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Determining the Rates for Scale Formation in Oil Wells

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ABSTRACT
Scale deposition is one of the most serious oil field problems that affect water injection systems adversely, when two incompatible waters are involved. Two waters are incompatible if they interact chemically and precipitate minerals when mixed. Typical examples are sea water, with high concentration of sulfate ion and formation waters, with high concentrations of calcium, barium, and strontium ions. Mixing of these waters, therefore, could cause precipitation of calcium sulfate, barium sulfate and/or strontium sulfate. This study was conducted to determine conditions for scientist and oil field Engineers to predict scale formation in oil wells. The solubility of common oil field scales formed and how their solubilities were affected by changes in salinity and temperatures (40-90^{0}C), scale prevention and removal methods were also studied. The results showed that at higher temperatures, the deposition of $CaCO_3$, $CaSO_4$ and $SrSO_4$ scales increases and the deposition of $BaSO_4$ scale decreases since the solubilities of $CaSO_3$ $CaSO_4$ and $SrSO_4$ scales decreases and the solubility of $BaSO_4$ increases with increasing temperature.

Keywords: Scale Formation, Solubility, Salinity, Temperature.

I. INTRODUCTION

The injection of seawater into oilfield 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 down hole equipment, generally in primary, secondary and tertiary oil recovery operation as well as scale deposits in the surface production equipment. The effect of scale can be short term and long term. In one North sea well in the Miller field, Engineers observed production fall from 30,000 B/D (4770 m^3/d) to zero in just 24 hours [1].

There are other reasons why scale forms, and the amount and location of which are influenced by several factors. Super saturation 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 super saturation, also known as the scaling index, is the driving force for the precipitation reaction and a high super saturation condition, therefore, implies higher possibilities for salt precipitation. Scale can occur at/or downstream of any point in the production system, at which super saturation is generated. Super saturation can be generated in single water by changing the pressure and temperature conditions or by mixing two incompatible waters. A typical example of incompatible waters are sea water with high concentration of SO_4^{-2} and low concentrations of Ca^{+2}, Ba^{+2}/Sr^{+2}, and formation waters with very low concentrations of SO_4^{-2} but high concentrations of Ca^{+2}, Ba^{+2} and Sr^{+2}. Mixing of these waters, therefore, causes precipitation of $CaSO_4$, $BaSO_4$, and/or $SrSO_4$. Field produced water (disposal water) can also be incompatible with seawater. In cases where disposal water is mixed with seawater for re-injection, scale deposition is possible [2]. Changes in temperature, pressure, pH, and CO_2/H_2S partial pressure could also contribute to scale formation [3].

The most common oilfield scales are listed in Table 1, along with the primary variables that affect their solubility [4]. These scales 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.

Table 1: Some common oilfield scales

Name	**Chemical Formula**	**Primary Variables**
Calcium Carbonate	$CaCO_3$	Partial pressure of CO_2, temperature, total dissolved salts, pH
Calcium Sulfate: Gypsum Hemihydrate Anhydrite	 $CaSO_4.2H_2O$ $CaSO_4.1/2H_2O$ $CaSO_4$	Temperature, total dissolved salts, pressure
Barium Sulfate	$BaSO_4$	Temperature, pressure
Strontium Sulfate	$SrSO_4$	Temperature, pressure, total dissolved salts
Iron Compounds: Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferrous Hydroxide	 $FeCO_3$ FeS $Fe(OH)_2$ $Fe(OH)_3$	Corrosion, dissolved gases, pH

This study details the procedure to determine the rates of scale formation in oil wells. This will enhance oil field Scientists and Engineers to predict operating conditions for oil systems. The use of appropriate equipment and tools can be achieved.

II. METHODOLOGY

The formation water contained calcium, strontium, and barium ions, and the seawater contained sulfate ions. It was clear that the mixing of these waters could lead to calcium, strontium, and barium sulfate precipitation. Seven salts used for the preparation of synthetic formation water and water injections are as follow; Sodium Chloride (NaCl), Potassium Sulfate (K_2SO_4), Magnesium Chloride ($MgCl_2.6H_2O$), Calcium Chloride ($CaCl_2.2H_2O$), Sodium Bicarbonate ($NaHCO_3$), Strontium Chloride ($SrCl_2.6H_2O$), Barium Chloride ($BaCl_2.2H_2O$).

Equipment used include; Beaker, Hot plate, Filter paper, Volumetric flask.

2.1 Experimental Procedure

The experimental procedures used in the determination of solubility of common oil field scales from mixing synthetic brines (formation water and sea water) at high salinity (high concentration of calcium and strontium), high concentration of barium, various temperatures (40 to 90 °C) and 1 atm. were:

I. For each experiment of common oil field scales, 100 ml of each filtered opposite waters were poured simultaneously into a beaker.
II. The synthetic brines were heated on hot plate, and the solution was stirred by magnetic stirrer and after that the solution was filtered through 0.45-μm filter paper.
III. After filtration, 5 ml of the filtrate was taken into a 50 ml volumetric flask and was diluted with distilled water to make up 50 ml of solution. This instantaneous dilution of $CaCO_{3,}$ $CaSO_{4,}$ $SrSO_4$, and $BaSO_4$ containing brines was performed in order to prevent $CaCO_{3,}$ $CaSO_{4,}$ $SrSO_4$, or $BaSO_4$ precipitation between filtering and analytical determination of the Ca, Ba, and Sr concentration.
IV. The calcium, barium, and strontium determinations were calibrated by measuring five standard solutions. Standard solutions were prepared from $CaCl_{2,}$ $BaCl_2$, and $SrCl_2$ solutions.
V. Calcium, barium, and strontium concentrations in the diluted filtrates were determined by Atomic Absorption Spectrometry. After multiplying with the dilution factor, the exact concentrations of calcium, barium, and strontium were computed.

VI. RESULTS AND DISCUSSION

The calcium, barium, and strontium concentrations in the diluted filtrates were determined using atomic absorption spectrometry. The solubilities of $CaCO_3$, $CaSO_4$, $BaSO_4$, and $SrSO_4$ at various temperatures of this study were calculated and are given in Tables 2 - 5. Graphical presentations are given in Figures 1 - 4. The expected trend in this temperature range is a decrease of $CaSO_4$, $SrSO_4$ solubilities, and $BaSO_4$ solubility increases with increasing temperature. The solubility of $CaSO_4$ and $SrSO_4$ decrease with increasing temperature because of dissociation of $CaSO_4$ and $SrSO_4$ which are exothermic reaction. But this phenomenal is different as compared to that of $BaSO_4$. Solubility of $BaSO_4$ increases with increasing temperature due to its endothermic reaction. A graphical presentation of the experimental results (Figures 1 - 4) illustrates this trend in these experiments. The sulfate ion content in the sea water brine was reacted with barium ions content in the formation water instantaneously but it was a reaction of both calcium and strontium ions during heating. The more precipitation of $CaCO_3$, $CaSO_4$, $SrSO_4$, and $BaSO_4$ results from the presence of a large concentration of calcium, strontium, and barium ions as compare to less precipitation at normal concentration of calcium, strontium, and barium ions.

Calcium carbonate scale can be formed by combination of calcium and bicarbonate ions, and this reaction is the major cause of calcium carbonate scale deposition in oilfield operations. This is because only a small percentage of the bicarbonate ions dissociated at the pH values found in most injection waters to form H^+ and CO_3^{-2} [5].

Solubility of $CaCO_3$ is greatly influenced by the carbon dioxide content of the water and temperature increases. $CaCO_3$ becomes less soluble as temperature increases. During heating CO_2 comes out of solution and precipitation of calcium carbonate. Super saturation was the most important reason behind mineral precipitation. Increased Super saturation would result in a more rapid rate of scale precipitation.

The experimental results conform to the general trend in solubility dependencies for common oil field scales with temperatures. This is similar to that observed in the earlier work [2], [3], [5], [6], [7], [8], [9], [10], [11], [12].

Table 2: Solubility of $CaCO_3$ at various temperatures

Temperature (°C)	**Solubility of $CaCO_3$ at high salinity (Ca = 30,000 ppm) (ppm)**	**Solubility of $CaCO_3$ at normal salinity (Ca = 7,000 ppm) (ppm)**
40	24776.00	6254.50
50	23301.34	5849.31
60	22698.14	4267.23
70	22502.21	3895.00
80	22045.20	3648.08
90	21712.06	3341.30

Table 3: Solubility of $CaSO_4$ at various temperatures

Temperature (°C)	**Solubility of $CaSO_4$ at high salinity (Ca = 30,000 ppm) (ppm)**	**Solubility of $CaSO_4$ at normal salinity (Ca = 7,000 ppm) (ppm)**
40	27030.12	5891.08
50	26918.52	5410.19
60	23120.04	5096.21
70	20154.26	4951.27
80	18923.17	3838.00
90	14772.01	3565.09

Table 4: Solubility of $SrSO_4$ at various temperatures

Temperature (°C)	**Solubility of $SrSO_4$ at high salinity (Sr = 1100 ppm) (ppm)**	**Solubility of $SrSO_4$ at normal salinity (Sr = 500 ppm) (ppm)**
40	913.08	369.36
50	851.15	363.01
60	705.03	351.17
70	680.28	293.32
80	620.24	260.58
90	430.02	241.25

Table 5: Solubility of $BaSO_4$ at various temperatures

Temperature (°C)	**Solubility of $BaSO_4$ at high (Ba=2200 ppm) (ppm)**	**Solubility of $BaSO_4$ at normal (Ba =250 ppm) (ppm)**
40	810.57	128.42
50	900.62	137.18
60	1300.10	169.24
70	1530.45	175.42
80	1620.39	181.21
90	1740.04	192.69

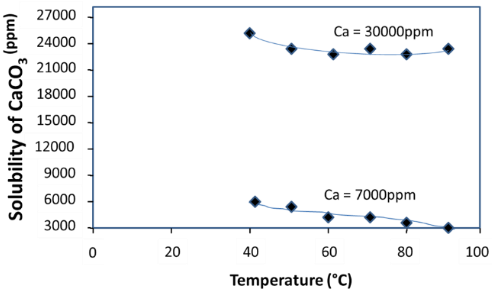

Fig 1: Solubility of $CaCO_3$ is largely dependent on temperature

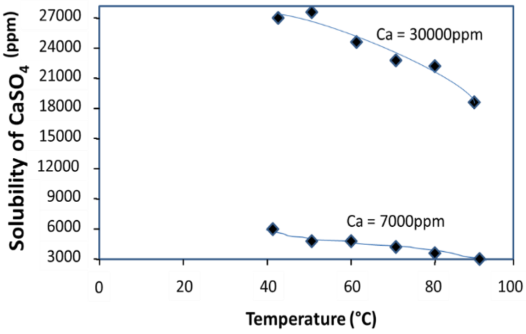

Fig 2: $CaSO_4$ solubility is dependent on temperature

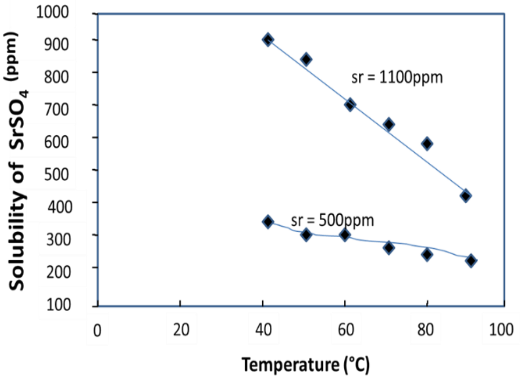

Fig 3: $SrSO_4$ solubility is dependent on temperature

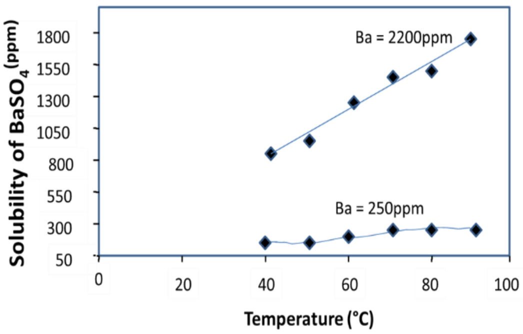

Fig 4: $BaSO_4$ solubility is dependent on temperature

V. CONCLUSION AND RECOMMENDATIONS

The experimental results conform to the general trend in solubility dependencies for common oil field scales, determined at various temperatures. A temperature rise from 40 to 90 °C causes an increase in $BaSO_4$ solubility and a decrease of $CaCO_3$, $CaSO_4$, and $SrSO_4$ solubilities. When synthetic seawater containing sulfate is mixed *in-situ* with formation water that contains a significant amount of dissolved calcium, strontium and barium ions, *in-situ* precipitation of calcium, strontium and barium sulfates occurs.

This scale is expected to form when pressure maintenance by seawater injection into the aquifer is started. More severe scaling by this material is to be expected when seawater breakthrough into production wells.

Based on the results and conclusions obtained from this study, the following suggestions for future work in the same area are recommended:

I. Instead of synthetic brines, real oil field brines can be employed in the study by mixing field disposal water and seawater.
II. The concentrations of calcium, barium, and strontium in effluent sample can be determined and much improved using an in–line ion analyzer or sophisticated analytical devices.

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