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Using silica nanoparticles to improve DETPMP scale inhibitor performance as a novel calcium sulfate inhibitor

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ABSTRACT

Among the EOR methods, water flooding is one of the oldest and also efficient methods that are used in reservoirs. The most challenging problem in water flooding processes is scale formation. Researchers are aimed to reduce the amount of scale precipitates during this process. Scale inhibitors are commonly used to minimize the formation of scale. One of the most commercial inhibitors that are used in the oil fields is DETPMP. The effects of silica nanoparticles, phosphonates, and silica nanoparticle/phosphonate blends on precipitation of calcium sulfate are presented in this work. Conductivity through static tests was measured in order to detect the amount of scale formed in the solution. Characterization of calcium sulfate crystals formed in the presence of nanoparticle/phosphonate blends was carried out by scanning electron microscopy technique. Also X-ray powder diffraction, transmission electron microscopy, and Fourier transform infrared studies have been performed to identify the novel inhibitor performance. It has been found that an optimum concentration of silica nanoparticles and DETPMP scale inhibitor could significantly reduce the rate of conductivity decreasing of the solution and consequently lower the scale deposition which is the aim of this challenging subject in the oil industry. It is concluded that silica nanoparticles and DETPMP could significantly control precipitation of calcium sulfate scale.

Keywords: Silica nanoparticles; DETPMP scale inhibitor; Calcium sulfate scale; Conductivity measurements

1. Introduction

As most of the reservoirs have reached the second half of their life, researchers must approach methods to produce more oil from the reservoirs that are called enhanced oil recovery (EOR) methods. Water injection is one of the oldest, effective, and most commonly used methods as secondary EOR methods in the oil fields. The most frequently used injected water is seawater (SW) because of high quantity and also availability (especially in offshore fields) and economic reasons. Injection of SW into the underground oil reservoir is applied in order to displace remaining oil from the reservoirs.

Injected and formation waters (FWs) mix each other and would chemically react with each other as soon as they mix with each other, because they contain different types and concentrations of ions (that is

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called incompatibility). Almost the injected water contains high concentration of the sulfate ions. Also the FW contains almost the high concentration of the cations with two positive charges such as calcium, barium, and strontium ions. This would cause the precipitation of salts that are known as scale precipitates [1–8].

The use of natural hard waters in oil field that causes the deposition of scale precipitates is one of the major oil field challenges that would result in severe technical and economic problems. More precisely, scale limits and sometimes blocks by plugging formation matrix, fractures, perforated intervals, tubing, production equipment, and surface facilities [3,9].

The most and less common composition of these waters is shown in Table 1.

In these cases, the removal of the precipitates needs discontinuous operation of production that results in higher operating costs.

Over the years, in order to prevent precipitation of different types of salts (scales) from aqueous solution, various approaches have been proposed. These approaches include physical (such as magnetic, electric, or the use of sonic waves) and chemical (such as acid addition, ion exchange, or scale inhibitor) processes [13–15].

Among the above techniques, the most effective approach for controlling scale formation is the use of chemical inhibitors. It is known that the addition of the scale inhibitor to the injected water would be an effective method to reduce or prevent scale formation.

The role of the scale inhibitors is reducing, minimizing, or preventing of scale deposition [13]. In the literature, the performance is dealt with so many different scale inhibitors. The commonly used inhibitors are organophosphorous compounds (organic), organic polymers (organic), and inorganic phosphates (inorganic) [16]. In the petroleum industry, polyphosphono Carboxylic acid (PPCA) and diethylene triamine pentamethylene phosphonic acid (DETPMP) are the two commonly used inhibitors [16]. The question is how such inhibitors (i.e. phosphonates and polyphosphates) could prevent scale formation. They adsorb onto the places where there would be the potential of crystal growth and by altering the morphology of crystals prevent the scale formation at amounts of less than stoichiometric relations [12].

The effect of polyphosphates and phosphonates on the calcium sulfate scale and the effect of polymeric inhibitors on the $CaSO_4·2H_2O$ scale have been investigated by many researchers.

Liu and Nancollas have used the seeded growth technique. They showed that using trace amounts of phosphonates could stabilize supersaturated calcium sulfate solutions and also could lengthen the induction period before commence of crystallization. The most important parameters that would affect the duration of induction periods (crystallization period) include concentration of phosphonates, amount of seed crystals added, and temperature [17].

Amjad showed that polymers containing carboxyl groups such as poly (acrylic acid), poly (aspartic acid), poly (itaconic acid), and poly (maleic acid) were especially effective for growth inhibition of $CaSO_4·2H_2O$ scale [18].

Also Dogan et al. studied the effect of various acrylic acid-based copolymers as gypsum scale inhibitor and arrived at similar conclusions as Amjad [19].

Amjad and Hooley in their seeded growth study on the evaluation of polymers containing different functional groups concluded that the most important factors influencing the inhibition activity of the polymers are polymer composition, type and amount of co-monomer, and molecular weight [20].

The influence of poly (ethylene oxide)-block-poly (meth (acrylic acid) and poly (butyl methacrylate)-block-poly (methacrylic acid) copolymers on precipitation of calcium sulfate scale is recently investigated by Dogan et al. They presented that by increasing the acid content of the copolymer, the calcium sulfate inhibition increases [21].

During the past years, various polymeric and non-polymeric additives were used in order to cure the problems that result from the water treatment applications. However, the calcium sulfate inhibition using additive inhibitors has been mostly researched.

In our previous work, we presented the results on the evaluation of silica nanoparticle inhibitors on amount of gypsum scale formation. In this work, it is showed that nanoparticles have considerable effect on reduction of scale precipitation. These particles have high surface charges, so that they might be effective in the scale formation processes. In the research, it showed that the addition of nanoparticles to the injected water will considerably decrease the amount of scale precipitation [12].

As previously mentioned, one of the most commercial inhibitors that widely used in the oil and gas industry is DETPMP. It is interesting to investigate the effect of nanoparticles scale inhibitors in the presence of DETPMP scale inhibitor. So, the main purpose of this work was to study the inhibition of the calcium sulfate precipitation using silica nanoparticles besides DETPMP as a novel scale inhibitor.

This study presents inhibitory data on the performance of nanoparticle/phosphonate blends as gypsum precipitation inhibitors. For this propose, through an experimental procedure this effect is investigated. The prepared formation and injected water with especial concentration of salts are added to each other alternatively. Then nanoparticles (as in the previous work) and inhibitor are added to the injected water at different concentrations lonely and together. By measuring the conductivity of the solution (before and after the scale inhibitors additive), it will be shown that nanoparticles could improve the effect of inhibitors on scale formation significantly and use of them simultaneously could decrease the amount of scale formation more than applying them separately.

2. Materials

2.1. Brines

Sodium sulfate and calcium nitrate are used as injected and formation water, respectively, as these salts causes common scale precipitates that are usually found in reservoirs as shown in Table 1. When these two salts react with each other leads to the generation of calcium sulfate salt that is a common scale in the reservoir. Also ethylenedinitro-tetraacetic acid disodium salt dihydrate (EDTA-Na_2) is used for core washing after each experiment as it could solve the calcium sulfate salts deposited in the core samples. A brief description of these chemical materials is given in the following.

1. Sodium sulfate (Na_2SO_4, MW = 142.04 g/mol, 99% purity) supplied by Merck Company.
2. Calcium nitrate tetrahydrate ($Ca\ (NO_3)_2{\cdot}4H_2O$, MW = 236.15 g/mol, 99% purity) supplied by Merck Company.
3. Ethylenedinitro-tetraacetic acid disodium salt dihydrate (EDTA-Na_2, $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$, MW = 372.24 g/mol, 99% purity) supplied by Merck Company.

2.2. Nanoparticles

Silica nanoparticles that are synthesized in a group containing some of the article authors are used with DETPMP to perform a new improved scale inhibitor. The properties of used nanoparticles are given in Table 2.

2.3. Chemical inhibitor

Diethylenetriamine pentamethylene phosphonic acid (DETPMP), provided from Changzhou New Future Chemical Company, is used here as a common commercial scale inhibitor. The properties of the DETPMP are given in Table 3. The chemical structure of the DETPMP scale inhibitor is shown in Fig. 1.

3. Mechanism of scale formation

Scale formation inhibition mechanism is a kind of physical process and does not require chemical reaction. The physical process includes ion pairing, aggregation, nucleation, crystal growth, and deposition [22].

Ions collide to form ion pairs in solution. These pairs then go on to form micro-aggregates, and some of these aggregates go on to become nucleation centers for crystallization. Microcrystals are formed in solution, which agglomerate and/or absorb to surfaces to grow into larger microcrystals and eventually fuse to form adherent macro-crystals. These macro-crystals continue to grow through the adsorption of additional ions from solution and eventually form the beginning

Table 1
Types of common oil field scales [2,3,7,10–12]

Category	Type	Cation	Name	Mineral	Chemical formula
Most common	Carbonates	Ca	Calcium carbonate	Calcite	$CaCO_3$
	Sulfates		Calcium sulfate	Anhydrite	$CaSO_4$
			Calcium sulfate	Gypsum	$CaSO_4{\cdot}2H_2O$
		Ba	Barium sulfate	Barite	$BaSO_4$
		Sr	Strontium sulfate	Celestite	$SrSO_4$
	Salt	Na	Sodium chloride	Halite	NaCl
	Metallic compounds	Fe	Iron sulfide	Pyrite	FeS_2
Less common	Carbonates	Ca	Calcium carbonate	Aragonite Vaterite	$CaCO_3$
	Metallic compounds	Fe	Iron sulfide	Mackinawite	FeS
		Zn	Zinc sulfide	Sphaerlite	ZnS
		Pb	Lead sulfide	Galena	PbS
		Ca	Calcium fluorite	Fluorite	CaF_2

Table 2
Properties of silica nanoparticles used in the experiments

Purity (on the basis of SiO_2)	98.3%
Na content (on the basis of Na_2O)	0.3%
Average particle size (on the basis of TEM image)	20–30 nm
Area of specific surface (on the basis of BET test)	200–400 m^2/g
Cumulative density	50–300 g/l
PH (5% suspension)	5–6
Appearance	White powder

Table 3
Properties of DETPMP scale inhibitor

Molecular formula	$C_9H_{28}N_3O_{15}P_5$
Molar mass	573.20
Appearance	White powder
Active acid	48–52%
Chloride (as Cl^-)	14–17%
Density (20˚C)	1.35–1.45 g/cm^3
PH (1% solution)	2.0 max
Fe	35 max mg/L

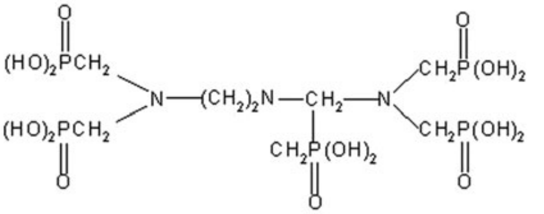

Fig. 1. Chemical structure of DETPMP scale inhibitor.

of a scale film on a surface. This scale film eventually grows into a deposit [23].

The fundamentals of inhibition processes especially from their quantitative aspects are not fully understood [24]. As said in the Introduction section, it is concluded that the trace quantities of additives (polymeric and non-polymeric) markedly reduce the precipitation of calcium sulfate dihydrate. The influence of these additives on the precipitation process may be explained in terms of three effects: (a) direct complexation of additive with crystal lattice ions in solution; (b) adsorption of additive on the gypsum crystal surface; and (c) additive may change the ionic strength of the calcium sulfate dihydrate solution and hence the effective solubility of calcium sulfate dehydrate [12].

The mechanism of scale formation is shown in Fig. 2.

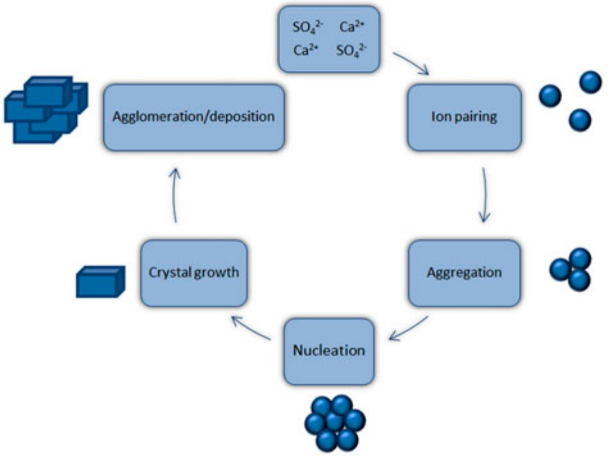

Fig. 2. Mechanism of scale formation [25].

4. Apparatus

Amount of ion concentration of a fluid could be measured by conductivity of the ion with conductivity meter. This property shows the amount of ions in the solution either before or after mixing of the two waters. Using this property, the amount of ions in the solution could be measured before and after the addition of the two incompatible waters.

The apparatuses that were used in this project are conductivity meter, ultrasonic, magnetic stirrer, and balance.

5. Experimental procedure

In this work, the static test part of scale formation experiments has been done. The procedure of the series of experiments is as follows.

(1) At first, the components of solutions (sodium sulfate and calcium nitrate) were weighted with the balance.
(2) Then, the weighted materials will be solved in deionized water in two different beakers. The solution that contains sodium sulfate will be named as SW and the one that contains calcium nitrate will be named as FW as said before.
(3) Then, 50 cc of FW is poured in another beaker, and the SW is added to it by 10 cc per time up to 50 cc (in order to SW per FW ratio to reach 50%). At each time after mixing them, the conductivity of the solution will be measured.
(4) After that in order to see the effect of silica nanoparticles on the deposition of calcium

sulfate, the nanoparticles are added to SW in a specific concentration (0.1, 0.2 wt.%, etc.). For doing this, nanoparticles are dispersed in the SW using ultrasonic apparatus for about 20 min. Then, the step 3 was done again for this new solution.

(5) Then, the steps 1 to 4 will be repeated for DETPMP scale inhibitor.
(6) The plot of conductivity vs. additive volume of SW to FW is plotted for steps 3 and 5. Also in order to see the difference between the plots, they could be merged.
(7) This work is done for different nanoparticles and inhibitor concentration. At the end, we could see the results between all the experiments as in the results section.
(8) At the end of the experiments, a new experiment was done at the optimum concentration of the nanoparticles and inhibitor and the result was compared with the previous experiments that only used nanoparticles or inhibitors.

6. Results and discussion

6.1. Static conductivity measurements

As illustrated in Fig. 3, addition of silica nanoparticles could decrease the reducing trend of the conductivity curves vs. time. As said before, conductivity represents the amount of ions in the solution. So, the nanoparticles could decrease the amount of scale precipitates. It might be because of the repulsive force between the silica nanoparticles that causes these particles to repel each other. However, these particles stay between the ions, so the ions repel each other too and the formation of precipitates decreases. Also by increasing the amount of silica nanoparticles, the conductivity of the solution increases up to a limit. As the concentration of the silica nanoparticles becomes more than this limit, the trend of increasing the conductivity is inversed and the conductivity of the solution decreases and this means that the amount of scale precipitates increases after this limit. It might be because of the nanoparticles agglomerate each other and could not be effective on scale inhibition. Also as it is clear from the figure, the existence of the silica nanoparticles, in addition to decreasing the reducing trend of the conductivity vs. time, decreases the rate of conductivity reduction of the solution [12].

As shown in Fig. 4, as the concentration of the DETPMP increases, the conductivity of the solution increases and so the amount of scale precipitates decreases. By increasing the concentration of DETPMP, the conductivity of the solution increases but the rate of increasing the conductivity increases up to a limit and after that the rate of increasing the conductivity decreases. If the addition of the DETPMP continues, there will be no or very small changes in the conductivity and also there will be no or small changes in the amount of scale precipitates. It might be because of that the molecules of DETPMP at this limit have maximum effect on formation of scale precipitates. Also increasing the concentration of DETPMP could not decrease the amount of scale precipitation. It might be because of agglomeration of these molecules that could not be effective on scale inhibition.

According to Fig. 5, the combination of both silica nanoparticles and DETPMP scale inhibitor is used. The concentration of them must be chosen so that their trends are in the opposite direction and the

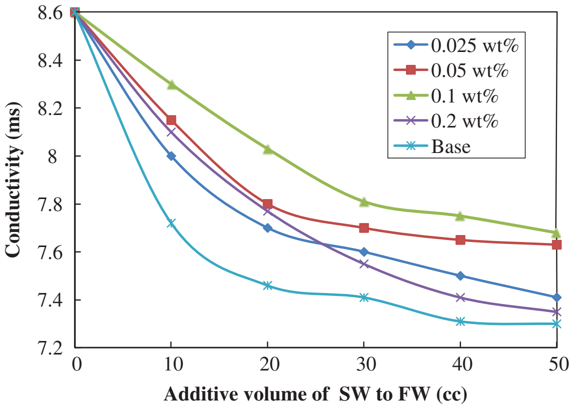

Fig. 3. Conductivity vs. additive pore volume of SW containing silica nanoparticles to FW [12].

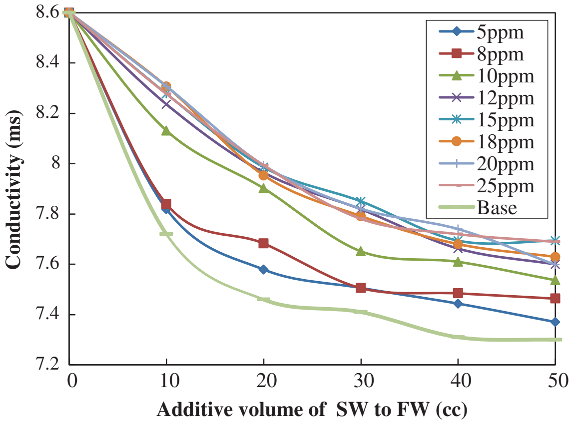

Fig. 4. Conductivity vs. additive pore volume of SW containing DETPMP scale inhibitor to FW.

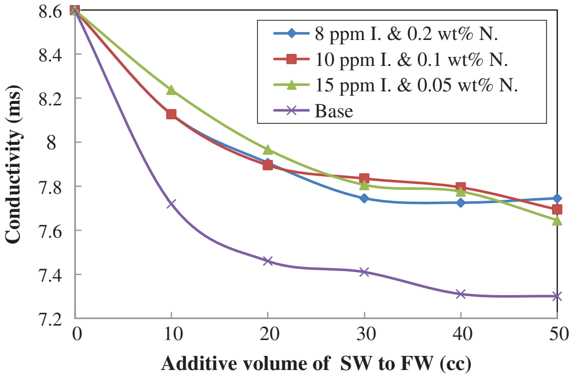

Fig. 5. Conductivity vs. additive pore volume of SW containing both DETPMP scale inhibitor and silica nanoparticles to FW (I.: DETPMP scale inhibitor, N.: Silica nanoparticles).

concentration of both must be in the optimum range of each other. As said before, the addition of silica nanoparticles and DETPMP inhibitor separately increases the conductivity of the solution. So by the addition of them together, the conductivity increases generally. However, as it is clear from the figure, the conductivity of the solution in the presence of them together does not change so much and its changes are negligible. By overall comparing this figure with the previous ones, it could be concluded that in each step, the conductivity reduction is less when both silica nanoparticles and DETPMP inhibitor are used in comparison with the conditions that only one of them is present.

It is clear from all of the figures in the discussion section that the rate of reduction of conductivity or the trend of conductivity in all of the figures is high at the beginning of addition of two waters. This results in that the more amount of scale precipitates would be formed at this range. Before the addition of the two waters, each of them contains some amount of ions. After the addition, many different ions with opposite charges would be presented in the solution. So because of difference in the ion concentrations between the two waters at the start of addition (that is called incompatibility of waters as said before), the reduction of conductivity is high and become less as the additive volume of the SW to FW gets more. Then, the electrical charges that exist in the solution are more, and the ions attract to each other more. So the inclination of the ions to react with each other and to form the precipitants is more. The idea of using and adding the nanoparticles to SW as scale inhibitors in order to decrease this high rate of reduction of conductivity was helpful [12].

As we see the addition of nanoparticles to SW will generally decrease this high rate of reduction of conductivity up to a limit. So up to this limit, the use of nanoparticles increases the conductivity of the solution and then decreases the amount of scale precipitates formation. As a result of this, we could use nanoparticles as scale inhibitors to reduce and also prevent the scale formation. So the precipitate formation is more important at the beginning of the addition of SW to FW and we should consider more to prevent the precipitate formation at the beginning of adding the two waters, which means as the injection of the SW in the reservoir, using nanoparticles. As we could see from all of the figures, the slope of all curves shows the conductivity of the solutions with and without nanoparticles will gradually decrease. As said before, this might be because of salt formation by difference in ion concentration between the two waters that will decrease as the additive volume of the SW to FW gets more. So the electrical charges that exist in the solution are less and the ions attract to each other less. Then, the inclination of the ions to react with each other and to form the precipitants is less. So the slope of the curves will gradually decrease and the importance of the precipitate formation is not as more as before and this will decrease as the addition of SW to FW increases.

The figures also show a limit of addition of the nanoparticles to SW. When the concentration of the nanoparticles is less than this limit, the performance of the nanoparticles is in the direction of decreasing the amount of precipitation. As the concentration of the nanoparticles becomes more than this limit, the performance of the nanoparticles is in the opposite direction, which means this will increase the amount of precipitation. So for each case, we should find this limit both for optimizing the amount of precipitates formation and optimizing the economic aspects of the case.

Using DETPMP like nanoparticles, the rate of conductivity reduction would be decreased. As the amount of DETPMP gets more, the conductivity would be increased gradually. The rate of increasing conductivity by increasing DETPMP concentration would be increased and then decreased up to a limit, and after that by increasing DETPMP concentration, the conductivity of the solution remains constant and there will be no significant changes. This means that the inhibitor could prevent the scale formation and no more scale would be formed so far. Nanoparticles and inhibitor could be used simultaneously. The concentration of each of them should be chosen in a manner that one of them increased and the other decreased in the vicinity of their optimum value (one of them smaller and the other bigger than optimum value). Then, we could see from the figure that in three cases, the conductivity does not change significantly and almost constant.

7. Nanoparticles characterization

As said before, several techniques (transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and Fourier transform infrared (FTIR)) were applied to characterize the properties of the used nanoparticles.

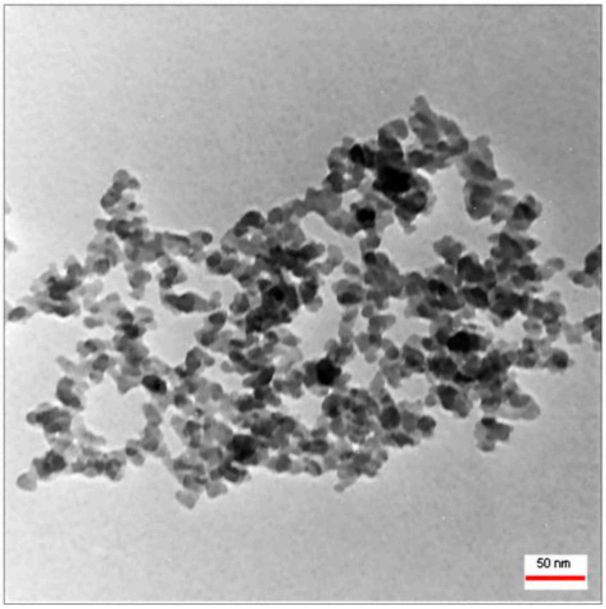

Fig. 6. TEM image of silica nanoparticles solution.

7.1. TEM test

In this research, TEM device was used to observe silica nanoparticles dispersed in the solution of SW. As shown in Fig. 6, the nanoparticles have mean diameter of 20–30 nm. Besides, the figure confirms that the synthesized nanoparticles are completely separated and placed in the solution in segregated fashion. This figure shows that the nanoparticles are well dispersed in the solvent and would remain in nanoscale.

7.2. XRD test

The XRD image of the nanoparticles is depicted in Fig. 7. As shown in this figure, the silica nanoparticles are in the amorphous form.

7.3. FTIR test

The result of FTIR test is shown in Fig. 8. It shows three peaks at about 1,100, 809, and 470 cm^{-1} due to Si–O bond. The band at 3,433 cm^{-1} indicates the carboxyl group attached at the surface of synthesized silica particles. The peak at about 1,633 cm^{-1} donates the hydroxyl group. In addition, these results have been shown by other researchers in the literature [26,27].

8. SEM test

The scanning electron microscopy (SEM) image of calcium sulfate precipitates is presented in Fig. 9 which demonstrates that the formed precipitates are calcium sulfate [12].

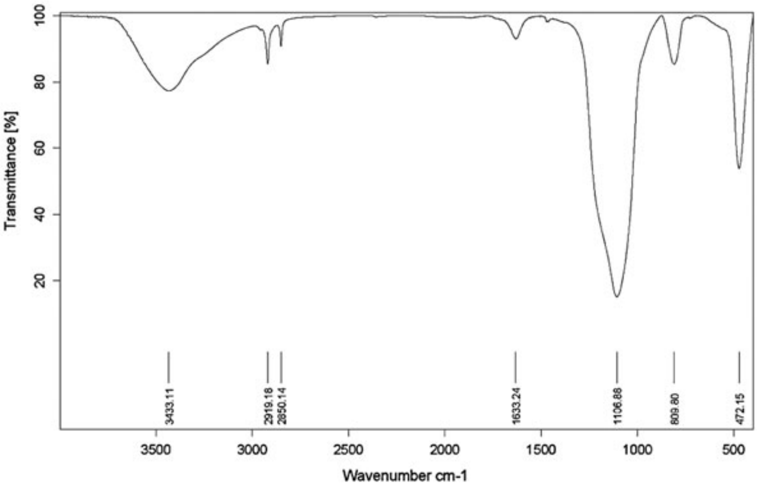

Fig. 7. XRD image of silica nanoparticles.

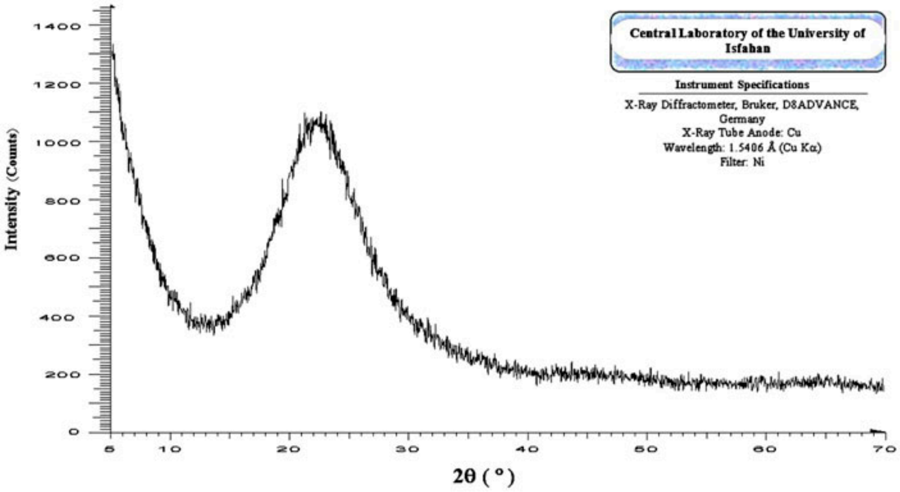

Fig. 8. FTIR spectrum of the silica nanoparticles.

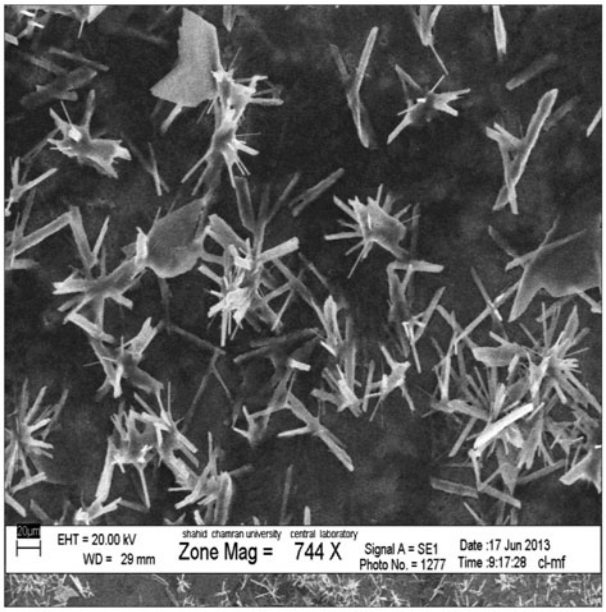

Fig. 9. SEM image of calcium sulfate precipitates [12].

9. Conclusion

Using silica nanoparticles, the reducing trend of the solution conductivity decreases up to a limit. After this limit, the trend of conductivity increasing would be reversed and the conductivity decreases, and as a result, the amount of precipitates increases. It could be concluded that silica nanoparticles were particularly effective as calcium sulfate crystal growth inhibitors. By the use of DETPMP scale inhibitor, the conductivity of the solution increases up to a limit. After this limit, the increasing DETPMP concentration could not change significantly the conductivity and the amount of precipitates would be constant. Using both nanoparticles and inhibitor simultaneously, it was showed that silica nanoparticles could improve the effect of DETPMP scale inhibitor significantly and could decrease the amount of scale formation more than before that each of them were used lonely. So it could be concluded that silica nanoparticles and DETPMP might be used as a novel scale inhibitor.

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