

# Distinguishing Anhydrate and Gypsum Scale in Mixing Incompatible Surface and Ground Waters During Water Injection Process

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**ABSTRACT:** *Determination of the type of precipitated calcium sulfate in mixing two incompatible injection and formation waters was studied experimentally in this work at two temperatures of 26°C and 80°C. Here the SEM, EDX and XRD techniques have been used to inspect the temperature effects on the morphology, type, and size of the precipitated calcium sulfate crystals. The results of this work show that the precipitated scales at these temperatures are calcium sulfate dihydrate and the temperature influences the size of crystals dramatically. The crystallization mechanism is the next issue which has been studied in this work. Measuring the amount of precipitated scale in the mixing of the incompatible waters versus time depicts the scale formation controlling mechanisms. According to the obtained results in this work, three primary nucleations, crystal growth, and secondary nucleation control the calcium sulfate scale precipitation.*

**KEYWORDS:** *Scale; Incompatible water; Nucleation; Crystallization; Calcium sulfate anhydrate; Gypsum.*

## INTRODUCTION

Water injection in reservoirs is a common method for pressure maintenance or pushing the oil toward production wells for increasing the oil recovery. The recovery of gas condensate reservoirs also can be enhanced by water injection. Determination of conditions at which the scale is formed in solution due to mixing incompatible waters is a crucial step in a water injection process for oil and gas reservoirs. Scale formation due to the mixing of injecting water with the reservoir formation water can induce serious damages in porous media as well as in surface facilities like boilers and pipes [1-5]. Prediction of the type of scales

which might be precipitated and the mechanisms affecting the process are two important issues which have been discussed in following.

Calcium sulfate is a common scale which is precipitated in porous media due to the mixing of injecting surface water with ground water which might cause serious problems. Calcium sulfate exists in three types of gypsum or dihydrate, bassanite or hemihydrate and halite or anhydrate. These three types have different characteristics and behavior so it is important to determine the type of calcium sulfate which might be precipitated.

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Despite the fact that the crystallization process of calcium sulfate has been investigated by different authors in the previous three decades, there is no clear specified temperature to distinguish the formation of calcium sulfate dihydrate and anhydrate. Calcium sulfate anhydrate is the most stable arrangement among others which is harder and more adherent and therefore more difficult to be removed [6, 7]. *Van't Hoff et al.*'s classical investigation [8] stated that the transition temperature for conversion of gypsum to anhydrate in pure water is 66°C while *Posnjak* [9], *MacDonald* [10] and *Bock* [11] based on the measurements of the solubility of gypsum and anhydrate in salt solution concluded this temperature to be in the range of 40 to 42°C. The reported temperatures for solutions with NaCl were lower. *Ostroff* states that all of these numbers are wrong as they are not compatible with the behavior of calcium sulfate [12]. Gypsum has been detected in core samples taken from reservoirs with temperatures much warmer than 42°C which shows that gypsum will not be converted to anhydrate for temperatures at this reported range. He experimentally and also with the thermodynamic calculations showed that gypsum will not be converted to anhydrate at a temperature below 97°C and for conversion of gypsum to anhydrate it must be first converted to hemihydrates. According to thermodynamic calculation, *Klepetsanis* [13] reported 50°C as the transition temperature although in his experiments at 80°C he faced with gypsum, not anhydrate. *Jamialhamadi and Muller* [6] studied the effect of temperature on the morphology of calcium sulfate experimentally for temperatures between 50 to 80°C and the results showed to be dihydrate[6]. It is surprising that in commercial software for predicting the type of calcium sulfate the transition temperature is between 42 to 97°C. So the results of this work could be very helpful as an indication of the experimental tests has been done to distinguish between these two types.

Doing experimental tests on the compatibility of mixed waters before injection tests could be very helpful in designing and interoperating of results. Supersaturation, contact time and nucleation are the main factors affecting the scale formation during water injection process [14]. Supersaturation is not enough condition for scale formation but is a necessary one. Changes in temperature, pressure, and mixing of incompatible waters are the parameters affecting the supersaturation in injection processes[15-18].

For scale formation, first, the ions consist the scale should be in contact to give the first nucleus. The time required for formation of the first nucleus is called induction time. There are several methods of predicting this time including measurement of turbidity of the solution at different time periods [19], temperature measurement technique [20], monitoring the solution specific conductivity[13]. Although there are several methods and lots of papers discussing the formation of the first nucleus in solution, the time at which the process ends or facing different behaviors is not fully described but it is very important when performing the dynamic injection tests[21]. When the injection studies in core samples are performed in labs, this time should be determined before to select an injection velocity which gives enough contact time for precipitation of scale due to mixing incompatible waters [21, 22].

Primary and secondary nucleation are two important stages of this process [23]. Primary nucleation is the stage that nucleus are generated in mixture with no crystalline matter. If the crystalline matters are formed in solution, they will be potential sites for generation of other crystals on them which is called secondary nucleation. *Mullin* [24] states that for a homogeneous reservoir there is a critical nucleolus that if the particle size is less than this size, it dissolves and if it is greater, it will continue to grow to minimize the free energy. Crystal growth happens in the metastable region and there is no nucleolus initiated at this stage[23].

In this study, the maximum amount of scale that might be produced by the mixing of injection and formation water first was examined by in-house software then examined by experiments. The amount of scale at different times was measured and attributed to different stages of crystallization. To confirm the results and also to measure the effect of temperatures on crystallization, the experiments have been done at both surface and reservoir temperatures. By comparing the amount of scale at different times for two temperatures, the importance of temperature on nucleation is also has been studied. The SEM, EDX and XRD techniques also were used to analyze the size and the type of crystals as well as differentiation of calcium sulfate anhydrates and anhydrate at low and high temperatures [25-30].

**Table 1: Ion concentration in both injection and formation water.**

Ion Type	Unit	Injection water	Formation water
Chloride (Cl <sup>-</sup> )	(mg/L)	23042	169597
Sodium (Na <sup>+</sup> )	(mg/L)	16857	82453
Calcium (Ca <sup>2+</sup> )	(mg/L)	0	24000
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	(mg/L)	4000	0
TDS	(mg/L)	43900	276050

## EXPERIMENTAL SECTION

### *The water samples preparation*

The injection (surface) and formation waters of the carbonate reservoir "A" in the south-west of Iran both have been prepared synthetically in the lab by adding the Merck<sup>®</sup> mineral salts to deionized waters. Then the formation and injection waters were mixed at different ratios. Finally, the amount of the precipitated scales has been measured at different times for two temperatures.

Table 1 shows the analysis of ions concentrations for both the injection and the formation used in this work. It should be noted that the real samples of this field contained other ions which are low in concentration (do not precipitate in experiments) and are not considered in synthetic water preparation. As it can be seen in this table, the formation and injection waters are reached in calcium and sulfate ions, respectively and chloride and sodium ions are the common ions in both glasses of water. It should be noted that the real water samples of this field contained other ions which are low in concentration and will not be precipitated for experiments in this work. So the other ions except those mentioned in Table 1 are not considered for synthetic water preparation. The Argentometric titration method in the lab was engaged to determine the concentration of chloride and Turbidimetric method was used for determination of sulphate ions [31]. The concentration of sodium ion was measured by atomic emission spectroscopy and the atomic absorption spectroscopy was used for the determination of calcium concentration (Device Model: Varian SpectrAA-10). The uncertainty of measurements is reported to be about 10 percent.

PSFSim<sup>®</sup> software (Pars Scale Formation Simulator, in-house software) has been used to predict the effect of the different thermodynamic conditions on scale formation at water injection in this reservoir. This software predicts the type and amount of scale formation

at static condition. The prediction of software for the amount of calcium sulfate at 26°C and 80°C were 0.44 and 0.48gr in 0.25 liter of solution, respectively which will be checked with experiments.

### *Experimental procedure*

There are lots of methods to predict the onset of nucleation and scale formation; however the conditions of the maximum potential of scale formation which occur at the end of the experiments are not well discussed.

In this work, more than 20 experiments have been done to find the maximum potential of scale formation (after which there would be no increase in the amount of the scales). It has been found that because of the low rate of reactions, reaching the maximum potential of scale which has been predicted by software takes time and is not instantaneous. The reported scale amount by commercial software is based on assuming the equilibrium thermodynamic condition. This time in this work was predicted by drawing the amount of scale by time. When the amount of scale was not changed with time, it shows that the equilibrium condition most probably is reached.

Tracing the number of precipitated scales in the mixing of waters versus time showed the dominant mechanisms in this process. Here after mixing of the injection and formation waters in 60/40 ratio and passage of time (reaction time), the mixtures were passed into a 0.4 μ filter paper. The dried precipitated scales on the filter paper were recorded as the amount of the scale for that time. Some of these samples then were analyzed by SEM, EDX, and XRD to check the size and type of the scale crystals.

## RESULTS AND DISCUSSION

### *Experimental results at the reservoir temperature*

Totally 11 mixtures of 60% injection and 40% formation water with the total volume of 250 cc prepared

**Table 2: Calcium Sulfate scale at reservoir condition.**

Sample Name	Time (hr)	The precipitated Scale (mg/0.25Liter)
S1	2	0.0613
S2	3.5	0.1748
S3	6	0.3239
S4	13	0.3350
S5	19	0.343
S6	23	0.3731
S7	25.5	0.3832
S8	32	0.4187
S9	48	0.4279
S10	70	0.4430
S11	80	0.4434

and were left at 80°C. Then the mixtures were filtered at different times. The amounts of the precipitated CaSO<sub>4</sub> scale versus time are shown in Table 2.

Fig. 1 shows the results of the amount of precipitated scale versus time at reservoir temperature. These results show three distinct zones. The first region duration is about 6 hours in which the amount of scale increases dramatically versus time. It seems that the controlling mechanism in this region is primary nucleation. At this region, the amount of precipitated scale increases dramatically with the passage of time; this behavior can be due to the formation of the nucleolus in solution by paring the calcium and sulfate ions. At the second region, which occurs between 6 and 19 hours, the amount of precipitated calcium sulfate scale remains almost constant and calcium sulfate crystal size increases; here this process is experimentally confirmed by SEM technique (section 3.3). At the last region, after 19 hours, the amount of the precipitated scale increases slowly and finally damped to a constant value at around 70 hours. It seems in the third region, the imperfection crystals can play the role of new crystallization sites to increase the scale formation. This region at which new nucleolus initiated on existing crystals is thought to be the secondary nucleation mechanism. At the end of 70 hours, the maximum of possible scale due to mixing the incompatible waters has been reached and no more scale will be formed by giving more time. The maximum precipitation of scale was 0.44 g in 0.25 liter of solution

which is in good agreement with the prediction of PSFSim<sup>®</sup> software at this temperature (0.50g).

#### **Experimental results at surface temperature**

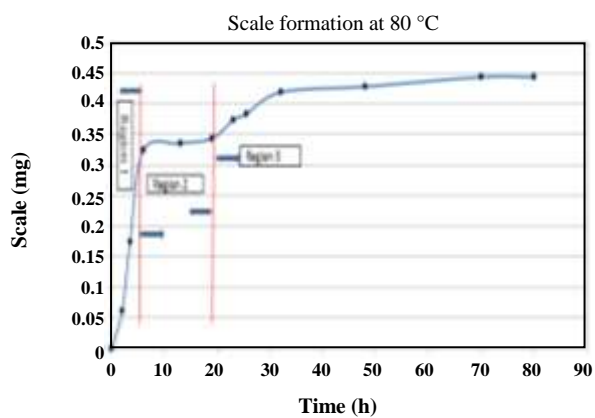
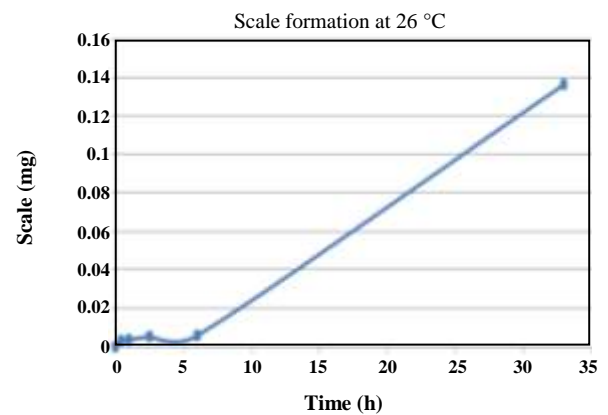
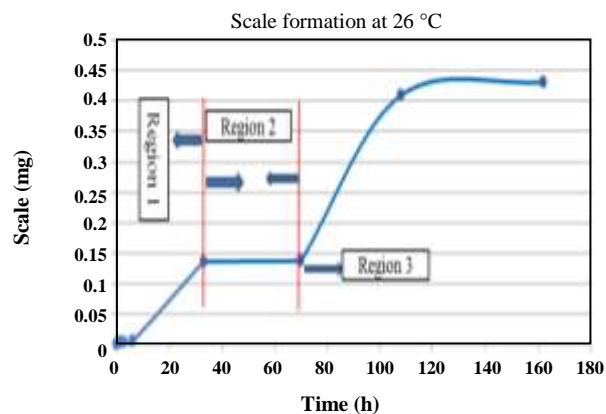
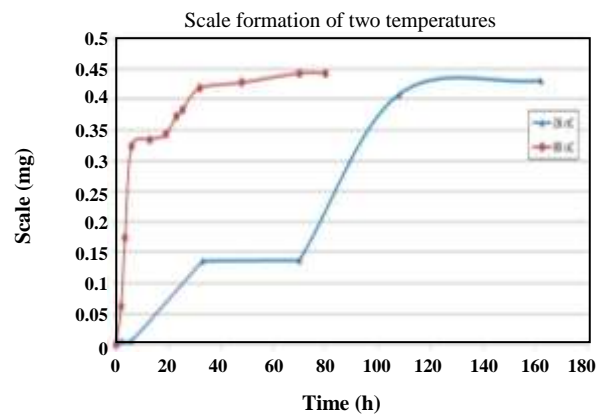
In order to study the temperature effects on the scale formation processes (mechanism and the amount of scale) and to confirm the distinguished zones, the experiments were repeated at 26°C. These tests have done for 8 samples at the same mixing ratios as the reservoir temperature. The results are reported in Table 3.

For experiments at 26°C the same as experiments at reservoir temperature, 3 regions with a different rate of scale precipitation were distinguished. At region 1 the nucleation is increasing then there is a transition region at which the crystals growth happens. In region 3, the secondary nucleation begins and the final amount of scale is getting at 162h.

To observe the trend of the plot at small times (between 0 and 35 hr), a zoom of data has been shown in Fig. 3. Fig. 4 shows the comparison of results of scale at two temperatures 80°C and 26°C. As it can be seen, the maximum potential of scale formation is reached in 70 h at 80°C while it is reached after 162h at 26°C. This shows that temperature is an important driving force for nucleation to occur. The maximum precipitation for the experiments at this temperature was 0.44g in 0.25 liter of solution which shows less than 10 percent difference with the prediction of PSFSim<sup>®</sup> software (0.48 g).

**Table3: Calcium Sulfate scale at surface condition.**

Sample Name	Time (h)	Scale (mg/0.25L)
W1	0.42	0.003
W2	1	0.0035
W3	2.5	0.0052
W4	6	0.0058
W5	32	0.1364
W6	70	0.1372
W7	108	0.4091
W8	162	0.4311

**Fig. 1: Amount of scale precipitated at reservoir temperature for different times.****Fig. 3: Calcium Sulfate at surface temperature (for times less than 35 h).****Fig.2: Amount of scale precipitated at surface temperature for different times.****Fig. 4: Comparing the Calcium Sulfate at reservoir and surface temperatures.**

According to the results at 26°C temperature, it can be concluded that the velocity of injection should be considered so that mixed injection and formation be in contact for at least 1 h. This means that at this

temperature for a core with 5 cm length, 11cm<sup>2</sup> surface area and porosity of 10 percent, the injection water velocity should be less than 5.5 cc/h to have enough contact time for precipitation of calcium sulphate scale.

Table 1: The summary of SEM and EDX results for the selected samples

Sample Name	Time	Temperature	Maximum length of crystals	Type of scale by EDX
	h	°C	Micron	
S2	2	80	200	Calcium Sulfate
W2		26	100	
S8	32	80	1100	
W5		26	170	

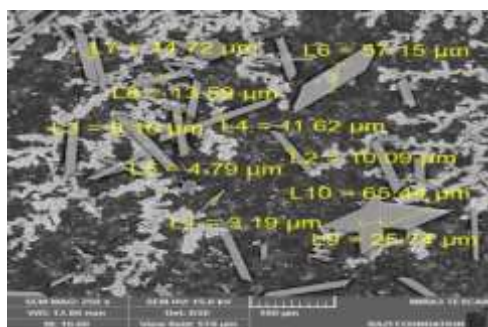
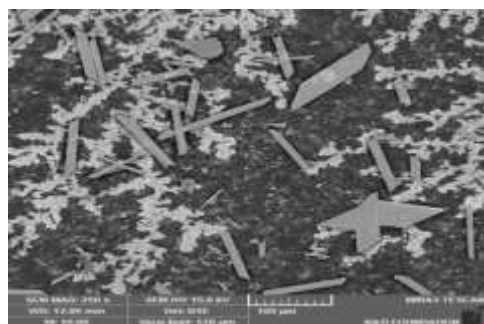
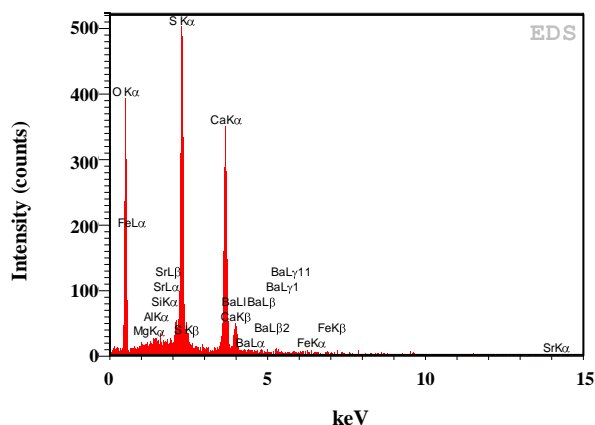


Fig.5: The EDX and SEM analysis results; a) EDX and b, c) SEM of the crystals of S2.

To confirm that these are the final potential of scales which can be achieved, two samples were left for 300 h at 80°C and 26°C. The amounts of scales were compared to the number of scales at these temperatures at 80°C and 26°C which showed no change.

#### Scale analysis by SEM, EDX, and XRD

To inspect the type of precipitated scale and also to investigate the size of formed crystals at different temperatures and times, four samples were selected to conduct the SEM and EDX analysis. The samples of the filtered scales have been collected at first 2 and 32 hours of the experiment. Table 4 gives the SEM and EDX analysis of the precipitated scales. Figs. 5 to 8 show the results of the SEM and EDX analysis of the samples. The scale type by EDX in all samples showed the calcium sulfate for all samples.

Comparing the size of crystals after 2 hours of the start of mixing the incompatible waters shows that the maximum size of crystals at 80°C is 2 times the one at 26°C. After 32 hours of mixing these waters, the maximum size of scales at 80°C would be almost 6.5 times the one at 26°C. This is probably because for samples at 80°C the crystal growth is already passed and for a sample at 26°C the crystal growth has been just started. The SEM results confirm the results of distinguished zones and attributed mechanisms at these zones.

The results of EDX have proved the type of scales to be calcium sulfate but to differentiate between gypsum and anhydrate, using the XRD technique was a must. So the scale precipitated at 26°C and 80°C very carefully kept without exposing in room humidity and were sent for XRD analysis to check the type of precipitated calcium sulfate. As has been shown in Figs. 9 and 10, the precipitated scale is gypsum. So the temperature in the range of 42°C could not be considered as the transition temperature of gypsum to anhydrate. The results of this work could have

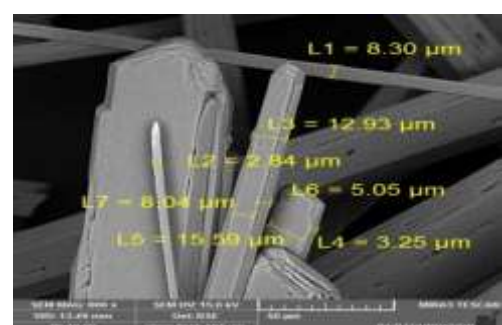
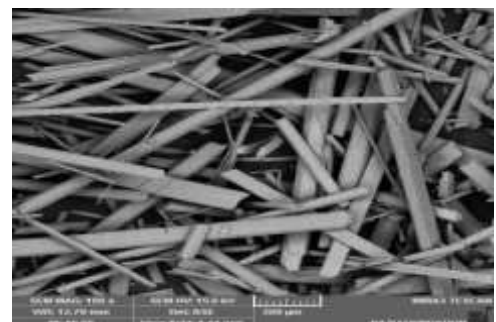
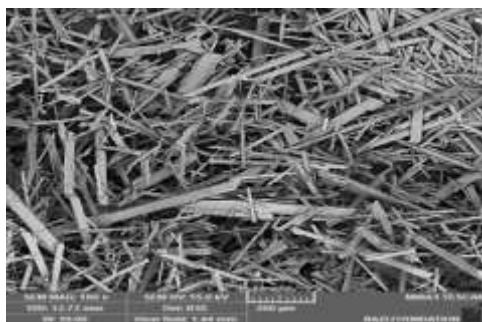
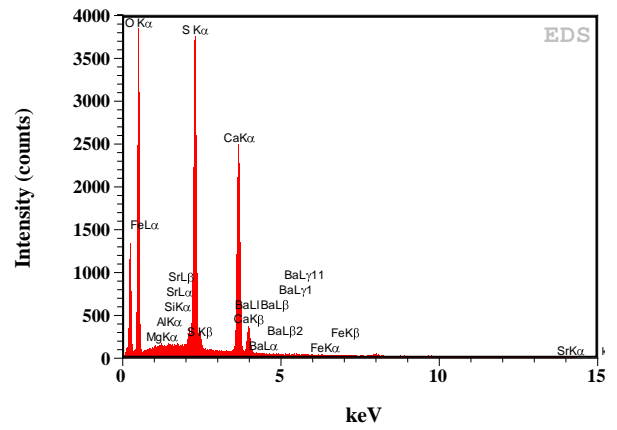
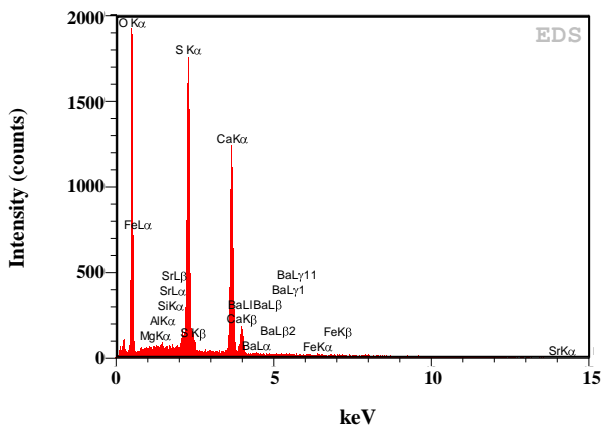


Fig. 6: The EDX and SEM analysis results; a) EDX and b, c) SEM of the crystals of W2.

Fig.7: The EDX and SEM analysis results; a) EDX and b, c) SEM of the crystals of S8.

many applications in the static and dynamic test. When it is required to know how long it takes to have precipitation happens in porous media like for designing the injection studies, the results of these tests could be helpful.

**CONCLUSIONS**

1- The mechanisms controlling the scale formation have been determined by plotting the amount of scale due to the mixing of incompatible water versus time.

2- Three regions, at which primary nucleation, transition, and secondary nucleation control the mechanism, have been distinguished by experiments.

3- The maximum potential of scale formation in the mixing of injection and formation waters occurred at 70 h and 162 h at 80°C and 26°C, respectively. This means the higher driving force at higher temperatures.

4- The SEM analysis confirms the crystal growth for times after the first region which is primary nucleation.

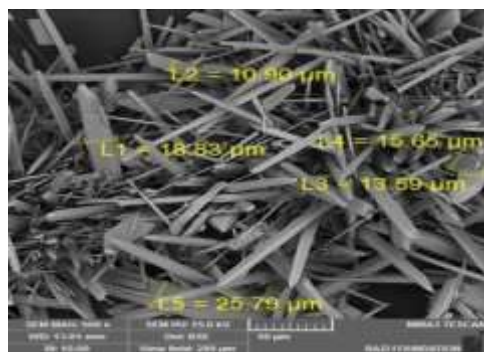
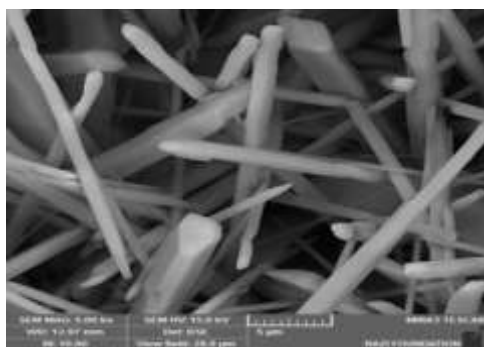
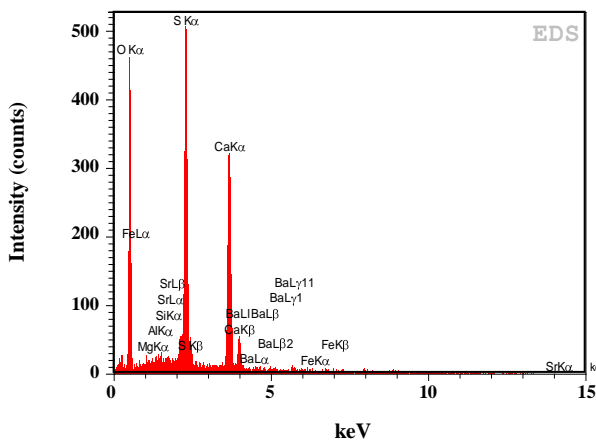


Fig. 8: The EDX and SEM analysis results; a) EDX and b, c) SEM of the crystals of W5.

5- The XRD results show that the precipitated scale at 26°C and 80°C are calcium sulfate dihydrate, not anhydrate and the reported temperatures in the range of 42°C could not be considered as the transition temperature of gypsum to anhydrate.

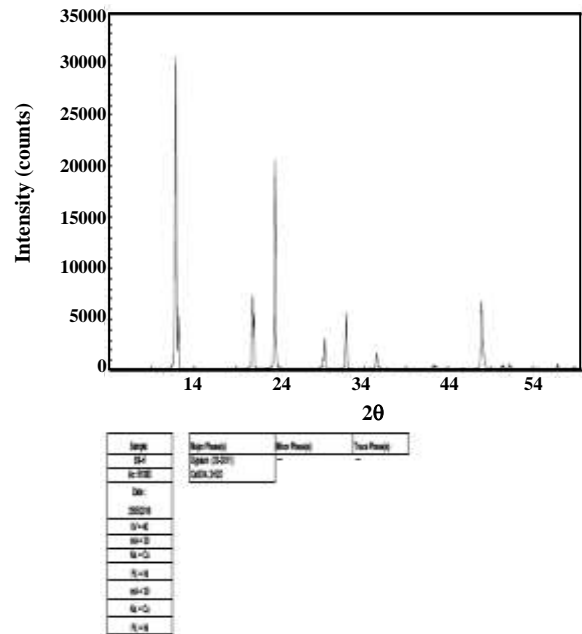


Fig. 9: The XRD analysis of sample S8.

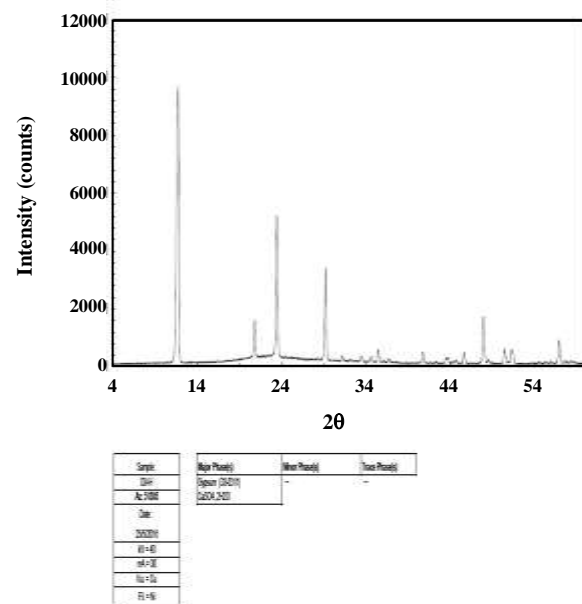


Fig. 10: The XRD analysis of sample W5.

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