# LABORATORY STUDY OF CALCIUM SULFATE SOLUBILITY CALCULATION BY USING SKILLMAN, McDONALD, AND STIFF METHOD

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## *ABTRACT*

*Calcium sulfate scale is one of serious problems and must be solved accurately in petroleum industry. It can plug pore media consequently decreases production rate. Therefore, it is very important to know injection water quality of S1, S2, S3 water samples by means of calculating* $CaSO_4$ *solubility. Each injection water sample has different* $CaSO_4$ *solubility.*

*The* $CaSO_4$ *solubility of S3 produced water is usually higher than S2 and S1 solubility. Because it contains the highest calcium and sulfate ion concentrations compared with S2 and S1. No* $CaSO_4$ *scale is found in all analyzed water sample.*

***Key words**: Calcium sulfate solubility, water, method, water analysis, calculation*

## I. INTRODUCTION

Oilfield scale is defined as the precipitation of hard, adherent deposits of inorganic solid originating from aqueous media. The types of scale found in oilfield are firstly, carbonate: such as calcium carbonate scale ($CaCO_3$) and secondly, sulfate: such as calcium sulfate scale ($CaSO_4$) or barium sulfate scale ($BaSO_4$). Generally, the process of the scale deposition occurs when the product solubility of a compound considered is exceeded (1,2,3). Calcium sulfate scale is one of the serious problems and commonly found in oil and gas production. In oilfield, water is injected into formation in order to displace crude oil that the crude oil can be produced. The function of water is as displacement to improve oil recovery factor (water flooding method). A lot of water is required for water flooding process, so injection water may be taken from different water sources, such as river water (S1) , water from gathering station (S2) and produced water from certain well (S3) located in Riau oilfield. So, the produced water is not thrown away into environment, but it will be treated and used as injection water. Before implementation water of injection method in oilfield, water quality test should be carried out. The objectives of this research are firstly, to analyze water completely by using API – RP 45. Secondly, to calculate calcium sulfate scale solubility at various temperature (at 77 $^oF$, 140 $^oF$ and 175 $^oF$) conditions on the three water sources using Skillman, McDonald and Stiff method. The results of water analysis and calcium sulfate solubility calculation will give valuable information about the S1, S2 and S3 water quality. If, the S1, S2 and S3 water samples can form scale, the quality of water samples are poor. Consequently, they should be treated by filtration or chemical process. On the other hand, if no scale is found in the S1, S2, S3 water samples, it means that these samples have good water quality. As a result they can be used as injection water without any treatment. Good injection water quality is required when they are used for water flooding process.

## II. $CaSO_4$ SOLUBILITY

The crystal structure of anhydrite calcium ions of tetrahedral $SO_4$ groups is shown in Figure 2.1. The large calcium ions are packed between $SO_4$ groups, while dark circles are sulfur atoms (2,4,8).

Solubility of calcium sulfate scale is affected by some factors (3,5,6), such as temperature, dissolved salts content and pressure.

### A. *Effect of temperature*

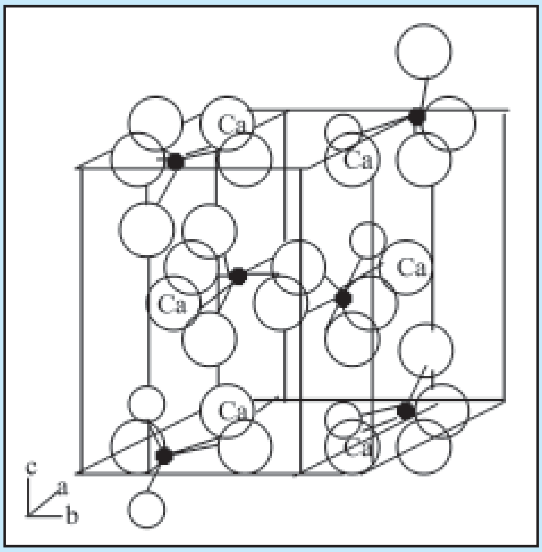
Generally, gypsum is the stable form at low temperature, whereas anhydrite is formed at higher temperature. Gypsum solubility increases with temperature up to about 40 °C, then decreases with temperature as shown in Figure – 2.2. This is quite different from the temperature-solubility behaviour of $CaCO_3$. Firtsly, gypsum is considerably more soluble than $CaCO_3$ in normal temperature range of interest. The solubility of $CaSO_4$ in distilled water is 2080 mg/l, while solubility of $CaCO_3$ 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 $CaCO_3$ where an 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 $CaSO_4$ in deeper, hotter wells. Actually, the temperature at which the scale changes form 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 $CaSO_4$ 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 $CaSO_4$ solubility. This case is described in Figure 2.3 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 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 2.4.



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

**Figure 2.1**
**Structure of anhydrite**

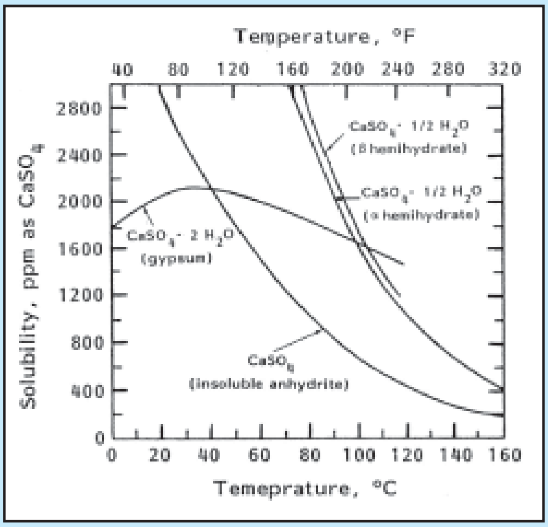


**Figure 2.2**
**Effect of temperature on calcium sulfate solubility**

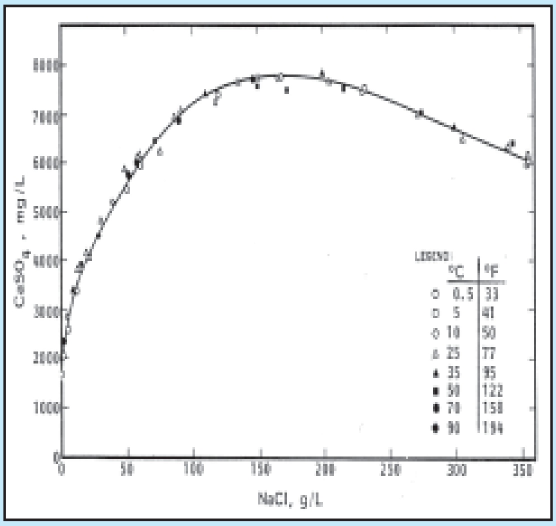


Figure 2.3
Effect of NaCl on $CaSO_4$ solubility

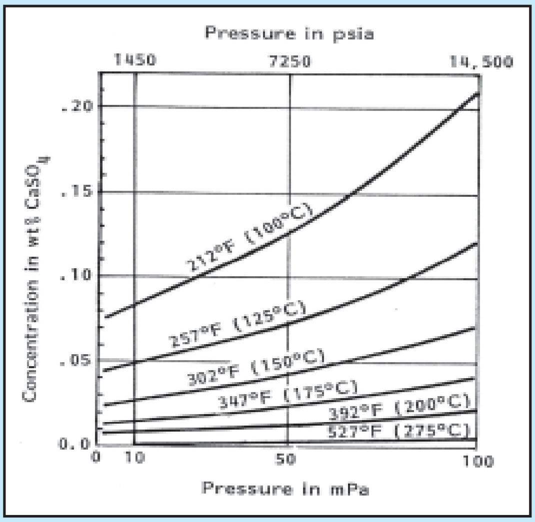


Figure 2.4
Effect of pressure on
concentration of calcium sulfate

Table 1
The Results of Different Water Source Analysis

| No | Laboratory Tests | Unit | Different Water Source | | |
|---|---|---|---|---|---|
| | | | S1<br>River water | S2<br>Injection Water | S3<br>Produced Water |
| 1 | Sodium, $Na^+$ (calc) | mg/L | 1,10 | 837,80 | 8.404,70 |
| 2 | Calcium, $Ca^{++}$ | mg/L | 12,10 | 109,10 | 230,30 |
| 3 | Magnesium, $Mg^{++}$ | mg/L | 4,90 | 15,90 | 41,70 |
| 4 | Iron, $Fe^{++}$ (total) | mg/L | 2,20 | 0,00 | 0,07 |
| 5 | Barium, $Ba^{++}$ | mg/L | 8,00 | 7,00 | 12,50 |
| 6 | Chloride, $Cl^-$ | mg/L | 17,90 | 1.338,90 | 12.496,80 |
| 7 | Bicarbonate, $HCO_3^-$ | mg/L | 33,60 | 379,10 | 1.357,30 |
| 8 | Sulfate, $SO_4^=$ | mg/L | 0,00 | 11,00 | 283,10 |
| 9 | Carbonate, $CO_3^=$ | mg/L | 0,00 | 0,00 | 0,00 |
| 10 | Hydroxide | mg/L | 0,00 | 0,00 | 0,00 |
| 11 | pH | | 6,90 | 7,85 | 7,80 |

## III. THE OCCURENCE OF $CaSO_4$ SCALE

The formation of $CaSO_4$ scale occurs via the following steps:

1. Dissolved salts in water mixture
2. Solution
3. Super saturation
4. Nucleation
5. Crystal growth
6. Scale formation

Salts (such as NaCl, $CaCl_2$ and $NaSO_4$ 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 followed by crystal growth process. The last stage is the occurrence of scale development. The process of the calcium sulfate scale deposition occurs when the $CaSO_4$ solubility value is less than actual $CaSO_4$ concentration. Whereas, when the $CaSO_4$ solubility value is higher than actual $CaSO_4$ concentration, $CaSO_4$ scale is not formed. The occurrence of calcium sulfate scale can be assumed as the following chemical reaction:

$$Ca^{+2}_{(aq)} + SO_{4\,(aq)}^{-2} \longrightarrow CaSO_{4\,(solid)}$$

**Table 2**
**The Results of Calcium Sulfate Solubilities Determination**
**For S1 – River water**

| Ion | Concentrations (mg/l) | Ionic Strength Calculation | |
|---|---|---|---|
| | | Conversion Factor | Results |
| $Na^+$ | 1,10 | 2,20E-05 | 2,42E-05 |
| $Ca^{++}$ | 12,10 | 5,00E-05 | 6,05E-04 |
| $Mg^{++}$ | 4,90 | 8,20E-05 | 4,02E-04 |
| $Cl^-$ | 17,90 | 1,40E-05 | 2,51E-04 |
| $CO_3^=$ | 0,00 | 3,30E-05 | 0,00E+00 |
| $HCO_3^-$ | 33,60 | 8,20E-06 | 2,76E-04 |
| $SO_4^=$ | 0,00 | 2,10E-05 | 0,00E+00 |
| | | | 1,56E-03 |
| Total Ionic Strength ( $\mu$ ) = | | | 0,00156 |

| Temp. °F | K | 4K |
|---|---|---|
| 77 | 1,20E-04 | 4,80E-04 |
| 140 | 1,20E-04 | 4,80E-04 |
| 175 | 1,10E-04 | 4,40E-04 |

| Ion | Concentrations (mg/l) | Conversion Factor | M (moles/l) |
|---|---|---|---|
| $Ca^{++}$ | 12,10 | 2,50E-05 | 3,03E-04 |
| $SO_4^=$ | 0,00 | 1,05E-05 | 0,00E+00 |
| | | **X = DM =** | **3,03E-04** |

S @ 77 °F = **21.61 meq/l**
S @ 140 °F = **21.61 meq/l**
S @ 175 °F = **20.68 meq/l**

| Ion | Concentrations (mg/l) | Equivalent Weight | Concentrations (meq/l) |
|---|---|---|---|
| $Ca^{++}$ | 12,10 | 20,00 | 0,6050 |
| $SO_4^=$ | 0,00 | 48,00 | 0,0000 |

Actual $CaSO_4$ concentration = 0.00 meq/l

**S > actual , so $CaSO_4$ scale is not formed**

## IV. METHODOLOGY FOR $CaSO_4$ SOLUBILITY CALCULATION

Solubility value for $CaSO_4$ can be calculated using the following equation values of Ksp are known for the compound :

Solubility (meq/L) =

$$S = 1000\,[(X^2 + 4\,K_{sp})^{½} - X]$$

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 $CaSO_4$ in water, where the $Ca^{+2}$ and $SO_4^=$ concentrations are equal:

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

$SO_4^=$ concentration = S moles / liter

$$Ksp = (S)\,(S) = S^2$$

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

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:

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

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

Rearranging:

$S^2 + SX - Ksp = 0$

Taking the positive root of the quadratic equation:

$$S = \frac{-X + (X^2 + 4Ksp)^{1/2}}{2}$$

For a divalentt ion:

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

Or:

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

The ”actual concentration” of CaSO4 in solution is equal to the smaller of the $Ca^{+2}$ or $SO_4^{=}$ concentrations (expressed in meq/liter) in the water of interest, since the smaller concentration limits the amount of calcium sulfate which can be formed. The calculated calcium sulfate solubility, S (meq/liter), is compared with the actual concentration to determine if scale formation is likely (6,7,8).

**Table 3**
**The Results of Calcium Sulfate Solubilities Determination**
**For S2 – Injection Water**

| Ion | Concentrations | Ionic Strength Calculation | |
|---|---|---|---|
| | (mg/l) | Conversion Factor | Results |
| $Na^+$ | 837,80 | 2,20E-05 | 1,84E-02 |
| $Ca^{++}$ | 109,10 | 5,00E-05 | 5,46E-03 |
| $Mg^{++}$ | 15,90 | 8,20E-05 | 1,30E-03 |
| $Cl^-$ | 1338,90 | 1,40E-05 | 1,87E-02 |
| $CO_3^=$ | 0,00 | 3,30E-05 | 0,00E+00 |
| $HCO_3^-$ | 379,10 | 8,20E-06 | 3,11E-03 |
| $SO_4^=$ | 11,00 | 2,10E-05 | 2,31E-04 |
| | | | 4,73E-02 |
| | | Total Ionic Strength ( $\mu$ ) = | 0,0473 |

| Temp. °F | K | 4K |
|---|---|---|
| 77 | 1,78E-04 | 7,12E-04 |
| 140 | 1,78E-04 | 7,12E-04 |
| 175 | 1,64E-04 | 6,56E-04 |

| Ion | Concentrations (mg/l) | Conversion Factor | M (moles/l) |
|---|---|---|---|
| $Ca^{++}$ | 109,10 | 2,50E-05 | 2,73E-03 |
| $SO_4^=$ | 11,00 | 1,05E-05 | 1,16E-04 |
| | | **X = DM =** | **2,61E-03** |

S @ 77 °F = **24.20 meq/l**
S @ 140 °F = **24.20 meq/l**
S @ 175 °F = **23.13 meq/l**

| Ion | Concentrations (mg/l) | Equivalent Weight | Concentrations (meq/l) |
|---|---|---|---|
| $Ca^{++}$ | 109,10 | 20,00 | 5,4550 |
| $SO_4^=$ | 11,00 | 48,00 | 0,2292 |

Actual $CaSO_4$ concentration = 0.2292 meq/l

**S > actual , so $CaSO_4$ scale is not formed**

| Case | Summary |
|---|---|
| S = Actual | The water is saturated with $CaSO_4$. |
| S > Actual | The water is undersaturated with $CaSO_4$.<br>Scale is not formed |
| S < Actual | The water is supersaturated with $CaSO_4$.<br>Scale is formed |

This formula is used to calculate the solubility of any divalent salt such as calcium sulfate ($CaSO_4$).

## V. RESULTS OF ANALYSIS

Water analysis and calcium sulfate scaling index tendency calculations were carried out on three different water sources, namely: S1 from river water, S2 from injection water and S3 from produced water. The results of water analysis gave valuable information whether the water is potential or not to form $CaSO_4$ scale.

The results of determination of chemical compositions in the S1, S2 and S3 water samples were tabulated in Table 1. Water analysis is carried out based on API-RP 45 standard operational procedure. Each water source show the different water analysis results. S1 river water has 12.10 mg/l calcium ion and 0.00 mg/l sulfate ions Concentrations with 6.90 pH value. Next, concentration of 109.10 mg/l calcium ion and 11.00 mg/l sulfate ion are obtained in S2 injection water with 7.85 pH value. Subsequently, S3 produced water has 230.30 calcium ion and 283.10 mg/l sulfate ion concentrations with 7.85 pH value.

The obtained water analysis data were used to calculate calcium sulfate solubility in the water samples with using equation as explained in Section V. The results of calcium sulfate solubility at different temperature conditions can be seen in Table 2 for S1 river water, Table 3 for S2 injection water, Table 4 for S3 produced water and Table 5 for summary of $CaSO_4$ solubility determination results.

S1 river water has calcium and sulfate ions concentrations lower than the concentrations of calcium and sulfate ions for S2 injection water. Therefore, the $CaSO_4$ solubility for S1 river water is lower than the $CaSO_4$ solubility for S2 injection water. The $CaSO_4$ solubility of S1 river water at various temperature conditions (77 $^{o}$F, 140 $^{o}$F and 175 $^{0}$F) is in a range of 20.68 – 21.61 meq/l. While, the $CaSO_4$ solubility of S2 injection water at various temperature conditions (77 $^{o}$F, 140 $^{o}$F and 175 $^{0}$F) is in a range of 23.13 – 24.206 meq/l. Lastly, the $CaSO_4$ solubility of S3 produced water at various temperature conditions (77 $^{o}$F, 140 $^{o}$F and 175 $^{0}$F) is in a range of 54.03 – 56.44 meq/l. The S3 produced water shows the highest $CaSO_4$ solubility than the $CaSO_4$ solubility of S2 injection water and S1 river water, because it has the highest calcium and sulfate ion concentrations. So, $CaSO_4$ scale was not formed in the all analyzed water source.

**Table 4**
**The Results of Calcium Sulfate Solubilities Determination For S3 – Produced Water**

| Ion | Concentrations (mg/l) | Ionic Strength Calculation | |
|---|---|---|---|
| | | Conversion Factor | Results |
| $Na^{+}$ | 8404,70 | 2,20E-05 | 1,85E-01 |
| $Ca^{++}$ | 230,30 | 5,00E-05 | 1,15E-02 |
| $Mg^{++}$ | 41,70 | 8,20E-05 | 3,42E-03 |
| $Cl^{-}$ | 12496,80 | 1,40E-05 | 1,75E-01 |
| $CO_3^{=}$ | 0,00 | 3,30E-05 | 0,00E+00 |
| $HCO_3^{-}$ | 1357,30 | 8,20E-06 | 1,11E-02 |
| $SO_4^{=}$ | 283,10 | 2,10E-05 | 5,95E-03 |
| | | | 3,92E-01 |
| | | Total Ionic Strength ( $\mu$ ) = | 0,3920 |

| Temp. $^{o}$F | K | 4K |
|---|---|---|
| 77 | 8,75E-04 | 3,50E-03 |
| 140 | 8,70E-04 | 3,48E-03 |
| 175 | 8,05E-04 | 3,22E-03 |

| Ion | Concentrations (mg/l) | Conversion Factor | M (moles/l) |
|---|---|---|---|
| $Ca^{++}$ | 230,30 | 2,50E-05 | 5,76E-03 |
| $SO_4^{=}$ | 283,10 | 1,05E-05 | 2,97E-03 |
| | | **X = DM =** | **2,78E-03** |

S @ 77 $^{o}$F = **56.44 meq/l**
S @ 140 $^{o}$F = **56.27 meq/l**
S @ 175 $^{o}$F = **54.03 meq/l**

| Ion | Concentrations (mg/l) | Equivalent Weight | Concentrations (meq/l) |
|---|---|---|---|
| $Ca^{++}$ | 230,30 | 20,00 | 11,5150 |
| $SO_4^{=}$ | 283,10 | 48,00 | 5,8979 |

Actual CaSO4 concentration = 5.8979 meq/l

**S > actual , so $CaSO_4$ scale is not formed**

**Table 5**
**Summary of $CaSO_4$ Solubility Determination Results For S1 (River Water), S2 (Injection Water) And S3 (Produced Water)**

| Water Source | $CaSO_4$ Solubility (meq/l) |
|---|---|
| S1 (river water)<br>$Ca^{+2}$ = 12.10 mg/L<br>$SO_4^{=}$ = 0.00 mg/L<br>pH = 6.90 | S at 77 $^{0}$F = 21.61<br>S at 140 $^{0}$F = 21.61<br>S at 175 $^{0}$F = 20.68<br>Actual $CaSO_4$ concentration = 0.00<br>So, $CaSO_4$ solublity > actual concentration<br>$CaSO_4$ scale is not formed |
| S2 (injection water)<br>$Ca^{+2}$ = 109.10 mg/L<br>$SO_4^{=}$ = 11.00 mg/L<br>pH = 7.85 | S at 77 $^{0}$F = 24.20<br>S at 140 $^{0}$F = 24.20<br>S at 175 $^{0}$F = 23.13<br>Actual $CaSO_4$ concentration = 0.2292<br>So, $CaSO_4$ solublity > actual concentration<br>$CaSO_4$ scale is not formed |
| S3 (produced water)<br>$Ca^{+2}$ = 230.30 mg/L<br>$SO_4^{=}$ = 283.10 mg/L<br>pH = 7.85 | S at 77 $^{0}$F = 56.44<br>S at 140 $^{0}$F = 56.27<br>S at 175 $^{0}$F = 54.03<br>Actual $CaSO_4$ concentration = 5.8979<br>So, $CaSO_4$ solublity > actual concentration<br>$CaSO_4$ scale is not formed |

## VI. CONCLUSIONS

1. Based on the results of water analysis, S3 produced water has the highest concentrations of calcium and sulfate ions ion ($Ca^{+2}$) compared with S2 injection water and S1 river water.
2. The results of calcium sulfate solubility calculation of S3 produced water is the highest compared with the $CaSO_4$ solubility of S2 injection water and S1 river water.
3. The results of $CaSO_4$ solubility calculation for the S1 river water, S2 injection water and S3 produced water are higher than actual $CaSO_4$ concentration, as a result $CaSO_4$ scale is not formed in the all analyzed water source samples.

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