

NORM Scale Formation, Control, And Relation To Gas Hydrate Control

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ABSTRACT

Some oil field scales have the potential to contain regulated levels of naturally occurring radioactive materials (NORM). It is estimated that between 300,000 and 1,000,000 tons of NORM scale are produced each year. The most common NORM containing scale is BaSO₄, or barite. Research at the Brine Chemistry Consortium have studied the causes of barite scale formation and control techniques. Recent research have shown that NORM scale formation can be adversely affected by the presence of gas hydrate inhibitors, e.g., methanol or glycols. Chemical threshold scale inhibitors have proven to be most efficient to inhibit barite scale formation in production systems. A semi-empirical mathematical model has been developed to predict inhibitor efficiency for barium sulfate scale control in industrial processes. This model can be used for selecting effective inhibitors and determining the minimal effective concentration needed for a given system. The model prediction for barium sulfate scale control was in good agreement with laboratory observations and field experience.

INTRODUCTION

Mineral scales are deposits produced in field production facilities due to temperature and pressure changes during the gas and oil recovery processes. Scale deposition in producing wells and associated facilities negatively impacts rates of production and is expensive to treat and remediate. Some oil field scales have the potential to contain regulated levels of NORM, generally in the form of radium-226 and radium-228. Chemically, radium is a metal cation with a charge of plus two (2+) and is slightly mobile in the produced water. Worldwide produced waters have from nil to a few thousand picocuries/l of radioactivity due to radium-226 and radium-228. The concentration of radium in the flowing brine is generally not high enough to be regulated, but when concentrated in scale deposits radiation levels can be in excess of regulated limits. It is estimated that between 300,000 and 1,000,000 tons of NORM scale are produced in the United States each year, if all NORM scales are included¹. However, these estimates drop dramatically to 15,000 to 50,000 tons/year if included scales are limited to >2,000 pCi/gram. Due to the uncertainties in the amount of material produced and the low average radionuclide content, it is difficult to assess the risk.

The most common NORM containing scale is barium sulfate, or barite². Although the radionuclides responsible for NORM in barium sulfate scales are radium-226 and radium-228, these radionuclides do not precipitate directly, but are co-precipitated in the barium sulfate scale causing the scale to be radioactive as in the following equation:



The concentration of radium in the barite solid is always far less than the concentration of barium. Barium sulfate scale occurs during gas and oil production in many places throughout the world and in the United States including the Michigan Basin, the Gulf Coast, Oklahoma and Alaska to name a few³. Unlike most other common scales, no economic method exists to chemically remove barium sulfate from field equipment. Furthermore, the scale often forms near or at the bottom of a well. The scale is usually removed by mechanical means. This results in lost production, damaged or ruined equipment and downtime. In addition, the recovery of solid NORM scale materials leads to storage problems of the regulated material.

Progress has been made toward the control and treatment of the scale deposits, although most of the reaction mechanisms are still not well understood. Often the most efficient and economic treatment for scale formation is to apply threshold chemical inhibitors via the "inhibitor squeeze". Threshold scale inhibitors are like catalysts and have inhibition efficiency at very low concentrations (commonly less than a few mg/L), far below the stoichiometric concentrations of the crystal lattice ions in solution. There are many chemical classes of inhibitors and even more brands on the market. Inhibitors are tested in the laboratory with either dynamic high pressure and temperature flow-through methods or in static beaker tests. In the following, the state of the art developments at Rice University Brine Chemistry Consortium on the prediction of barite scale formation and inhibition will be discussed. Some recent work on the adverse effect of hydrate inhibitors on barite scale formation and inhibition will also be discussed.

Scale Prediction

The thermodynamic-based solubility of mineral salt is defined as the ion activity product at equilibrium (See Eq. 1 for an anhydrous, divalent ion salt).

$$K_{sp}(T, P) = \{ \text{Me}_{eq}^{2+} \} \cdot \{ \text{A}_{eq}^{2-} \} = (\text{Me}_{eq}^{2+}) \cdot (\text{A}_{eq}^{2-}) \cdot \gamma_{\text{Me}} \cdot \gamma_{\text{A}} \quad 1$$

The solubility product is a function of temperature and pressure and its temperature and pressure dependence is typically well known^{4,5}. Mineral scale is generally predicted with saturation indexes that compare the amount of the scaling constituents in solution to the solubility. There are several commercial and non-commercial computer programs available, all with severely limited utility in practical scale control in the oil and gas industry. Most of these programs [e.g., SOLMINEQ.88, PHREQ.PITZ, EQ3/EQ6, and EQPITZER] are simply general-purpose chemical speciation codes, not intended specifically for oilfield brine and conditions. In addition to the standard difficulties with brine sampling and analyses, all the above programs require measurement of the brine pH. In oil and gas wells, realistic pH measurement is rarely feasible. The measured pH depends strongly on the conditions of sampling and analysis. In addition to the procedural difficulties of measuring pH, the theoretical meaning of usable pH in complex oilfield brines is ambiguous, at best.

To overcome these shortcomings, a computer program, ScaleSoftPitzerTM, has been developed by the authors. The program is written in MicrosoftTM ExcelTM designed to calculate the pH, scaling tendency, and inhibitor needs of oil and gas wells for commonly encountered minerals: 1. Calcite (CaCO₃); 2. Barite (BaSO₄); 3. Gypsum (CaSO₄·2H₂O); 4. Hemihydrate (CaSO₄·1/2H₂O); 5 Anhydrite (CaSO₄); 6. Celestite (SrSO₄); 7. Fluorite (CaF₂); 8. Sphalerite (ZnS); 9. Iron-sulfide (FeS); 10. Siderite (FeCO₃); and 11. Halite (NaCl). The program has incorporated a subroutine for simulating mixing of brine from different zone or seawater. The calculations are based on Pitzer theory of electrolytes and the latest version of Pitzer coefficients⁶. The unique feature of this program is the rigorous approach used to handle the conservation of all brine components (total mass of oil, water, gases, all mineral components, and alkalinity). pH from bottomhole to surface can be calculated from the continuous partition of CO₂ in gas/oil/water phases due to temperature and pressure changes. The Rice University Brine Chemistry Consortium, an industrial consortium of both the production and chemical companies, supported the development of ScaleSoftPitzerTM.

In ScaleSoftPitzer, the most reliable temperature and pressure dependence of solubility product is used. Scaling tendency is represented by the ratio of the ion activity product and the thermodynamic-based saturation index, SI, and is defined as Eq. 2.

$$SI \equiv \text{Log}_{10} \left\{ \frac{\{Me^{2+}\} \cdot \{A^{2-}\}}{K_{sp}(T, P)} \right\} \quad 2$$

The program results have been tested extensively against other computer programs, published solubility data, and published activity coefficient results. In each case, typically three levels of testing have been done 1. the overall layout, logic, and assumptions have been tested against field experience and published results; 2. the detailed equations have been tested for mathematical rigor and typographical errors (presently, the program is about 1500 lines of VBA code); and 3. the calculation results have been checked against published solubility data and activity coefficients and against other tested computer programs, which calculate similar results. Emphasis has been placed on the calcite, sulfate, and halite systems. The bubble point is calculated in either of two ways: 1. given the oil API gravity and the gas specific gravity, the Vasquez & Beggs correlation is used to calculate the bubble point; or 2. an average set of partition coefficients is used to calculate whether a gas phase exits at a given T and P. The first method does not consider the water phase and is therefore probably better for oil wells while the second method considers both the oil and the water phases and might be preferred for gas wells that produce predominantly gas and water. Fugacity coefficients of gases are calculated via a modified Peng-Robinson equation of state method, recommended in Reid, Prausnitz, and Poling⁷; it can easily be extended to include more complicated gas mixtures and hydrocarbon liquids.

There are three primary modes of running ScaleSoftPitzerTM. First, the program divides the bottom hole to surface into ten even intervals in temperature and pressure and calculates the saturation index for

each mineral at the specified (T, P) and composition and plots the results. For several minerals the change in SI from the bottom to the top is also calculated. Second, the program allows for convenient what-if calculations at different (T, P) and %CO₂ values. Third, a second brine (more could be added, if needed) can be defined and mixed in any proportions with the produced brine; the default second brine is sea water, but any composition can be used. Finally, the inhibitor needs to control either the calcite or barite scale formation under the given well condition are calculated based upon our previous research on nucleation inhibition.

The variation of SI with temperature and pressure at various locations in the production system is presented in the program. In addition, both the absolute SI and ΔSI are calculated. The ΔSI concept (1) is based on an assumption that the brine is in equilibrium with carbonate (or sulfate) minerals present in the reservoir rock and thus a zero-SI exists with respect to that mineral under these conditions. Therefore, the ΔSI at a given location is the SI calibrated with the reference point (the reservoir condition). It is especially useful when analytical parameters are not complete or in doubt, because it reflects the changes in the degree of supersaturation of the fluid in response to changes in temperature and pressure.

Inhibitor Needs And Selection

Recently, the authors have made progress in estimating the inhibitor efficiency through a semi-empirical nucleation inhibition model and in characterizing the solubility and phase transformation behavior of metal-inhibitor precipitates. With the nucleation inhibition model, we are able to predict the minimum effective inhibitor concentration needed for a specific well condition and then select the most effective inhibitor for a squeeze application. With the solubility model, it is possible to describe the flow-back curve of the inhibitor after a squeeze treatment. Which inhibitor to use among many commercial options and the minimum effective concentration needed are often critical in scale treatment. Common inhibitor types include various aminopolyphosphonates, polyacrylates, polysulfonates, their derivatives and mixtures. The inhibition calculation in this program is based on a semi-empirical nucleation inhibition model. The currently available inhibitors in this program include: NTMP [nitrilotri(methylene phosphonic) acid], HDTMP [hexamethylenediamine tetra(methylene phosphonic) acid], DTPMP [diethylenetriamine penta(methylene phosphonic) acid], BHPMP [bis-hexamethylenetriamine penta(methylene phosphonic) acid], PAA (polyacrylic acid), PPCA (phosphinopolycarboxylic acid), and SPA (sulfonated polyacrylic acid)⁸⁻¹⁰. Other inhibitors and inhibitor blends can be easily added into the program once their inhibitory properties are measured and become available. Also the model parameter set is presently limited to calcite and barite, the most common oilfield scales. Preliminary data are available for additional scale types and will be included later when they become available.

The efficiency of inhibitors has been modeled as a function of field conditions, such as saturation index (SI), temperature (T), pH, and lattice ion ratios (R, for example [Ba²⁺]/[SO₄²⁻] in the case of barite scale, [Ca²⁺]/[HCO₃⁻] used for calcite instead of [Ca²⁺]/[CO₃²⁻] for convenience) as in Eq. (3) to Eq. (6).

$$C_{inh} \text{ (mg/l)} = \frac{1}{b_{inh} \text{ (l/mg)}} \log \left\{ f_{safety} \frac{t_{inh} \text{ (sec)}}{t_0 \text{ (sec)}} \right\} \quad 3$$

$$\log[b_{inh} \text{ (l/mg)}] = \beta_0 + \beta_1 \cdot SI + \frac{\beta_2}{T \text{ (K)}} + \beta_3 \cdot \text{pH} + \beta_4 \log R \quad 4$$

$$\log t_0 \text{ (BaSO}_4 \text{, sec)} = 1.83 - \frac{12.1}{SI} - \frac{885.8}{T \text{ (K)}} + \frac{5460.3}{SI \cdot T \text{ (K)}} \quad 5$$

$$\log t_0(\text{CaCO}_3, \text{sec}) = 4.22 - \frac{13.8}{\text{SI}} - \frac{1876.4}{\text{T(K)}} + \frac{6259.6}{\text{SI} \cdot \text{T(K)}}$$

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where C_{inh} is the minimum effective inhibitor concentration needed, f_{safety} is the safety factor generally set from two to three, b_{inh} is the inhibition efficiency, t_{inh} is the time period for the system to be protected from scaling which is approximately equal to the time for the brine to travel from the bottom-hole to surface facility plus the surface detention time, t_0 is the induction time for the supersaturated solution to nucleate without inhibitors, β_0 to β_4 are constants listed in Table 1 for calcite and barite. An advantage of this approach, as suggest via Eq. 3 to Eq. 6, is that the effect of the inhibition is separated from the effect of the mineral nucleation and therefore it is only necessary to do a few inhibition experiments to characterize a new inhibitor or blend.

In general, the inhibitor efficiency was expressed in terms of its b_{inh} values at a given condition as a function of field variables such as pH, T, SI, and R as in Eq. 4. The selection of inhibitors is based on the calculated b_{inh} values for a scale type at a given condition. Generally the higher the b_{inh} value, more efficient is the inhibitor. Therefore, the inhibitor with the maximum b_{inh} will be chosen. In addition, the inhibitor can be manually selected if the user prefers to use other inhibitors or blends rather than the one recommended by the program.

Effect Of Hydrate Inhibitors On Barite Scale Formation.

In the oil and gas industries, methanol and ethylene glycol are often used to inhibit gas hydrate formation during production. Gas hydrate is a crystalline solid consisting of gas molecule surrounded by a cage of water molecules, which forms at certain high pressure and low temperature regimes. Gas hydrate formation is particularly troublesome for offshore gas wells where the producing temperature is low due to both adiabatic expansion of gas and seawater cooling. Once gas hydrate forms, it can plug up the well and prevent gas production. One economic solution to prevent hydrate formation is to inject a large quantity of methanol or ethylene glycol. However, methanol or ethylene glycol may cause adverse scaling problems in the associated brine solution, which often contains high concentrations of dissolved minerals. There is little research on the solubility of mineral salt in methanol/water/salt or ethylene glycol/water/salt solutions. The authors have studied the solubility of mineral salts in these mixed solvent systems and inhibition of scale formation in the presence of methanol or ethylene glycol. The impact of methanol on barite scale formation are predicted by ScaleSoftPitzer[®] with a neutral species activity coefficient, $\gamma_{\text{MA}}^{\text{N}\pm}$ 11,12.

$$\text{SI}^{\text{Barite}} = \log \left\{ \frac{[\text{Ba}^{2+}] \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{Ba}^{2+}}^{\text{S}} \cdot \gamma_{\text{SO}_4^{2-}}^{\text{S}} \cdot \gamma_{\text{BaSO}_4}^{\text{N}\pm 2}}{K_{\text{sp}}^{\text{Barite}}} \right\} \quad 7$$

The model parameters for γ^{N} and $\gamma_{\text{MA}}^{\text{N}\pm}$ can be depicted in the nomogram of Figure 1 or calculated from the equations in Table 2. Figure 1 can be used to estimate activity coefficients (γ^{N} and $\gamma_{\text{MA}}^{\text{N}\pm}$) and dielectric constant values in methanol solutions at 25 °C, as well as to correlate between vol%, wt%, and mole fraction. Combining γ^{N} and $\gamma_{\text{MA}}^{\text{N}\pm}$ with common activity coefficient calculations, e.g., Pitzer theory, the saturation index of calcite, barite, celestite, gypsum, and halite at a given methanol concentration can be predicted.

In Figure 2 is plotted the predicted change in mg/L of scale formation and saturation index of calcite and barite versus the methanol concentration (% vol) under realistic field condition. The calculations were done with ScaleSoftPitzer[®], which is written in Microsoft Excel[®] program specifically for oil field application. The above methanol activity coefficient (γ^N and $\gamma_{MA}^{N\pm}$) have been incorporated into the program. The calcite simulation is done for a brine containing 4,972 mg/L Ca, 660 mg/L bicarbonate alkalinity, 69,801 mg/L total dissolved solid, equilibrated with 1% CO₂ in the gas phase, at 25 °C and 2,940 psig pressure. The barite scaling tendency was simulated for a brine containing 57,211 mg/L TDS, 15 mg/L Ba, and 11 mg/L sulfate at 25 °C and 2,940 psig pressure. In both simulations, the brine composition is adjusted such that the SI is zero when $x_{MeOH} = 0$. The simulation shows that considerable barite or calcite scale will form in the presence of as little as 5-20% methanol (by volume). The effect of methanol on halite scale formation can be evaluated from Figure 3. In Figure 3 is plotted the amount of halite that will precipitate from brines versus TDS (assumed to be equal to NaCl concentrations) where different methanol concentrations (Vol%) are compared. In the absence of methanol, NaCl is soluble in water up to 6.1 m or approximately 318,000 mg/L TDS. However, NaCl will precipitate out of a brine containing 250,000 mg/L TDS when 30% methanol is added to the system. At 50% methanol, the system may experience halite problem if the brine contains > 210,000 mg/L TDS, etc.

Effect Of Methanol And Ethylene Glycol On Barite Scale Nucleation And Inhibition

It has been observed that barite nucleation rate is significantly affected by the addition of methanol. We have systematically measured the barite nucleation time at both a varied methanol concentrations (0 - 40% by wt.) and a varied barium and sulfate (at equal molal) concentrations from 0.5 -1.1 mmoles/Kg H₂O¹³. The experiments were done by first mixing a barium containing solution and a sulfate containing solution. The onset of nucleation was monitored by a turbidity meter over time using a data logger. The induction time is operationally defined as the time when the rapid increase in turbidity is observed. In Figure 4a is plotted the turbidity reading versus logarithmic reaction time in seconds for seven nucleation kinetic experiments where the only variable is the methanol concentrations. In this example, the barium solution contains 1 m NaCl, 0.09 m Ca, 1.50 mm Ba and 5 mm PIPES buffer at pH 6.4. The sulfate solution contains 1 m NaCl, 0.09 m Ca, 1.44 mm sulfate, and 5 mm PIPES buffer at pH 6.4. Methanol was added to both the cationic and anionic solution to a fixed concentration. An equal volume of these two solutions were then mixed and the turbidity of the solution was monitored. As shown in Figure 4a, barite induction time was affected by as little as 5% (by wt) of methanol and the induction time is shortened more at higher methanol concentrations.

It has been observed that barite nucleation time (t_{ind}^0 , sec) is related to the supersaturating state of the solution (SI), temperature (°K) and methanol concentration by Eq. 6:

$$\log_{10}(t_{ind}^0, \text{sec}) = \left\{ -2.235 + \frac{[1087.2 - 0.297 \cdot T]^2}{T^2 SI_{Brine}} - 0.123 \frac{[1087.2 - 0.297 \cdot T]^3}{T^3 SI_{Brine}^2} \right\} - 13.68 \cdot x_{MeOH} \quad (6)$$

In Eq. 6, the first term represents the effect of ions and temperature on barite nucleation and the second term is an empirical function to account for the effect of methanol on nucleation rate. Very good agreement ($r = 0.97$) between the observed and calculated induction time ($\log_{10}(t_{ind}^0)$) are observed (Figure 4b).

The inhibitory effect of a phosphonate scale inhibitor (BHPMP, Bis-hexamethylene triamine-penta(methylene phosphonic) acid) on barite nucleation has been studied at 0-40% methanol or ethylene glycol and 0.7 to 1.1 mm barium and sulfate concentrations. BHPMP is one of the most effective barite

inhibitors. In Figure 5 is plotted a typical set of nucleation studies where barium and sulfate concentrations are 1.1 mm (SI=2.0). The solutions also contain 1 m NaCl, 0.09 m Ca, 5 mm PIPES buffer (pH 6.4) and various concentrations of BHPMP and methanol or ethylene glycol. The six plots in Figure 5 are grouped by different methanol or ethylene glycol concentrations. In each plot of Figure 5, multiple nucleation data are plotted. These nucleation experiments were done at identical solution compositions, except for BHPMP concentrations. Increasing concentrations of BHPMP were added to successive experiments until a BHPMP concentration capable of inhibiting barite precipitation up to ~24 hours ($\log t=4.94$) was observed. As shown in Figure 5a, only 0.33 mg/L BHPMP was needed to inhibit the barite nucleation for 24 hours when no methanol was present. However, more BHPMP was needed at higher methanol concentrations. For example, 0.65, 1.90 2.52 mg/L BHPMP were needed to inhibit barite nucleation in 10-30% methanol. Even though only 2.52 mg/L BHPMP was needed to inhibit barite precipitation in 30% methanol, low turbidity was observed at 3-5.3 mg/L BHPMP for the same solution. The reason for the deteriorating inhibition effect at higher BHPMP concentrations is probably caused by the precipitation of Ca-BHPMP at higher methanol concentrations. The solubility of BHPMP in a similar sulfate free solution is measured to be ~2.0 mg/L in 30% methanol concentration and ~1.2 mg/L in 40% methanol concentration. If the phosphonate inhibitor solubility in methanol solution is limited, there should be a limiting methanol concentration that no phosphonate inhibitor will work. As shown in Figure 5e, no inhibitory effect was observed for BHPMP up to 5.8 mg/L concentration at 40% methanol. Interestingly, only 0.38 mg/L BHPMP is needed to inhibit barite precipitation from a similar solution containing 40% ethylene glycol (Figure 5f). These results are consistent with the solubility data, indicating a significant advantage in using ethylene glycol to control hydrate formation.

CONCLUSION

Some oil field scales have the potential to contain regulated levels of naturally occurring radioactive materials (NORM). However, NORM problem can be prevented if barite scale formation is properly monitored and controlled. The common cause for sulfate scale is commingling of different sources of brines either due to breakthrough of injected seawater, incompatible brine or mixing of different brines from different zones of the reservoir formation from different wells. A decrease in temperature tends to cause barite to precipitate. In addition, pressure drops tend to cause all scale minerals to precipitate due to the pressure dependence of the solubility product.

In subsea gas wells, hydrate formation is often problematic due to the large temperature drop. Methanol, ethanol, and ethylene glycol are often added in large quantity to control hydrate formation. Such practice has significant adverse effect on scale formation. A new activity model (ScaleSoftPitzer[®]) is proposed to model the mineral salt scaling tendency in oil and gas production system. The model uses Pitzer theory to model the effect of salt and Born equation to model the effect of hydrate inhibitors. The model predicts potentially significant barite and calcite scaling problem with as little as 5% to 20% methanol in a well. Halite scale problem can occur at >210,000 mg/L TDS when 50% (vol.) methanol is present in the production system. Barite nucleation rate is accelerated in as little as 5% methanol. A semiempirical equation has been developed to predict the kinetics of barite scale formation as a function of methanol concentration. More scale inhibitors are needed to inhibit barite scale when methanol is added to the production system. Barite scale control may become impossible when substantial amount of methanol are used for hydrate control. Ethylene glycol has less adverse effects than methanol in both scale formation and inhibition.

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Table 1 - Empirical coefficients used in the nucleation inhibition model (eqn (4)) to calculate inhibitor efficiency coefficient, b_{inh}^* .

Inhibitors	Calcite					Barite				
	β_0	β_1	β_2	β_3	β_4	β_0	β_1	β_2	β_3	β_4
BHPMP	-3.21	-1.45	1918.7	0	0.27	-0.999	-1.28	1143.3	0.134	0.106
NTMP	-0.53	-1.61	1226.0	0	0.13	-3.227	-1.13	1254.8	0.337	0.225
HEDP	0.23	-1.69	1082.0	0	0.14	-1.403	-1.05	639.5	0.290	0.181
HDTMP	-3.15	-1.22	1813.1	0	0.27	-0.006	-1.40	968.6	0.102	0.137
DTPMP	-1.53	-1.63	1396.4	0	0.29	-0.113	-1.76	1076.7	0.154	0.087
PAA	-2.54	-1.55	1734.6	0	0.27	0.645	-1.53	1051.1	0	0.102
SPA	-2.96	-1.59	1768.8	0	0.20	0.780	-1.76	1068.7	0	0.074
PPCA	-3.04	-1.41	1745.3	0	0.33	0.366	-1.58	1131.9	0	0.079

$$* \log[b_{inh}(\text{l/mg})] = \beta_0 + \beta_1 \cdot \text{SI} + \frac{\beta_2}{T(\text{K})} + \beta_3 \cdot \text{pH} + \beta_4 \log F$$

Table 2. The correlation of activity due to methanol effect (γ^N and $\gamma^{N\pm}$) with methanol concentrations (mole fraction), ionic strength and temperature.

$$\log(\gamma_{\text{CO}_2, \text{aq}}^N) = (-6.029 + 1444.9/T(^{\circ}\text{K})) \cdot x_{\text{MeOH}} - 1.170 \cdot x_{\text{MeOH}}^2 \quad r = 1.00$$

Standard deviations for the three parameters are 0.612, 175.4, and 0.135, respectively.

$$\log(\gamma_{\text{HCO}_3^-}^N) = (-3.338 + 955.9/T(^{\circ}\text{K})) \cdot x_{\text{MeOH}} + 0.565 \cdot x_{\text{MeOH}}^2 \quad r = 0.85$$

Standard deviations for the three parameters are 0.929, 260.8, and 0.211, respectively.

$$\log(\gamma_{\text{CO}_3^{2-}}^N) = (-1.957 + 1580.9/T(^{\circ}\text{K})) \cdot x_{\text{MeOH}} - 1.601 \cdot x_{\text{MeOH}}^2 \quad r = 0.99$$

Standard deviations for the three parameters are 0.520, 150.9, and 0.097, respectively

$$\log(\gamma_{\text{Ca}^{2+}}^N) = (19.343 - 4714.2/T(^{\circ}\text{K}) - 0.333 \cdot I) \cdot x_{\text{MeOH}} - 2.519 \cdot x_{\text{MeOH}}^2 \quad r = 0.97$$

Standard deviations for the three parameters are 0.861, 247.2, 0.0316 and 0.189, respectively

$$\log(\gamma_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}^{N\pm}) = (4.706 - 0.423 \cdot I) \cdot x_{\text{MeOH}} - 4.153 \cdot x_{\text{MeOH}}^2 \quad r = 0.97$$

Standard deviations for the three parameters are 0.314, 0.092, and 1.205, respectively

$$\log(\gamma_{\text{SrSO}_4}^{N\pm}) = (4.963 - 0.206 \cdot I) \cdot x_{\text{MeOH}} - 4.017 \cdot x_{\text{MeOH}}^2 \quad r = 1.00$$

Standard deviations for the three parameters are 0.221, 0.0484, and 0.613, respectively

$$\log(\gamma_{\text{BaSO}_4}^{N\pm}) = (3.022 + 1167.6/T(^{\circ}\text{K})) \cdot x_{\text{MeOH}} - 10.89 \cdot x_{\text{MeOH}}^2 \quad r = 0.99$$

Standard deviations for the three parameters are 2.507, 723.2, and 1.046, respectively

$$\log(\gamma_{\text{BaSO}_4}^{N\pm}) = 2.590 \cdot x_{\text{EG}} - 5.316 \cdot x_{\text{EG}}^2 \quad r = 0.52$$

Standard deviations for the three parameters are 0.623 and 1.684, respectively

$$\log(\gamma_{\text{NaCl}}^{N\pm}) = 1.385 \cdot x_{\text{MeOH}} - 1.104 \cdot x_{\text{MeOH}}^2 \quad r = 0.96$$

Standard deviations for the three parameters are 0.070 and 0.110, respectively

$$\log(\gamma_{\text{NaCl}}^{N\pm}) = 1.366 \cdot x_{\text{EtOH}} \quad r = 0.99$$

Standard deviations for the parameter is 0.018.

$$\log(\gamma_{\text{NaCl}}^{N\pm}) = -0.429 \cdot x_{\text{EG}} \quad r = 0.90$$

Standard deviations for the parameter is 0.118.

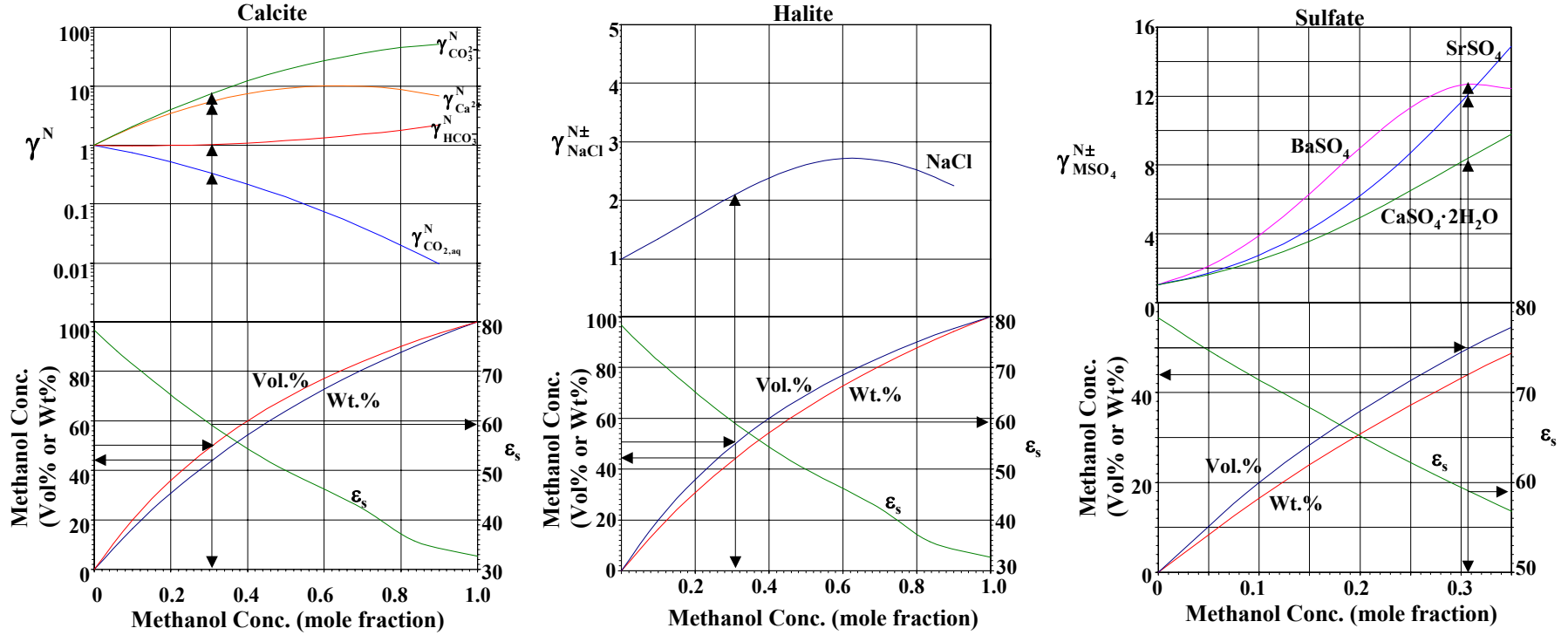


Figure 1. Nomograms to determine γ^N , $\gamma_{MA}^{N\pm}$ and solution dielectric constants for calcite, barite and halite from either methanol vol%, wt%, or mole fraction concentrations, where γ^N and $\gamma_{MA}^{N\pm}$ values are calculated from equations listed in Table 3. For illustration, arrows are drawn to show the users how to find all parameters at 50% (vol) methanol concentrations. All data is for 25 °C. For example, 50 vol % methanol = 44 wt % = 0.308 mole fraction; $\gamma_{CO_3^{2-}}^N = 7.5$, $\gamma_{Ca^{2+}}^N = 5.6$, $\gamma_{HCO_3^-}^N = 1.0$, $\gamma_{CO_2,aq}^N = 0.3$, $\gamma_{NaCl}^{N\pm} = 2.1$, $\gamma_{SrSO_4}^{N\pm} = 12.1$, $\gamma_{BaSO_4}^{N\pm} = 12.7$, $\gamma_{CaSO_4 \cdot 2H_2O}^{N\pm} = 8.4$, and $\epsilon_s = 59$.

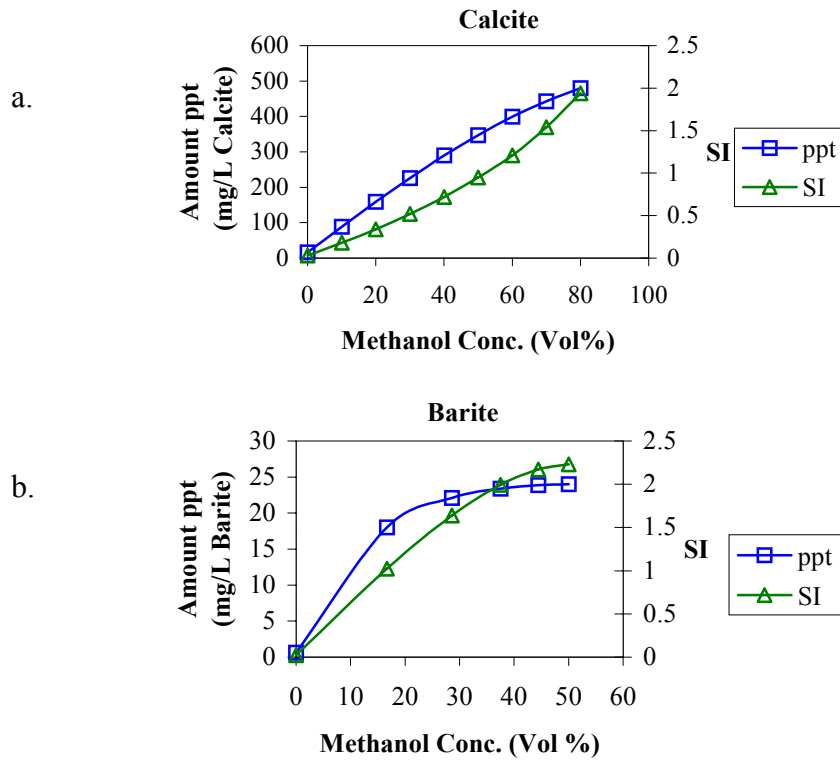


Figure 2. Plots of (a) amount of calcite scale precipitated (mg/L) and calcite SI and (b) amount of barite scale precipitated (mg/L) and barite SI versus the methanol concentrations where the condition for the simulation is discussed in text.

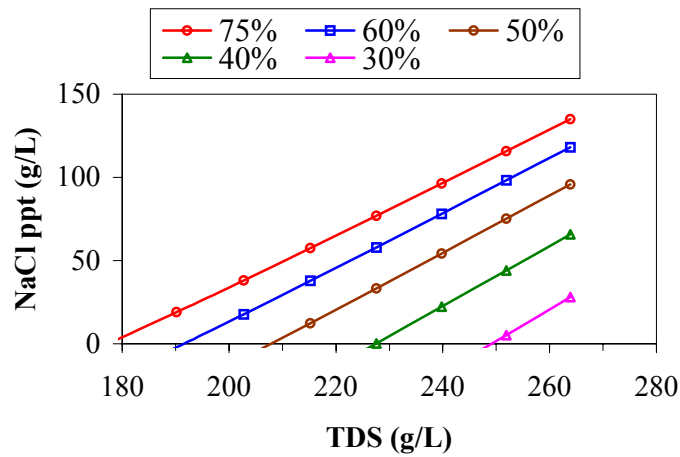
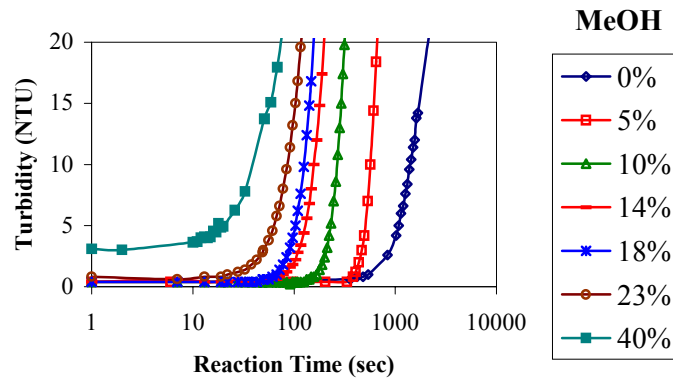


Figure 3. Plot of the amount of NaCl precipitated (mg/L) versus the brine TDS when various volume % of methanol is present in the brine. The condition for the simulation is discussed in the text.

a.



b.

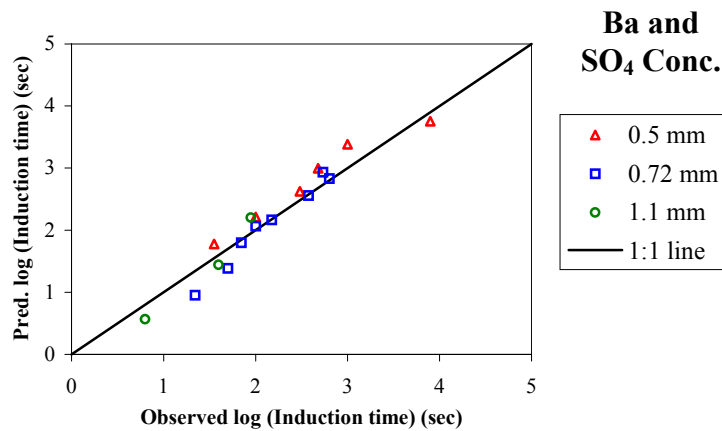


Figure 5. Plots of (a) the turbidity reading of a solution after mixing an equal volume of a cationic solution (1 m NaCl, 0.09 m Ca, and 1.50 mm Ba) and an anionic solution (1 m NaCl, 0.09 m Ca, and 1.44 mm SO₄) at 25 °C versus time (sec). The final Ba and SO₄ concentrations are 0.75 and 0.72 mm, which correspond to $SI_{\text{barite}} = 1.6$ in the absence of methanol; and (b) the predicted logarithmic induction time (sec) by Eq. 8 versus observed logarithmic induction time (sec). The data were from nucleation kinetics experiments at three different Ba and SO₄ concentrations and 0 - 40% methanol concentrations.

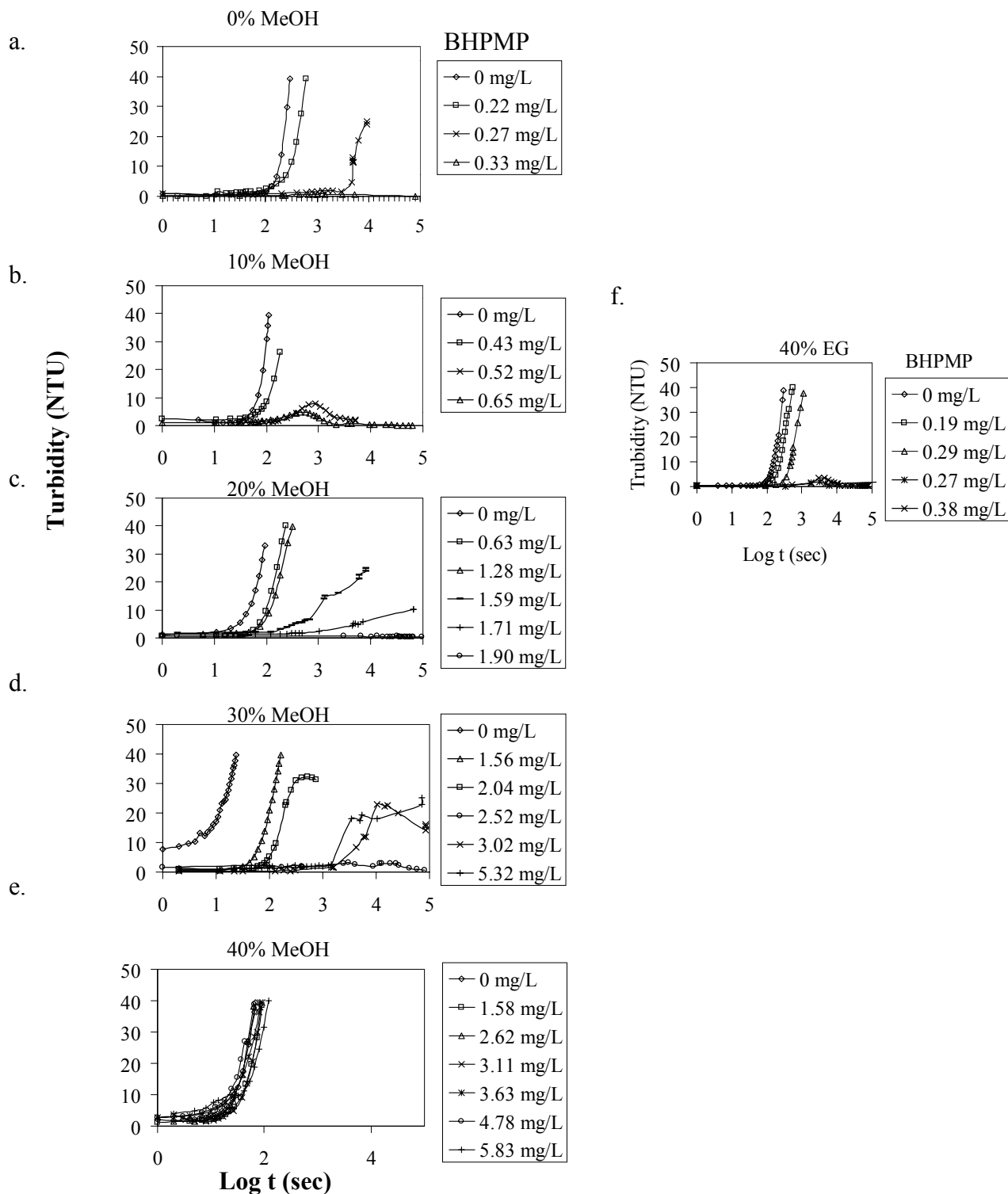


Figure 6. Plots of the turbidity reading versus time following the mixing of a barium containing solution (1 m NaCl, 0.09 m Ca, 1.1 m Ba, pH 6.4) and a sulfate containing solution (1 m NaCl, 0.09 m Ca, 1.1 m SO₄, pH 6.4) in the presence of 0 - 40% (wt) methanol or ethylene glycol and various concentrations of BHPMP at 25 C. The mixed solution is supersaturated with respect to BaSO₄. In the absence of methanol, the SI for barite = 2.0.