CHAPTER II
LITERATURE SURVEY

2.1 Equilibrium Precipitation

The solution that is in the equilibrium with the solid phase is said to be saturated with respect to that solid. Precipitation of soluble alkaline earth metal salts can be done via nucleation and growth from supersaturated aqueous solutions. At high supersaturation ratios, the reaction is determined by the rate of diffusion from the bulk of the solution to the surface of the particles (Mersmann. 1994). Murthy demonstrates the growth mechanism and shapes of barium sulfate crystals by electron microscope techniques (Murthy, 1994). Antonious studied the kinetics of the crystallization of barium chromate by conductometric method for spontaneous and seed growth systems and found that the growth rate depends upon the relative supersaturation and the order of reaction of barium chromate was 2 at 298 K in the spontaneous condition. Furthermore. the growth rate is accelerated by the presence of seed crystals. Some inhibitors have affected on the crystal growth. Diffusion control of growth leads to rounding of growth contours. At lower supersaturation ratios, the reaction rate is controlled by polynuclear surface mechanism (Antonious et al.,1996, Xyla et al., 1991). Ramis studies the effect of polyphosphate and phosphonates on crystallization of barium chromate and interpreted in terms of a Langmuir type adsorption isotherm (Ramis et al.,1996). Although precipitation from solution is a very common operation in the chemical industries, it remains rather difficult to predict the mean crystal size which depends on the nucleation and crystal growth rate.

2.2 Binding on Polyelectrolyte

The complex formation between metal ion and polyelectrolyte can be candidates for removing metal ions from dilute solution or wastewater for economical and toxicological reasons. The polyelectrolyte is the macroion carrying anionic or cationic groups and low molecular counterions for electroneutrality. Application such as polyelectrolyte uses in separations requires high molecular weight polymers greater than 10^6 g/mole (Dautzenberg et al., 1994). The complicating factor of polyelectrolyte properties are the coupling of charge-charge interactions along the chain backbone with the distribution of mobile ions. To model the complicated system. the interaction is assumed a particular distribution of fix charges and then treated the electrostatic potential energy and counterion distribution separately. The most simplified chain model for description of a polyion is the rod limit. With rodlike models the distribution of charge can be considered as continuously smear along its surface (Hara. 1993, Dunaway, 1997).

Generally, low molecular weight substances bind to macromolecules by intermolecular forces, mainly ionic or complex bond or the combination of both. Ion exchange is a common technique concerned in the ionic interactions such as the removal of arsenate anions by polycation polymer. Complex bonding is more selective than ionic interaction. The complex formation between ions and water soluble polymers occur such as resins containing amino and imino groups form stable chelates with copper, nickel. and other transition metal ions (Geckeler et al.. 1996). The polymer that is required in the separation process should have the high selectivity toward target ions, chemical and mechanical stability, low toxicity and low cost. The pH affects polymeric binding, since either hydrogen ions or hydroxyl anions can complete with target ions to bind the polymer. Bourikas reports on chromium species in aqueous solution that $HCrO_4^-$ is predominant in pH range of 4.5 to 5

and CrO_4^{2-} in pH range of 6 to 10 (Bourikas et al., 1997). Furthermore, the standard pH value of wastewater drains to the environment is in pH range of 5.5 to 9 (Ministry of industries, 1992) therefore most wastewater presents the mainly product of chromium (VI) in form of chromate (CrO_4^{2-}).

2.3 Crystallizer Design

Precipitation is a separation process to remove particles using on gravitational force (Peavy et al., 1985, David et al., 1991). The particles that settle within a reasonable period of time can be removed in a sedimentation basin. Normally this reservoir is rectangular or circular with a radial or upward water flow and sludge goes down. Settling properties are often categorized into one of four classes :

Type 1 Precipitation or free settling type : Particles settle discretely at a constant settling velocity. They fall as individual and do not stick to other particles during the precipitation process. Examples are sand and grit material.

Type 2 Precipitation or flocculate settling type : Particles flocculate during the process so their sizes are constantly changed that result in changing of settling velocity. This type occurs in alum or ion coagulation.

Type 3 Zone settling type : Particles are high concentration (greater than 1000 mg/l) and tend to settle as a mass. Lime softening is one example in this type.

Type 4 Precipitation or compression settling type : Particles settle in high concentration until particles stiff, so the feed cannot pass through the layer of sludge particles and causes a lower settling velocity.

Barium chromate precipitation corresponding to Type 3 tends to settle as a compact waste. Its settling velocity and overflow rate are important terms in study of precipitation design. The overflow rate is the flowing of solution over the top of a column as same as liquid velocity. And the settling velocity is

the sedimentation rate to reach the bottom of the basin during retention time. To remove particles from the solution, the settling velocity is greater than overflow rate and expected 100% removal which means the overflow concentration equals zero. Force balance of the falling particles is determined by relating of the solid mass flux by gravity to bulk movement of underflow.