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Kinetics of magnesium hydroxide precipitation from sea bittern

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Abstract

Magnesium hydroxide is a valuable chemical produced almost in pure form from seawater and its bitterns through precipitation process. Product size distribution of magnesium hydroxide affects the ease of downstream processes of filtration and drying. Therefore, gaining insight into kinetic information in order to improve the size distribution of product particles is essential. In this work, a mechanistic model has been developed for precipitation of magnesium hydroxide from sea bittern. The parameters of model equations based on the population balance concept have been determined using the experimental data of precipitation from a pure synthetic solution containing 3% Mg²⁺ and a sea bittern from salt production unit of a local petrochemical complex. The model suggests a higher nucleation rate coefficient and a lower growth rate coefficient for precipitation from the sea bittern compared to that from pure synthetic solution. The nucleation increase and growth decrease which were attributed to the effects of impurities in the bittern, would decrease the settling velocity of the product particles and therefore make the filtration process in industrial use more difficult. However, a larger coefficient of agglomeration rate was predicted by the model for precipitation from the bittern favor to product settling.

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1. Introduction

Magnesium hydroxide, the intermediate of magnesium oxide, is used mainly in industries of pharmaceutical, refractory, water and wastewater treatment and desulphurization of fuel gases [1]. Seawater is the main source for production of Mg(OH)₂ due to containing of soluble salts of magnesium such as MgCl₂ and MgSO₄. The concentration of magnesium ion is about 1272 ppm in seawater and about 30,000 ppm in the end bitterns of NaCl production units from seawater [2].

A chemical reaction between magnesium ions of seawater and an alkaline such as caustic soda will result in magnesium hydroxide precipitates as:

$$Mg^{2+} + 2NaOH \rightarrow Mg(OH)_2 + 2Na^+$$
 (1)

Lime milk may also be used instead of caustic soda [2], but due to a low solubility of lime in water (0.159 g/100g H₂O at 25 °C, [3]), however, lime particles and insoluble impurities in lime may enter the solid product of magnesium hydroxide caus-

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ing a detrimental effect on product purity. Use of lime as an alkaline solution in precipitation of magnesium hydroxide may also result in precipitation of calcium sulfate when the solution contains a high concentration of sulfate ions. Desulfation may be necessary when lime is used as a reagent for introduction of hydroxyl ions to the solution containing Mg^{2+} . Rabadzhieva et al. [2] desulfated natural brine using CaCl₂ solution prior to precipitation of magnesium hydroxide. However, the impurity content of the product they obtained was high. Therefore, use of caustic soda as alkaline is more reasonable than lime when a very high pure product is desirable and when calcium compounds in the product have a detrimental effect on Mg(OH)₂ applications as in refractory industry.

Turek and Gnot [4] investigated the effect of temperature on the precipitation of $Mg(OH)_2$ in the range 10–40 °C when the precipitating agent was NaOH. They observed that precipitation at higher temperatures reduced the sedimentation rate and increased the humidity of the filter cake. These observations were apparently due to higher rates of reaction and consequently higher rates of supersaturation release and nucleation at higher temperatures. However, a higher rate of diffusion at higher temperature due to a lower viscosity increases the mass deposition on precipitates.

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The size enlargement of product is desired in industrial production of $Mg(OH)_2$ due to difficult filtration of very fine particles. Products containing a large portion of fine particles will also cause dustiness problems in the drying process. Therefore, in industrial applications every effort is made to produce a relatively coarse product with a size distribution as narrow as possible. Gaining insight into kinetic information in order to increase the average size of product particles and improve the distribution is, therefore, indispensable. The present investigation is aimed at gaining kinetic information of magnesium hydroxide precipitation from sea bittern, wasted from salt production units. Kinetic information is helpful in design and optimization of the precipitation process in industrial production of magnesium hydroxide.

2. Experimental

Experiments were carried out both batch and semi-batch wise at room temperature in a one-liter crystallizer equipped with a stirrer using both synthetic solution and sea bittern. Caustic solution (250 ml, 1N) was added drop-wise by a burette to the crystallizer containing 100 ml of sea bittern or synthetic 3% Mg²⁺ solution. Preliminary precipitation experiments were carried out to adjust the supersaturation release rate at which the primary nucleation was not dominant. Therefore, the flow rate of caustic addition thereafter was adjusted to 4 ml/min to avoid primary nucleation. In order to prevent excessive nucleation, enough mass of Mg(OH)₂ powder as seed (15 g) was added to the solution prior to commencement of the reaction. This amount of seed provides a suspension density of around 15% at the commencement of the precipitation runs, almost the common suspension density utilized in industrial trials. The size distribution of seed particles is shown in Fig. 1.

After addition of the first half of the caustic soda solution (31 min), the reaction was paused and the suspension in the crystallizer was filtered. The filter cake was washed and the size distribution of particles was analyzed. Then, the particles were returned to the mother solution in the crystallizer, and the reaction was restarted with the same flow rate of caustic



Fig. 1. Experimental size evolution of particles during the course of precipitation from sea bittern.

addition. The reaction was terminated when the second half of the caustic solution had been consumed (62 min). The product particles were filtered and analyzed for size distribution. During the course of reaction at specified time intervals the mother solution was sampled and analyzed for pH and the magnesium ion concentration. The method of titration with EDTA was used to determine the concentration of Mg^{2+} in the mother solutions.

Due to measurement limitations of the sieve set for fine size ranges of particles, size distribution was analyzed by the hydrometry method where size is calculated based on measurements of suspension density changes with time due to settling of particles in a fluid. Hydrometry is a standard method for measuring sizes of particles less than 75 μ m [5]. In order to verify the consistency of hydrometry method with sieve analysis, an initial powder sample of magnesium hydroxide was split into two almost identical samples using method of multiple divisions and then the resulting two samples were analyzed by wet screening and hydrometry. In order to find how the particles are agglomerated together the method of Scanning Electron Microscopy (SEM) was performed using an Oxford 5526 (Link Pentafet) microscope operating at 20 kV.

3. Mathematical modeling

Equations of mass and population balances were coupled together with appropriate initial and boundary conditions in order to model the precipitation of $Mg(OH)_2$. Considering an interval of particle size and number of particles entering and exiting the interval because of growth and agglomeration, the population balance equation for a batch or semi-batch precipitation process in the absence of particle breakage is written as [6]:

$$\frac{\partial n(v,t)}{\partial t} + \frac{\partial (n(v,t)G_v)}{\partial v}$$

$$= \frac{1}{2} \int_0^v C(t,u,v-u)n(v-u,t)n(u,t) du$$

$$-n(v,t) \int_0^\infty C(t,v,u)n(u,t) du$$
(2)

where n(v, t) is the population density of v size particles at time t, G_v the growth rate defined based on particle volume as size, C the agglomeration kernel, and u is a dummy variable of size. The first term on the right side of Eq. (2) represents the rate of formation of new v size particles by agglomeration of smaller ones. The second term on the right is for death of v size particles which agglomerate with other particles. The kernel function C(t, v, u) represents the frequency at which particles of size v and size u collide and then agglomerate.

The relation between mass deposition on $Mg(OH)_2$ particles and the changes in Mg^{2+} concentrations in solution is represented by the mass balance equation. The reaction between Mg^{2+} and NaOH generates solute mass in the solution and the particle growth consumes mass from the solution and deposits it on the solid phase. Since there is no outflow of mass from the solution, the mole balance equations on ions of OH⁻ and Mg²⁺ Download English Version:

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