

# STUDY OF CALCIUM SULFATE SCALING INDEX TENDENCY CALCULATIONS AT DIFFERENT TEMPERATURE CONDITIONS IN INJECTION WATER SAMPLES FROM OILFIELDS

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## ABSTRACT

Calcium sulfate scale is a type of scale found in petroleum industry and shows serious problem, because it can plug pore media and cause a decrease in production rate.

Actual calcium sulfate ( $\text{CaSO}_4$ ) concentrations of S1, S2, S3 and S4 injection water samples were in the range of 0.0208 to 0.4583 meq/l. While, the values of solubility of S1, S2, S3 and S4 water samples at 77,145 and 177°F are in a range of 23.20 to 27.43 meq/l. Based on the results of calcium sulfate scaling tendency calculations showed that the values of solubility of S1, S2, S3 and S4 water samples at various temperature conditions (77,140 and 175°F) are higher than actual  $\text{CaSO}_4$  concentrations for the same water samples. No occurrence of  $\text{CaSO}_4$  scale was found in all analyzed injection water samples at different temperature conditions (77,140 and 175°F).

Key words : calcium sulfate scale, scaling index tendency calculation, solubility of injection water sample and actual  $\text{CaSO}_4$  concentration.

## I. INTRODUCTION

Calcium sulfate scale has long been recognized as one of the serious problems in oil and gas production leading to reduced production rates as flow becomes restricted.

Calcium sulfate scale is defined as the precipitation of hard, adherent deposits of inorganic solid originating from aqueous media. This constitutes sulfate of the alkaline earth metals calcium, barium and strontium and complex salts of iron. Generally, the process of the scale deposition occurs when the product solubility of a compound considered is exceeded. The main purpose of this study was firstly, to determine chemical compositions of four injection water samples (S1, S2, S3 and S4). Secondly, to know calcium sulfate scaling index tendency calculations at various temperatures (at 77,140 and 175°F) conditions in injection water samples from the oilfield.

## II. STRUCTURE AND NATURAL FORM OF ANHYDRITE

The structure of anhydrite is a three dimensional view shown in Figure 1 and illustrates the packing

together of the Ca ions and tetrahedral  $\text{SO}_4$  groups. The large calcium ions are packed between  $\text{SO}_4$  groups, and dark areas are sulfur atoms<sup>(1,2,3)</sup>.

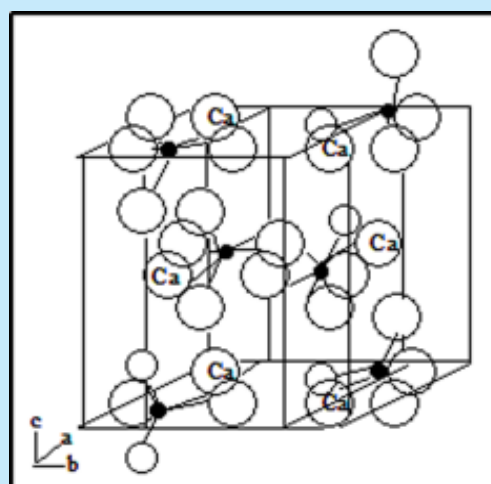


Figure 1  
Structure of anhydrite

Source: Crystal structure of minerals, 1965,  
Bell. G and Sons, Cornell University

The natural form of anhydrite and clear gypsum crystal with yellow sulfur band along bottom can be seen Figures 2 and 3 below.

### III. $\text{CaSO}_4$ SOLUBILITY

Solubility of calcium sulfate scale is affected by some factors<sup>(4,5,6)</sup>, such as temperature, dissolved salts content and pressure. The explanations are as follows:

#### A. Effect of temperature

Generally, gypsum is the stable form at low temperature, whereas anhydrite is formed at higher tem-

perature. Gypsum solubility increases with temperature up to about 40°C, then decreases with temperature as shown in Figure 4. This is quite different from the temperature-solubility behaviour of  $\text{CaCO}_3$ . Firstly, gypsum is considerably more soluble than  $\text{CaCO}_3$  in normal temperature range of interest. The solubility of  $\text{CaSO}_4$  in distilled water is 2080 mg/l, while solubility of  $\text{CaCO}_3$  in distilled water is 53 mg/l. Secondly, the maximum in the gypsum curve explains that an increase in temperature could either increase or decrease the solubility of gypsum depending on which part of the temperature curve it is concerned with. This is decidedly different from  $\text{CaCO}_3$  where an

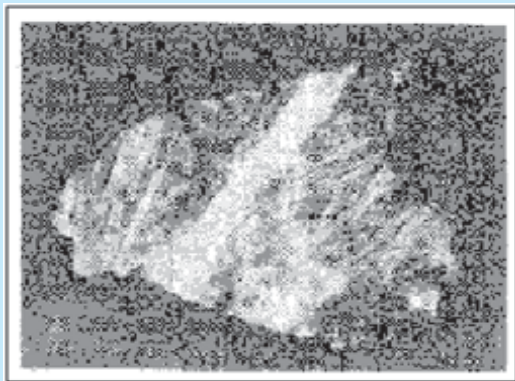


Figure 2  
Anhydrite (the natural form)

Source : Courtesy U.S. National Museum

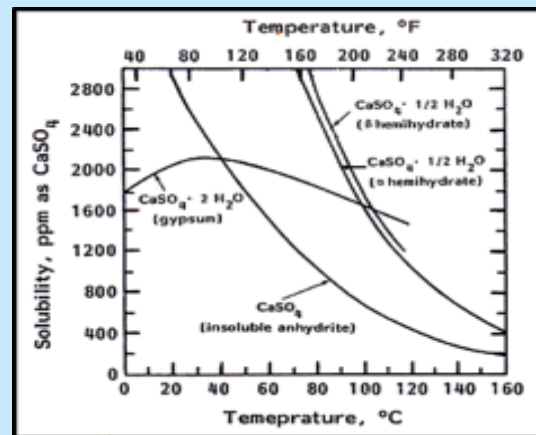


Figure 4  
Effect of temperature on calcium sulfate solubility

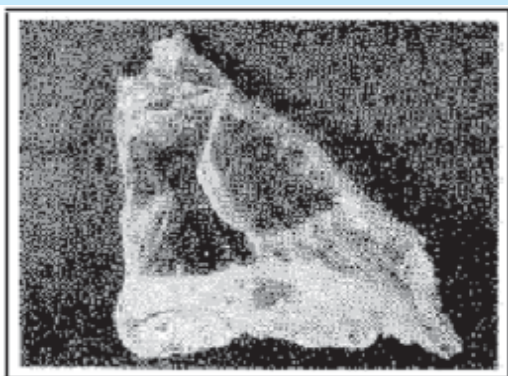


Figure 2.3  
Clear gypsum crystal with yellow sulfur band along bottom

Source : Courtesy U.S. National Museum

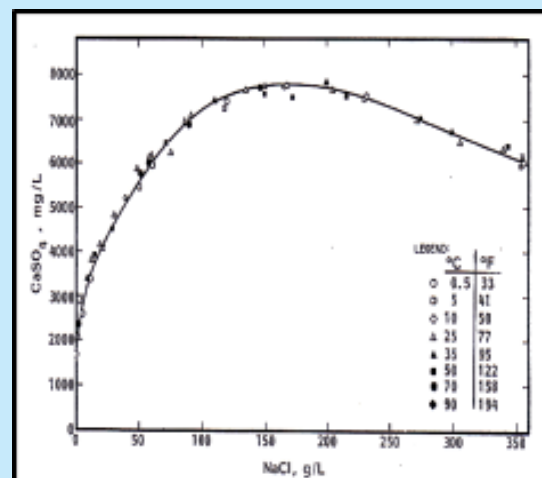


Figure 5  
Effect of NaCl on  $\text{CaSO}_4$  solubility

increase in temperature always decreases the solubility. Note that above about 40 °C, anhydrite becomes less soluble than gypsum, so it could reasonably be expected that anhydrite might be the preferred form of CaSO<sub>4</sub> in deeper, hotter wells. Actually, the temperature at which the scale changes from gypsum to anhydrite or hemi-hydrate is a function of many factors, including dissolved salt content, pressure, flow conditions and the speed at which different forms of CaSO<sub>4</sub> can precipitate from solution.

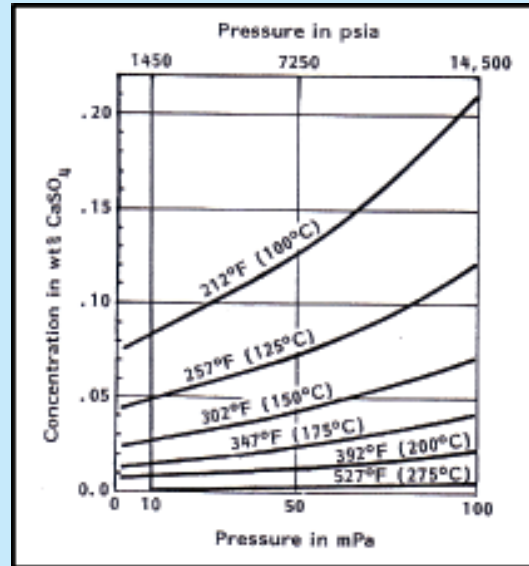
The curve for the solubility of anhydrite intersects the solubility curve for gypsum at 42°C. This is transition point of gypsum-anhydrite. Above 100°C, anhydrite will precipitate directly in a stirred or flowing system. If the system is quiescent, hemi-hydrate solubility becomes limiting. Conversion to anhydrite could be expected with time.

**B. Effect of dissolved salts**

The presence of NaCl or dissolved salts other than calcium or sulfate ions increases the solubility of gypsum or anhydrite, up to a salt concentration of about 150,000 mg/l. Further increases in salt content decrease CaSO<sub>4</sub> solubility. This case is described in Figure 5 below.

**C. Effect of pressure**

The solubility of calcium sulfate in water increases with pressure. The effect of increased pressure is physical, resulting in a reduction in the size of the



Effect of pressure on concentration of calcium sulfate

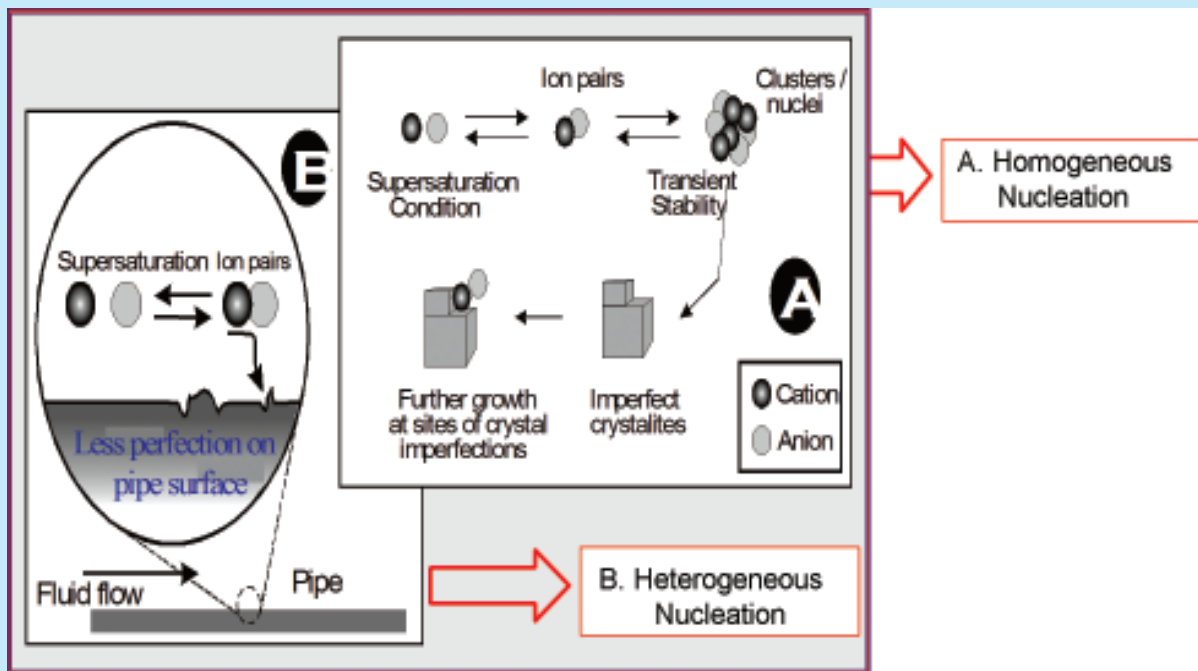


Figure 7  
Mechanism of the occurrence of calcium sulfate scale

calcium sulfate molecule. Although rather large increases in pressure are necessary to effect a significant change in molecular size, the effect of pressure can be important and beneficial in injection wells where appreciable pressure may be developed. The effect of pressure and temperature on anhydrite solubility is shown in Figure 6.

#### IV. MECHANISM OF CaSO<sub>4</sub> OCCURENCE

One of the most successful methods of secondary recovery is water flooding, a process in which water is pumped down an injection well to flush or remove oil from the formation as it moves along to a producing well. The oil, along with the injected water and connate water, is recovered at the well. Although

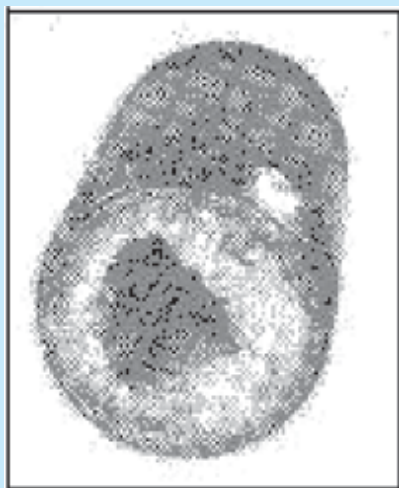


Figure 8  
The form of CaSO<sub>4</sub> scale in pipe

Table 1  
The results of determination of chemical compositions and ionic strength calculation for S1 - injection water sample

Ion	Concentrations (mg/l)	Ionic Strength Calculation	
		Conversion Factor	Results
Na <sup>+</sup>	772,10	2,20E-05	1,70E-02
Ca <sup>++</sup>	12,86	5,00E-05	6,43E-04
Mg <sup>++</sup>	2,85	8,20E-05	2,33E-04
Cl <sup>-</sup>	356,78	1,40E-05	4,99E-03
CO <sub>3</sub> <sup>=</sup>	0,00	3,30E-05	0,00E+00
HCO <sub>3</sub> <sup>-</sup>	1240,78	8,20E-06	1,02E-02
SO <sub>4</sub> <sup>=</sup>	22,00	2,10E-05	4,62E-04
Total Ionic Strength ( μ ) =			0,0335



Figure 9  
Calcium sulfate scale on meter-run screens

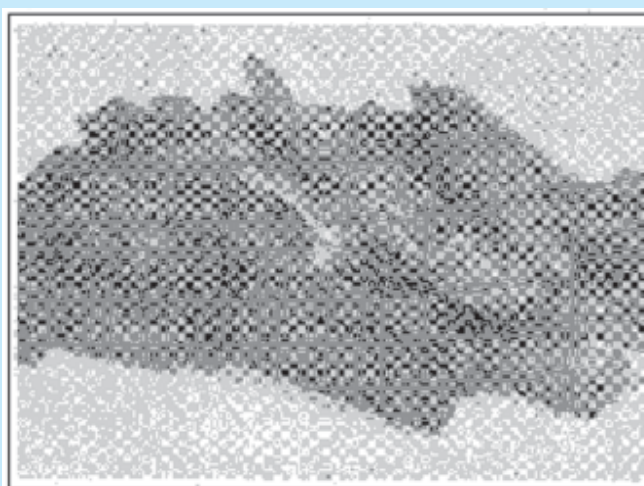


Figure 10  
Large crystal of gypsum produced from brine recovery operation



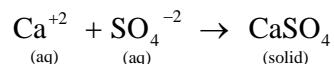
this method has been highly successful and is in wide use today, it is fraught with many problems. A major one is *scale*, such as calcium sulfate scale (CaSO<sub>4</sub>). Scale is formed through several stages :

1. mixture of water and dissolved salts.
2. solution.
3. supersaturation.
4. nucleation.
5. crystal growth.
6. scale.

Salts (such as NaCl, CaCl<sub>2</sub> and NaSO<sub>4</sub> etc ) are dissolved into water and the mixtures of water and salts form solution. When the water as solvent can not dissolve the salts anymore, this condition is called supersaturation. Next stage is nucleation process, from time to time after nucleation process is followed by crystal growth process. Last stage is the occurrence of scale.

Generally, the process of the calcium sulfate scale deposition occurs when the product solubility of a compound considered is exceeded.

Chemical reaction of the occurrence of calcium sulfate scale can be written as follows:



Mechanism of the formed calcium sulfate scale is described clearly in Figure 4.1.

Some examples of calcium sulfate scale were found in the petroleum industry can be seen in Figures 8, 9 and 10.

## V. METODOLOGY

Solubility value for CaSO<sub>4</sub> can be calculated using the following equation values of K<sub>sp</sub> are known for the compound:

**Table 2**  
The results of caso<sub>4</sub> scaling index tendency calculations at Different temperature in S1 - injection water sample

Temp. °F	K	4K		
77	1,89E-04	7,57E-04		
140	1,89E-04	7,57E-04		
175	1,54E-04	6,14E-04		
Ion	Concentrations (mg/l)	Conversion Factor	M (moles/l)	
Ca <sup>++</sup>	12,86	2,50E-05	3,22E-04	
SO <sub>4</sub> <sup>=</sup>	22,00	1,05E-05	2,31E-04	
		X = Δ M =	9,05E-05	
S @ 77°F =	27.43 meq/l			
S @ 140°F =	27.43 meq/l			
S @ 175°F =	24.70 meq/l			
Ion	Concentrations (mg/l)	Equivalent Weight	Concentrations (meq/l)	
Ca <sup>++</sup>	12,86	20,00	0,6430	
SO <sub>4</sub> <sup>=</sup>	22,00	48,00	0,4583	
Actual CaSO <sub>4</sub> concentration = 0.4583 meq/l				
S > actual , so CaSO <sub>4</sub> scale is unlikely				

**Table 3**  
The results of determination of chemical compositions and ionic strength calculation for S2 - injection water sample

Ion	Concentrations (mg/l)	Ionic Strength Calculation	
		Conversion Factor	Results
Na <sup>+</sup>	725,40	2,20E-05	1,60E-02
Ca <sup>++</sup>	22,13	5,00E-05	1,11E-03
Mg <sup>++</sup>	3,03	8,20E-05	2,48E-04
Cl <sup>-</sup>	356,78	1,40E-05	4,99E-03
CO <sub>3</sub> <sup>=</sup>	24,05	3,30E-05	7,94E-04
HCO <sub>3</sub> <sup>-</sup>	1197,99	8,20E-06	9,82E-03
SO <sub>4</sub> <sup>=</sup>	8,00	2,10E-05	1,68E-04
			3,31E-02
Total Ionic Strength (μ) =			0,0331

Solubility (meq/L) =

$$S = 1000 [(X^2 + 4 K_{sp})^{1/2} - X]$$

Derivation of this equation follows the common ion effect. The maximum solubility of a slightly soluble salt is obtained when the concentrations of the cation and anion are equal. For example : given s saturated solution of  $\text{CaSO}_4$  in water, where the  $\text{Ca}^{+2}$  and  $\text{SO}_4^{-}$  concentrations are equal :

$\text{Ca}^{+2}$  concentration = S moles/liter.

$\text{SO}_4^{-}$  concentration = S moles / liter

$$K_{sp} = (S)(S) = S^2$$

$$S = (K_{sp})^{1/2}$$

The solubility of calcium sulfate is equal to S moles/liter, which is simply the square root of the molar solubility product constant.

However, in most natural waters, the cation and anion concentration are not equal. In this case, the difference between the two concentration is called the excess common ion concentration. The presence of excess common ion reduces the solubility of the salt unless a complex ion or ion pair, such as neutral magnesium sulfate, forms and offsets the effect. For example:

$\text{Ca}^{+2}$  concentration = S moles/liter.

$\text{SO}_4^{-}$  concentration = S moles / liter

In this case, the sulfate ion concentration as the larger of the two has been selected randomly. The amount by which the sulfate ion concentration exceeds the calcium concentration, X, is the excess common ion concentration.

$$K_{sp} = (S)(S + X) = S^2 + SX$$

The calcium sulfate solubility is equal to S moles/liter, since that is the maximum amount of calcium sulfate which can be performed by combining S moles of  $\text{Ca}^{+2}$

**Table 4**  
The results of  $\text{CaSO}_4$  scaling index tendency calculations at different temperature in S2 - injection water sample

Temp. °F	K	4K		
77	1,89E-04	7,54E-04		
140	1,89E-04	7,54E-04		
175	1,53E-04	6,12E-04		
Ion	Concentrations (mg/l)	Conversion Factor	M (moles/l)	
$\text{Ca}^{++}$	22,13	2,50E-05	5,53E-04	
$\text{SO}_4^{-}$	8,00	1,05E-05	8,40E-05	
		X = Δ M =	4,69E-04	
S @ 77°F =	26.99 meq/l			
S @ 140°F =	26.99 meq/l			
S @ 175°F =	24.27 meq/l			
Ion	Concentrations (mg/l)	Equivalent Weight	Concentrations (meq/l)	
$\text{Ca}^{++}$	22,13	20,00	1,1065	
$\text{SO}_4^{-}$	8,00	48,00	0,1667	
Actual $\text{CaSO}_4$ concentration = 0.1667 meq/l				
S > actual , so $\text{CaSO}_4$ scale is unlikely				

**Table 5**  
The results of determination of chemical compositions and ionic strength calculation for S3 - injection water sample

Ion	Concentrations (mg/l)	Ionic Strength Calculation	
		Conversion Factor	Results
$\text{Na}^{+}$	559,70	2,20E-05	1,23E-02
$\text{Ca}^{++}$	12,89	5,00E-05	6,45E-04
$\text{Mg}^{++}$	3,52	8,20E-05	2,89E-04
$\text{Cl}^{-}$	89,19	1,40E-05	1,25E-03
$\text{CO}_3^{-}$	24,05	3,30E-05	7,94E-04
$\text{HCO}_3^{-}$	1210,22	8,20E-06	9,92E-03
$\text{SO}_4^{-}$	1,00	2,10E-05	2,10E-05
			2,52E-02
Total Ionic Strength (μ) =			0,0252

with  $(S + X)$  moles of  $SO_4^{2-}$ .

Rearranging :

$$S^2 + SX - K_{sp} = 0$$

Taking the positive root of the quadratic equation :

for a divalent ion:

$$S \text{ (equiv./L)} = (X^2 + 4 K_{sp})^{1/2} - X$$

or :

$$S \text{ (meq/L)} = 1000 [X^2 + 4 K_{sp}]^{1/2} - X$$

The "actual concentration" of  $CaSO_4$  in solution is equal to the smaller of the  $Ca^{+2}$  or  $SO_4^{2-}$  concentrations (expressed in meq/liter) in the water of interest, since the smaller concentration limits the amount of calcium sulfate which can be formed <sup>(4,5,7,8)</sup>.

The calculated calcium sulfate solubility,  $S$  (meq/liter), is compared with the actual concentration to determine if scale formation is likely.

Case	Summary
$S = \text{Actual}$	The water is saturated with $CaSO_4$ .
$S > \text{Actual}$	The water is undersaturated with $CaSO_4$ . Scale is unlikely.
$S < \text{Actual}$	The water is supersaturated with $CaSO_4$ . Scale is likely

This formula can be used to calculate the solubility of any divalent salt such as calcium sulfate ( $CaSO_4$ ), barium sulfate ( $BaSO_4$ ) or strontium sulfate ( $SrSO_4$ ).

## VI. RESULTS

Water analysis and calcium sulfate scaling index tendency calculations were focused on four injection water samples, namely: S1, S2, S3 and S4. Before injection water used as displacement fluid in water flooding process, initial stage must be carried out, was water analysis. It plays important role not only in water analysis, but also re-

**Table 6**  
The results of  $CaSO_4$  scaling index tendency calculations at different temperature in S3 - injection water sample

Temp. °F	K	4K		
77	1,73E-04	6,91E-04		
140	1,73E-04	6,92E-04		
175	1,38E-04	5,53E-04		
Ion	Concentrations (mg/l)	Conversion Factor	M (moles/l)	
$Ca^{++}$	12,89	2,50E-05	3,22E-04	
$SO_4^{2-}$	1,00	1,05E-05	1,05E-05	
			$X = \Delta M = 3,12E-04$	
S @ 77°F =	25.97 meq/l			
S @ 140°F =	25.99 meq/l			
S @ 175°F =	23.20 meq/l			
Ion	Concentrations (mg/l)	Equivalent Weight	Concentrations (meq/l)	
$Ca^{++}$	12,89	20,00	0,6445	
$SO_4^{2-}$	1,00	48,00	0,0208	
Actual $CaSO_4$ concentration = 0.0208 meq/l				
S > actual , so $CaSO_4$ scale is unlikely				

**Table 7**  
The results of determination of chemical compositions and ionic strength calculation for S4 - injection water sample

Ion	Concentrations (mg/l)	Ionic Strength Calculation	
		Conversion Factor	Results
$Na^+$	578,90	2,20E-05	1,27E-02
$Ca^{++}$	7,32	5,00E-05	3,66E-04
$Mg^{++}$	2,50	8,20E-05	2,05E-04
$Cl^-$	169,47	1,40E-05	2,37E-03
$CO_3^{2-}$	12,02	3,30E-05	3,97E-04
$HCO_3^-$	910,72	8,20E-06	7,47E-03
$SO_4^{2-}$	11,00	2,10E-05	2,31E-04
			2,38E-02
Total Ionic Strength ( $\mu$ ) =			0,0238

lated to many factors, such as : water quality, injection - formation water compatibility, water-rock compatibility, and even water flooding analysis. The results of laboratory water analysis gave valuable informations, among of them, namely:

- a. Type of cations and anions were found in water samples.
- b. Concentrations of cations and anions in water samples.
- c. Which ions have potential to form calcium sulfate scaling tendency.

The results of determination of chemical compositions in the analyzed water samples were tabulated in Tables 1, 3, 5 and 7.

The obtained water analysis data were used to calculate calcium sulfate scaling tendency in the water samples with using equation as explained in Section V. The results of calcium sulfate scaling index tendency calculations at different temperature conditions can be seen in Table 2 ( for S1-water sample), Table 4 (for S2-water sample),

Table 6 ( for S3- water sample), Table 8 (for S4-water sample). Concentration of calcium ( $Ca^{+2}$ ) and sulfate ( $SO_4^{-}$ ) ions in the water samples were tabulated briefly in Table 9. All results of scaling index tendency calculations at different temperature ( 77,

**Table 8**  
The results of  $CaSO_4$  Scaling index tendency calculations at different temperature in S4 - injection water sample

Temp. °F	K	4K		
77	1,70E-04	6,79E-04		
140	1,70E-04	6,80E-04		
175	1,36E-04	5,42E-04		
Ion	Concentrations (mg/l)	Conversion Factor	M (moles/l)	
$Ca^{++}$	7,32	2,50E-05	1,83E-04	
$SO_4^{-}$	11,00	1,05E-05	1,16E-04	
		$X = \Delta M =$	6,76E-05	
S @ 77°F =	25.99 meq/l			
S @ 140°F =	26.02 meq/l			
S @ 175°F =	23.21 meq/l			
Ion	Concentrations (mg/l)	Equivalent Weight	Concentrations (meq/l)	
$Ca^{++}$	7,32	20,00	0,3662	
$SO_4^{-}$	11,00	48,00	0,2292	
Actual $CaSO_4$ concentration = 0.2292 meq/l				
S > actual , so $CaSO_4$ scale is unlikely				

**Table 9**  
Summary of the results of calcium and sulfate ions concentration determinations in injection water samples (S1, S2, S3 and S4) from oilfield

Ions	Concentrations of ions (mg/l) in Injection Water Samples			
	S1	S2	S3	S4
Calcium ( $Ca^{+2}$ )	12,86	22,13	12,89	7,32
Sulfate ( $SO_4^{-}$ )	22,00	8,00	1,00	11,00



**Table 10**  
**Summary of the results of scaling index tendency calculations**  
**at different temperature conditions in injection water samples from oilfield**

Water Sample	Solubility (meq/l)	Actual CaSO <sub>4</sub> Concentration (meq/l)	REMARKS	
S1	S at 77 <sup>0</sup> F = 27.43	0,4583	S > actual	CaSO <sub>4</sub> scale was unlikely
	S at 140 <sup>0</sup> F = 27.43	0,4583	S > actual	CaSO <sub>4</sub> scale was unlikely
	S at 175 <sup>0</sup> F = 24.70	0,4583	S > actual	CaSO <sub>4</sub> scale was unlikely
S2	S at 77 <sup>0</sup> F = 26.99	0,1667	S > actual	CaSO <sub>4</sub> scale was unlikely
	S at 140 <sup>0</sup> F = 26.99	0,1667	S > actual	CaSO <sub>4</sub> scale was unlikely
	S at 175 <sup>0</sup> F = 24.27	0,1667	S > actual	CaSO <sub>4</sub> scale was unlikely
S3	S at 77 <sup>0</sup> F = 25.97	0,0208	S > actual	CaSO <sub>4</sub> scale was unlikely
	S at 140 <sup>0</sup> F = 25.99	0,0208	S > actual	CaSO <sub>4</sub> scale was unlikely
	S at 175 <sup>0</sup> F = 23.20	0,0208	S > actual	CaSO <sub>4</sub> scale was unlikely
S4	S at 77 <sup>0</sup> F = 25.99	0,2292	S > actual	CaSO <sub>4</sub> scale was unlikely
	S at 140 <sup>0</sup> F = 26.02	0,2292	S > actual	CaSO <sub>4</sub> scale was unlikely
	S at 175 <sup>0</sup> F = 23.21	0,2292	S > actual	CaSO <sub>4</sub> scale was unlikely

145 and 177<sup>0</sup>F) conditions in the injection water samples from oilfield have been tabulated and summarized in Table - 10 briefly. Generally, the values of solubility of S1, S2, S3 and S4 water samples at various temperature conditions (77, 140 and 175<sup>0</sup>F) were in a range of 23.20 to 27.43 meq/l. While, actual CaSO<sub>4</sub> concentrations of S1, S2, S3 and S4 water samples were in a range of 0.0208 to 0.4583 meq/l. In this case, the values of solubility of S1, S2, S3 and S4 water samples at certain temperature above are higher than actual CaSO<sub>4</sub> concentrations of the same water samples. So, CaSO<sub>4</sub> scale was unlikely or not formed in S1, S2, S3 and S4 water samples at various temperature conditions (77,140 and 175<sup>0</sup>F).

## VII. CONCLUSIONS

All results of water analysis and calcium sulfate scaling index tendency calculations have been obtained and can be concluded as follows:

1. Based on the results of water analysis, concen-

trations of calcium ion (Ca<sup>+2</sup>) were in a range of 7.32 to 22.13 mg/l, and concentrations of sulfate (SO<sub>4</sub><sup>=</sup>) ion are in a range of 1 to 22 mg/l for S1, S2, S3 and S4 injection water samples.

2. The results of calcium sulfate scaling index tendency calculation indicated that the values of solubility of S1, S2, S3 and S4 water samples at 77,145 and 177<sup>0</sup>F are in a range of 23.20 to 27.43 meq/l.
3. Actual CaSO<sub>4</sub> concentrations of S1, S2, S3 and S4 water samples were in a range of 0.0208 to 0.4583 meq/l.
4. The values of solubility of S1, S2, S3 and S4 water samples at various temperature conditions (77,140 and 175<sup>0</sup>F) are higher than actual CaSO<sub>4</sub> concentrations for the same water samples.
5. CaSO<sub>4</sub> scale was not formed in all analyzed injection water samples at different temperature conditions (77,140 and 175<sup>0</sup>F).

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