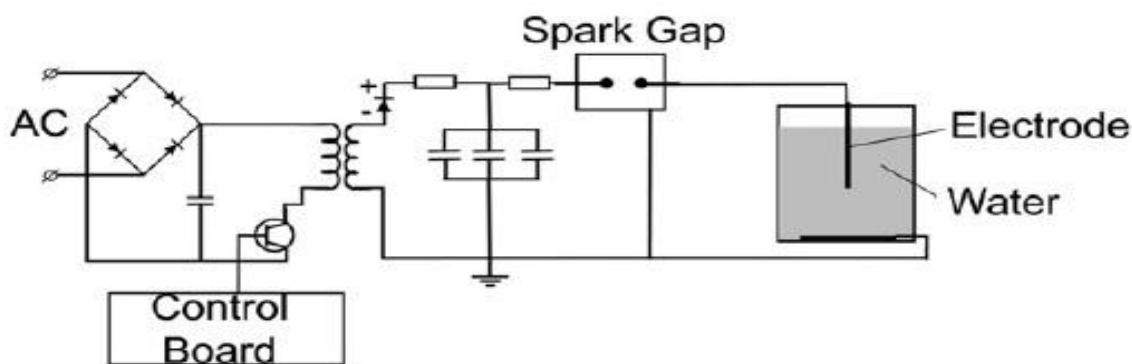


Fig.2.3. Schematic diagram of a pulsed power system [31]

(Leonard et al., 2011) studied the effect of the voltage and frequency of high-frequency electric field generated between two graphite flat-plate electrodes on the precipitation of

calcium carbonate, producing less dense, less adherent, and easily-removed calcite crystal structures, mitigating fouling of copper tube surfaces.[33]

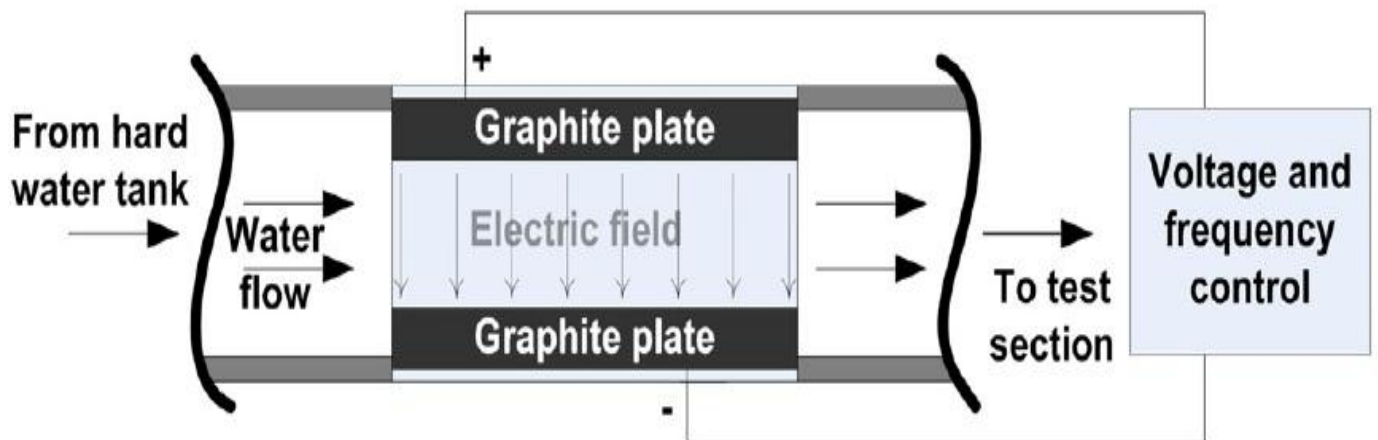


Fig.2.3. Schematic layout of a high frequency electric field device using graphite flat-plate electrodes [32]

In this work, we are using UV light, ultrasound, and electric field as alternative green physical methods to mitigate the precipitation of calcium carbonate in water since antiscalants are environmental unfriendly due to their chemical effect on the treated water, and the surrounding environment over a long period of time; beside the high cost of

chemicals. UV light will be used to inhibit the calcium carbonate scale formation, while ultrasound and electric field will enhance the scale formation leading to prior removal of calcium carbonate from water, preventing scaling at undesirable locations like desalination membranes.

CHAPTER 3

Materials and methods

3.1. Materials

Calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), sodium chloride (NaCl), sodium bicarbonate (NaHCO_3), and ethylene diamine tetra acetic acid (EDTA) of analytical grade were supplied by Sigma Aldrich, Germany. Hydrex 4102 RO antiscalant, and polypropylene and polysulfone membranes was supplied by VEOLIA WATER STI, Khobar, Saudi Arabia. Hydrex 4102 chemical constituents are amino tris (methylenephosphonic acid), and phosphonic acid, with pH of 11.00-12.00, and specific gravity of 1.35 – 1.45.

3.2. Methods

Synthetic sea water solution was prepared by mixing 86.0 mM sodium chloride, 4.50 mM calcium chloride, and 9.50 mM sodium bicarbonate solutions prepared from standardized stock solutions, prepared using deionized water using a Millipore Q-Plus 185 system. The pH of the solutions was measured by a glass / saturated calomel electrode (Metrohm), calibrated before and after each experiment with 4, 7, and 10 standard buffer solutions. The pH of the working solution was adjusted by the addition of hydrochloric acid and ammonia buffer. Calcium carbonate precipitation was initiated when adding Calcium chloride and Sodium bicarbonate.

UV light was generated by a UV lamp source having a 15 mm diameter, $106\mu\text{W}/\text{cm}^2$ intensity, 54V operating voltage, and 12W output power, emitting a broad band of UV light, with eight filters for specific wavelength selection, producing an average intensity of $2\text{mW}/\text{cm}^2$ at a distance of 2 cm from the working solution. Fig. 3.1 shows the experimental setup of UV treatment experiment.

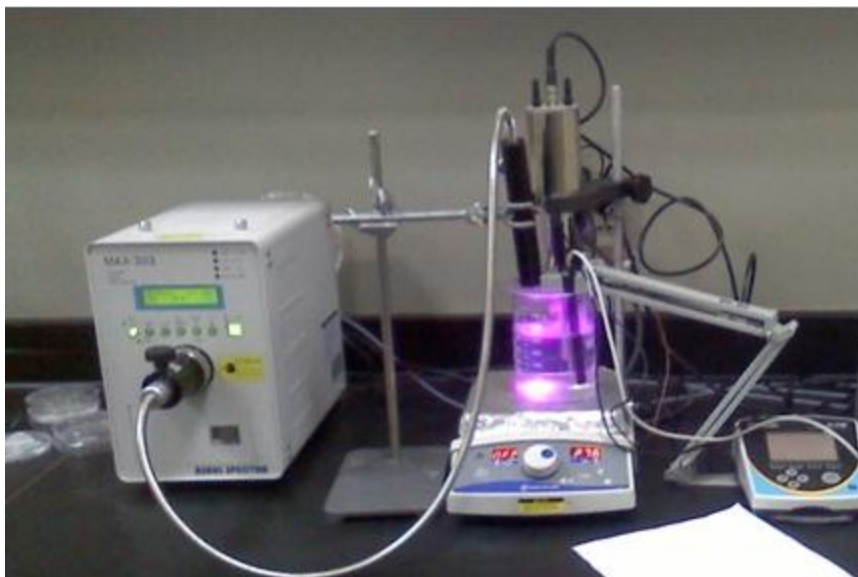


Fig.3.1. Experimental setup of UV treatment experiment

Ultrasonic radiation was generated by an ultrasonic homogenizer working at a frequency of 20 KHz and power 750 W, with a horn immersed in the center of the reaction solution. Reaction solution of 0.500 dm^3 was put inside a vessel of 13 cm diameter and 14 cm height to achieve a solution surface height of 10 cm. Fig. 3.2 shows the experimental setup of sonication experiment.



Fig.3.2. Experimental setup of ultrasonication experiment

For the electric field experiments; the electric field was applied at 3 different magnitudes 1, 5, and 10 V and 3 different frequencies 0, 10, and 20 MHz on 2 parallel graphite electrodes 5 cm apart inside the working solution.

For determination of the calcium ion concentration, 10 ml of the working solution were taken every 15 min, filtered by 0.025 μm membrane filter, and titrated versus EDTA standardized solution.

The weight measurements of the calcium carbonate scale deposits were carried out by weighing the polypropylene and polysulfone membranes using a Mettler weighing

balance with 4 decimal places, keeping them inside the working solutions for 30, and 60 minutes, drying in an oven for 1 h at 110 °c, and then weighing the membranes together with the deposits.

At the end of the experiments, the solutions were filtered, and the precipitates were collected and examined by XRD for the determination of the crystal types of the deposited CaCO₃ scales. Sample sizes of 10×10 mm were prepared by manual cutting using a saw blade for each fouled tube and were analyzed at diffraction angles of 10 to 110°.

CHAPTER 4

RESULTS AND DISCUSSION

The effect of chemical treatment on calcium carbonate scale formation in water has been studied and compared with physical techniques, including UV light, ultrasound, and electric field.

Calcium carbonate scale inhibition has been monitored by measuring the calcium concentration in solution every 15 minutes for 1 hour by complexometric titration versus standardized EDTA solution.

$$\text{CCI \%} = \frac{[\text{Ca}^{2+}]_{\text{sample}}}{[\text{Ca}^{2+}]_{\text{initial}}} \times 100\% \quad (4)$$

Where $[\text{Ca}^{2+}]_{\text{initial}}$ is the calcium ion concentration at $t=0$, and $[\text{Ca}^{2+}]_{\text{sample}}$ is the calcium ion concentration at time (t).

4.1. Chemical treatment

The effect of antiscalants on calcium carbonate scale formation has been investigated by using ATMP [amino tris (methylenephosphonic acid)] as a scale inhibitor. ATMP, commercially named as Hydrex 4102, is one of the commonly used antiscalants used for calcium carbonate scale inhibition in water since it has an excellent chelating ability with calcium ions, low threshold inhibitory dosage, and powerful lattice distortion process.

In chemical treatment experiments, different dosages of ATMP have been used ranging from 1 to 10 ppm to test for the threshold concentration suitable for calcium carbonate scale inhibition.

Starting with 1 ppm, CCI has increased by about 1% compared to the untreated system as shown in Fig.4.1. When the dosage to 2 and 3 ppm, the scale inhibition has increased by about 4%. Meanwhile, adding 5 ppm has increased CCI to about 80% compared to 65% obtained for the control experiment. The 10 ppm dosage achieved the best performance in terms of scale inhibition, increasing CCI% to about 82% after 60 minutes. This finding indicates that 10 ppm is the threshold inhibitory dosage of ATMP as calcium a scale inhibitor for calcium carbonate.

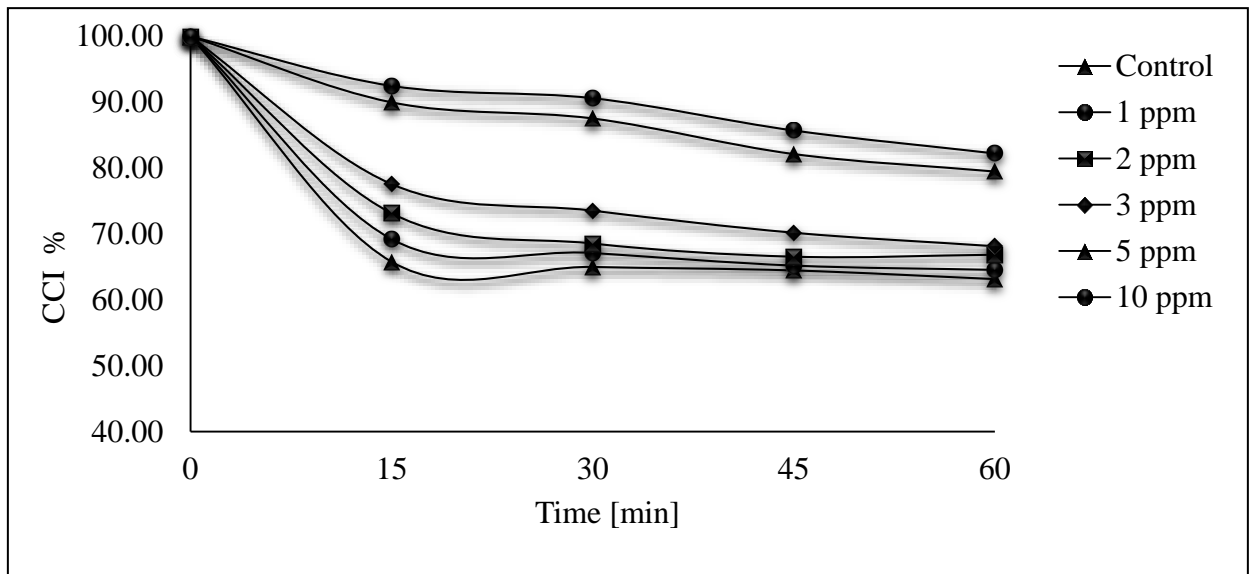


Fig. 4.1. Effect of ATMP concentration on calcium carbonate scale formation

4.2. UV light

Calcium carbonate scale mitigation in water using UV light was only reported by [29]. Calcium carbonate is a sparingly soluble salt, growing by a parabolic rate law. Hence, the rate limiting step of its crystal growth involves the dehydration of the growth units, and the surface diffusion of these dehydrated growth unit into the lattice from the adsorption site. [29]

4.2.1. Effect of pH

Fig.4.2 depicts the effect of pH on calcium carbonate scale inhibition using UV light of 265 nm radiation during 60 minutes. At pH 7.00, the scale inhibition was almost steady reaching 97.15% after 60 minutes, while decreasing to 91.80 % at pH 8.00. On the other hand, increasing pH to 9.00 had a drastic effect on the scale inhibition behavior, decreasing slowly in the first 15 minutes and then sharply in the next 15 minutes, while

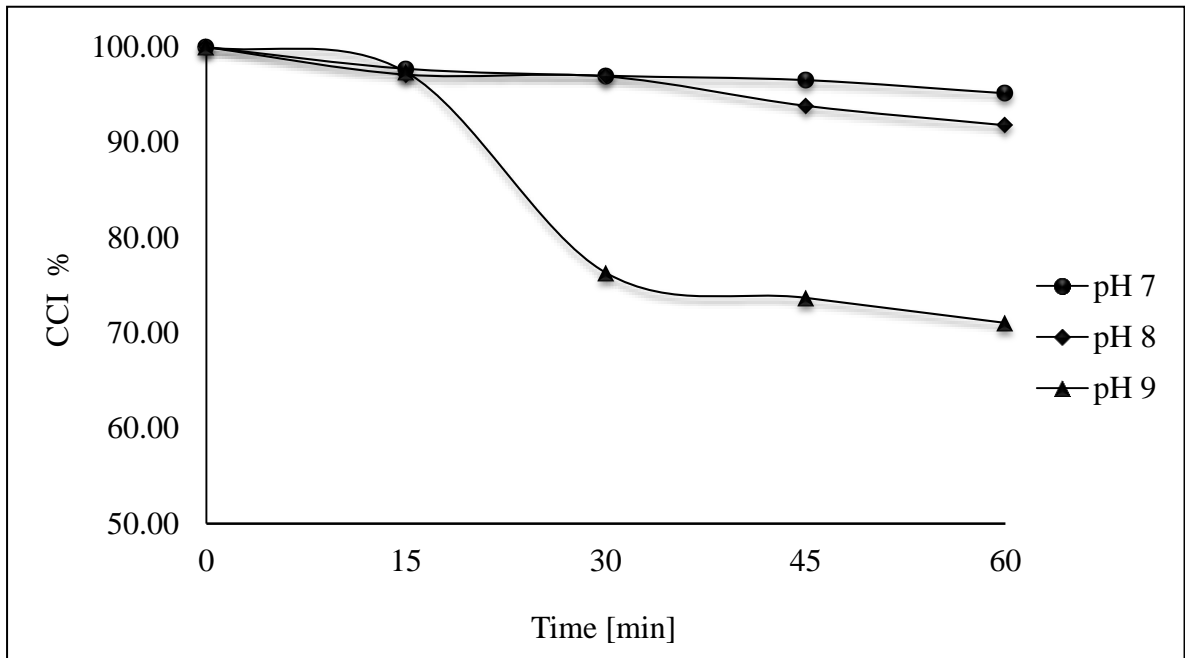


Fig.4.2. Effect of pH on calcium carbonate scale inhibition

giving an asymptotic trend during the last 30 minutes, reaching 71.06% at 60 minutes.

This dramatic effect of pH can be interpreted based on the pH dependence of carbonate concentration in solution. Bicarbonate dissociates into carbonate according to the equation:



According to Henderson-Hasselbalch equation, as pH increases, the carbonate concentration increases as indicated in Table 4.1.

Table 4.1. Effect of pH on carbonate concentration in 9.50 mM bicarbonate solution

pH	[CO ₃ ²⁻]/ mM
7	4.44 x 10 ⁻⁹
8	4.44 x 10 ⁻⁸
9	4.44 x 10 ⁻⁷

$$\text{pH} = \text{p}K_a + \text{Log} [\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (9)$$

Increasing pH by 2 units increases the carbonate concentration by 2 orders of magnitude, increasing the chance of calcium and carbonate ions recombination, hence increasing the rate of calcium carbonate precipitation. This finding can be supported by the fact that in a carbonate system, the dissolved carbon is distributed among three species H₂CO₃, HCO₃⁻ and CO₃²⁻ as a function of pH. This distribution of carbonate species can be derived from the

Henderson-Hasselbalch relationship knowing pH and pK's. As shown in Fig.4.3.at low pH, H₂CO₃ is the dominant species. Starting from pH 5, HCO₃⁻ will appear until being dominant from pH 6-10. When increasing pH to 8, CO₃²⁻ will appear in the system, being the prevalent species at 9 and above.

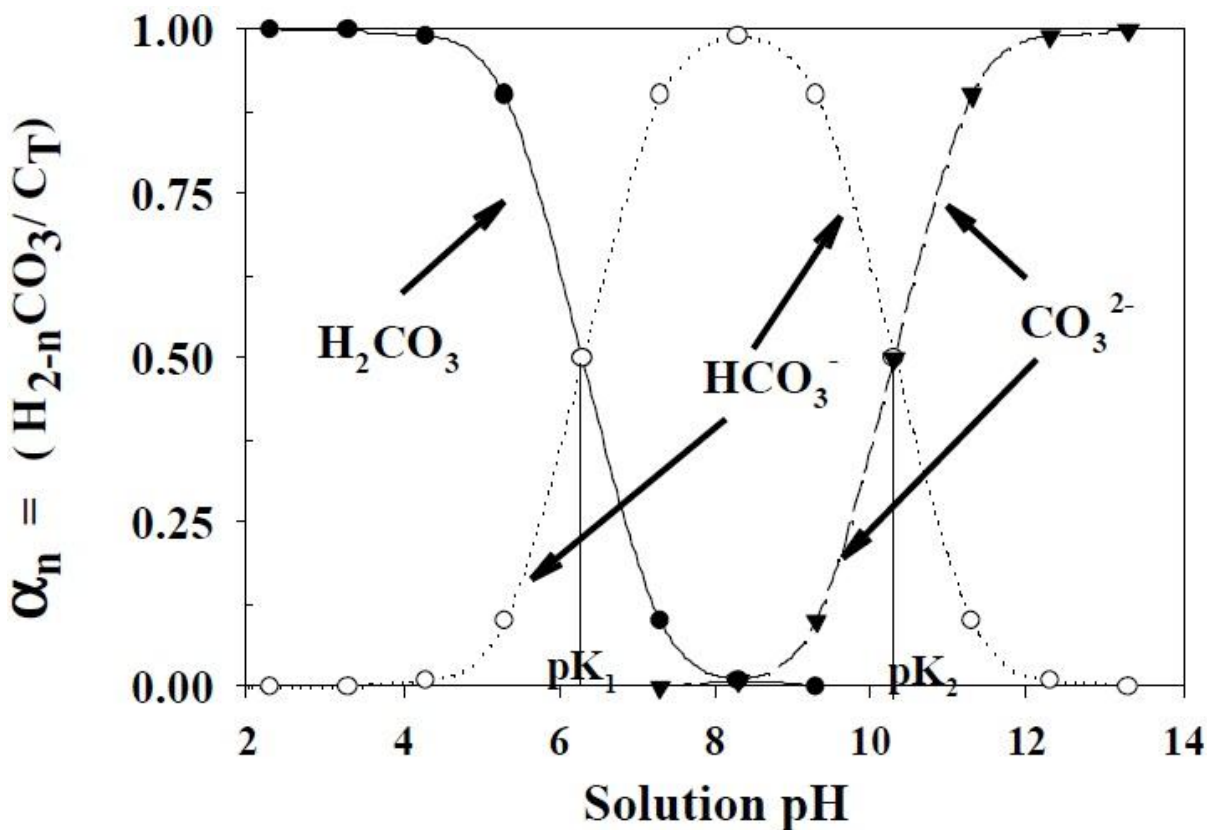


Fig4.3. Distribution of carbonate species as a fraction of total dissolved carbonate in relation to solution pH

4.2.2. Effect of radiation energy

The effect of radiation energy was studied in UV and visible regions. For the visible region, the solution was irradiated with 385 nm radiation, providing scale inhibition of

80.90% after 120 minutes, compared to 95.66% when irradiating with 265 nm UV radiation, as shown in Fig. 3.4.

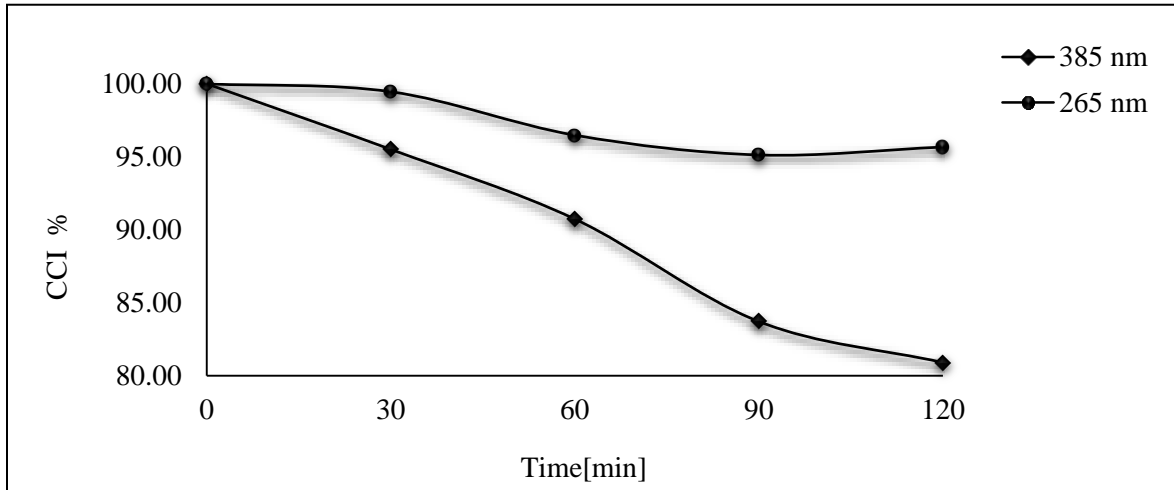


Fig.4.4. Effect of radiation energy on calcium carbonate scale inhibition

The effect of UV radiation can be explained in terms of the calcium ion acid base character. Since calcium ion is a weak acid, and when excited becomes much weaker, irradiating the calcium solution with 385 nm visible radiation, excites some of the energetic calcium ions becoming weakly acidic, hence not able to recombine with the carbonate ion present in solution, and eventually retarding calcium carbonate precipitation. When shifting from visible to UV region, the radiation energy increases, exciting more calcium ions, resulting in much more efficient scale inhibition.

4.2.3. Effect of ATMP concentration

The effect of the addition of ATMP during UV irradiation of the working solution has been investigated by the addition of the antiscalant at different dosages from 1 to 10 ppm. As depicted in Fig. 4.5., the addition of 1 and 2 ppm increased the precipitation of calcium carbonate relative to the control case because UV radiation has dissociated the antiscalant into fragments unable to inhibit the scale formation. When increasing the dosage to 3 ppm, the scale inhibition has been enhanced because the antiscalant molecules have blocked some of the active sites that are available for crystal growth. Meanwhile, increasing the antiscalant concentration to 5 ppm and 10 ppm has raised the scale inhibition to 96% compared to 36% for the untreated case.

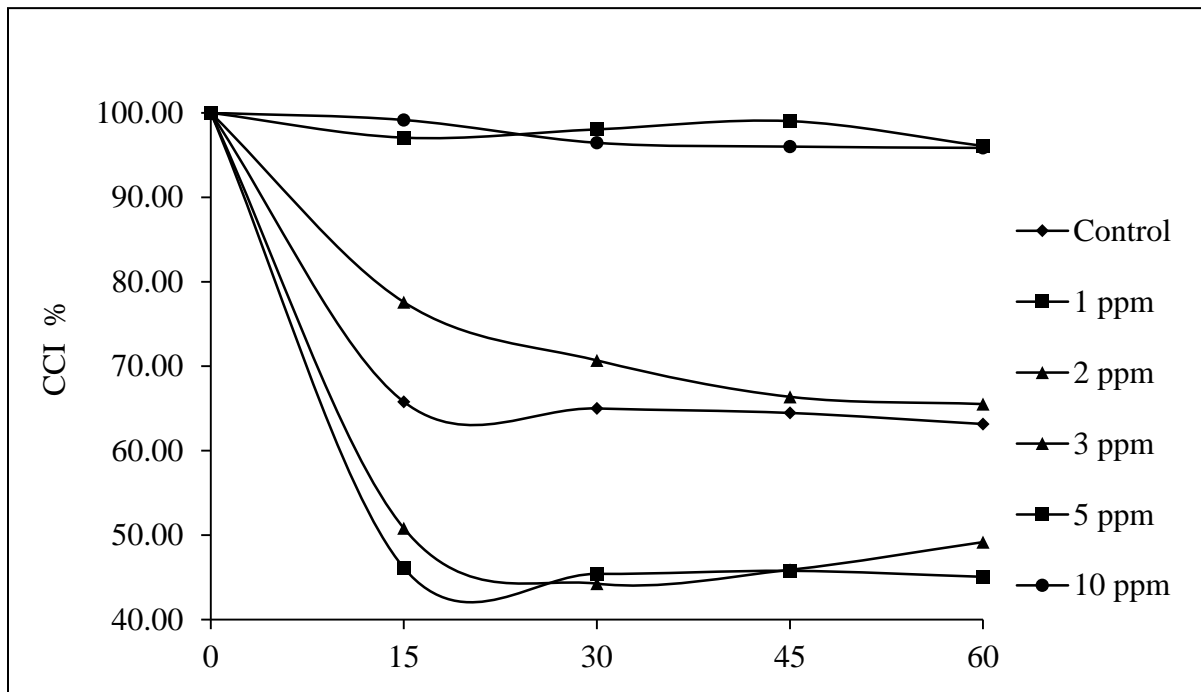


Fig.4.5. Effect of ATMP concentration on calcium carbonate scale inhibition during UV irradiation

4.2.2. Water chemistry

1) pH

Fig.4.6 illustrates the variation of pH in case of control and UV treated water. The pH of untreated sample decreased from 9.00 to 8.9, while that of the UV treated sample decreased from 9.00 to 8.80, because of the release of the protons resulting from calcium carbonate precipitation according to:

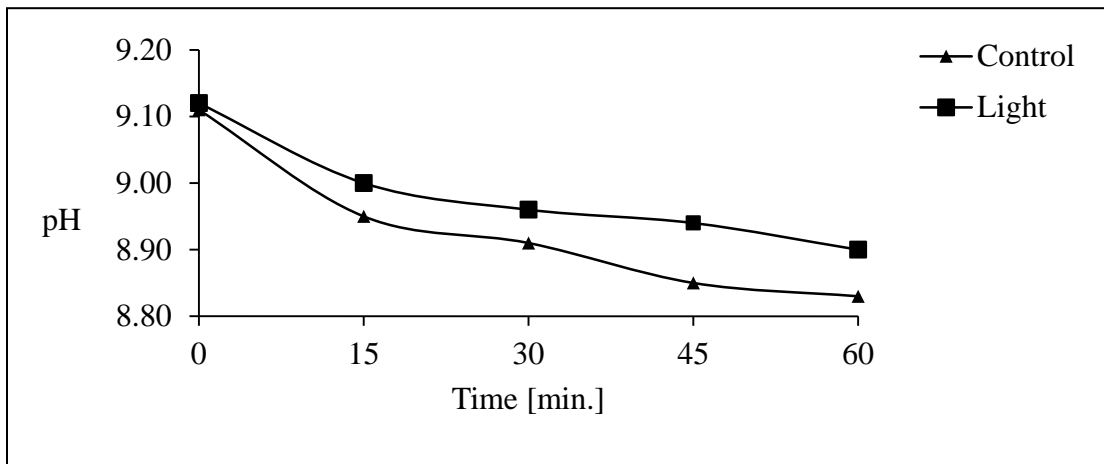
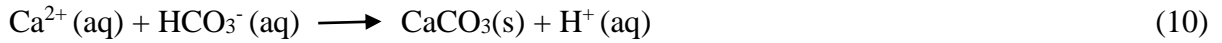


Fig.4.6.pH variation with and without UV treatment

II) Conductivity

The electrical conductivity of solution is a measure of the extent of precipitation because as precipitation occurs, more ions will be driven off from the solution, lowering the electrical conductivity. Fig. 4.7. shows that the conductivity drop in case of untreated water is higher compared to that in case of the UV irradiated water since calcium carbonate has precipitated more in case of the untreated sample leading to more calcium and bicarbonate ions consumption from solution, lowering the electrical conductivity with time.

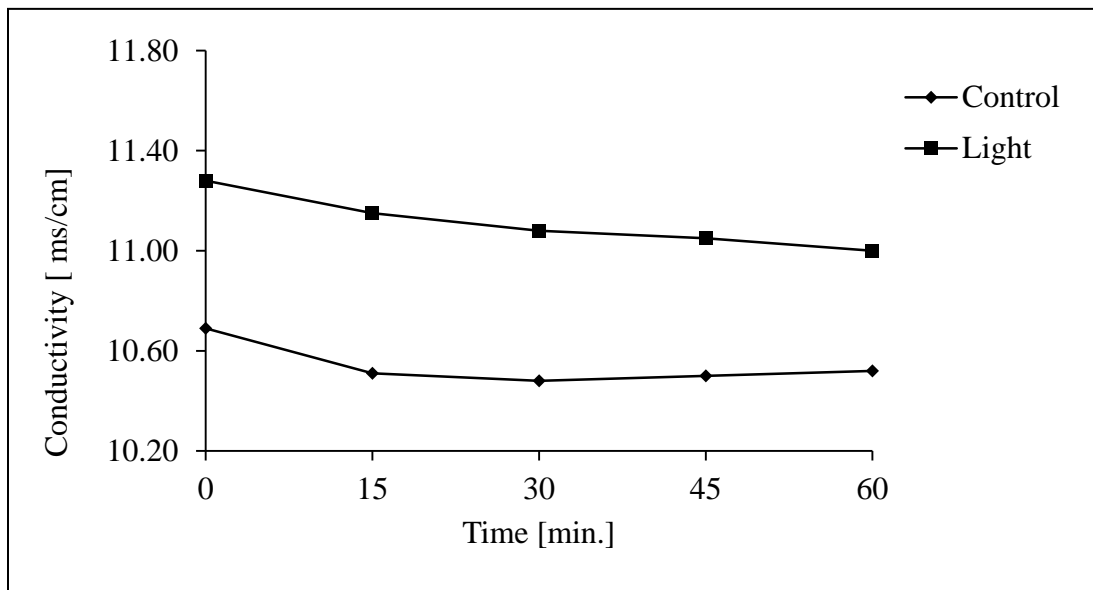


Fig.4.7. Comparison of conductivity variation with and without sonication

4.2.3. Calcium carbonate crystal growth rate

Calcium carbonate scale formation involves supersaturation, nucleation, crystal growth, and precipitation. Thus, affecting any of these steps can retard the crystal growth rate.

Table 2 shows the rate of crystal growth of calcium carbonate for the untreated,

chemically treated, and irradiated water samples. The rate of crystal growth decreased by about 43% when adding 3 ppm of ATMP, which was assumed to block some of the

Table 4.2. Rate of calcium carbonate crystal growth for UV treated and untreated water

Water sample	<i>f</i>(<i>s</i>)	R ($\times 10^{-8} \text{ molm}^{-2}\text{s}^{-1}$)
Untreated	1.05	7.36
Hydrex 4102	0.92	4.22
385 nm	0.92	1.87
265 nm	0.68	1.12

active sites of the calcium carbonate nuclei, decreasing the number of calcium carbonate crystals precipitated. The effect of UV radiation can be explained in terms of the calcium ion acid-base character. Since calcium ion is a weak acid, and when excited becomes basic; irradiating the calcium solution with UV radiation, excites some of the energetic calcium ions becoming weakly acidic, hence not able to recombine with the carbonate ion present in solution, and eventually retarding calcium carbonate crystal growth. The crystal growth rate decreased by about 75% when water was irradiated with 385 nm. When shifting from visible to UV region, 265 nm, the radiation energy increases, exciting more calcium ions, retarding

the crystal growth by about 85%. Thus, 265 nm UV radiation was used for further studies. Hence, UV light treatment is much more efficient in calcium carbonate scale inhibition compared to commercial antiscalants. Application of UV light has more advantages than chemical treatment. UV radiation is commonly used in water treatment to get rid of pathogens without have any harmful effect when compared to chemical antiscalants.

The rate of crystal growth depends on the relative supersaturation, and the number of available surface active sites according to the equation:

$$R = k_g \cdot f(s) \cdot \sigma^n \quad (11)$$

Where k_g is the crystal growth rate constant, $f(s)$ is a function of the number of available active sites for crystal growth, σ is the relative supersaturation, and n is the order of crystal growth respectively.

4.2.4. Characterization of scale deposits

I) Membrane scale deposit measurements

Fig.4.8. shows the mass of calcium carbonate deposited on polypropylene and polysulfone membranes kept inside the working solutions for 30, and 60 minutes. It is very clear that the amount of scale deposited in case of UV-treated sample is insignificant compared to that of the untreated one. This observation is extremely valuable regarding the life time of the desalination membranes that is affected by the amount of scale deposit. Thus, using UV light for scale inhibition increases the life time of the membrane due to the reduced membrane fouling.

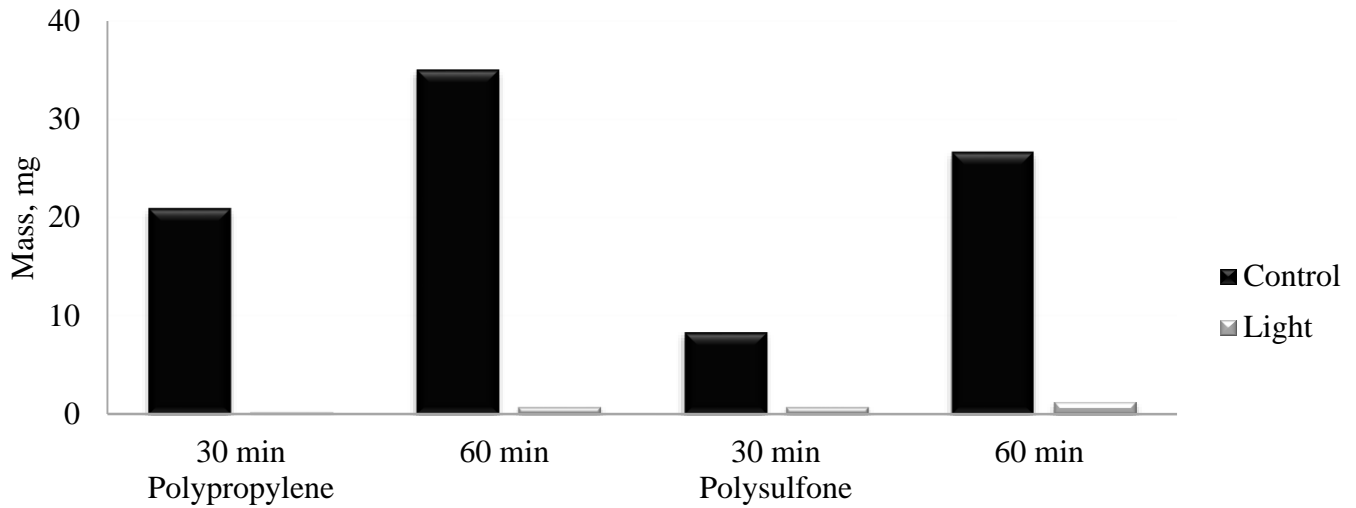


Fig. 4.8. Weight measurements of calcium carbonate deposits with and without UV light treatment

II) XRD analysis

Fig.4.9. shows XRD images of the deposits obtained from untreated, and UV- Light treated water. Calcium carbonate deposited in case of untreated sample contains calcite and vaterite, only calcite was formed in case of the UV light treated, that is less dense, less adherent, and easily-removed when deposited. The formation of calcite scale in the treated case may be due to the formation of CaCO_3 in the bulk water due to the supersaturated condition, precipitating in bulk water at lower temperatures than those directly precipitated on the surface, hence resulting in the formation of calcite scales rather than aragonite. [10]

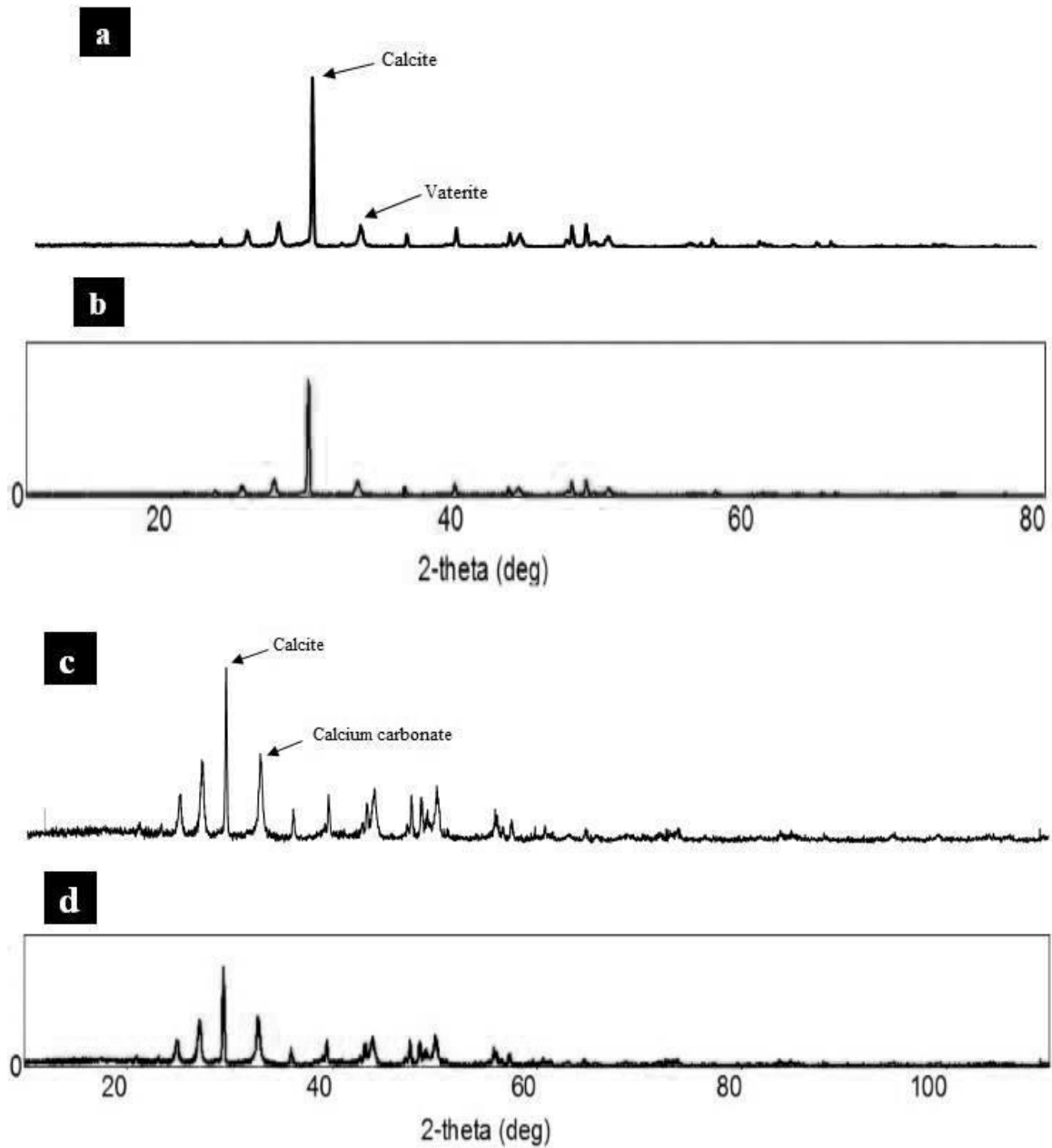
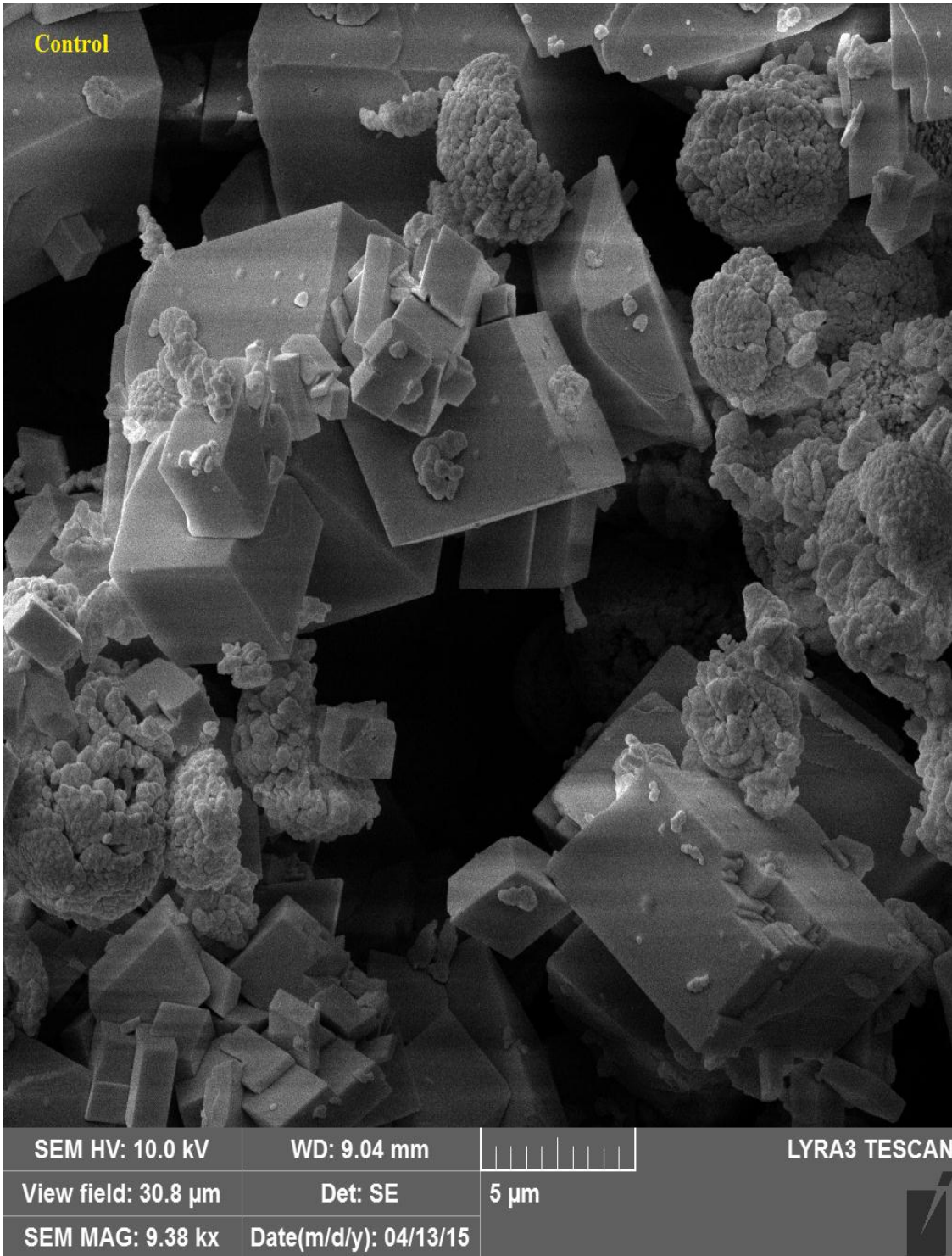


Fig. 4.9. XRD spectra for: (a) Untreated case (b) standard peaks of calcite and vaterite; (c) UV treated case; (d) standard peaks of calcite and calcium carbonate

III) SEM analysis

Fig.4.10. shows SEM images of the deposits obtained from untreated, and UV light treated water. The SEM images also show the deposition of calcite crystals in case of the

UV light treated sample, while the calcium carbonate deposited in case of untreated sample consists of calcium carbonate, and vaterite.



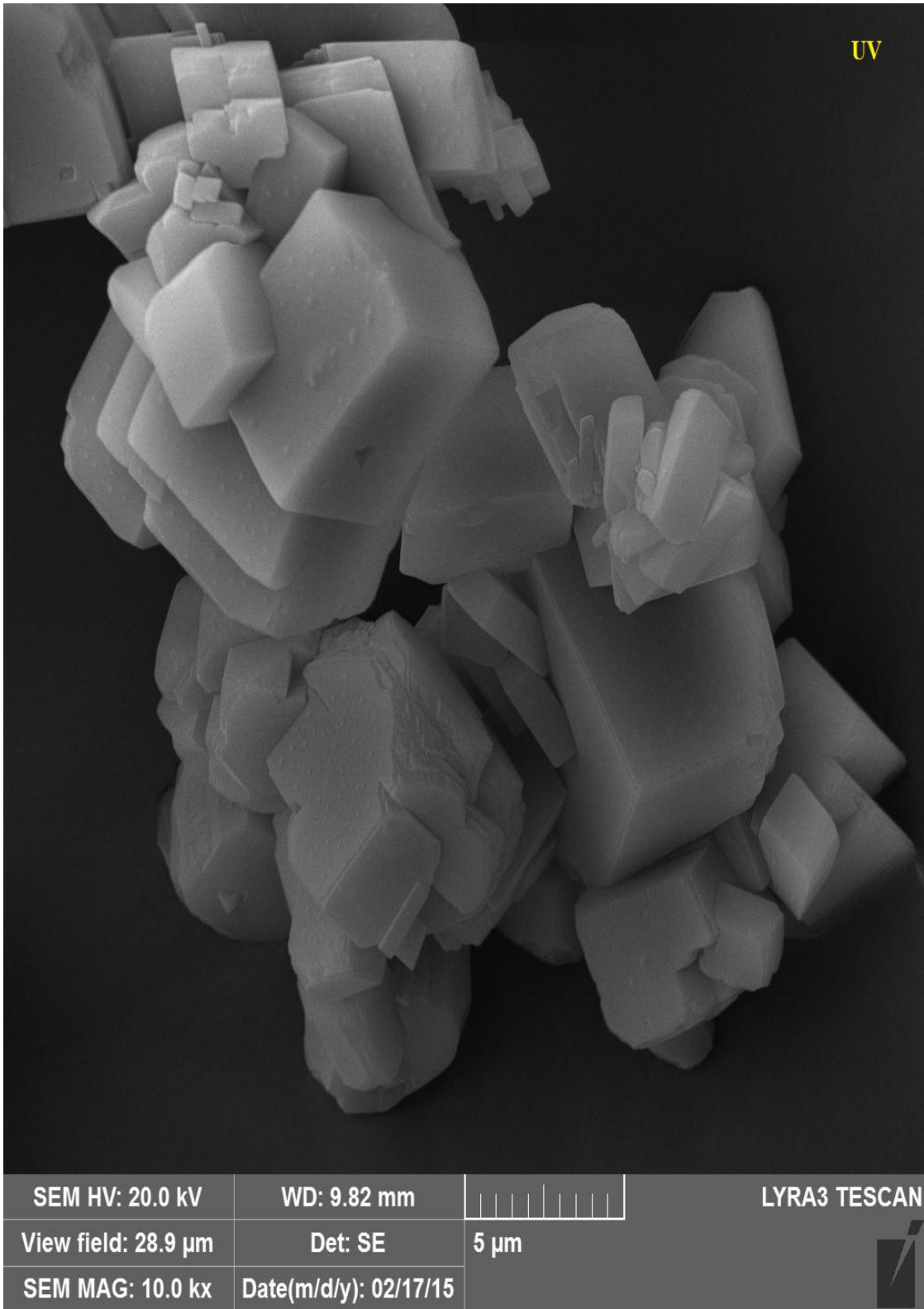


Fig.4.10.SEM images for deposits of untreated water and UV treated water

4.3. Ultrasound

4.3.1. Effect of pH

Fig.4.11 depicts the effect of pH on calcium concentration during the application of ultrasonic radiation for 60 minutes. Calcium concentration in solution decreased steeply at pH 9.00 from 4.50 to 4.19 mM, compared to 4.24 at pH 8.00, and 4.39 at pH 7.00.

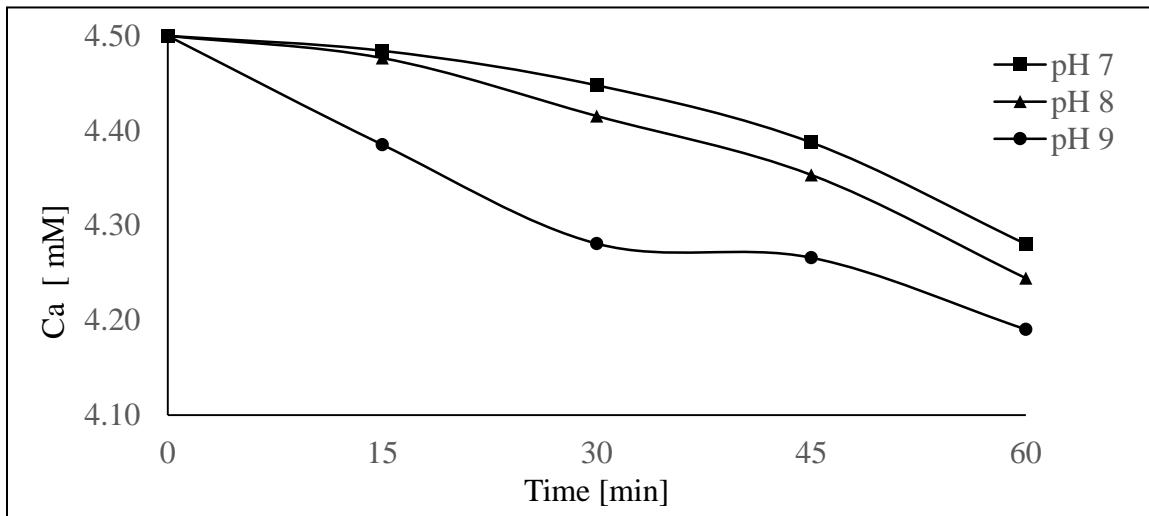


Fig.4.11. Effect of pH on calcium concentration during sonication

The effect of pH can be explained based on the pH dependence of carbonate concentration in solution. Bicarbonate dissociates into carbonate according to the equation:



According to Henderson-Hasselbalch equation, as pH increases, the carbonate concentration increases as indicated in Table 4.1:

$$\text{pH} = \text{p}K_a + \text{Log} [\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (13)$$

Increasing pH by 2 units increases the carbonate concentration by 2 orders of magnitude, increasing the chance of calcium and carbonate ions recombination, hence increasing the rate of calcium carbonate precipitation.

4.3.2. Effect of ultrasound amplitude

The effect of ultrasound amplitude was studied at two different amplitudes, 150 and 450 W as shown in Fig.4.12. After 60 minutes, calcium concentration in solution decreased from 4.50 to 4.24 mM at 150 W amplitude, which is higher compared to 3.09 mM at 450 W. The reason is that at the lower amplitude, the effect of physical mixing of solutions was lower compared to that at the higher one, showing a lower precipitation rate.

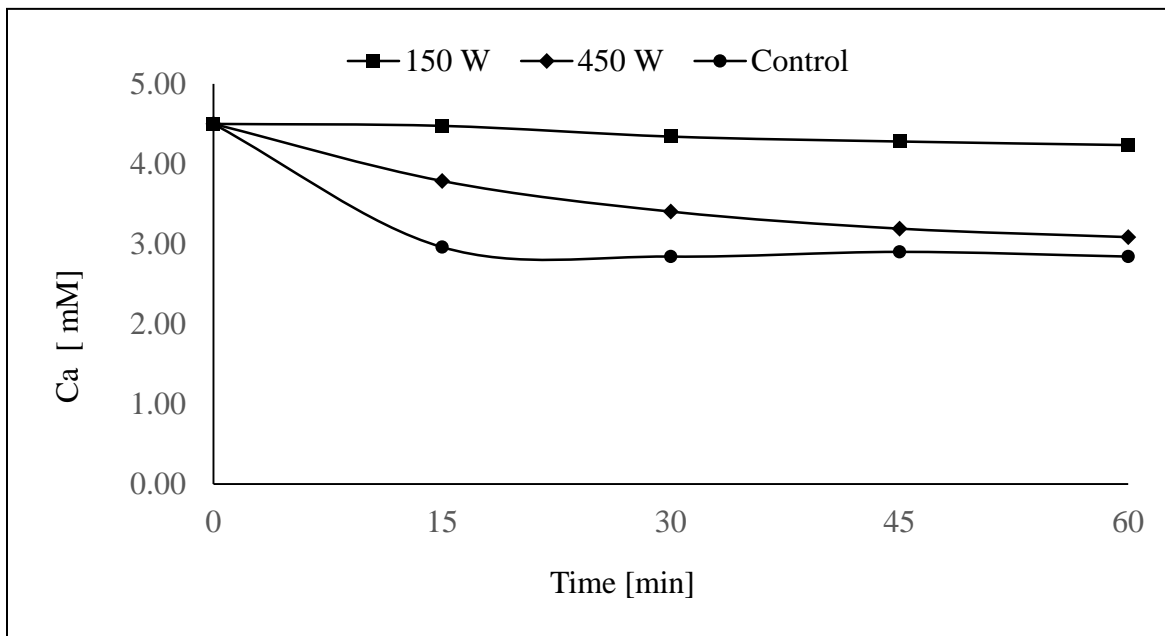


Fig.4.12. Effect of ultrasound amplitude on calcium concentration

4.3.3. Effect of ATMP concentration

Fig.4.13 shows the effect of the addition of different dosages of ATMP on scale inhibition during 60 minutes. Application of ultrasound resulted in the splitting of water molecules, resulting in solvating more calcium and carbonate ions so they will not be able to react forming calcium carbonate, inhibiting calcium carbonate scale formation on surface to 94.32% compared to 63.16% of the untreated sample. Furthermore, the addition of tris (methylenephosphonic acid) decreased the scale inhibition. The addition of 5 ppm, the threshold concentration, again increased the scale inhibition, above which there will be a reversal effect.

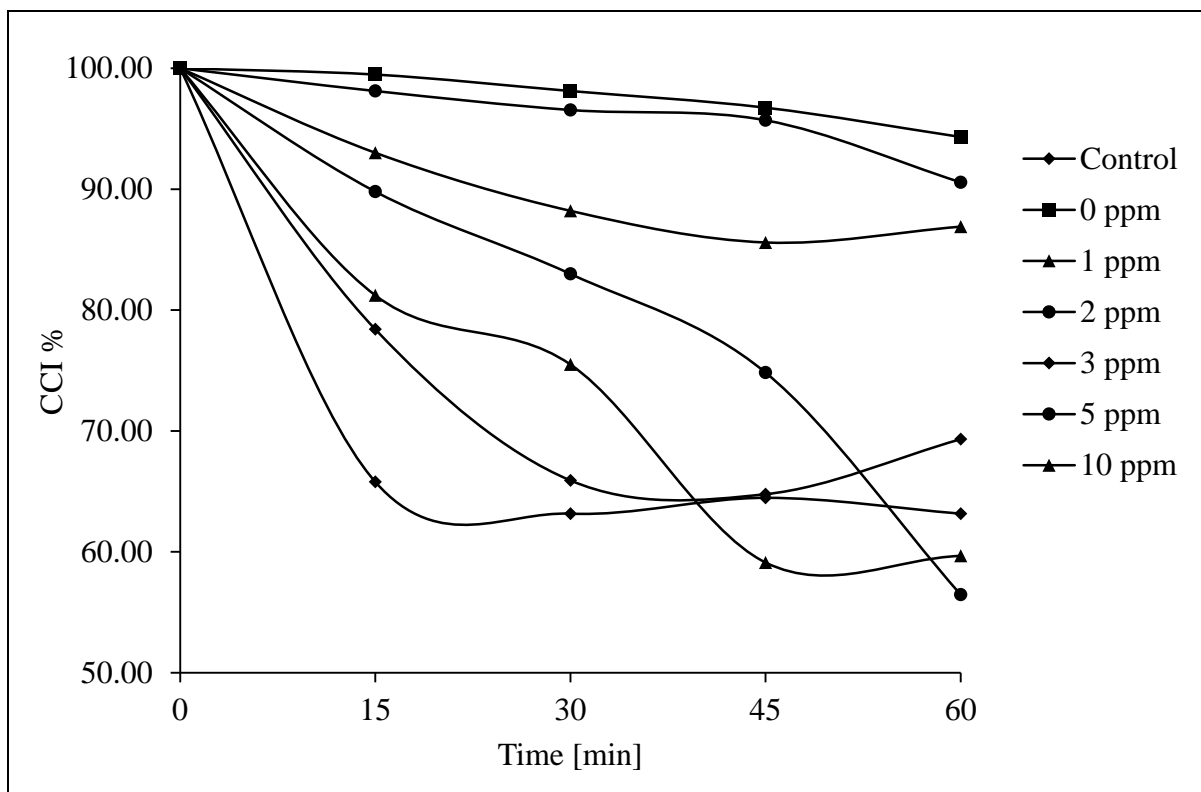


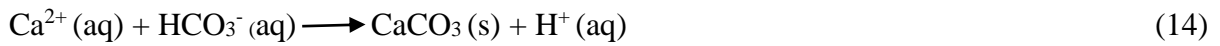
Fig.4.13. Effect of Amino tris (methylenephosphonic acid) dose on sonication scale inhibition

4.3.4. Water chemistry

I) pH

Calcium carbonate precipitation has also been monitored by measuring pH every 15 minutes in order to track the extent of precipitation with time.

Fig.6 illustrates the variation of pH in case of control and sonicated cases. As calcium carbonate precipitates, the protons are released according to:



The pH of untreated sample decreased from 9.00 to 8.93, while that of the sonicated sample decreased from 9.00 to 7.83, indicating that less calcium carbonate has been precipitated in case of the sonicated water.

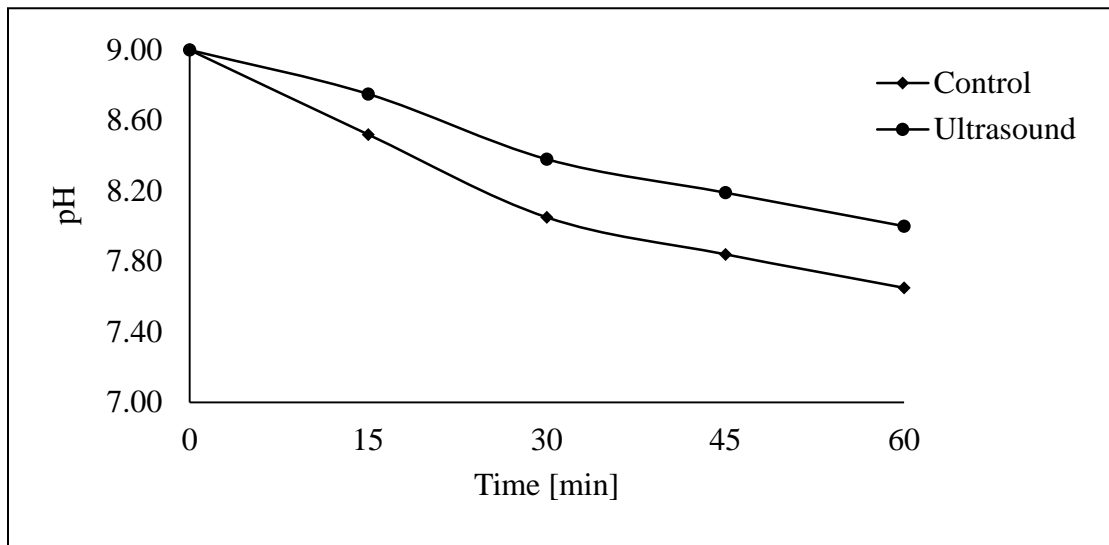


Fig.4.14. Comparison of pH variation with and without ultrasound treatment

II) Conductivity

Fig. 4.15 shows the conductivity measurements of untreated and sonicated water for 60 minutes. In both cases, the conductivity decreases with time. However, the conductivity drop in case of untreated water is higher compared to that in case of the sonicated water since calcium carbonate has precipitated more in case of the untreated sample leading to more calcium and bicarbonate ions consumption from solution, lowering the electrical conductivity with time.

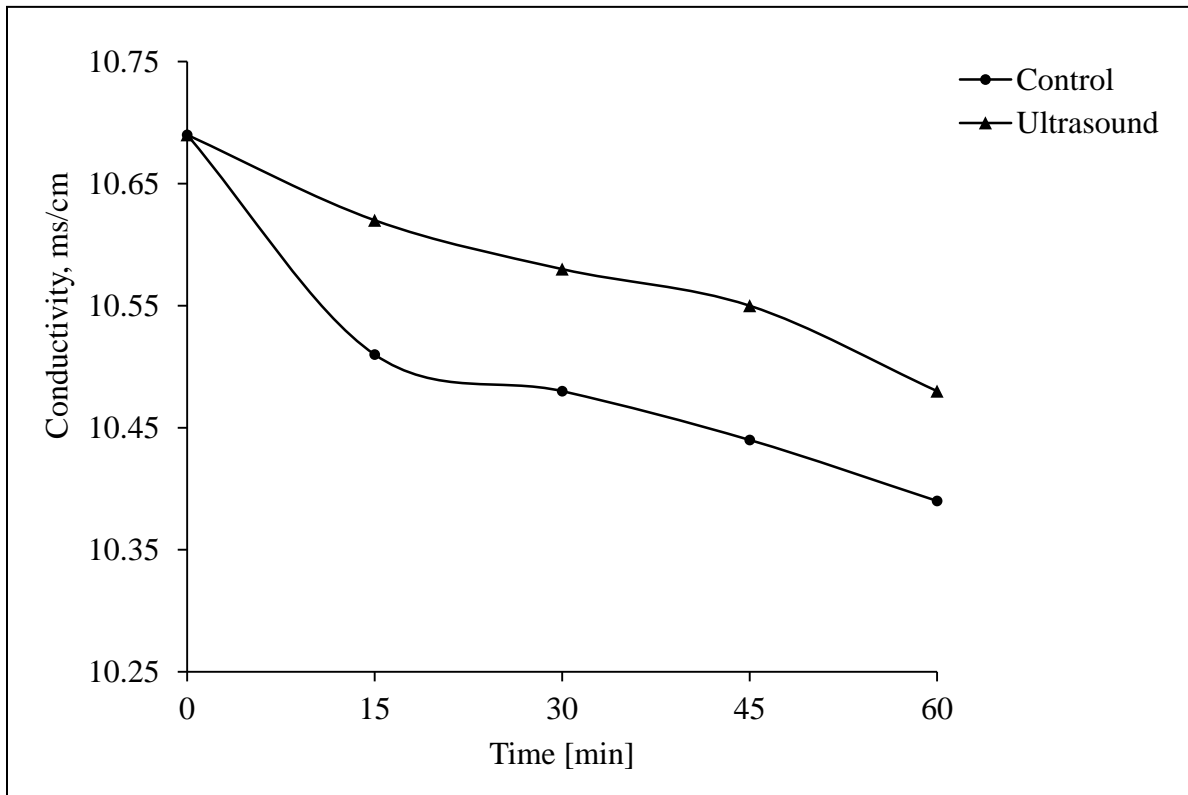


Fig.4.15. Comparison of conductivity variation with and without sonication

4.3.5. Characterization of scale deposits

I) Membrane scale deposit measurements

Fig.4.16. shows the mass of calcium carbonate deposited on polypropylene and polysulfone membranes kept inside the working solutions for 30, and 60 minutes. As shown in the figure, the amount of scale deposited in case of sonicated sample is insignificant compared to that of the untreated one since the rate of precipitation in case of ultrasound application is very low compared to that of the untreated case.

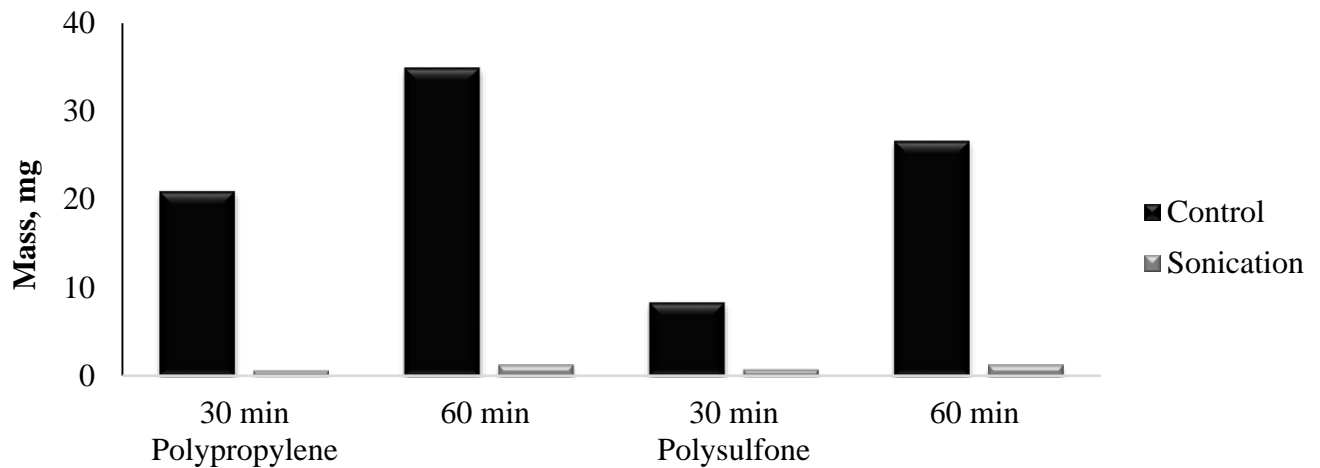


Fig.4.16. Weight measurements of calcium carbonate deposits with and without ultrasound application

II) XRD analysis

Fig.4.17 shows XRD images of the deposits obtained from untreated, and sonicated water. Calcium carbonate deposited in both cases contains calcite and vaterite, indicating that the morphology of the crystals formed was unaffected by ultrasonic irradiation.

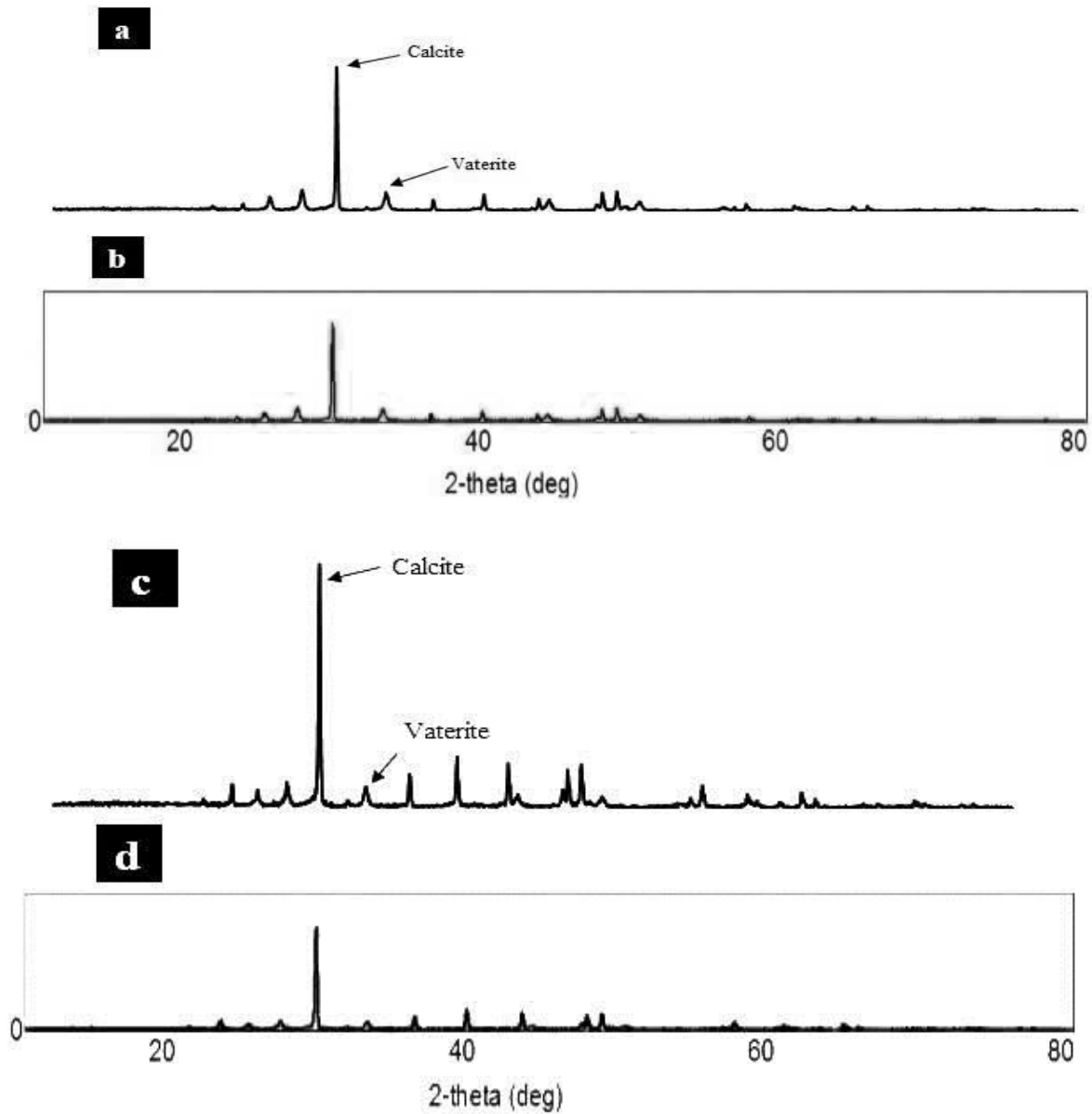
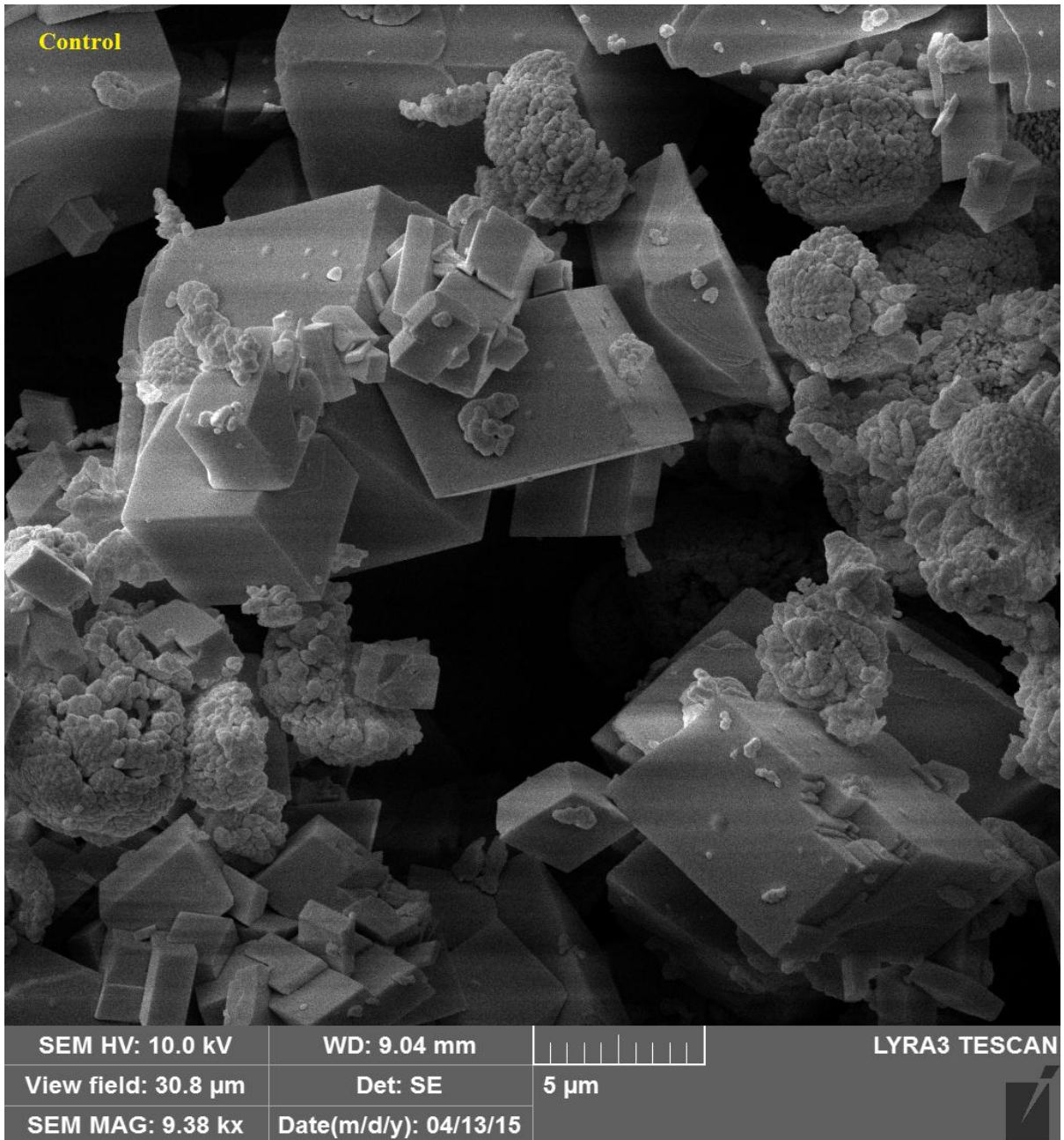


Fig. 4.17. XRD spectra for: (a) Untreated case (b) standard peaks of calcite and vaterite; (c) UV treated case; (d) standard peaks of calcite and vaterite

III) SEM analysis

Fig.4.18 shows SEM images of the deposits obtained from untreated, and sonicated water. The SEM images also show that the calcium carbonate crystals deposited in both cases are calcite and vaterite, indicating that the morphology of the crystals formed was unaffected by ultrasonic irradiation.



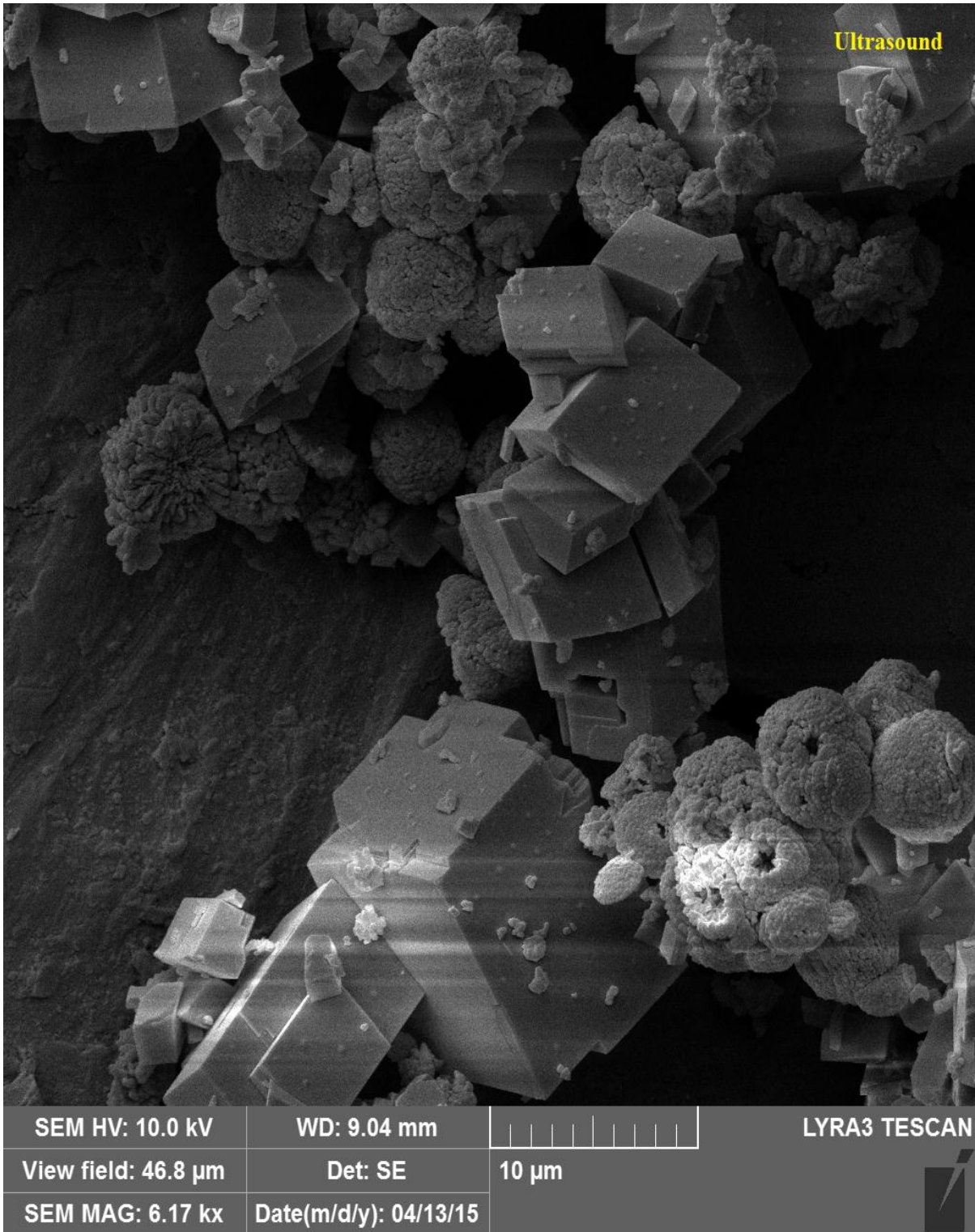


Fig.4.18. SEM images for deposits of untreated water and sonicated water

4.3.6. Comparison of ultrasound with commercial antiscalants

Fig.4.19 shows the rate of calcium carbonate precipitation of untreated, chemically treated, and sonicated samples. A glance at the figure reveals that the rate law of precipitation is parabolic, having a peak at 15 minutes – the induction period of calcium carbonate precipitation under these conditions ; since calcium carbonate is a sparingly soluble salt. Also evident is the sharp decrease of the precipitation rate in case of the treated samples. However, the sonicated water showed a sharper decline compared to the chemically treated one; due to the splitting of the solution water molecules under the effect of ultrasound, solvating more calcium and carbonate species, preventing their recombination, hence decreasing the rate of calcium carbonate precipitation.

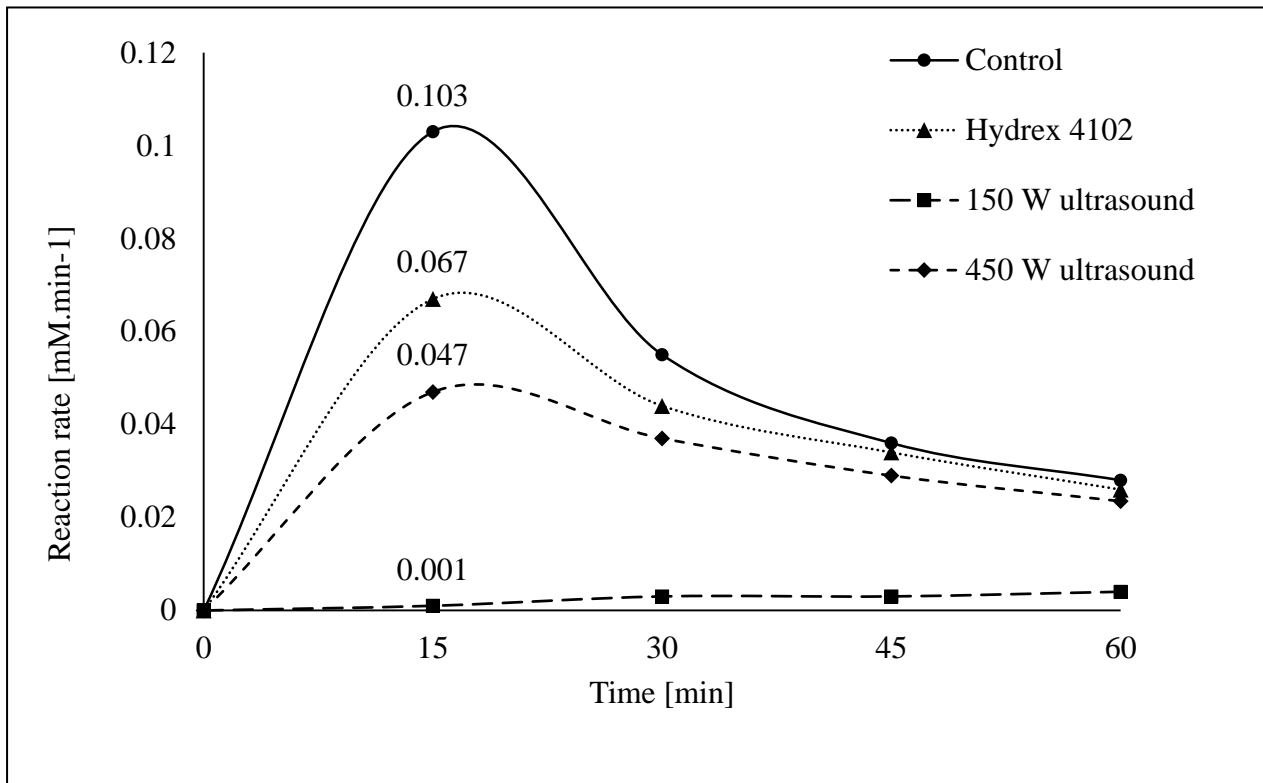


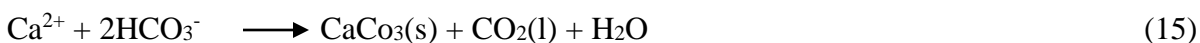
Fig.4.19. Calcium carbonate precipitation rate of treated and untreated water sample

4.4. Electric field

The effect of electric field on calcium carbonate scale formation has been studied by applying an electric field on 2 graphite electrodes immersed in the working solution at different levels of voltage, frequency, and degree of supersaturation.

4.4.1. Effect of Voltage:-

The effect of voltage has been studied at a wide range of voltage from 1 to 20 V. Afterwards, 10 V has been used as the upper level above which the effect of electric field on the precipitation of calcium carbonate did not change. Hence, electric field at 3 different levels; 1, 5, and 10 V has been applied on a solution composed of 0.01 M CaCl₂ and 0.02 M NaHCO₃ for 60 minutes. Fig.4.20 illustrates the effect of electric field on calcium carbonate formation behavior. When applying 1 V, the calcium concentration has decreased to 26% compared to 48% in case of the untreated solution, while increasing the voltage to 5V increased lowered the calcium concentration by 20%. Application of 10 V increased calcium carbonate precipitation significantly, decreasing the calcium content in solution by 16%. . The reason is that the application of electric field induces the decomposition of water into hydrogen and oxygen gases, causing significant bubbling in solution, expelling CO₂ from solution. Once CO₂ is expelled from solution, the bicarbonate to CO₂ ratio increases according to the equation:-



Increasing the bicarbonate concentration raises the chance for calcium carbonate precipitation because the electric field provides the energy needed to decompose the

bicarbonate into carbonate, which further recombine with calcium ions, precipitating as calcium carbonate.

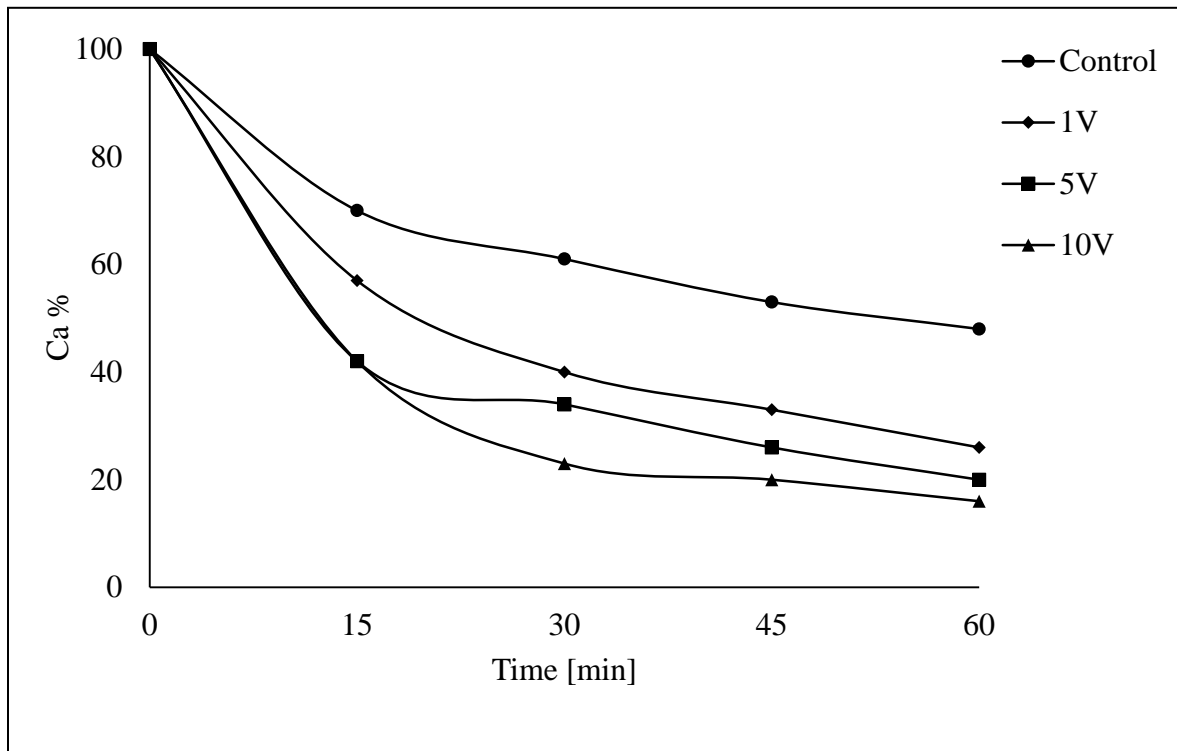


Fig.4.20. Ca % in solution in presence and absence of electric field

The precipitation reaction has also been monitored by measuring pH and conductivity of solution every 15 minutes. As it is shown in Fig.4.21, pH of the untreated water has decreased with time due to the liberation of H^+ resulting from the precipitation of calcium

carbonate. Meanwhile, application of electric field resulted in the expulsion of CO₂ from solution, so the solution became more basic with time.

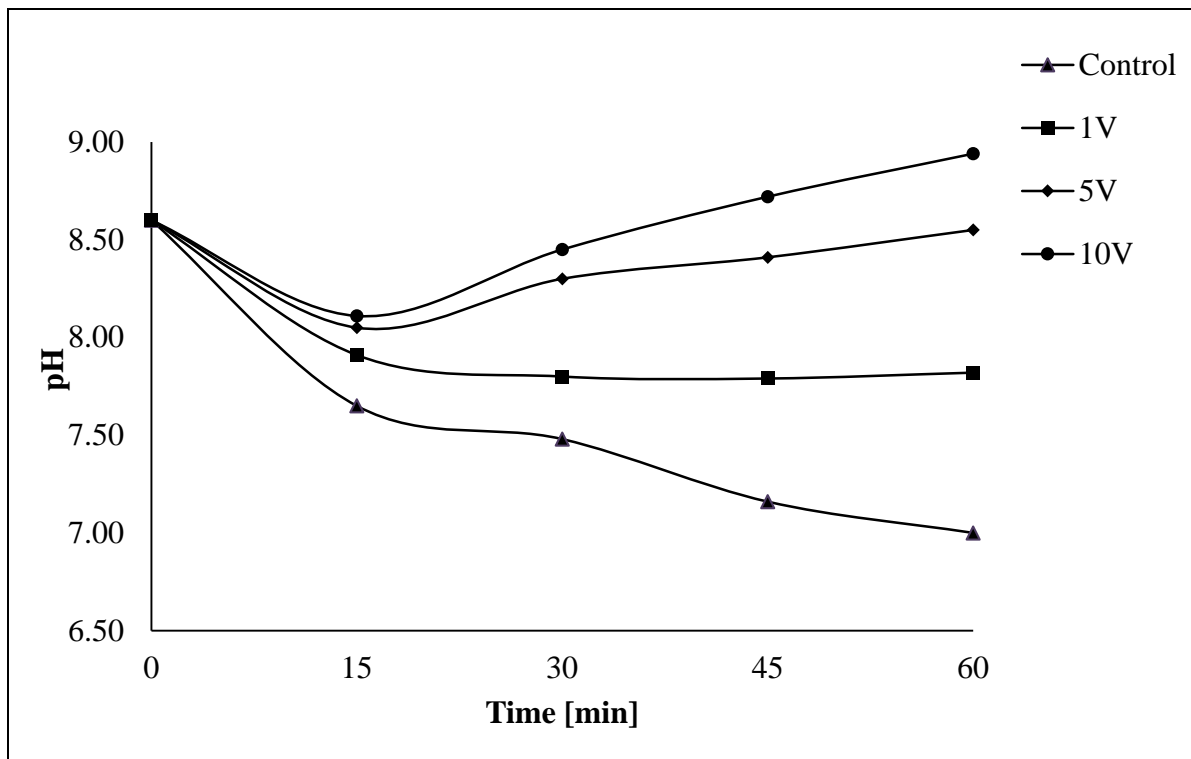


Fig.4.21. pH variation for control and electric field experiments

The electrical conductivity of solution is also a measure of the extent of calcium carbonate precipitation in solution. When calcium carbonate precipitates, calcium and carbonate ions are taken away from the solution; and since these are the ions responsible for conductivity, taking these ions from solution lowers the electrical conductivity of solution. Fig.4.22 shows that the conductivity drop while applying the electrical field is higher than that for the control experiments indicating that more ions have been consumed due to more calcium carbonate precipitation.

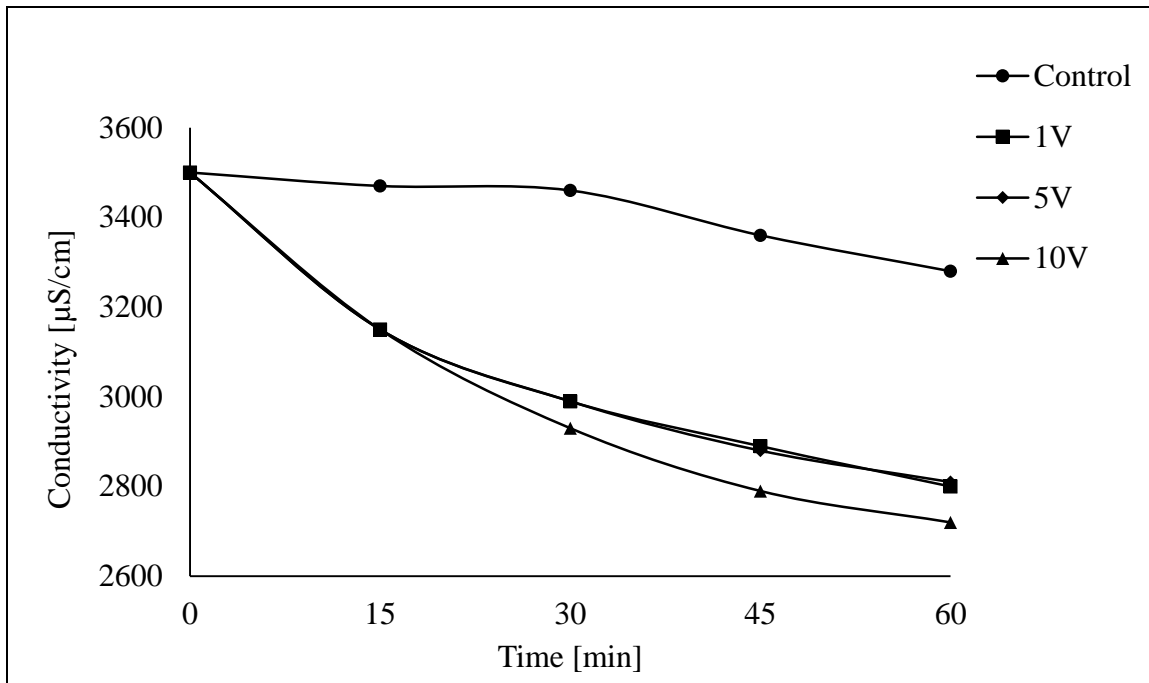


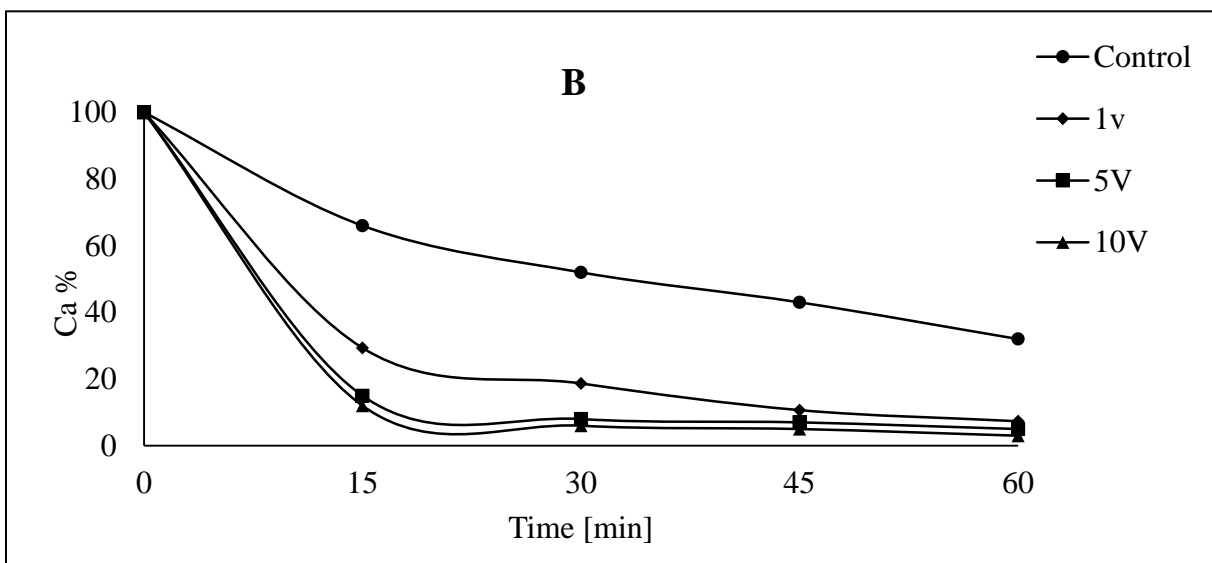
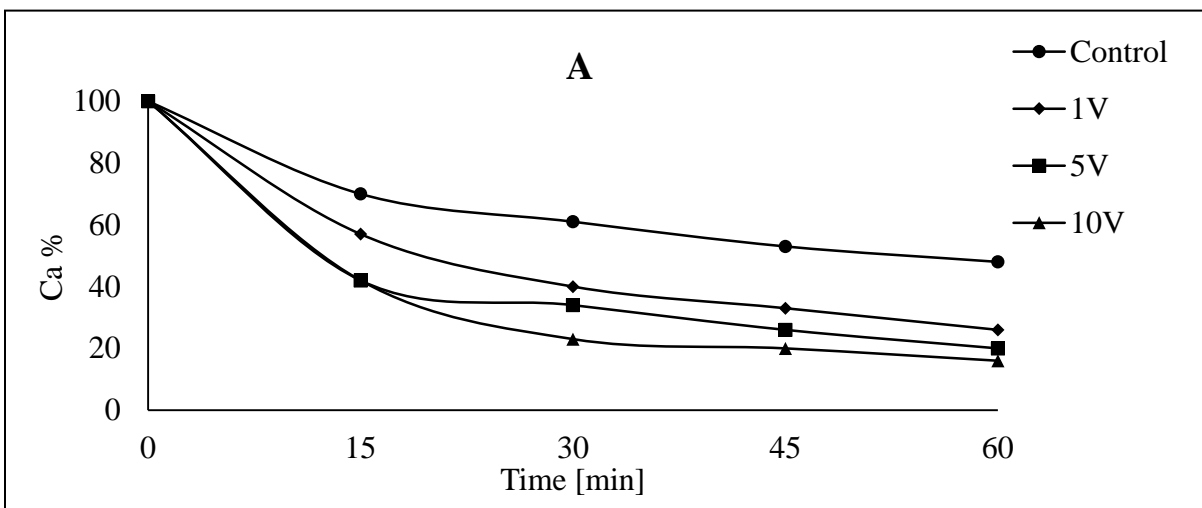
Fig.4.22. Conductivity variation for control and electric field experiments

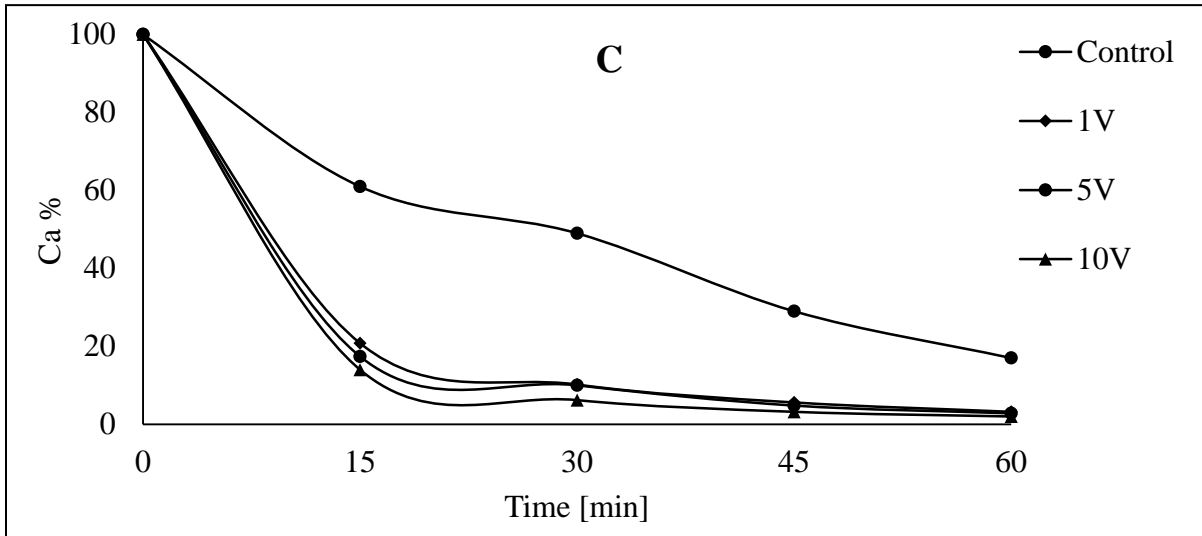
4.4.2. Effect of degree of supersaturation

The effect of degree of supersaturation on the behavior of electric field has been studied at 3 different concentrations of calcium chloride and sodium bicarbonate as shown in table4.3. As the degree of supersaturation increases, the tendency of calcium carbonate precipitation increases as depicted in Fig.4.23. When using 0.01 M CaCl₂, the application of 10 V has lowered the calcium content to 16% after 60 minutes, compared to 48% for the untreated water. However, when increasing the initial solution concentration to 0.03 M, the calcium content decreased to 3% and then 2% at 0.05 M solution. Thus, as the solution becomes more saturated, applying electric field results on more calcium carbonate precipitation.

Table.4.3. Initial concentration of the working solution

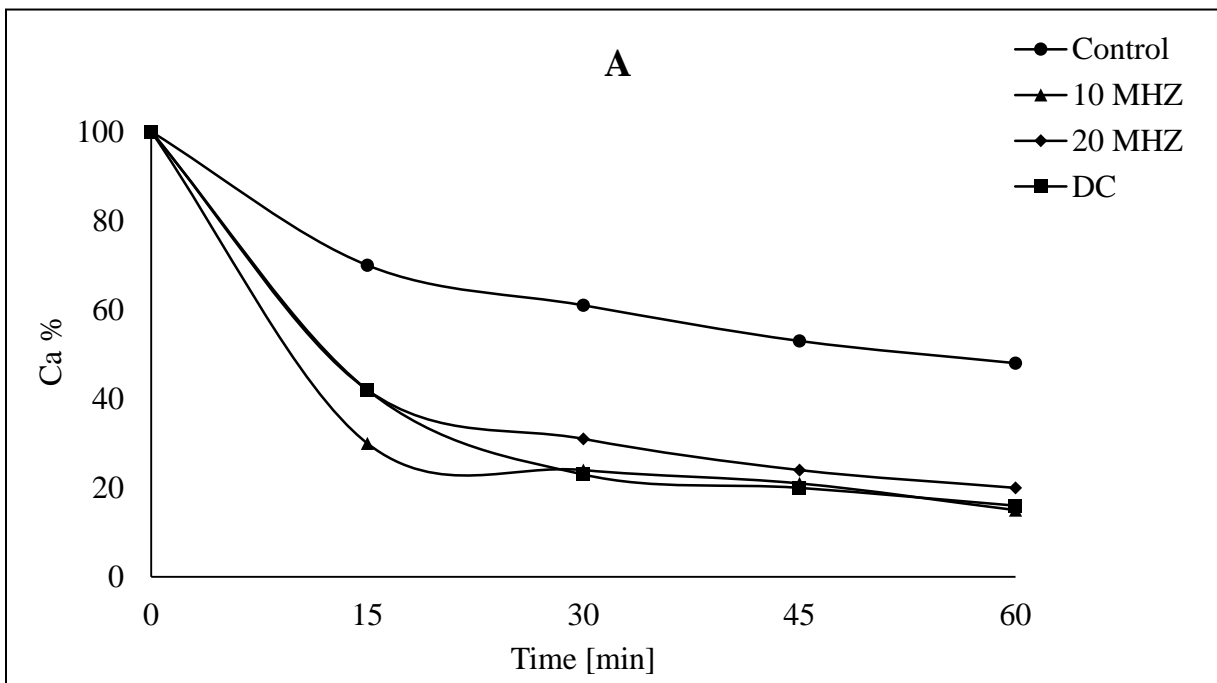
Solution	CaCl ₂ [M]	NaHCO ₃ [M]
A	0.01	0.02
B	0.03	0.06
C	0.05	0.1





4.4.2. Effect of frequency

The effect of the frequency of the alternating current has been investigated applying the electric field at 10 and 20 MHz. As it is shown in Fig.4.24, the frequency of the electric field had no effect on the behavior of the electric field toward calcium carbonate precipitation at all degrees of supersaturation.



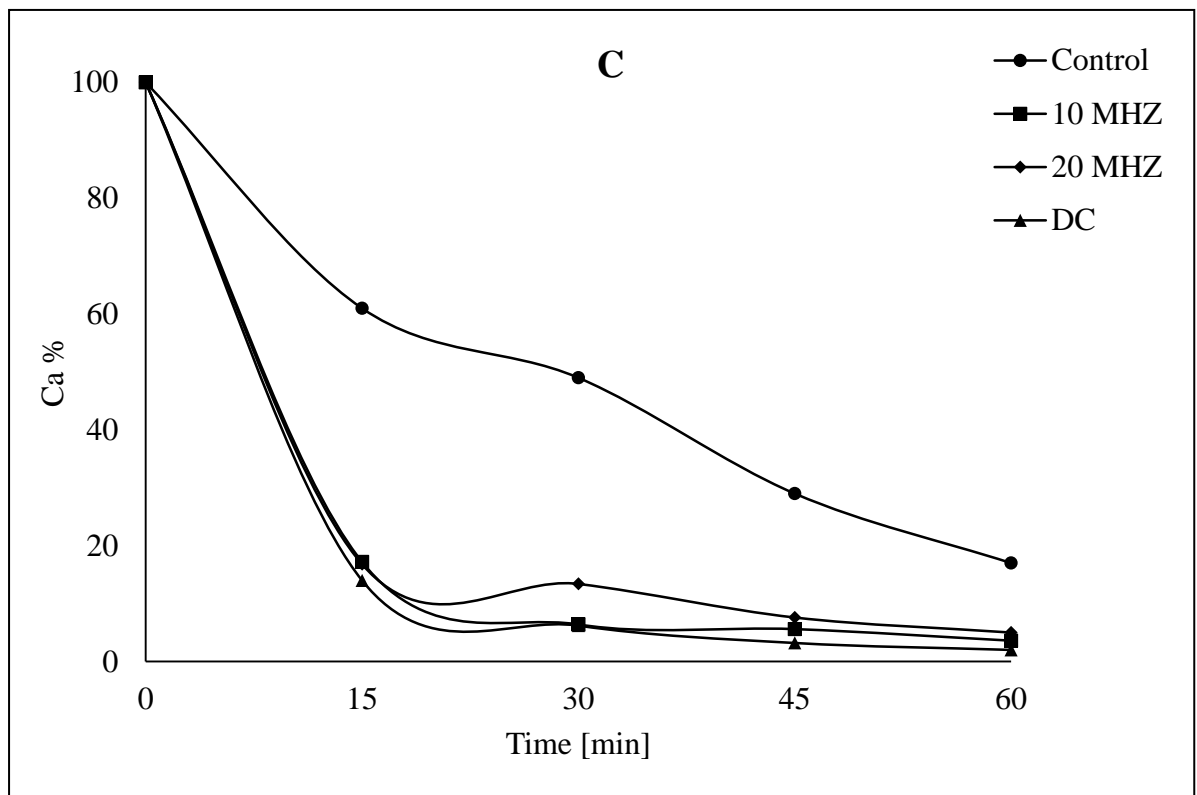
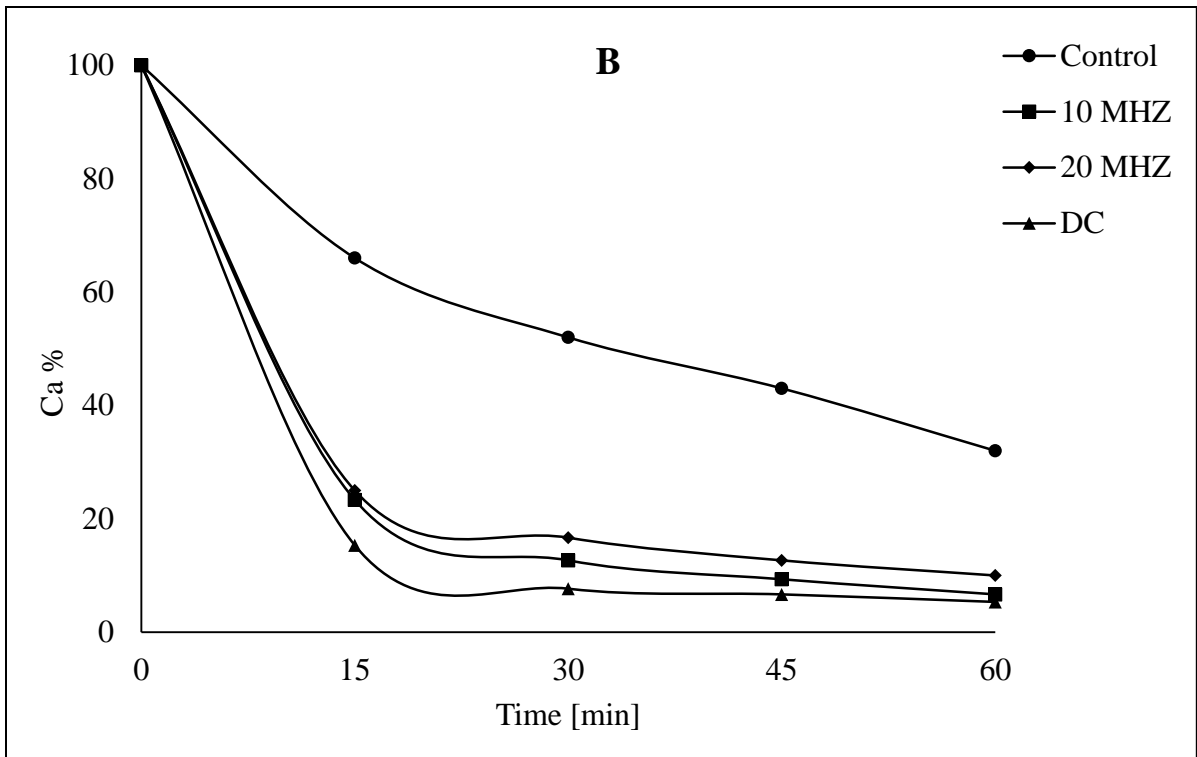


Fig.4.24. Effect of electric field frequency on electric field behavior

4.4.4. Characterization of scale deposits

I) *Scale deposit measurements*

The weight measurements of deposits of CaCO_3 have been done in the absence and presence of electric field at 10 V each 15 minutes at initial 0.05 M CaCl_2 . In agreement with the Ca concentration determined by complexometric titration, the amount of CaCO_3 deposited in the presence of electric field is higher than that in the untreated solution as illustrated in Fig.4.25.

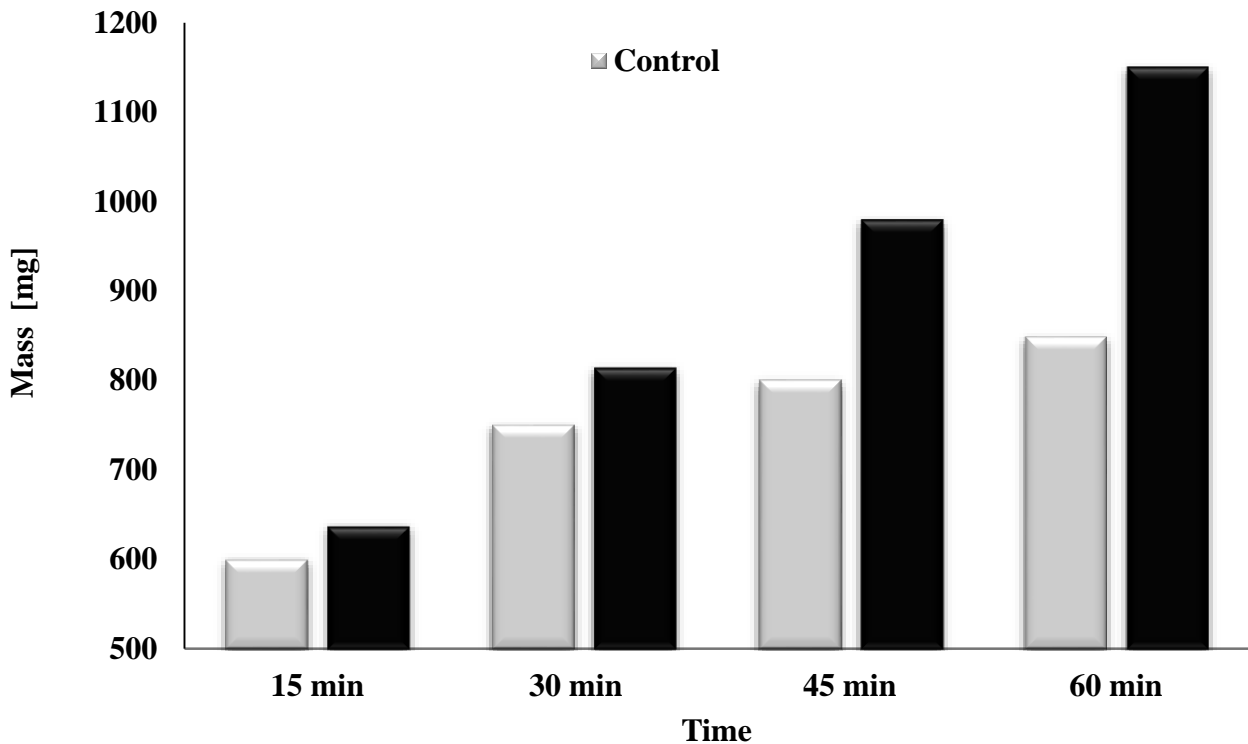


Fig.4.25. Weight measurements of calcium carbonate deposits with and without electric field

II) XRD analysis

Fig.4.26 shows XRD images of the deposits obtained from untreated, and sonicated water. Calcium carbonate deposited in both cases contains calcite and vaterite, indicating that the morphology of the crystals formed was unaffected by ultrasonic irradiation.

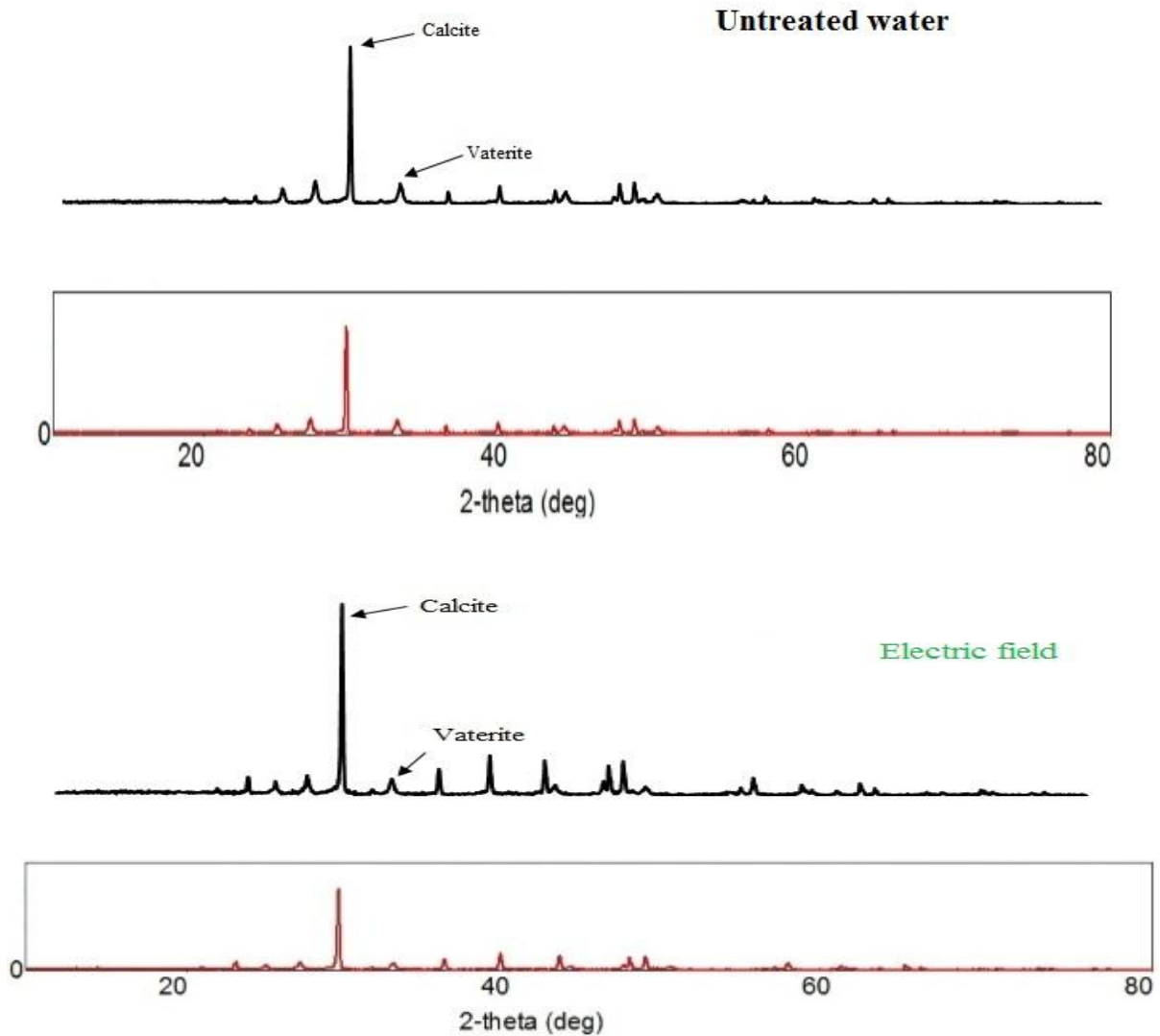


Fig. 4.26. XRD spectra for untreated and electrical field treated water

III) SEM analysis

Fig.4.27 shows SEM images of the deposits obtained after application of electric field at 15, 30, 45, and 60 minutes. The SEM images show that the electric field did not change the morphology of the crystals formed. In addition, the size of the calcite and vaterite crystals formed increases with time indicating the crystal growth increase with time.

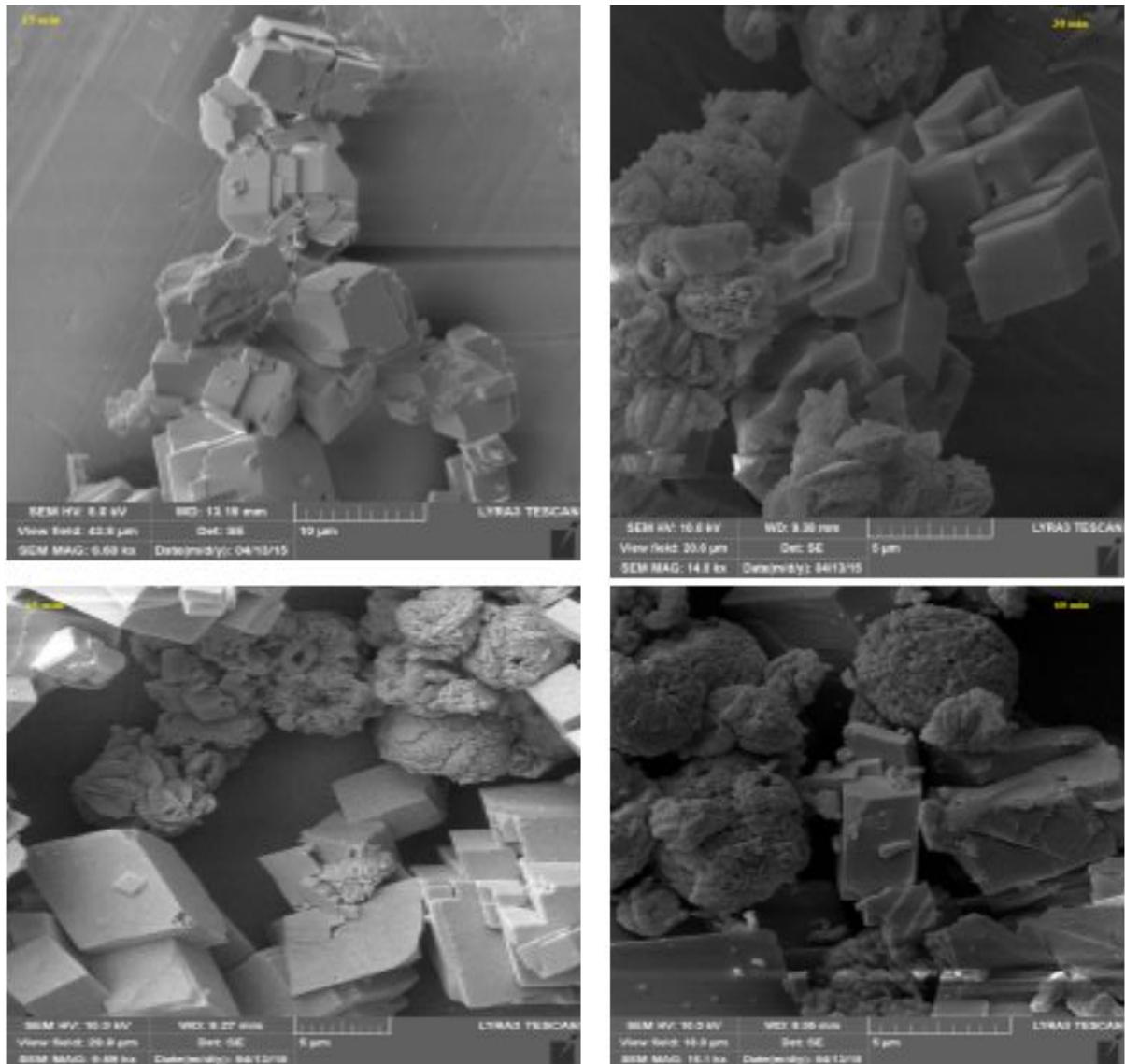


Fig.4.27.SEM images for deposits during the application of electric field at different time intervals

Chapter 5

Conclusion

Calcium carbonate scale inhibition was studied using UV light, ultrasound, and electric field.

UV light

1. Using UV light; the calcium carbonate crystal growth rate decreased by about 85%, compared to 43% after the addition of 3 ppm of amino tris (methylenephosphonic acid) antiscalant
2. Calcium carbonate scale inhibition experiments on polypropylene and polysulfone membranes used in desalination plants revealed that the amount of scale deposited in case of UV-treated sample is insignificant compared to that of the untreated one, increasing the life time of the desalination membrane
3. XRD, and SEM analyses revealed that UV light treatment produced mostly calcite crystals, that are less dense, less adherent, and easily removed than other types of calcium carbonate phases; increasing the life time of the desalination membrane
4. Thus, UV radiation is an efficient green approach for calcium carbonate scale mitigation on desalination membrane surfaces.

Ultrasound

1. Application of ultrasound is an effective green approach for calcium carbonate scale inhibition on water desalination membranes, compared to the chemical treatment.
2. Monitoring the water chemistry parameters unveiled the inhibition behavior in case of treated and untreated cases; pH and conductivity values of the untreated sample were very low compared to the sonicated one, reflecting more calcium carbonate precipitation compared to the sonicated case.
3. Applying ultrasound produced small quantity of calcium carbonate scale deposit; confirmed by SEM, and XRD to be vaterite crystals, indicating that ultrasound application did not affect the morphology of the formed crystals. Hence, ultrasound can be applied to retard the calcium carbonate fouling on the pipes surfaces in oil and gas plants.

Electric field

Applying electric field enhanced the precipitation of calcium carbonate, independent of the degree of supersaturation of solution and frequency.

Future work

1. Intensive study of factors affecting CaCO_3 scale formation under the effect of UV light, ultrasound, and electric field
2. Pilot and large scale application of UV, ultrasound, and electric field techniques for CaCO_3 scale inhibition
3. Studying the effect of these approaches on CaSO_4 scale formation

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3. Saudi – Japan Symposium on “Catalyst in Refining and Petrochemicals” KFUPM, December, 2013

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1. Mokhtar Noor El Deen, Chanbasha Basheer, Than Htun, Calcium carbonate scale inhibition by UV radiation, Green Chemistry letters and Reviews journal (submitted)
2. Mokhtar Noor El Deen, Chanbasha Basheer, “Effect of ultrasound on calcium carbonate scale inhibition”, Ultrasonics Sonochemistry (submitted)
3. Mokhtar Noor El Deen, Chanbasha Basheer, Eid Al Mutairi, Khurram Qureshi, Sowrirajan Subbaiah, SaravananSankaran, and Idris Khan Mohd Ali, “Innovative techniques to remove calcium carbonate scale from water”, Lab tech 2014 conference, Manamah, Bahrain, 28-30th Oct., 2014
4. Mokhtar Noor El Deen, Chanbasha Basheer, “Calcium carbonate scale inhibition by UV radiation”, US patent (submitted)
5. Mokhtar Noor El Deen, Chanbasha Basheer, “Effect of ultrasound on calcium carbonate scale formation”, US patent (submitted)