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Prediction the Amount of Barium Sulfate Scale Formation in Siri Oilfield using OLI ScaleChem Software

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Abstract: OLI ScaleChem software predicts mineral scaling potentials of 54 solids for virtually any oil and gas well and processing facility in the world. There are several advantages over other commercially available scaling software: (1) By including all brines in the calculations, the well and processing facility are modeled more accurately, (2) scaling potential and scale buildup are reported at each calculation point, (3) automatic correction of pH and charge balance, therefore the chance of unexpected problems from bad water analyses decreases. Also, more effective treatment can be made (4) automatically removal organic acid concentrations from the measured alkalinity, therefore producing a true brine alkalinity and (5) accurately predict the behavior of any mixture of chemicals in water and mixed solvent. This study presents the amount of barium sulfate precipitation of formation water, injection water and mixing of injection water with formation water at different temperatures, pressures and mixing ratio of injection water with formation water. The experimentally measured chemical analysis of formation water and injection water were used by OLI ScaleChem software to determine the tendency of scale formation at different conditions. As pressure and temperature was increased, the amount of barium sulfate precipitation was found to decrease, as was predicted by OLI ScaleChem software.

Key words: Scale, BaSO₄, temperature, pressure, mixing ratio

INTRODUCTION

The injection of seawater into oil field reservoirs to maintain reservoir pressure and improve secondary recovery is a well established mature operation. Moreover, the degree of risk posed by deposition of mineral scales to the injection and production wells during such operations has been much studied.

Scale formation in surface and subsurface oil and gas production equipment has been recognized to be a major operational problem. It has been also recognized as a major cause of formation damage either in injection or producing wells. Scale contributes to equipment wear and corrosion and flow restriction, thus resulting in a decrease in oil and gas production.

Experience in the oil industry has indicated that many oil wells have suffered flow restriction because of scale deposition within the oil producing formation matrix and the downhole equipment, generally in primary, secondary and tertiary oil recovery operation as well as scale deposits in the surface production equipment.

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There are other reasons why scale forms and the amount and location of which are influenced by several factors. And, supersaturation is the most important reason behind mineral precipitation.

A supersaturated condition is the primary cause of scale formation and occurs when a solution contains dissolved materials which are at higher concentrations than their equilibrium concentration. The degree of supersaturation, also known as the scaling index, is the driving force for the precipitation reaction and a high supersaturation condition, therefore, implies higher possibilities for salt precipitation.

Scale can occur at/or downstream of any point in the production system, at which supersaturation is generated. Supersaturation can be generated in single water by changing the pressure and temperature conditions or by mixing two incompatible waters. Changes in temperature, pressure, pH and CO₂/H₂S partial pressure could also contribute to scale formation (Mackay, 2003; Moghadasi *et al.*, 2003).

SCALE PROBLEMS IN OILFIELDS

Scale deposition is one of the most important and serious problems which water injection systems are generally engaged in. Scale sometimes limits or blocks oil and gas production by plugging the oil-producing formation matrix or fractures and perforated intervals. Scale also deposited in downhole pumps, tubing, casing flowlines, heater treaters, tanks and other production equipment and facilities. Scale can occur at /or downstream of any point in the production system, at which supersaturation is generated. Supersaturation can be generated in single water by changing the pressure and temperature conditions or by mixing two incompatible waters. The most common oilfield scales deposited are calcium carbonate, calcium sulphate, strontium sulphate and barium sulphate. Calcium carbonate scale generally causes a sharp reduction in pressure such as that exists between the formation and the wellbore and across any constriction in the production tubing, e.g., checks and safety valves. The reduction in pressure liberates CO₂ into the gas phase leaving a solution, which is supersaturated in calcium carbonate. The various forms of calcium sulphate scale, i.e., gypsum, anhydrate and hemihydrate can be formed due to an increase in temperature.

TYPE OF SCALES IN OILFIELDS

The most common scales encountered in oil field operations are sulfates such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite) and Strontium sulfate (celestite) and calcium carbonate. Other less common scales have also been reported such as iron oxides, iron sulfides and iron carbonate. Lead and zinc sulfide scale has recently become a concern in a number of North Sea oil and gas fields, these scales are shown in Table 1, along with the primary variables, which affect their solubility.

Where Does Oilfield Scale Form?

The scaling reaction depends on there being adequate concentrations of sulfate ions in the injected seawater and barium, strontium and calcium divalent cations in the formation brine to generate sulfate scale or on there being enough bicarbonate and calcium ions to generate carbonate scale.

Therefore, scale precipitation may occur wherever there is mixing of incompatible brines, or there are changes in the physical condition such as pressure decline. An overview of all

Table 1: Most common oilfield scales (Moghadasi *et al.*, 2003)

Name	Chemical formula	Primary variables
Calcium carbonate	CaCO ₃	Partial pressure of CO ₂ , temperature, total dissolved salts, pH
Calcium sulphate		
Gypsum	CaSO ₄ .2H ₂ O	Temperature, total dissolved salts, pressure
Hemihydrate	CaSO ₄ .1/2H ₂ O	
Anhydrite	CaSO ₄	
Barium sulphate	BaSO ₄	Temperature, pressure
Strontium sulphate	SrSO ₄	Temperature, pressure, total dissolved salts
Iron compounds		
Ferrous carbonate	FeCO ₃	Corrosion, dissolved gases, pH
Ferrous sulphide	FeS	
Ferrous hydroxide	Fe(OH) ₂	
Ferrous hydroxide	Fe(OH) ₃	

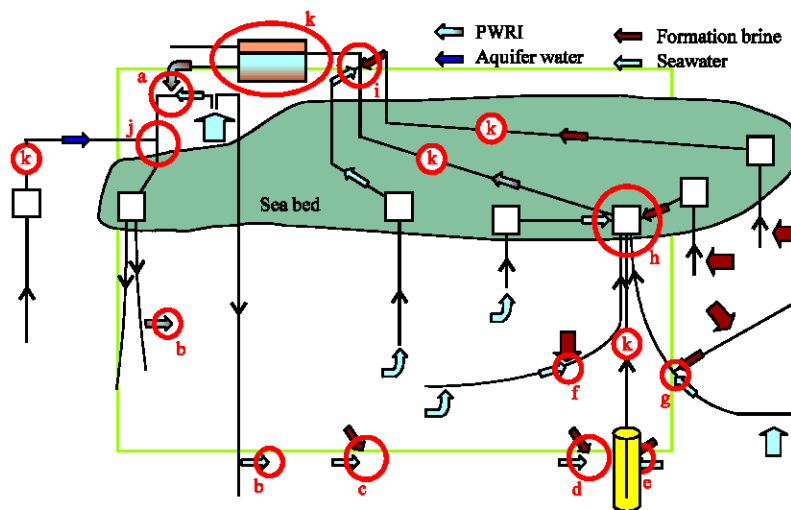


Fig. 1: Locations throughout the flow system where scale deposition may take place (Jordan *et al.*, 2006)

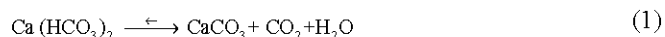
the possible scale formation environments for seawater, aquifer, natural depletion and produced water re-injection is shown in Fig. 1 (Jordan and Mackay, 2005; Jordan *et al.*, 2006).

- Prior to injection, for example if seawater injection is supplemented by Produced Water Re-Injection (PWRI)
- Around the injection well, as injection brine enters the reservoir, contacting formation brine
- Deep in formation, due to displacement of formation brine by injected brine, or due to meeting flow paths
- As injection brine and formation brine converge towards the production well, but beyond the radius of a squeeze treatment
- As injection brine and formation brine converge towards the production well and within the radius of a squeeze treatment
- In the completed interval of a production well, as one brine enters the completion, while other brine is following up the tubing from a lower section, or as fluid pressure decreases

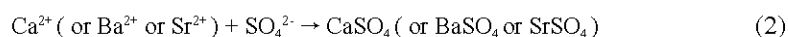
- At the junction of a multilateral well, where one branch is producing single brine and the other branch is producing incompatible brine
- At a subsea manifold, where one well is producing single brine and another well is producing different brine
- At the surface facilities, where one production stream is flowing one brine and another production stream is flowing another brine
- During aquifer water production and processing for re-injection could lead to scale formation within self-scaling brine or mixing with incompatible formation brine
- During pressure reduction and/or an increase in temperature within any downhole tube or surface processing equipment, leading to the evolution of CO₂ and to the generation of carbonate and sulfide scale if the suitable ions are present. Temperature reductions could lead to the formation of halite scales if the brine was close to saturation under reservoir conditions

Oilfield scales are inorganic crystalline deposits that form as a result of the precipitation of solids from brines present in the reservoir and production flow system. The precipitation of these solids occurs as the result of changes in the ionic composition, pH, pressure and temperature of the brine. There are three principal mechanisms by which scales form in both offshore and onshore oilfield system (Mackay, 2005; Jordan and Mackay, 2005; Collins *et al.*, 2006):

- Decrease in pressure and/or increase in temperature of a brine, goes to a reduction in the solubility of the salt (most commonly these lead to precipitation of carbonate scales, such as CaCO₃)



- Mixing of two incompatible brines (most commonly formation water rich in cations such as barium, calcium and/or strontium, mixing with sulfate rich seawater, goes to the precipitation of sulfate scales, such as BaSO₄)



Other fluid incompatibilities include sulfide scale where hydrogen sulfide gas mixes with iron, zinc or lead rich formation waters:



- Brine evaporation, resulting in salt concentration increasing above the solubility limit and goes to salt precipitation (as may occur in HP/HT gas wells where a dry gas stream may mix with a low rate brine stream resulting in dehydration and most commonly the precipitation of NaCl)

BARIUM SULPHATE SCALE

BaSO₄ scale (barite) in oil fields can be precipitated easily on the basis of already available information relating to the thermodynamic condition and the kinetics (Collins and Leinweber, 1956; Davis and Collins, 1971; Hunton and Gilbert, 1982; Nancollas and Liu, 1975;

Templeton, 1960; Weintritt and Cowan, 1967) of precipitation. Solubility data for barium sulphate are available for a complete scale deposition prediction model. Therefore, BaSO₄ solubility increases with temperature increase, with increasing ionic strength of brine and with pressure. BaSO₄ precipitation is affected most strongly by temperature.

Barium Sulfate Scale Removal Method

One of the most common reasons for production loss is the development of scales inside the production strings, blocking the flow of the reservoir fluid to the surface facilities. Barium sulfate scale is among the toughest scales to remove, whether mechanically or chemically (Guimaraes *et al.*, 2007).

Barium sulfate could only be removed by mechanical means. However, chemicals based on EDTA are now available which have had some success in dissolving barium sulfate.

CALCULATION OF THE AMOUNT OF SCALE FORMED

It is possible to estimate the maximum amount of scale, which could form, assuming that the system is in equilibrium. If a solution is supersaturated with a salt (such as CaCO₃, CaSO₄, BaSO₄, or SrSO₄), precipitation can be expected.

In this case, let us consider the general case of the formation of a mineral scale, MA. The general reaction is given as:



Assuming that the solution is supersaturated with respect to MA:

$$[M] [A] > K_{sp} \quad (5)$$

If the solution is allowed to reach equilibrium, MA will precipitate until the solution reaches its saturation point with MA. Since one mole of M²⁺ and one mole of A²⁻ are required to make one mole of MA, the concentration of both ions will be decreased by one mole for each mole of scale which precipitates.

Let, p equal the number of moles of MA, which precipitate in the act of reaching saturation, then:

$$K_{sp} = [M-p] [A-p] \quad (6)$$

Rearranging:

$$p^2 - (M + A) p + MA - K_{sp} = 0 \quad (7)$$

Taking the negative root of the resulting quadratic equation:

$$p = \frac{(M + A) - [(M - A)^2 + 4K_{sp}]^{0.5}}{2} \quad (8)$$

Let,

$$G = (M + A) \quad \text{and} \quad X = (M - A) \quad (9)$$

Then:

$$p(\text{moles L}^{-1}) = \frac{G - (X^2 + 4K_{sp})^{0.5}}{2} \quad (10)$$

Gives the following relationship:

$$p(\text{mg L}^{-1}) = 500(\text{MW})[G - (X^2 + 4K_{sp})^{0.5}] \quad (11)$$

This equation can be used to calculate the maximum amount of any scale, which could precipitate.

USE OF THE OLI SCALECHEM SOFTWARE FOR SCALING PREDICTION

ScaleChem predicts mineral scaling potentials of 54 solids for virtually any oil and gas well and processing facility in the world. The program computes the gas-liquid-oil-solid chemistry of produced fluids and provides the operator and engineer with vital chemical data about their wells, surface facilities and water injection and disposal operations. ScaleChem works with brines, gases and hydrocarbons, collected as samples and input into the program. Calculation types include a generalized scale scenario for well profiles; mixing waters to find safe (non-scaling) ratios; reservoir saturation to simulate downhole conditions and facilities with simple mix and separate abilities to simulate collection and disposal. Output includes the (thermodynamic) scale tendencies for all solids in the model, as well as scale amount produced, if any. ScaleChem is predictive up to 600 °F, 22,000 psi and 700,000 ppm TDS. Thus, almost any production operation can be modeled.

There are several advantages over other commercially available scaling software:

- The presence or absence of carbon dioxide is critical for calcium carbonate scale formation but in most scaling softwares this is not considered
- All reactions simulated in OLI ScaleChem software are pressure and temperature dependent
- Accurately predict the behavior of any mixture of chemicals in water and mixed solvent
- All possible scenarios are simulated, to obtain optimum flow rates and flow regimes. This minimizes the risk of mixing incompatible waters
- Automatic correction of pH and charge balance. Therefore the chance of unexpected problems from bad water analyses decreases. Also, more effective treatment can be made
- Calculate brine conditions at reservoir condition (Downhole Wizard). This is useful when lab data is incomplete, but the brine is known to be saturated downhole
- Automatically removal organic acid concentrations from the measured alkalinity, producing a true brine alkalinity
- By including all brines in the calculations, the well and processing facility are modeled more accurately
- Scaling potential and scale buildup are reported at each calculation point
- In this software Potential scale buildup can be found before they occur, allowing preventive measures to be taken. This decreases production costs and lost production
- Accurate scaling rates give the operator a time window to make decisions about potential problems

RESULTS AND DISCUSSION

Siri field has a weak water drive and produces from Mishrif formation. This field consists of Siri-A, Siri-B, Siri-C, Siri-D, Siri-E and Nosrat. Seawater injection was started in 1980 in this field. This section deals with the results taken from running of the model for injection water, formation water and mixing of injection water with formation water of Siri oilfield. It is quite essential to be mentioned that condition chosen for modeling are not exact the same of the reservoir formations. Table 2 shows the analysis of the Persian Gulf water and Mishrif formation water in Siri field.

Table 2: Water analysis of Persian Gulf water and Mishrif formation water in Siri field

Ions (mg L ⁻¹)	Siri- C	Siri- D	Siri- E	Nosrat	Sea water
Cl ⁻	73942	70740	83324	86900	23000
SO ₄ ⁻²	635	310	142	340	3350
HCO ₃ ⁻	579	528	397	244	166
Mg ⁺²	759	766	552	2010	2996
Ca ⁺²	3032	4525	8917	7920	267
Na ⁺	42215	35391	42800	43700	11750
K ⁺	1986	-	88	-	-
Ba ⁺²	-	-	-	18	0.09
Fe ⁺²	17	5.6	246	-	0.42
Sr ⁺²	547	760	-	610	3.4
Li ⁺	-	-	-	-	-
TDS	131472	129225	137370	141000	40270
pH	6.82	5.86	6.25	5.6	7.7
CO ₂	-	100	-	-	-
H ₂ S	-	14	-	-	-
SG	1.050	1.052	1.055	1.053	1.045
Flow rate (bbl/day)	20000	20000	20000	20000	10000

BaSO₄ Scale Tendency Prediction for the Persian Gulf Water Injection into Mishrif Formation in Siri Oilfield (Offshore) at Different Temperatures

As in Table 2, the amount of Ba²⁺ ions are equal to zero for formation water of Siri-C, Siri-D and Siri-E oilfields, so there is not any possibility for the BaSO₄ scale formation in these fields at different temperatures.

Figure 2 show the amount of BaSO₄ precipitation of Nosrat oilfield at different temperatures. As in Fig. 2, there is tendency of BaSO₄ scale formation in this field.

Also, Ba²⁺ ions is negligible (0.09 mg L⁻¹) in injected water and as in Fig. 2, BaSO₄ scale will be precipitated only at low temperatures.

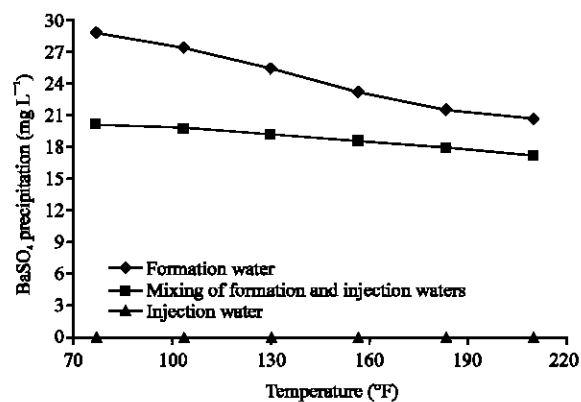


Fig. 2: BaSO₄ precipitation in Nosrat oilfield (P = 4800 psia)

When injection water is mixed with formation water, the amount of $BaSO_4$ precipitation of formation water is decreased in Nosrat oilfield.

BaSO₄ Scale Tendency Prediction for the Persian Gulf Water Injection into Mishrif Formation in Siri Oilfield (Offshore) at Different Pressures

As in Table 2, the amount of Ba^{2+} ions are equal to zero for formation water of Siri-C, Siri-D and Siri-E oilfields, so there is not any possibility for the $BaSO_4$ scale formation in these fields at different pressures.

Figure 3 show the amount of $BaSO_4$ precipitation of Nosrat oilfield at different pressures. As in Fig. 3, there is tendency of $BaSO_4$ scale formation in this field.

Also, Ba^{2+} ions is negligible (0.09 mg L^{-1}) in injected water and as in Fig. 3, the $BaSO_4$ precipitation of injected water is equal to zero at different pressures.

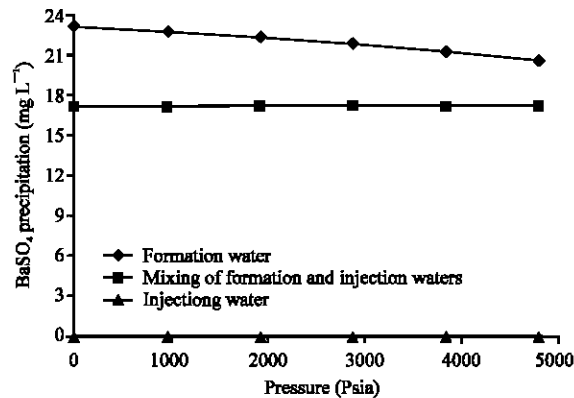


Fig. 3: BaSO₄ precipitation in Nosrat oilfield (T = 210°F)

BaSO₄ Scale Tendency Prediction for Siri Oilfield (Offshore) at Different Mixing Ratio of Injection Water with Formation Water

Results of the compatibility modeling of the Persian Gulf water and Siri field formation (Siri C, D, E and Nosrat) water are shown in Fig. 4.

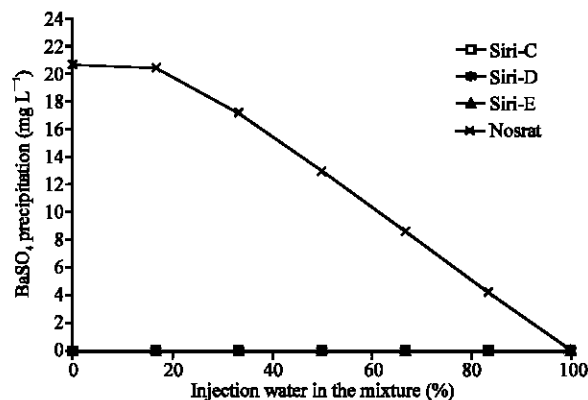


Fig. 4: BaSO₄ precipitation in Siri oilfield (T = 210°F, P = 4800 psia)

As in Table 2, the amount of Ba^{2+} ions are equal to zero for Siri-C, Siri-D and Siri-E, so there is not any possibility for the $BaSO_4$ scale formation in these fields. Also Ba^{2+} ions is negligible (0.09 mg L^{-1}) in injected water and $BaSO_4$ scale does not form in this water at reservoir conditions. In Nosrat field, formation water contain some Ba^{2+} ions (18 mg L^{-1}) and as in Fig. 4, for different percent of injected water some $BaSO_4$ scale can be formed.

CONCLUSIONS

The results obtained in this study may be summarised in the following items:

- This software calculates the precipitation of scale forming compounds under all pertinent field conditions
- Using valid water (brine) analysis data is the key concept behind using ScaleChem. If the water analysis is not valid then the resulting calculations are not valid
- Barium sulfate is the most insoluble scale that can be precipitate from oilfield water, the formation of this scale is a big problem in Nosrat field that for solving this problem, we use EDTA
- Formation of $BaSO_4$ in Iranian oilfields is very low
- When pressure and temperature was increased, the scaling tendency of the barium sulfate scale was found to decrease

ACKNOWLEDGMENTS

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NOMENCLATURES

EDTA = Ethylene diamine tetra acetic acid
 K_{sp} = Solubility product, M^2
P = Pressure, psi
SG = Specific gravity
SI = Scaling index, dimensionless
ST = Scaling tendency, dimensionless
T = Temperature, °F
TDS = Total dissolved salts

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