



## CHAPTER II LITERATURE REVIEW

### 2.1 Scale Formation

Scale formation can occur due to the changes in temperature, pressure or mixing of two incompatible waters. There are many kinds of scales in oilfields: calcium carbonate (calcite,  $\text{CaCO}_3$ ), calcium sulfate ( $\text{CaSO}_4$ ), barium sulfate (barite,  $\text{BaSO}_4$ ), strontium sulfate (celestite,  $\text{SrSO}_4$ ). In case of some scales such as carbonate scales, when the pressure decreases and/or temperature increases, the solubility of salt decreases and leads to precipitation:

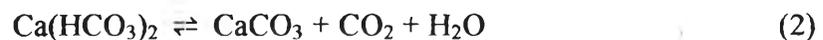
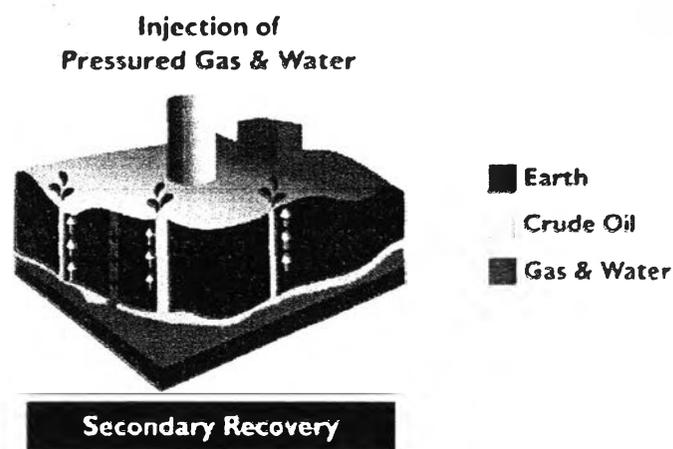


Figure 2.1 shows the mixing of two incompatible waters due to injection of seawater into the reservoir for maintaining reservoir pressure and improving the secondary recovery.



**Figure 2.1** Schematic of mixing of two incompatible waters; seawater and formation water (<http://www.fabtechinc.net/EnhancedOilRecovery.aspx>).

## 2.2 Barium Sulfate Precipitation/Deposition

The precipitation of barium sulfate is created by a nucleation. Nucleation can be divided into two categories, primary nucleation and secondary nucleation. Primary nucleation is a nucleation which takes place in a bulk solution. Primary homogeneous nucleation occurs by a supersaturated solution itself. On the other hand, primary heterogeneous nucleation occurs when foreign particles or container surface act as nuclei. After nuclei are formed, growing particle can continuously grow and aggregate in the bulk solution and/or on the surface of the container as called secondary nucleation (Ring *et al.*, 1991; Kashchiev *et al.*, 2003; Kind *et al.*, 2004). Although barium sulfate precipitation has been investigated but it is still unclear how the deposition of barium sulfate occurs in pipelines. There are many possible ways in which barium sulfate can deposit in pipelines. For example, barium sulfate precipitates, grows in the bulk solution and then deposits in pipelines or barium sulfate deposits directly and then grows on the surface of the pipelines.

Induction time, which is defined as the time between the formation of the supersaturated solution and the first observed change in turbidity or absorbance, can be used to explain barium sulfate precipitation. In order to determine the induction time of barium sulfate formation, light spectroscopy techniques have been used.

Klein *et al.*, 1964 investigated the heterogeneous and homogeneous nucleation of barium sulfate. They conducted their experiments in a batch reactor by mixing 0.01 M of barium perchlorate ( $\text{Ba}(\text{ClO}_4)_2$ ) with 0.05 M of sodium thiocyanate ( $\text{NaSCN}$ ). A current was applied to generate sulfate ions. Turbidity, ion product, which is the product of barium ion and sulfate ion, and number of particles were measured as a function of time as shown in Figure 2.2. The results showed that the turbidity was detected within less than 1 min for the heterogeneous nucleation. At about 1 hr, the turbidity started to increase again, the authors stated that the turbidity increased because of homogeneous nucleation and growth of barium sulfate.

Symeopoulos *et al.*, 1992 investigated the spontaneous precipitation process of barium sulfate in aqueous solutions. They conducted experiments by using equimolar solutions of barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) in 500 mL double-walled Pyrex glass vessel at 25 °C. The absorbance of the solution was

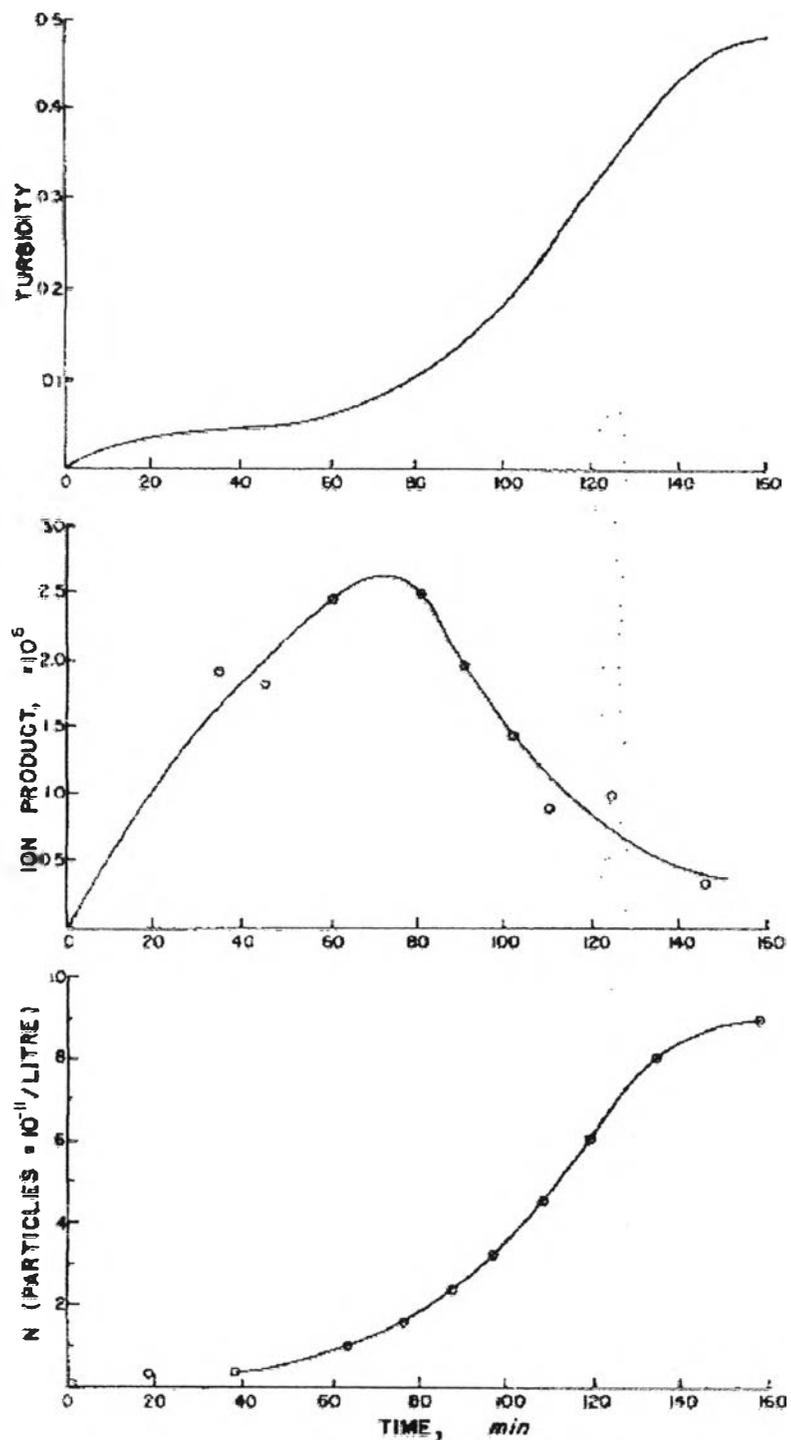
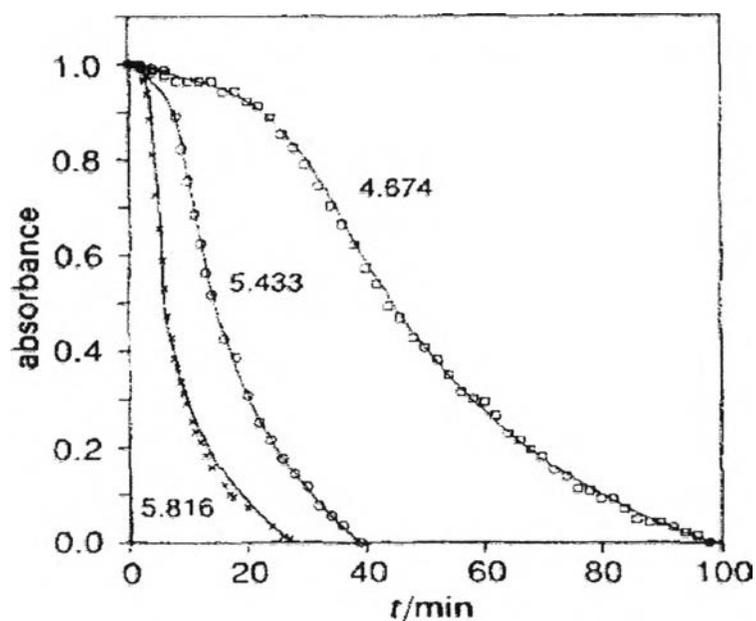


Figure 2.2 Turbidity, ion product and number of particles as a function of time (Klein *et al.*, 1964).

measured by using UV-VIS spectrophotometer as a function of time and the change of the slope of the absorbance vs. time is determined as the induction time. They reported that their experiments are not truly homogeneous nucleation because of the reactor walls or dust particles in the system. However, they found that when the concentration of barium ions gradually increases, rate of spontaneous precipitation dramatically increases but induction time considerably decreases as shown in Figure 2.3. These results indicated that supersaturation has stronger effect on induction time and rate of spontaneous precipitation of barium sulfate.

Similarly, Morizot *et al.*, 1999 determined the induction time of barium sulfate formation by using spectrophotometer. 150 mg/L of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) solution was fed at 6 mL/min into 300 mg/L of barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) solution and turbidity was measured every 30 s for the first 10 mins and every 10 mins for the remainder of the experiment. Results, as shown in Figure 2.4 and 2.5, showed that the turbidity changed within 1 min ( $\pm 0.5$  mins). In addition, the induction time is consistency with Klein *et al.*, 1964 and Symeopoulos *et al.*, 1992.



**Figure 2.3** Variation of the absorbance as a function of time. Numbers in the graph are driving forces, which were calculated from the concentration of two solutions used for precipitation of barium sulfate (Symeopoulos *et al.*, 1992).

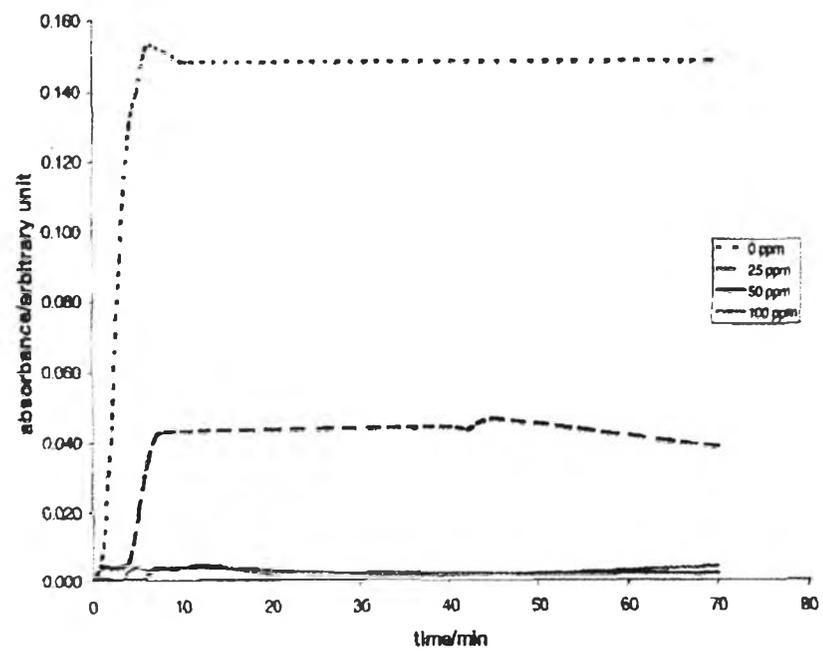


Figure 2.4 Turbidity of BaSO<sub>4</sub> solution in absence and presence of different inhibitor concentrations (Morizot *et al.*, 1999).

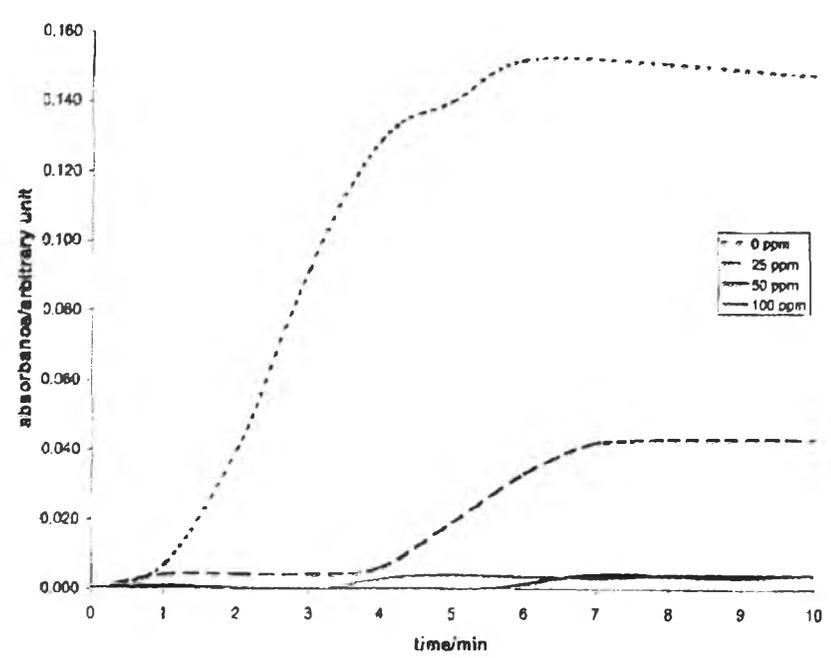


Figure 2.5 Zoom of Figure 2.4 for the first 10 minutes (Morizot *et al.*, 1999).

### 2.3 Factors Effect on Barium Sulfate Precipitation/Deposition

There are many factors that affect scale precipitation and scale deposition: supersaturation ratio, free lattice ion ratio, temperature and pressure.

The first factor is supersaturation ratio which is defined as the ratio of the ion activity product to the solubility product (Scaling and Particulate Fouling in Membrane Filtration Systems):

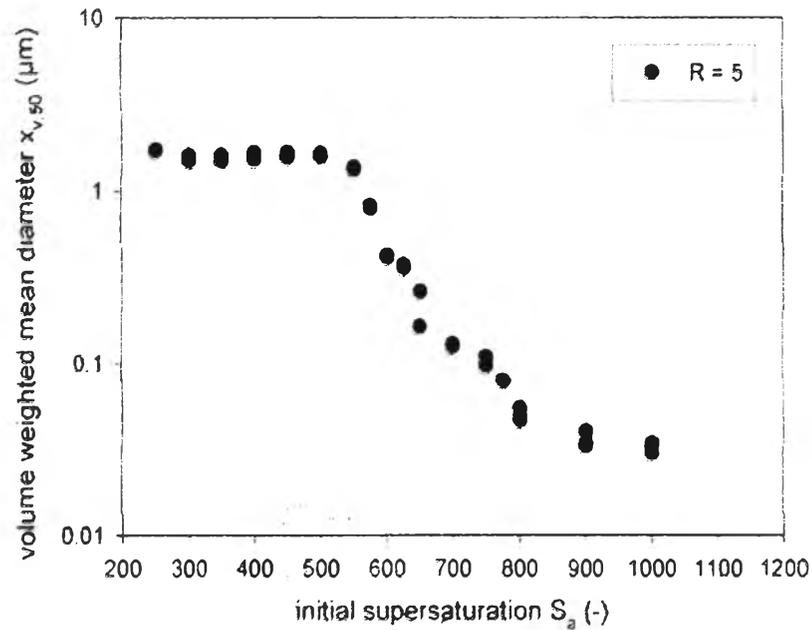
$$S_a = \left[ \frac{a_{\text{cation}} a_{\text{anion}}}{K_{sp}} \right]^{\frac{1}{2}} \quad (3)$$

Where

- $a_i$  is the activity of cation/anion ( $\text{molL}^{-1}$ )
- $K_{sp}$  is the solubility product of barium sulfate ( $\text{mol}^2\text{L}^{-2}$ )

Figure 2.6 showed that, at low supersaturation ratios, heterogeneous nucleation is dominant and larger particles can be formed. Moreover, at low supersaturation ratios, scale formation will occur slowly because there are fewer barium and sulfate ions in the solution. At high supersaturation ratios, homogeneous nucleation is dominant; scale formation will occur faster and small particles can be formed (O'Hern *et al.*, 1963; Klein *et al.*, 1964; Pelizzetti *et al.*, 1984; Jaworski *et al.*, 2001; Boerlage *et al.*, 2002; Kucher *et al.*, 2006; Boodhoo *et al.*, 2007).

In addition, Yuan *et al.*, 1994 studied sulfate scaling problems in various brines. They conducted their experiment by injecting seawater into formation water and found that  $\text{BaSO}_4$  tends to precipitate at low mixing ratio of seawater as compared to other sulfate salt. Moreover, at low mixing ratio, supersaturation of barium sulfate increased drastically. These results also indicate that precipitation of barium sulfate depends on supersaturation.



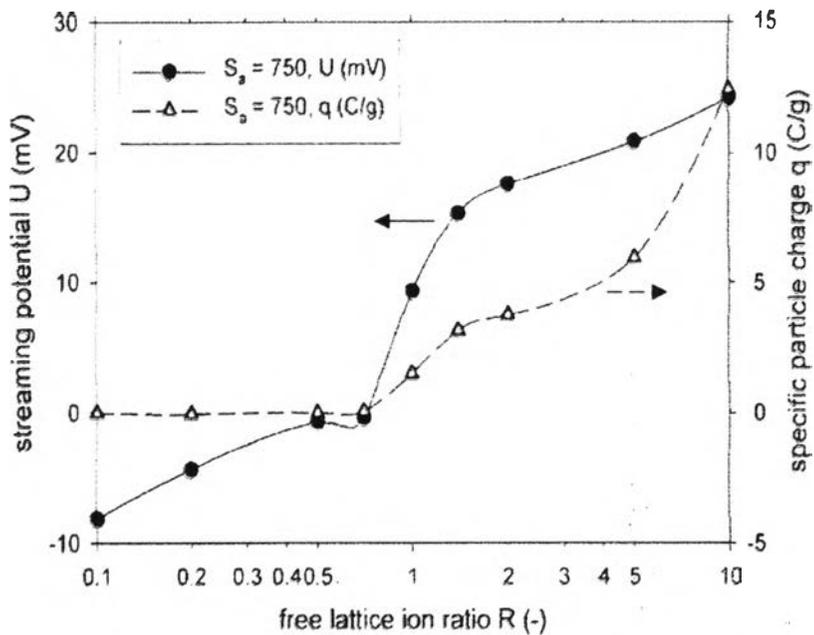
**Figure 2.6** Mean volume weighted particle size as a function of supersaturation at constant free lattice ion ratio  $R=5$  (Kucher *et al.*, 2006).

The next factor is free lattice ion ratio,  $R$ , which is defined as the ratio of the concentration of barium ions and sulfate ions.

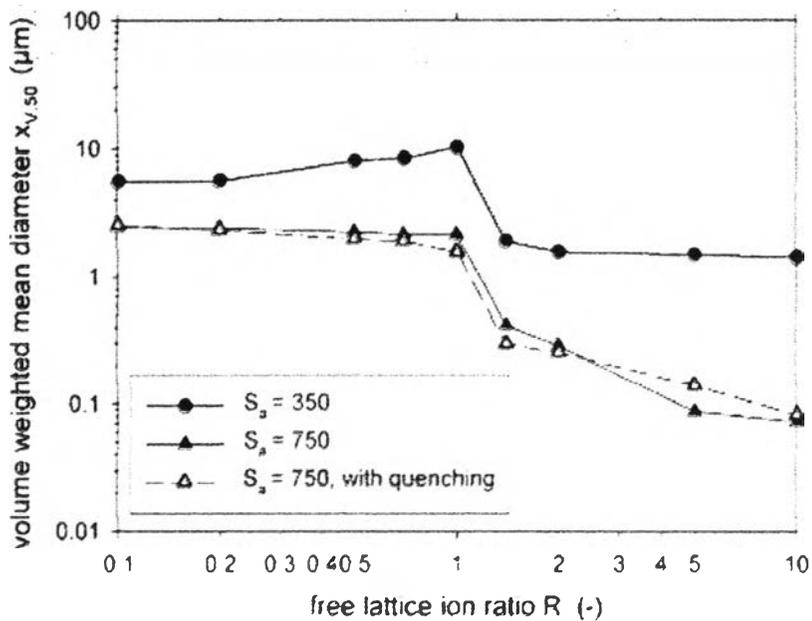
$$R = \frac{C_{Ba^{2+}}}{C_{SO_4^{2-}}} \quad (4)$$

Where  $C_i$  is the concentration of  $Ba^{2+}$  and  $SO_4^{2-}$  ( $\text{molL}^{-1}$ )

Kucher *et al.*, 2006 studied the effect of free lattice ion ratio on the particle size and morphology of barium sulfate by mixing barium chloride and sodium sulfate solutions at equal volumetric flow rates. They conducted experiments at  $25 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$  and samples were analyzed by Scanning Electron Microscope (SEM). As can be seen in Figure 2.7 and 2.8, they found that when  $R > 1$ , excess of barium ions, there is high adsorption of barium ions on the surface of barium sulfate particles and a positive charge on the surface of the particles was created. These positive charges on the surface of the particles cause repulsive interaction between particles so particle



**Figure 2.7** Streaming potential and particle charge measurement as a function of ion ratio at supersaturation ratio  $S_a=750$  (Kucher *et al.*, 2006).



**Figure 2.8** Mean volume weighted particle size as a function of free lattice ion ratio for  $S_a=350$  and 750 (Kucher *et al.*, 2006).

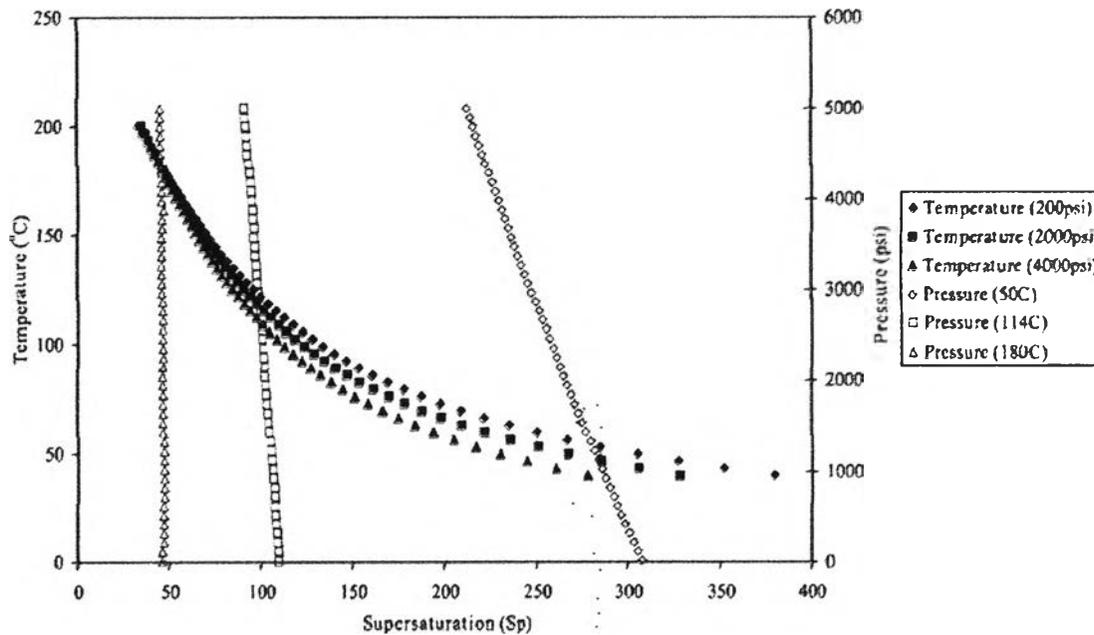
size will be small. For  $R \leq 1$ , they found that there is no effect of charges on the surface of the particles because the diffusion and adsorption of sulfate ions on the surface of the particles are significantly too low and particles can be grown to become larger.

The next factor which affects the solubility of barium sulfate and scale formation is temperature (Templeton, 1960; Jiang, 1996). Binmerdhah *et al.*, 2010 investigated the solubility of barium sulfate scale formation by changing the temperature (40-90 °C). They conducted experiments in batch reactor; 100 mL of each filtered seawater and formation water, which were prepared by dissolving salt in deionized water, were poured simultaneously into a beaker. The solution was stirred by magnetic stirrer and heated on the hot plate. Then, 5 mL of the solution was passed through a filter and then diluted to 50 mL in a volumetric flask with distilled water and the barium concentration was measured by atomic absorption spectrometry. They found that increasing temperature, increases barium sulfate solubility because the dissociation of barium sulfate is endothermic.

Similarly, another work has studied the effect of temperature and pressure on the supersaturation of barium sulfate (Graham *et al.*, 2002). Results are shown in Figure 2.9. They reported that when temperature increases, the solubility of barium sulfate will increase and cause a decrease in the supersaturation of barium sulfate. This also indicates that the temperature affects the barium sulfate scale formation. Moreover, they found that increasing pressure at low temperature, supersaturation will be slightly decreased but at high temperature the reduction of supersaturation was more significant. However, the effect of pressure on the supersaturation of barium sulfate is still less significant effect when compared with temperature.

#### **2.4 Technique to Investigate Scale Deposition**

There are many techniques which have been used for investigating the scale deposition: Morizot *et al.*, 1999 and Quddus *et al.*, 2000 conducted their experiments



**Figure 2.9** Predicted barium sulfate supersaturation with changing temperature at the fixed pressure and changing pressure at the fixed temperature for the low sulfate scaling brine (Graham *et al.*, 2002).

by using rotating disk electrode (RDE) and rotating cylinder electrode (RCE), respectively. Moreover, Binmerdhah *et al.*, 2010 conducted their experiments with a core flooding system. However, in order to compare the results with real situations in which scale deposition occurs in the pipeline, there is a technique called capillary technique which has been used by Graham *et al.*, 2002 and Yindee, 2010 for studying the effect of temperature and pressure on scale formation and scale deposition, respectively. Initially, two brine solutions,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$ , will be injected through a capillary at constant flow rate. Pressure drop ( $\Delta P$ ) across the capillary will be measured. When  $\Delta P$  increases, it indicates that scale has started to deposit inside the capillary. Increasing of  $\Delta P$  can be used to calculate mass of barium sulfate deposit inside the capillary by using Hagen-Poiseuille equation, Eq. (5), under the assumption of laminar flow and uniform deposit.

$$\Delta P = \frac{8\mu QL}{\pi r^4} \quad (5)$$

Where

- $\mu$  is the viscosity (Pa·s)
- $Q$  is the volumetric flow rate ( $\text{m}^3\text{s}^{-1}$ )
- $L$  is the length of capillary (m)
- $r$  is the radius of capillary (m)

## 2.5 Scale Prevention/Dissolution

There are three possible ways to prevent or remove scale formation. First, removal sulfate ions from seawater before injecting to the reservoir by reverse osmosis technique. Unfortunately, seawater contains high concentration of sulfate ions so in order to reduce the concentration of sulfate ions, the efficiency of the reverse osmosis system has to be very high. Moreover, due to the large volume of the seawater, this technique requires high energy and high production cost (Putnis *et al.*, 1995).

Secondly, using nucleation inhibitors such as poly vinyl sulphonate (PVS), sulphonated polyacrylate (VS-Co), polyphosphinocarboxylic acid (PPCA) to reduce or inhibit the scale precipitation (Van Der Leeden *et al.*, 1992; Morizot *et al.*, 1999; Graham *et al.*, 2002). However, maintaining the concentration of inhibitors in well bore is too difficult and scale can still be formed and causes the reduction in oil production (Putnis *et al.*, 1995).

The third way is to remove scale that has been formed by using chelating agents. Ethylenedinitrilotetraacetic acid (EDTA) and diethylenetrinitrilopentaacetic acid (DTPA) are chelating agents which are widely used in the industry for dissolution and formation of complex with metal ions.

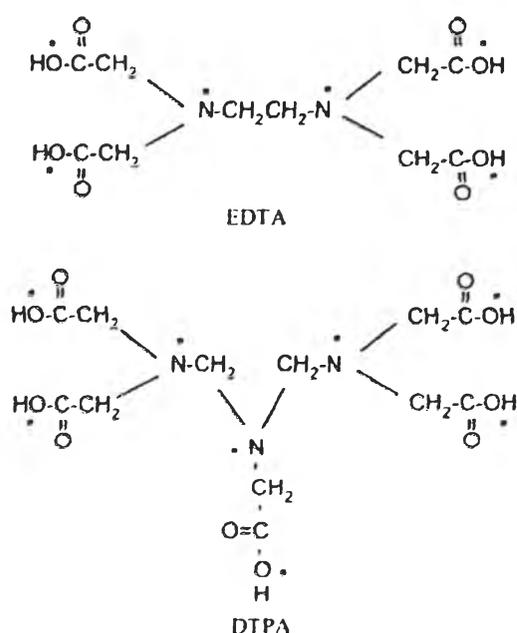
Yen *et al.*, 1999 conducted their experiments in aqueous system to study the dissolution kinetics and surface phenomena on the barium sulfate particles by using barium sulfate dissolved in 100 mL of 0.18 M chelating agent, EDTA or DTPA. They also investigated the effect of temperature on the dissolution of barium sulfate.

They found that at the same temperature, DTPA is more effective to dissolve barium sulfate than EDTA and when temperature increases, more barium sulfate can be dissolved. This indicates that dissolution rate is strongly affected by temperature.

Putnis *et al.*, 2008 conducted their experiment in batch reactor by mixing 1 g of BaSO<sub>4</sub> with 100 mL DTPA solution at various temperatures and concentrations of DTPA solution. They have reported that DTPA has 8 active metal-complexing sites which are able to form a complex with barium ions as shown in Figure 2.10 (Putnis *et al.*, 1995):

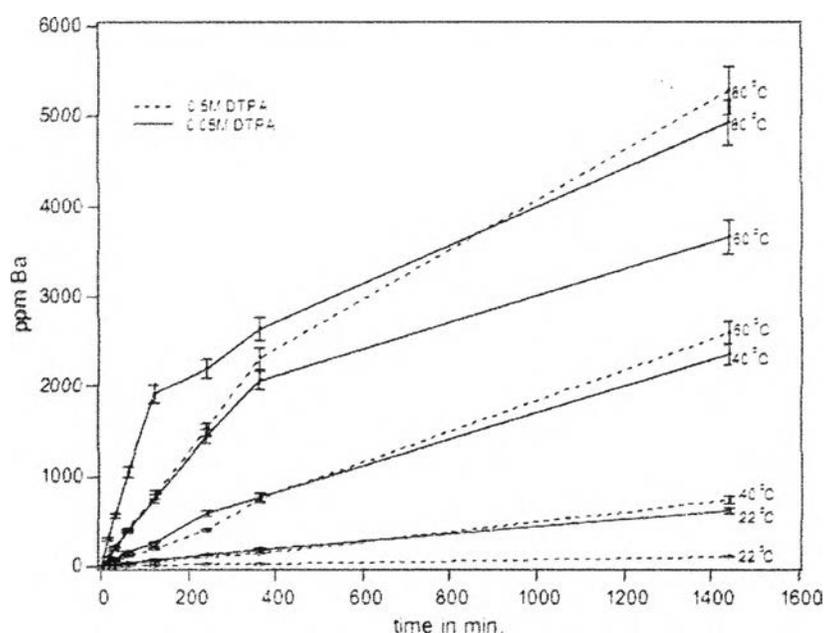


The results as shown in Figure 2.11 and 2.12 showed that, at higher temperature, DTPA solution can dissolve barium sulfate particles more than at lower temperature. When the concentration of DTPA solution is higher than the concentration of barium chloride solution, which was used as a feed solution, DTPA may block the barium sulfate particle and prevent effective dissolution. However, when the concentration

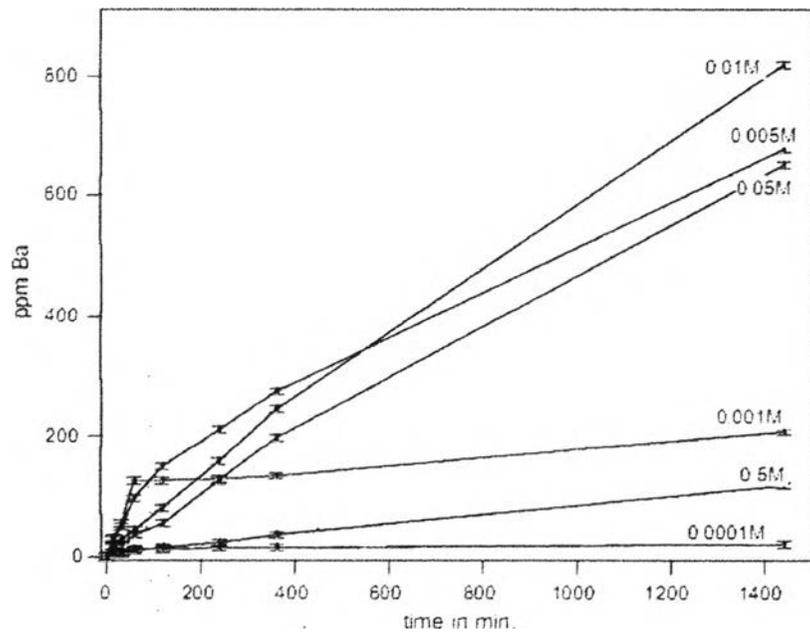


**Figure 2.10** Schematic diagrams of the structures of EDTA and DTPA (Putnis *et al.*, 2008).

of the chelating agent is lower than the concentration of barium chloride solution, a precipitate of barium hydroxide can be formed. Thus, when the concentration of DTPA solution equal to the concentration of barium chloride solution, all barium sulfate particles can be dissolved. They also proposed the mechanism of barium sulfate dissolution which is as follows: DTPA will attach to barium ion on the surface of the particle, then detach barium ion from the particle and form a complex, Ba-DTPA, in the solution. Moreover, they stated that at high pH, pH 11-12, DTPA is effectively deprotonated and the active ionic species become negatively charged. Thus, DTPA can form strongly complex with barium ions and BaDTPA complex has the greatest stability. In this study, DTPA will be used to dissolve barium sulfate scale deposited inside the capillary.



**Figure 2.11** The dissolution of barium sulfate at different DTPA concentrations, 0.05 M and 0.5 M, in the temperature range 22-80 °C (Putnis *et al.*, 2008).



**Figure 2.12** The dissolution of barium sulfate at various DTPA concentrations, 0.0001-0.5 M, at room temperature (22 °C) (Putnis *et al.*, 2008).