

Novel scalechem programe for monitoring and enhancing dissolution of scale deposits near wellbore.

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ABSTRACT

The phenomena of desalination processes of the waters containing a considerable amount of calcium occurs both in cases of the pressure-driven membrane and electro- membrane processes, and is usually referred to as membrane scaling. Formation of mineral scale deposits is undesirable in various industrial processes where water and water treatment are involved, such as cooling systems, boilers, heat exchangers, filtration, mineral processing, oil and gas production, and geothermal systems. Common water formed scales include calcium carbonate, calcium sulfate, and barium sulfate. Most of scale found in Egyptian oil reservoirs was formed by direct precipitation from the formation water in high temperature and salinity reservoirs (Gulf of Suez Area), or from chemical incompatibility between injection water and formation water. In this study, ScaleChem software and laboratory Jar-testing were applied to evaluate the scale tendency of two Egyptian oil reservoirs existed in Gulf of Suez area. The two reservoirs were characterized by high temperature of 90-127 °C, and high salinity of 100,000-230,000 ppm. The salinity of injected water was 35,000 ppm. Both of theoretical software and laboratory Jar-testing results were comparing using an ion chromatograph (IC). Results ensured that the scales formation of calcium carbonate, calcium sulfate, barium sulfate and strontium sulfate, and their relative quantities have been functions of pressure, temperature and mixing ratio. Validity of ScaleChem software results has been checked by conducting Jar test at reservoir conditions. The produced scales formed from the Jar test have been analyzed using X- ray diffraction (XRD) and their results have been compared with the output data of ScaleChem software. It have been found that an excellent agreement obtained between results of ScaleChem software and Jar test, in addition the results of Jar test have been founded to be in a good agreement with field observations.

Key words: Desalination, scale deposition; scale prediction; OLI system and ScaleChem program.

INTRODUCTION

In the reservoir, the natural water is in equilibrium with its surroundings at ambient temperature and pressure. As the brine flows up through the well, both temperature and pressure decrease considerably and the equilibrium is disturbed. This will generally lead to solid-phase deposition¹. In offshore oilfield developments, mixing of incompatible waters as a result of water-flooding is the main cause of sulfate scale formation. Two waters are incompatible if they interact chemically and precipitate minerals when mixed. When sulfate-

carbonate rich injection water (often seawater) is mixed with the Ba²⁺, Ca²⁺ and Sr²⁺ rich formation water it is very likely that calacite (CaCO₃), barite (BaSO₄), celestite (SrSO₄) and/or anhydrite (CaSO₄) precipitation will take place². Mineral scale deposition causes serious damage in utilization systems and reduces flow areas. Well production and injection rates and capacities thus drop, with consequent economical loss: for example, BP loses around 4 million bbls per year in the North Sea³. The cross-section decrease caused by solid deposition onto the inner wall of a pipe is shown in Fig.1⁴. In some cases the choke of the flow line is so large that the

well needs to be closed. Scaling can also cause safety problems caused by blockage and failure of valves³. As scaling may be difficult to prevent, there is a need for an accurate method to evaluate the risk of occurrence and, if any, quantify its extent.

El-Manharawy, S., *et al.*,⁶⁻⁷ have developed empirical models, to make accurate prediction calculations and understanding the detailed thermo kinetic processes which causes the scale. The need for reliable predictive numerical models of scale formation is illustrated by the many commercial numerical codes developed over the past few years,^{8&9}. These numerical models are intended to help the management of scale deposition to minimize the costs of control and mitigation of scaling problems. Among these codes, ScaleChem was specifically developed at OLI Systems Inc. The ScaleChem Program estimates scale formation under CO₂ and water flood conditions, also can be used to evaluate stimulation compatibility amongst formation waters. The performance of using a ScaleChem Version 2.2,

downhole completion equipment, thereby clogging the wellbore and restriction fluid flow¹⁰. There by ScaleChem (V 2.2) is the one of the technique used to calculate queens' speciation mineral saturation indices, mineral solubility's and the effect of mixing between different fluids¹¹. The quantitative calculations of Scaling Tendency (ST) are performed using a specific software designed to theoretically estimate the scale formation conditions and scale quantities that may result from mixing two incompatible waters at one or more specified temperature and pressure and any specified ratio of mixing to simulate the reservoir conditions. The input data to the software are the results of two mixing waters. Reservoir pressure and temperature as well as mixing ratios are also a must to complete the run.

In this study, ScaleChem (V2.2) was used to evaluate and quantify scaling precipitated from two Egyptian oil reservoirs existed in Gulf of Suez area at high temperature of 90-127 °C, high pressure of 3600 psi, and high salinity of 100,000-230,000 ppm and 35,000 ppm for formation and injected water, respectively. The cations and anions of such waters were determined experimentally using ion chromatography (IC), also, the produced scales formed from the Jar test have been analyzed using X-ray diffraction (XRD). Both of output data of theoretical software and laboratory Jar-testing results were compared.

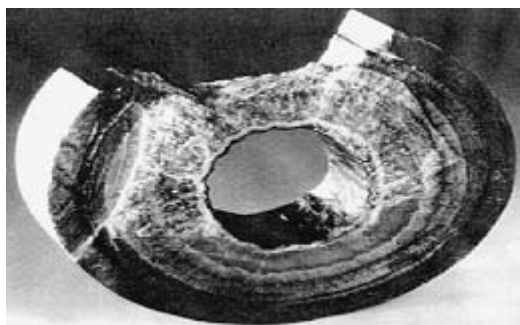


Fig. 1: Solid deposition in tubing⁴

designed to measure the theoretical quantitative calculations of scale tendency result from mixing of two incompatible waters at one or more specified temperature, pressure and at any specified ratio to simulate the reservoir conditions.

The ScaleChem Thermo Kinetic Modeling Software

Deposition of scale has been shown to be a widespread problem, that cake perforations, casing; production tubing, valves, pumps, and

Water analysis

Formation water normally is a highly saline brine of a composition typical for each geological formation. The major component is sodium chloride, mostly at concentrations higher than 10000 ppm. To characterize these water samples a lot of different anions and cations have to be analyzed. Anions of interest are sulfate, chloride and bromide which can be measured by ion chromatography (IC) in a single run, and also carbonate and hydrogen carbonate. In this respect, cations and anions of formation and injected brine water were determined experimentally according to ASTM D4327¹² using Dionex ion chromatography (IC) model DX 600 equipped with high capacity columns. Alkaline species (CO₃²⁻, OH⁻, and HCO₃⁻) were determined experimentally according to ASDTM D3875¹³ calculations were

Table 1: Complete formation water analysis (West Bakr H-12)

Physical Properties			
Total Dissolved Solids	48865.8mg/L	pH	7.1 @25°C
Conductivity	7.47×10 ² mohs/cm@30.4°C	Density	1.03081g/ml@60F
Resistivity	0.13387 ohm-m @30.4°C	Specific gravity	1.03183
Salinity	46741.7mg/l	Hardness	14770.94 mg/L
Chemical Properties			
Cations	mg/L	Anions	mg/L
Lithium	0.017	Chloride	28328.3
Sodium	10707	Bromide	149.86
Potassium	192.94	Bicarbonate	110
Magnesium	840.39	Sulfate	7.82
Calcium	4529.52		
Aluminum	Nil		
Iron	1.47		
Copper	0.17		
Strontium	117.72		
Barium	4.94		

Table 2: Complete injection water analysis (West Bakr K)

Physical Properties			
Total Dissolved Solids	24230mg/L	pH	7.7 @25°C
Conductivity	3.39×10 ² mohs/cm@30.9°C	Density	1.00934 g/ml @60 F
Resistivity	0.28653 Ohm-m @30.4°C	Specific gravity	1.01035
Salinity	20337.8mg/L	Hardness	7299.1 mg/L
Chemical Properties			
Cations	mg/L	Anions	mg/L
Sodium	4864	Chloride	12325.95
Potassium	159.5	Bromide	187
Magnesium	926	Bicarbonate	125.1
Calcium	1396	Sulfate	387
Aluminum	Nil		
Iron	0		
Copper	0		
Strontium	25.92		
Barium	0.9		

done using Alkalinity calculator ver.2.10 (USGS). The traces and ultra traces of metals were determined using inductively coupled plasma spectro instrument (ICP)¹⁴. The total dissolved solids, which are simply the total amount of matter dissolved in a given volume of water, was determined experimentally according to ASTM D-1888¹⁵. Conductivity and resistivity was determined experimentally using digital conductivity meter WTW 330I according to ASTM D1125¹⁶. Density and specific gravity were determined experimentally according to ASTM D1429¹⁷, pH was determined experimentally according to ASTM D1293¹⁸. Salinity value was calculated upon chloride content value. The ScaleChem software was run using the complete water analysis of such reservoir, i.e., from formation and injection water respectively, and the output data were given in Tables (1 and 2).

Jar-Test Procedure

The tested incompatibility brines were firstly pre-filtered to remove any suspended materials. Then complete water analyses were carried out to determine the concentration of the initial composing and scaling ions. After that the brines were mixed at different Formation water: injected water of 20:80, 40:60, 60:40 and 80:20, respectively, and incubated at the 150°F test temperature for 48 h. Then the mixtures were left for 24h the filtered through 0.42-micron filter paper to catch any precipitate. The filter papers were dried at 150°F for 2h and then the precipitates were weighted. Then the maximum scaling ratio was determined based on the weight of the precipitates.

Suspended Solid

The chemical composition of suspended solids filtered from mixing a certain volume of two incompatible waters using a membrane filter (0.45, pore size) are weighted to estimate the possible plugging tendency of water such as corrosion product, scale particles, formation sand, etc. The precipitated results from mixing different ratio of 80,60,40,20 from formation water with 20,40,60,80 from injection water, respectively, are given in Table (1 and 2).

Theoretical Compatibility Test

Scale Prediction In order to determine the

scale deposition, the ScaleChem (V2.2) computer software program was applied to predict the scale precipitation ScaleChem (V2.2) used to predicate and calculates the queens' speciation mineral saturation indices, mineral solubility's and the effect of mixing between different fluids (formation and injected waters)^{9&19}.

Calculating a Scaling Tendency

The Scaling Tendency is defined as the ratio of the activity product of an equilibrium equation to the solubility product for the same equation, the activity products is define as Q, therefore the Scaling Tendency can be written as the following equation:

$$(ST) = Q / K_{sp}$$

where K_{sp} = Solubility products

The solubility products of gypsum can be expressed as the following equilibrium equation taken in the consideration that the chemical formula of gypsum is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, therefore the equilibrium expression is:



The activity product, Q is defined as:

$$Q = a_{\text{Ca}^{++}} a_{\text{SO}_4^{-2}} a_{2\text{H}_2\text{O}}$$

where a_i is the activity of the species:

$$a_i = g_i m_i$$

where g_i is the activity coefficient for species i. and m_i is the molal concentration.

The solubility product, K_{sp} is a thermodynamic quantity and is a function of the temperature and pressure (although in most cases, the pressure functionality for solids can be ignored). The software has stored the K_{sp} for all of the solids used in the chemistry model.

When the ratio Q/K_{sp} is greater than 1.0, then the solid has tendency to form. When the ratio is less than 1.0, then there is little tendency to form.

Calculating a Scale Index.

The scale prediction results are expressed as Saturation Index (SI) and the amount of potential

precipitation. The scale index is the logarithmic volume of the scaling tendency, so that scale index (SI),

$$(SI) = \log_{10} (ST)$$

Table 3: Maximum scale mass in mg/L for all possible scales for ratios of H12-K mixture type of scale

% of formation water	BaSO ₄ (Barite)	CaCO ₃ (Calcite)	CaSO ₄ .2H ₂ O (Gypsum)
Ambient Conditions (P=14.73 psi & T= 60 °F)			
100	0	12.197	0
80	5.7648	13.247	0
60	5.0789	14.047	0
40	3.9426	14.502	0
20	2.6879	14.454	0
0	1.3851	13.607	0
At Reservoir Conditions (P=1000 psi & T=149 °F)			
100	0	30.594	0
80	0.66697	20.189	0
60	2.6246	9.397	0
40	2.4648	0	0
20	1.7247	0	0
0	0.74317	0	0

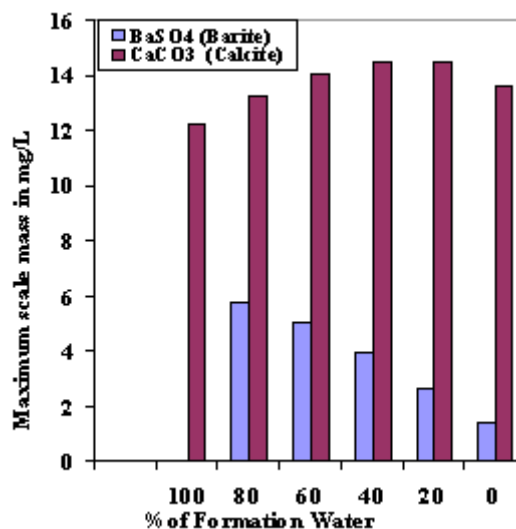


Fig. 2: Maximum Scale Mass in mg/L for All Possible Scales for ratios of H12-K Mixture at Standard Conditions (P=14.73 psi & T= 60 °F)

Table 4: Scale Tendency for all possible scales for ratios of H12-K mixture types of scale

% of Formation water	BaSO ₄ (Barite)	CaCO ₃ (Calcite)	CaSO ₄ .2H ₂ O (Gypsum)	FeCO ₃ (Siderite)	SrSO ₄ (Celestite)
Ambient Conditions (P=14.73 psi & T= 60 °F)					
100	0.56987	2.752	0.006388	0.0989	0.008
80	5.6683	3.1635	0.06425	0.1058	0.076
60	9.787	3.6347	0.11364	0.1087	0.131
40	12.505	4.1546	0.15236	0.1026	0.169
20	13.116	4.6843	0.17665	0.0759	0.182
0	10.342	5.1052	0.17968	0	0.157
At Reservoir Conditions (P=1000 psi & T=149 °F)					
100	0.11212	6.493	0.004426	0.099987	0.009
80	1.108	2.9548	0.044849	0.043285	0.087
60	1.9007	1.5796	0.079982	0.021151	0.15
40	2.4126	0.91106	0.10823	0.010294	0.194
20	2.5132	0.53175	0.12683	0.004034	0.21
0	1.9672	0.29468	0.13065	0	0.183

The positive SI ($SI > 0$) can be indicating that the solution (brine) is supersaturated, i.e., from the view of thermodynamic chemistry the scaling ions will have a tendency to form. On the contrary, the negative SI ($SI < 0$) indicates that the solution (brine) is unsaturated and there is no potential for the scale to form.

Laboratory Compatibility Test

In water handling operations we are primarily concerned with those ions and physical properties, which are important from the standpoint of plugging or corrosion.

RESULTS AND DISCUSSION

Results of simulator

The data in Table (1&2) indicated that the input data of formation and injection waters to the software is completely analyzed. The result show high concentration of scaling species (i.e., Ca^{++} , Ba^{++} , and SO_4^{--}).

Results of Water Analysis

The results in Table 1 indicated that the conductivity of formation water is 7.47×10^{-2} mhos/cm @30.4 °C, where as the corresponding conductivity of injection water is 3.39×10^{-2} mhos/cm @30.4 °C, on the contrary it have been found that the resistivity of electrical current flow as a function of an ion dissolved in water decreases from 0.28653 ohm-m @30.4 °C to 0.13387 Ohm-m @30.4 °C for injection, and formation water, respectively. Moreover, it has been found that the salinity (ionic strength) of formation water is higher by 26403.9 times than that of injection water According to all this data and in addition to the knowledge about the inversely relation between the dissolved ions and the resistivity, one can predict that the formation water has an ability to form undissolved ions than injection water.

In Table 1, it has been observed that the rank of increasing of the concentration of the dissolved cations and anions of formation water measuring using Dionex ion chromatograph (IC), are $Li^+ < Cu^{++} < Fe^{++} < Ba^{++} < Sr^{++} < K^{++} < Mg^{++} < Ca^{++} < Na^+$, for cations and $SO_4^{--} < HCO_3^- < Br^- < Cl^-$ for anions, respectively, taking into account the nature of dissolved salts with respect to pure NaCl brine.

Thereby, the probabilities of formation of sparingly soluble salts of $CaCO_3$ and $BaSO_4$ are dominant. The same rank of increasing of the concentration of the dissolved cations and anions of the injection water are also found in Table 2.

Prediction of Scales Formed at Different Conditions

In this part the two brines water used in current study were mixed at both of 60°F and 149°F which represents the ambient and reservoir conditions, respectively. After that the scale tendency of all possible scales have been predicted using a ScaleChem (V2.2) program, in this respect, the relation between the percentage of formation water in X axis plotted individually against all of maximum scale, scale tendency (ST) & scale index (SI), in Y axis, respectively.

The Prediction of Maximum Scale Masses at Ambient and Reservoir Conditions

The maximum scale masses in mg/l at ambient conditions (pressure of 14.73 psi and temperature of 60 °F), and different mixing ratios of 100, 80, 60, 40, 20 and 0 of formation water are shown in Figure (2), it is clear that the large quantities of barite ($BaSO_4$) and calcite ($CaCO_3$) are initiated at the ratio of 80:20 of formation water. Where as the maximum scale masses at reservoir conditions (pressure of 1000 psi and temperature of 149 °F) are given in Table 3. The result of maximum scale masses of calcite ($CaCO_3$) is 20.189 mg/L, and beginning at formation: injection water ratio of 80: 20, in the contrary the maximum scale mass of barium sulfate is 2.6246 mg/L recorded at ratio of formation water: injection water (60: 40). Such date is plotted in Fig. 5. Thus the mixing ratio should be designed suitably.

The Prediction of Scale Tendency at Ambient and Reservoir Conditions

The results in Tables (4) reveled that the higher scale tendency (ST) of barite values at ambient conditions are 5.6683, 9.787, 29.505, 13.116 and 10.342, which corresponding to 80, 60, 40, 20, and 0 of formation water, respectively. Meanwhile, the results of higher values of ST of calcite are 2.752, 3.1635, 3.6347, and 4.1546, which corresponding to 100, 80, 60, and 40 of formation water, respectively. It is clear that scale tendencies

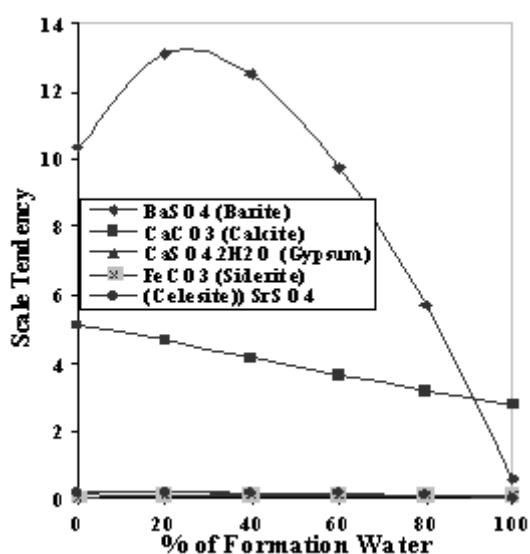


Fig. 3: Scale Tendency for All Possible Scales for ratios of H12-K Mixture at Standard Conditions (P=14.73 psi & T= 60 °F)

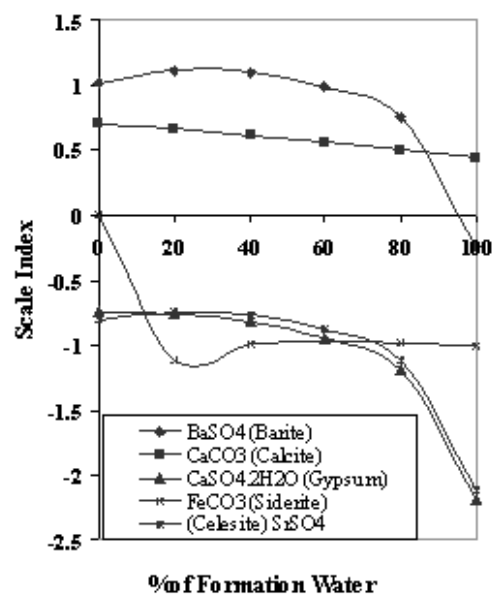


Fig. 4: Scale Index for All Possible Scales for ratios of H12-K Mixture at Standard Conditions (P=14.73 psi & T= 60 °F)

Table 5: Scale Index for all possible scales for ratios of H12-K mixture
Type of scale

% of formation water	BaSO ₄ (Barite)	CaCO ₃ (Calcite)	CaSO ₄ .2H ₂ O (Gypsum)	FeCO ₃ (Siderite)	SrSO ₄ (Celestite)
At Ambient Conditions (P=14.73 psi & T= 60 oF)					
100	-0.2442	0.4396	-2.1938	-1.0048	-2.11
80	0.7535	0.5002	-1.1918	-0.9755	-1.12
60	0.9906	0.5605	-0.9446	-0.9638	-0.88
40	1.0971	0.6185	-0.817	-0.9889	-0.77
20	1.1178	0.6706	-0.7528	-1.1198	-0.74
0	1.0146	0.708	-0.7455	0	-0.8
At Reservoir Conditions (P=1000 psi & T=149 oF)					
100	-0.95	0.8121	-2.3565	-1.0004	-2.06
80	0.0444	0.85	-1.3487	-0.9867	-1.06
60	0.2783	0.8834	-1.0975	-0.9935	-0.82
40	0.3813	0.9101	-0.9666	-1.0424	-0.71
20	0.3985	0.9265	-0.8983	-1.2007	-0.68
0	0.2915	0.9234	-0.8861	0	-0.74

Table 6: Maximum Scale Mass in mg/l for ratios of H12-K Mixture in jar test at Reservoir Conditions (P=1000 psi & T= 149 °F)

%of Formation water	Amount of Scale
Water	formed
20	3.8
40	4.5
60	12.9
80	19.92

Table 7: Results of XRD-Test for Scales result from possible ratios of H12-K Mixture at Reservoir Conditions (P=1000 psi & T= 149 °F)

%of Formation water	Amount of Scale, Wt %	
	CaCO ₃ (Calcite)	BaSO ₄ (Barite)
20	0	100
40	29.22784	70.77216
60	48.03045	51.96955
80	55.69265	44.30735

Table 8: The results of maximum scale amount of jar test and ScaleChem (V 2.2) at reservoir conditions

% of Formation water	Maximum amount scale (jar test)	Maximum amount scale (Software)	The conformity ratio %
80	19.92	20.85597	104.6986446
60	12.9	12.0216	93.19069767
40	4.5	2.4648	54.77333333
20	3.8	1.7247	45.38684211

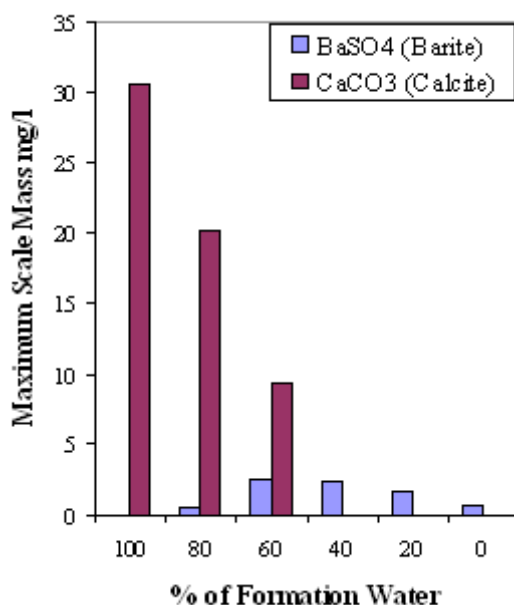


Fig. 5: Maximum scale mass in mg/L for all possible scales for ratios of H12-K mixture at reservoir conditions (P=1000 psi & T=149 °F)

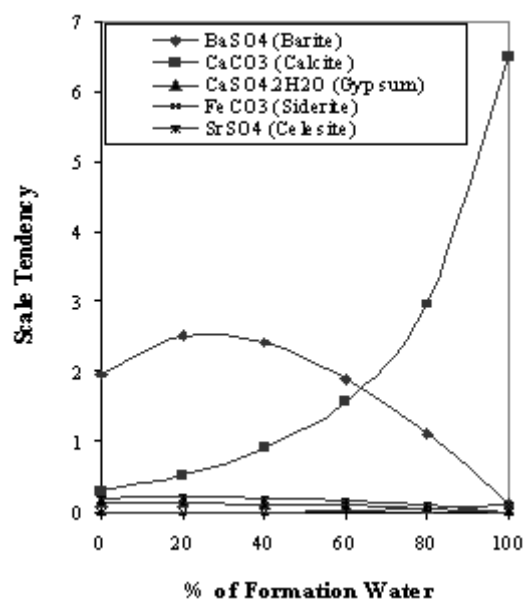


Fig. 6. Scale Tendency for all possible Scales for ratios of H12-K Mixture at Reservoir Conditions (P=1000 psi & T= 149 °F)

of barite and calcite are greater than 1.0 ($ST > 1.0$), which indicates a severe barite and calcite-scaling tendency. The ST of Gypsum is less than 1.0 [$ST < 1.0$], then there is little tendency to form, accordingly, it was not cause any problem.

The results of higher scale tendency (ST) of barite values at reservoir conditions are 1.108, 1.9007, 2.4126, 2.5132 and 1.9672, which corresponding to 80, 60, 40, 20, and 0 of formation water, respectively. Meanwhile, the results of higher values of ST of calcite are 6.493, 2.9548, 1.5796, and 0.91106, which corresponding to 100, 80, 60, and 40 of formation water, respectively.

Table (4) represents the scale tendency of all possible scales resulting from mixing different ratio of formation water and injection water. They also indicate that, calcium carbonate and barium sulfate are superiors in being formed at any mixing ratio between formation water and injection water.

The Prediction of Scale Index at Ambient and Reservoir Conditions

The scale index at ambient conditions are shown in Figure (4), the Figure illustrated that the higher scale index (SI) values of barite are 0.7535, 0.9906, 1.0971, 1.1178 and 1.0146 which corresponding to 80, 60, 40, 20, and 0 of formation

water, respectively. Meanwhile, the higher values of SI of calcite are 0.4396, 0.5002, 0.5605, and 0.6185, which corresponding to 100, 80, 60, and 40, of formation water, respectively. Such values illustrated that the SI are greater than zero ($SI > 0$), then such solid are supersaturated and have a tendency to form hard scales.

Meanwhile, in the case of reservoir conditions the higher values of scale index (SI) are shown in Figure (7), in this respect, the higher values of scale index (SI) of barite are 0.2783, 0.3813, 0.3985, and 0.2915, which corresponding to 60, 40, 20, and 0 of formation water, respectively. Where as, the higher values of SI of calcite are 0.8121, 0.85, 0.8834, and 0.9101 which corresponding to 100, 80, 60, and 40, of formation water, respectively.

On the contrary as indicated in Table (5), SI of the calcium sulfate (gypsum), and ferric carbonate recorded negative values ($SI < 0$), this mean that gypsum and ferric carbonate are undersaturated, and did not cause any problem. It is clear that from all these results the superior scales formed are calcite and barite.

Jar test was conducted to confirm the results of the simulator, and the results are given in

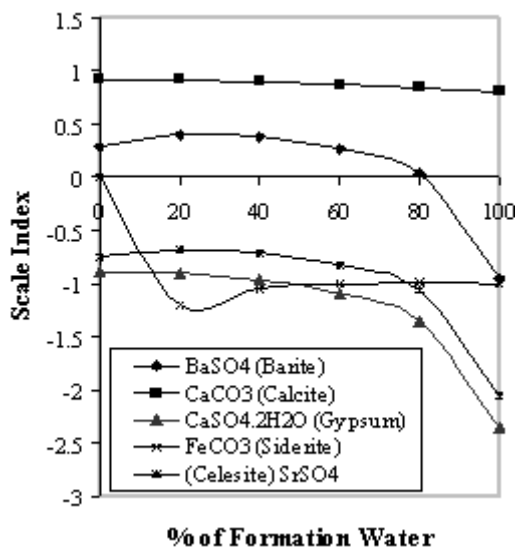


Fig. 7. Scale Index for all possible scales for ratios of H12-K Mixture at Reservoir Conditions (P=1000 psi & T=149 °F)

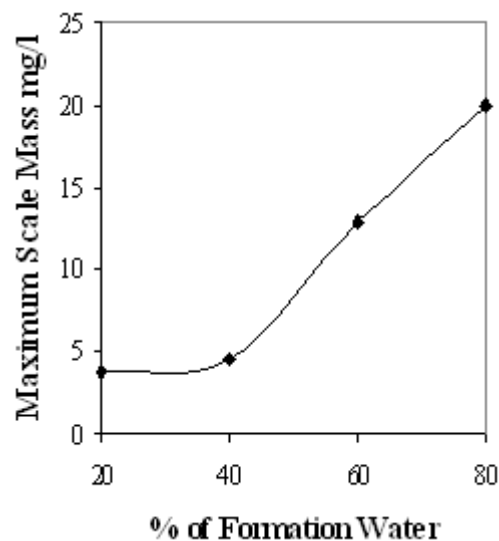


Fig. 8. Maximum scale formed for H12-K mixture at reservoir conditions (P=1000 psi & T= 149 °F)

Table 6 and plotted in (Fig. 8). The maximum scale formed 19.92mg /l is attained at formation: injection waters 80: 20. The results of XRD are given in table (7) and plotted in Figure (9) illustrate that the maximum calcium carbonate formation is 96.80202mg/l that occur at formation water: injection water of 80: 20, where as the maximum barite

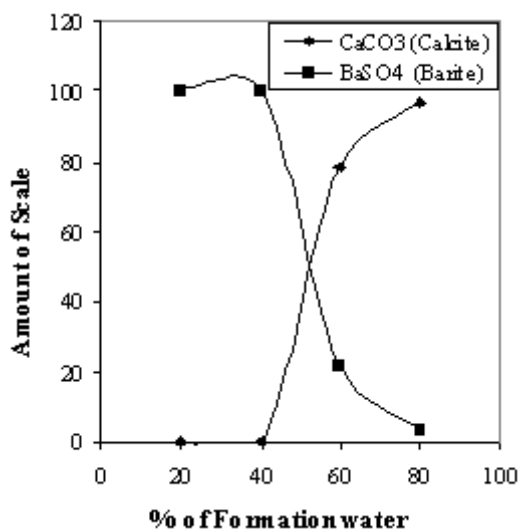


Fig. 9: Results of XRD-Test for scales result from possible ratios of H12-K mixture at reservoir conditions (P=1000 psi & T= 149 °F)

formation is 21.83237 mg/l that obtained at formation: injection waters of 60:40. The results of maximum scale amount of jar test and ScaleChem (V 2.2) at reservoir conditions that represent in Table (8) evident a good conformity between both tools used to calculate and understanding the meticulous thermo kinetic process that causes the scale. Accordingly, the ratios of 80 and 60 of formation water are the most performance ratios that can be apply safely in oilfield.

Conclusions

A wide range of field brines was examined using a ScaleChem (V2.2). The results indicate that the model is capable for predicting the scaling tendencies of BaSO₄, CaCO₃ and CaSO₄ at various water compositions, temperatures and pressures covering oilfield conditions. Also it is confirmed that, to achieve the correct prediction of scale precipitations in the complex field waters, the possible competitive co precipitation of scale minerals in the same solution and the temperature and pressure changes should be taken into consideration. The maximum scale amounts of jar test and ScaleChem (V 2.2) at reservoir conditions are obtained at 80:20 of formation water; consequently, one can say that both of the simulation results and jar test results are in good agreement with each other.

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