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SOLUBILITY OF COMMON OIL FIELD SCALES OF INJECTION WATER AND HIGH-BARIUM CONCENTRATION AND HIGH-SALINITY FORMATION WATER

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Abstract. 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 the perforated intervals. This paper presents a summary of the laboratory measurements of the solubility of common oil field scales in synthetic brines (formation water and sea water) of high-barium and high-salinity formation waters at 40 to 90°C and atmospheric pressure. The experimental results confirm the general trend in solubility dependencies for common oil field scales at these conditions. At higher temperatures the deposition of $CaCO_3$, $CaSO_4$ and $SrSO_4$ scale increases and the deposition of $BaSO_4$ scale decreases since the solubilities of $CaCO_3$, $CaSO_4$ and $SrSO_4$ scales decreases and the solubility of $BaSO_4$ increases with increasing temperature.

Keywords: Scaling problems; solubility of scale; high salinity; high barium

Abstrak. Kerak pemendapan merupakan satu daripada masalah paling penting dan serius dalam sistem suntikan air. Kerak kadangkala mengehadkan atau menghalang penghasilan gas dan minyak melalui penyumbatan matrik atau perpecahan pembentukan minyak dan jeda yang berlubang. Makalah ini mengetengahkan kesimpulan pengukuran makmal bagi kerak terbentuk di dalam keterlarutan medan minyak biasa dalam sintetik air masin (pembentukan air dan air laut) bagi pembentukan air yang mengandungi barium dan kandungan garam yang tinggi pada suhu 40 hingga 90°C pada tekanan atmosfera. Keputusan uji kaji mengesahkan pola kebergantungan keterlarutan bagi kerak medan minyak biasa pada keadaan ini. Pada suhu yang lebih tinggi, kerak bagi $CaCO_3$, $CaSO_4$, dan $SrSO_4$ meningkat manakala kerak $BaSO_4$ menurun disebabkan oleh keterlarutan $CaCO_3$, $CaSO_4$, dan $SrSO_4$ menurun dan keterlarutan $BaSO_4$ meningkat dengan kenaikan suhu.

Kata kunci: Masalah pengskalaan; skala keterlarutan; paras kandungan garam tinggi; logam barium tinggi

1.0 INTRODUCTION

The injection of seawater into oil field reservoirs to maintain reservoir pressure and improve secondary recovery is a well-established and matured operation. Moreover, the degree of risk posed by deposition of mineral scales to the injection and production

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wells during such operations has been studied extensively. Scale deposition is one of the most serious oil field problems that inflict water injection systems primarily when two incompatible waters are involved.

Precipitation of mineral scales causes many problems in oil and gas production operations such as formation damage, production losses, increased workovers in producers and injectors, poor injection water quality, and equipment failures due to under-deposit corrosion. The most common mineral scales are sulfate and carbonate-based minerals. However, scale problems are not limited to these minerals and there have recently been reports of unusual scale types such as zinc and lead sulfides [1].

1.1 Source of Oil Field Scale

The chief source of oil field scale is mixing of incompatible waters. Two waters are called incompatible if they interact chemically and precipitate minerals when mixed. 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 – 6].

1.2 Scale Deposition Mechanisms

Scale deposition can occur from one type of water because of super-saturation with scale-forming salts attributable to changes in the physical conditions under which the water exists. Scale also deposited in down-hole pumps, tubing, casing flow-lines, heater treaters, tanks and other production equipment and facilities. Scale can occur near the downstream of any point in the production system where super-saturation is generated. Super-saturation can be generated in water by changing the pressure and temperature conditions or by mixing two incompatible waters. The most common oil field scales deposited are calcium carbonate, calcium sulfate, strontium sulfate and barium sulfate. Scale also can deposit when two incompatible waters are mixed and super-saturation is reached [7 – 12].

1.3 Oil Field Scale Types

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.

1.4 Calcium Carbonate Scale

In many oil fields, the deposition of calcium carbonate scale on surface and subsurface production equipment creates an operation problem. The formation water in which the carbonate-scale-forming components are initially dissolved becomes supersaturated with calcium carbonate because of the drop in pressure during production. The continuous flow of a supersaturated solution through the production equipment results in the growth of a dense layer of calcium-carbonate crystals [13].

The water is drained to the surface and suffers from significant pressure drop and temperature variations during the production. The continuous pressure drops lead to degassing of the carbon dioxide with an increase in pH value of the produced water and precipitation of calcium carbonate [14 – 15].

Carbonate scale formation occurs when connate water or aquifer water passes through the bubble point and carbon dioxide is evolved. As carbon dioxide is evolved, the solubility with respect to carbonate declines rapidly and forms a precipitate with divalent ions, such as iron, and more commonly calcium, as outlined in the following equation [16]:

$$\mathrm{Ca(HCO_3)_2} \rightleftharpoons \mathrm{CaCO_3 + CO_2 + H_2O} \tag{1}$$

1.5 Calcium Sulfate Scale

Calcium sulfate scale poses a unique problem for the salts under consideration because it occurs with one of three different phases. Gypsum, the most common scale formed occurs at relatively low temperatures. At high temperatures (above 100°C), the stable phase predicted is anhydrite ($CaSO_4$). However, hemi-hydrate has been known to form at 100 to 121°C, especially in non-turbulent systems and in high ionic strength brines [17].

According to Oddo *et al.* [18], calcium sulfate scale formation is somewhat dependent on temperature, but is typically precipitated because of a decrease in pressure or an increase in the relative concentrations of calcium or sulfate. $CaSO_4$ solubility is fairly independent of pH and hence, can readily precipitate in an acid environment. Solubility of calcium sulfate is also affected by temperature, salinity and excess common ions.

The case where water injection (seawater, river, aquifer, or produced water) is used for pressure maintenance and sweep, the mixing of incompatible brines can lead to the formation of sulfate scales when the injection water contains sulfate ions [16].

$$\mathrm{Ba^{2+}\left(or\ Sr^{2+}\ or\ Ca^{2+}\right) + SO_4^{2-}} \rightleftharpoons \mathrm{BaSO_4\,(or\ SrSO_4\ or\ CaSO_4)} \tag{2}$$

1.6 Barium Sulfate Scale

Barium sulfate scale (barite) in oil fields can be precipitated easily on the basis of already available information relating to thermodynamic conditions and the kinetics of precipitation [19 – 20]. Barium sulfate solubility increased with increases of the temperature, the ionic strength of brine and the pressure. However, barium sulfate precipitation is affected most strongly by temperature [17].

1.7 Strontium Sulfate Scale

Strontium sulfate scale formation has become a growing concern in oil-production systems [7]. Until recently, the appearance of strontium in oil field scales has been primarily in the presence of barium sulfate scale.

Jacques and Bourland [21] have described a solubility study of strontium sulfate in sodium chloride brine. Their study has showed that the solubility of strontium sulfate increases with increasing ionic strength and decreases with increasing temperature.

Strontium sulfate behaves like barium sulfate except the former is more soluble under the same conditions. Most of the field scale barium sulfate deposits contain strontium sulfate too [22 – 23].

1.8 Solubility of Scale Formation

Solubility is defined as the limiting amount of solute that can dissolve in a solvent under a given set of physical conditions. The chemical properties of interest to us are present in aqueous solutions as ions. Certain combinations of these ions lead to compounds which have low solubility. Once the solubility capacity is exceeded the compounds precipitate from solution as solids. Therefore, precipitation of solid materials, which may form scale, will occur if:

(i) The water contains ions which are capable of forming compounds of limited solubility.
(ii) There are changes in the physical conditions or water compositions which are lowering the solubility.

Factors that affect scale precipitation, deposition and crystal growth are supersaturation, temperature, pressure, ionic strength, evaporation, contact time and pH.

The solubilities of typical oil field scales are given in Figure 1. Although the solubility curves (Figure 1) of these crystalline forms versus temperature show that above about 40°C (104°F), anhydrite is the chemically stable form, it is known from experience that gypsum is the form most likely to precipitate up to a temperature of about 100°C (212°F). Above this temperature, hemihydrate becomes less soluble than gypsum and will normally be the form precipitated. This, in turn, can dehydrate

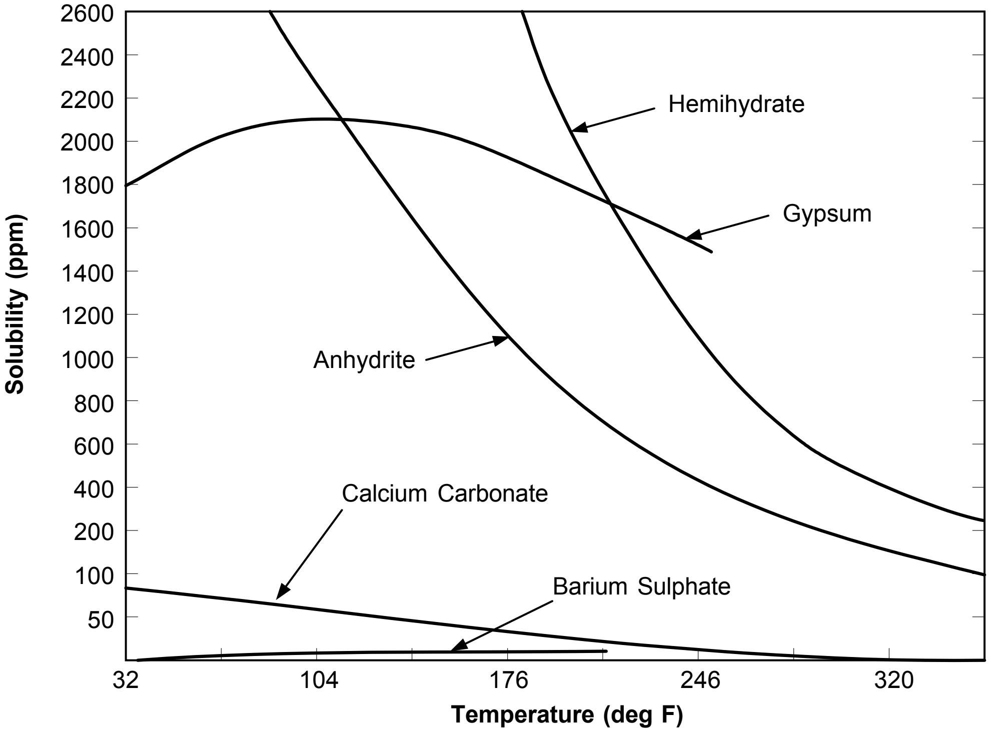

Figure 1 Solubilities of common scales

to form a scale at temperatures below 100°C and hemihydrate forms above this temperature [24].

Because of the solubility of the sulfates of calcium, strontium and barium can all be estimated; the amount of super-saturation of each can be predicted for any given system of different waters. Caution, however, must be exercised when working with estimated values of solubility and super-saturation. Many different variables, including temperature, pressure, other ions, pH, turbulence, rate of kinetics of precipitation and seeding or nucleation all have an effect on the behavior of mixtures of incompatible waters. Some of these variables are beyond the scope of definition in an oil field situation. They introduce unknown factors that make any estimate of solubility, super-saturation, and the likelihood of precipitation and scaling uncertain.

According to Lindlof and Stoffer [25], strontium sulfate solubility is decreased by the common ion effect; the super-saturation becomes a disproportionately higher percentage of total strontium sulfates in the solution. The super-saturation represents the amount of strontium sulfate present in excess of the solubility and thus represents the amount available for precipitation from solution and possible scaling. The super-saturation exists in a metastable state and, as such, the manner in which it exists in solution or comes out of solution by crystallization and precipitation is entirely unpredictable.

Solubility of calcium carbonate is greatly influenced by the carbon dioxide content of the water. $CaCO_3$ solubility increases with increased CO_2 partial pressure. The effect becomes less pronounced as the temperature increases. The reverse is also true. It is one of the major causes of $CaCO_3$ scale deposition.

2.0 MATERIALS AND METHODS

The intention of this study was to determine solubility of common oil field scales from mixing synthetic brines (formation water and sea water) contain high salinity (high concentration of calcium and strontium) and high concentration of barium at 40 to 90°C and 1 atm.

The ionic compositions of synthetic formation waters and injection waters (Barton and Angsi seawaters) are given in Tables 1 and 2. The formation water has calcium, strontium and barium ions, and the sea water contains sulfate ions. It was clear that the mixing of these waters can lead to calcium, strontium and barium sulfate precipitation.

The experimental procedures used in the determination of solubility of common oil field scales from mixing synthetic brines (formation water and sea water) are:

(i) For each experiment of common oil field scales, 100 mL of each filtered opposite waters was poured simultaneously into beaker.

(ii) The mixture was heated on hot plate and the mixture was stirred by magnetic stirrer and after that the mixture was filtered through 0.45 μm filter paper.

(iii) After filtration, 5 ml of the filtrate was pipetted into a 50 ml volumetric flask and filled up with distilled water to 50 ml. This instantaneous dilution

Table 1 The ionic compositions of synthetic formation and injection waters

Ionic	Normal salinity formation water (ppm)	High salinity formation water (ppm)	Normal barium formation water (ppm)	High barium formation water (ppm)	Barton seawater (ppm)	Angsi seawater (ppm)
Sodium	52,132	52,132	42,707	42,707	9,749	10,805
Potassium	1,967	1,967	1,972	1,972	340	375
Magnesium	4,260	4,260	102	102	1,060	1,295
Calcium	7,000	30,000	780	780	384	429
Strontium	500	1,100	370	370	5.4	6.577
Barium	10	10	250	2,200	<0.2	–
Chloride	99,653	146,385	66,706	67,713	17,218	19,307
Sulfate	108	108	5	5	2,960	2,750
Bicarbonate	350	350	2,140	2,140	136	158.80

Table 2 Compounds of synthetic formation and injection waters

Ionic	Normal salinity formation water (ppm)	High salinity formation water (ppm)	Normal barium formation water (ppm)	High barium formation water (ppm)	Average between Barton and Angsi seawater (ppm)
Sodium Chloride	132,000	132,000	106,500	106,500	26,100
Potassium Sulfate	–	–	–	–	5,180
Magnesium Chloride	35,625	35,625	853	853	9,846
Calcium Chloride	25,677	110,045	–	–	–
Sodium Bicarbonate	482	482	–	–	–
Strontium Chloride	1,521	3,347	–	–	–
Barium Chloride	–	–	445	3,914	–

of the $CaCO_{3,}$ $CaSO_{4,}$ $SrSO_4$ and $BaSO_4$ containing brines just after filtration was performed in order to prevent $CaCO_{3,}$ $CaSO_{4,}$ $SrSO_4$ or $BaSO_4$ precipitation during the period between filtering and analytical determination of the Ca, Ba and Sr concentrations.

(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.

3.0 RESULTS AND DISCUSSION

The concentrations of calcium, barium and strontium in the diluted filtrates were determined by atomic absorption spectrometry. The solubilities of $CaCO_{3,}$ $CaSO_{4,}$ $BaSO_4$ and $SrSO_4$ at various temperatures (40 – 90°C) of this study were calculated. Graphical presentations are given in Figures 2 – 5.

The expected trend in this temperature range is a decrease of $CaSO_4$ and $SrSO_4$ solubilities, but an increase of $BaSO_4$ solubility with increasing temperature. The solubility of $CaSO_4$ and $SrSO_4$ derease 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 2 – 5) illustrates this trend in these experiments. The SO_4^{-} content of the sea water brine reacts with the barium ions of the formation water instantaneously, but it reacts of both calcium and

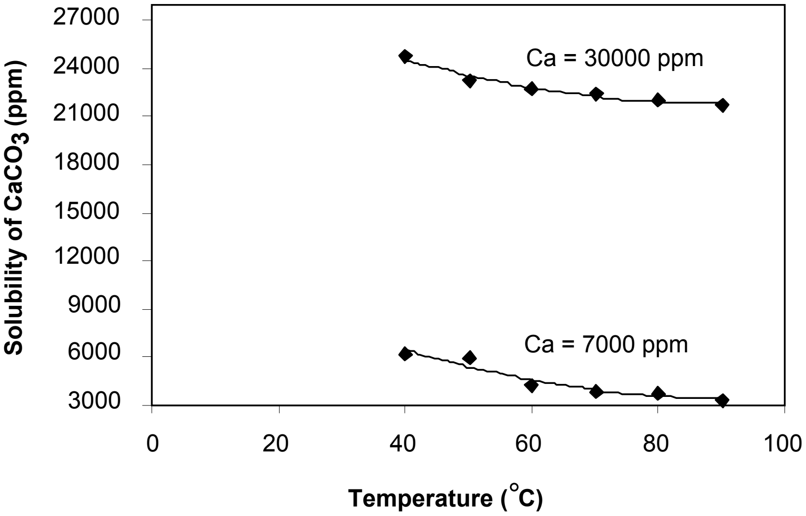

Figure 2 Solubility of $CaCO_3$ is largely dependent on temperature

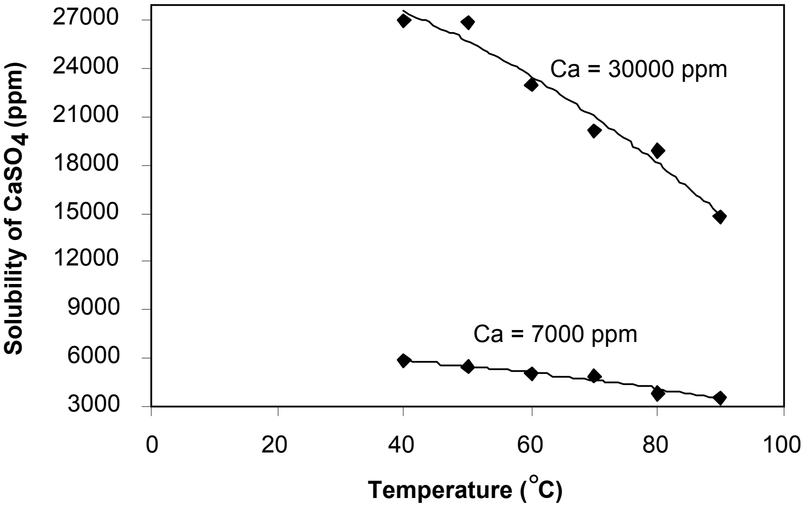

Figure 3 $CaSO_4$ solubility is dependent on temperature

strontium ions during heating. More precipitation of $CaCO_3$, $CaSO_4$, $SrSO_4$ and $BaSO_4$ are resulted from the presence of high concentration of calcium, strontium and barium ions with comparison to less precipitation at normal concentration of calcium, strontium and barium ions.

Calcium carbonate scale can be formed by the reaction of calcium and bicarbonate ions, and the reaction is the major cause of calcium carbonate scale deposition in oilfield operations. This is because only a small percentage of the bicarbonate ions

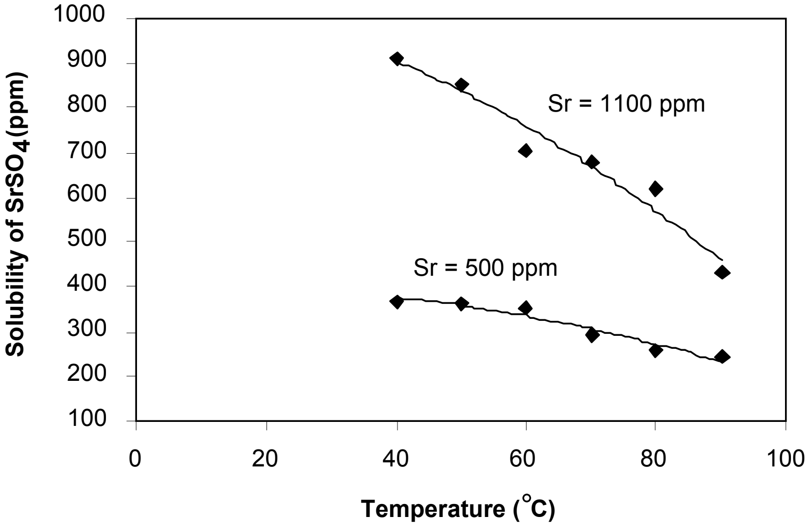

Figure 4 $SrSO_4$ solubility is dependent on temperature

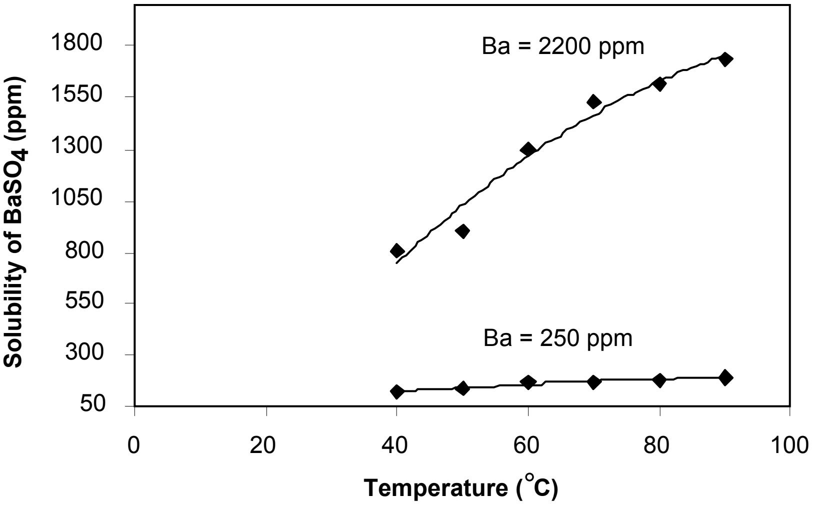

Figure 5 $BaSO_4$ solubility is dependent on temperature

dissociated at the pH values found in most injection waters. 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.

The experimental results confirm the general trend in solubility dependencies for common oil field scales with temperature. They are obvious and similar to that observed in the earlier works [21, 25, 18, 17, 14, 15, 16].

4.0 CONCLUSIONS

The experimental results confirm the general trend in solubility dependencies for common oil field scales at various temperatures (40 to 90°C) and 1 atm. A temperature rise from 40 to 90°C causes an increase in $BaSO_4$ solubility, but a decrease in $CaCO_3$, $CaSO_4$ and $SrSO_4$ solubilities. 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 the pH of the water rises may cause $CaCO_3$ precipitation. Super-saturation was the most important reason behind mineral precipitation. Increased super-saturation would result in a more rapid rate of scale precipitation.

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