

CHAPTER II

LITERATURE REVIEW

2.1 Precipitation Process

Precipitation is a thermodynamically driven process of mass transfer from solution to the solid phase. It is the result of several parallel and successive mechanisms: nucleation, growth, and secondary processes, i.e., agglomeration, attrition, and breakage. In nanoparticulate system, the latter two are negligible due to low collision energies (Hans et al., 2002).

In order to investigate the precipitation of barium sulfate from aqueous solutions, barium chloride and sodium sulfate were chosen as reactants according to Eq. (1)



The driving force for crystal nucleation and growth is supersaturation, a measure of thermodynamic offset from equilibrium. A concentration-based supersaturation S_c is defined as follows:

$$S_c = \sqrt{\frac{[\text{Ba}^{2+}][\text{SO}_4^{2-}]}{K_{sp}}} \quad (2)$$

The value of solubility product found by Monnin ($K_{sp} = 9.82 \times 10^{-11} \text{ mol}^2/\text{l}^2$ at 25 °C) will be used in this calculations (Monnin, 1999). It can be seen from Eq. (2) that the supersaturation can be either created by stoichiometric or non-stoichiometric conditions.

Therefore, the molar ratio of barium ions to sulfate ions is defined as free lattice ion ratio R .

$$R = \frac{[\text{Ba}^{2+}_{free}]}{[\text{SO}_4^{2-}_{free}]} \quad (3)$$

Graham investigated the effect of temperature and pressure on barium sulfate scale formation using a dynamic tube blocking rig (Graham et al., 2002). The results showed that the solubility of barium sulfate increases with increasing temperature and causes a decrease in supersaturation of barium sulfate. This is in a good agreement with thermodynamic point of view according to the enthalpy of barium sulfate and Van't Hoff equation.

Several investigations regarding salt kinetics precipitation utilizes the concept of induction time. The induction time is the time lag between the formations of supersaturated solution until the appearance of the first measurable changes in the physic-chemical properties of the solutions (Sorbie et al., 2000) and it should be interpret as the time that it take for different systems to reach a certain criteria. Symepoulos studied the spontaneous precipitation in aqueous solutions containing relatively high barium and sulfate concentrations (Symepoulos et al.,). It was found that the induction time is inversely proportional to the solution supersaturation and is linearly dependent on the molar ratio of barium to sulfate.

2.1.1 Nucleation and Growth

In general, solid formation depends on transport mechanism and interactions (Schwarzer et al., 2002). The transport may be diffusive or convective. Moreover, the mass transfer may also be contributed by field forces such as gravity or electric fields. The interactions may be divided into dispersive, electrostatic and magnetic forces, as well as structural forces in fluids and forces due to material bridges.

Nucleation is the formation of new particles and it can be divided in two categories, homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation takes place in bulk solution while heterogeneous nucleation occurs when foreign particles, such as growth particles and reactor walls. The nucleation rate is a strongly dependent of supersaturation and homogeneous nucleation mechanism becomes dominant at relatively high supersaturations. After nucleation is completed, the particles begin to grow further. This transport and integration of ions into the

crystal structure of the particles are considered as particle growth (Schwarzer et al., 2002). It was found that solid formation is complete after 10-100 ms and the particles do not grow further after 30 minutes (Schwarzer and Peukert, 2002, 2004a, 2004b). According to Mersmann (Mersmann, 2001) growth can be considered to be diffusion-controlled at high supersaturation and the growth rate is a linear function of supersaturation and much less dependent on supersaturation.

2.1.2 Aggregation and Agglomeration

Aggregation is the formation of collections of primary particles held together by van-der-Waals forces, and agglomeration is the formation of collections held together by chemical bonds (material bridges). Aggregation must have occurred almost completely after solid formation ended. Schwarzer studied the particle-size distribution in continuous precipitation (Schwarzer et al., 2002). It was found that the size of precipitated primary particle (approximately 50 nanometers in diameter) can be generated by controlling the mixing intensity. They also found that increasing electrostatic repulsion forces and the surface charge by changing the barium ion concentration can stabilize the particles against agglomeration.

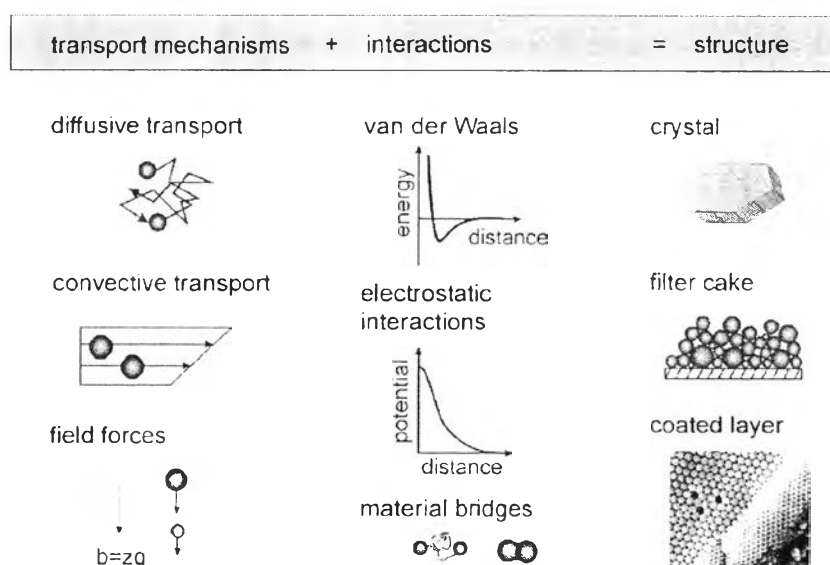


Figure 2.1 Principles of structure formation.

Several models have been developed in literature to account for aggregation and agglomeration. These models are based on population balance equation developed by Shmolochowski (Schwarzer et al., 2002).

$$\frac{\partial n(x)}{\partial t} = B_{agg}(n, x) - D_{agg}(n, x) \quad (4)$$

Where: n = number density concentration of particles, m^{-4}

x = particle size (volume equivalent diameter), m

t = time, s

B_{agg} = birth rate of aggregation, $m^{-4}s^{-1}$

D_{agg} = death rate of aggregation, $m^{-4}s^{-1}$

Figure 2.2 shows the comparison between experimental and simulated results of the particle size distribution with time. It can be seen, experimental and simulated PSDs agree fairly well with the tendency, that the simulated distributions are less broad than the experimental ones (Schwarzer et al., 2002).

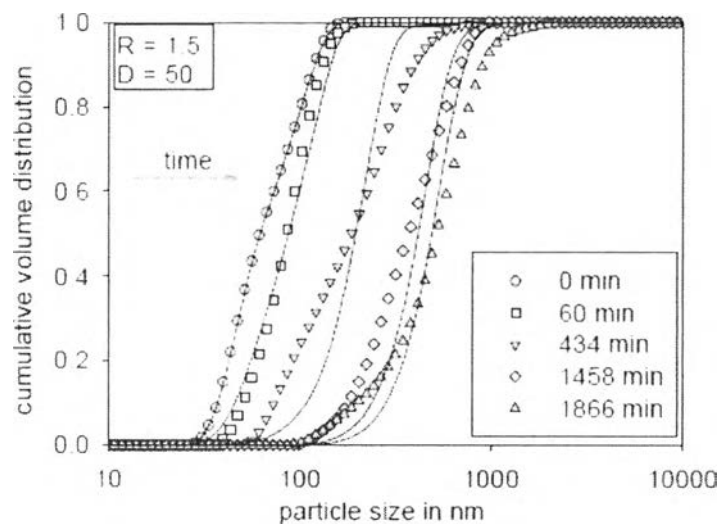


Figure 2.2 Comparison of experimental and simulated evolution of the PSD.

2.2 Technique to Investigate Scale Deposition

There are several techniques that have been used for investigating BaSO₄ deposition. Quddus (Quddus et al., 2000) conducted the experiments using a rotating cylinder electrode (RCD) technique to study the effect of fluid hydrodynamics on the deposition of barium sulfate. They found that the deposition rate increases with increasing Reynolds number during agitation of the solution. Furthermore, there is a technique called capillary technique which has been used by Graham (Graham et al., 2002) to study scale deposition occurring in pipelines. Two brine solutions, BaCl₂·2H₂O and Na₂SO₄, were injected through a capillary at constant flow rate. Pressure drop (ΔP) was measured across the capillary. It was found that the scale started to deposit on the capillary wall as the pressure drop increases.

2.3 Scale Prevention and Removal

There are three possible methods that have been used for prevent and remove barium sulfate scale formed. The first method is done by removing sulfate ions from seawater using osmosis technique before water injection is injected to the reservoir. This technique, however, requires a lot of energy and high operating costs due to the large volume of seawater (Putnis et al., 1995).

The second way is using scale inhibitors such as poly vinyl sulfonate (PVS), sulfonated polyacrylate (VS-Co), and polyphosphinocarboxylic acid (PPCA) to inhibit barium sulfate from precipitation. However, it is impracticable to maintain the inhibitor concentrations in the reservoir, the scale can still form and get deposited.

The third way, a promising technique, is to remove the scale formed chemically. Most of these techniques have been done by using chelating or complexing agents (Putnis et al., 1995). The strong chelating agents for barium ions that are widely used in the oil industry are diethylenetrinitrilopentaacetic acid (DTPA) and ethylenedinitrilotetraacetic acid (EDTA).

Yen studied the dissolution kinetics and surface phenomena on the barium sulfate particles by dissolving barium sulfate in different dissolving agents, DTPA

and EDTA (Yen et al., 1999). They also investigated the effect of temperature on the dissolution of barium sulfate. Their results showed that DTPA is more effective than EDTA at the same temperature. As temperature increases, barium sulfate becomes more soluble. This indicated that the dissolution rate is a strong function of temperature.

The effects of temperature and concentration on the dissolution of barium sulfate have been investigated by Putnis (Putnis et al., 1995) They reported that one molecule of DTPA has 8 active metal-complexing sites which can form a complex with barium ions, compared 6 active sites in EDTA, as shown in Figure 2.3.

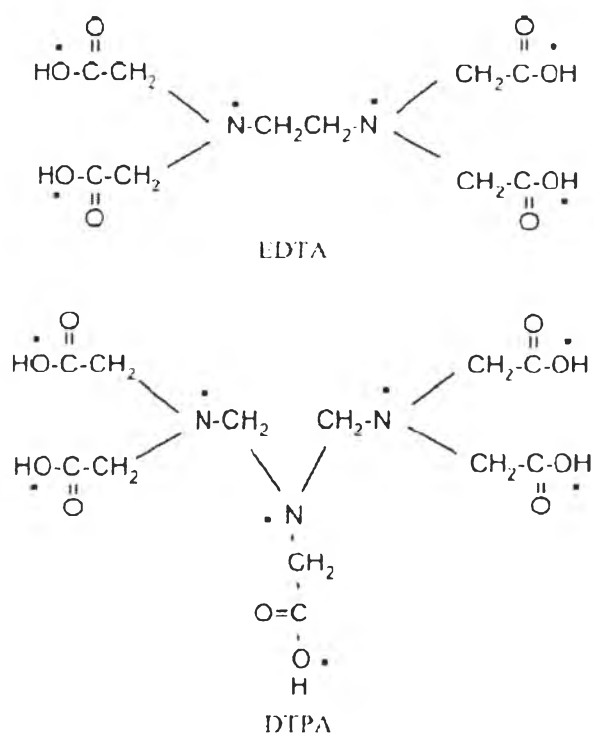


Figure 2.3 Chemical structures of EDTA and DTPA.

Figure 2.4 and Figure 2.5 showed that barium sulfate particles can be dissolved more at higher temperatures. These results are consistent with the previous work as discussed above. It is found that the dissolution rate is inversely related to the DTPA concentration in solution. Diluted DTPA solution is shown to be more

efficient as a solvent for the dissolution of barium sulfate. They also suggested that pH of the solution influences the dissolution rate. The molecule becomes more negatively charged due to the deprotonation at high pH (11-12). Thus, DTPA can form strong complex with barium ions since it shows the greatest stability. In this work, DTPA will be used to dissolve barium sulfate in the samples.

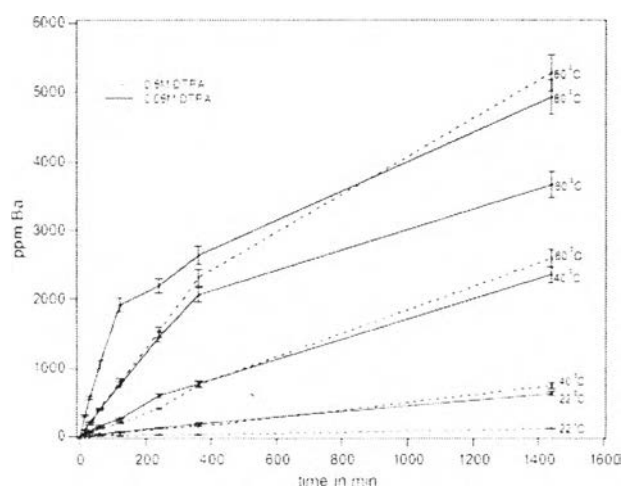


Figure 2.4 The dissolution of barium sulfate at different DTPA concentrations, 0.05 M and 0.5 M, in the temperature range 22-80 °C.

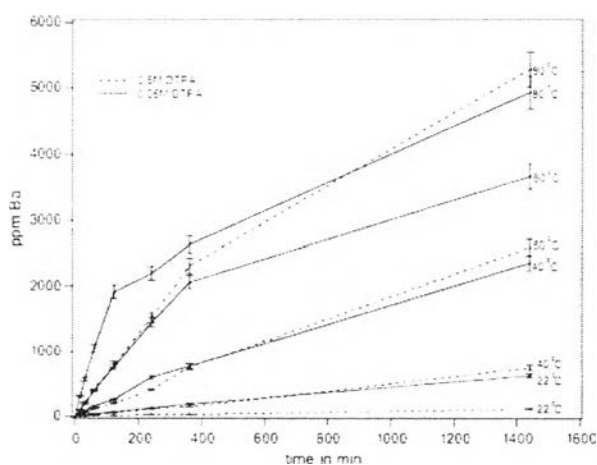


Figure 2.5 The dissolution of barium sulfate at various DTPA concentrations, 0.0001-0.5 M, at room temperature (22 °C).