A STUDY OF THE RATE OF SEDIMENTATION OF MAGNESIUM HYDROXIDE OBTAINED FROM BITTERN

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ABSTRACT

During the production of magnesium oxide from seawater or brine (bittern), the rate of sedimentation of magnesium hydroxide often represents the bottleneck of this process.

The influence of addition of seeds of magnesium hydroxide, flocculent (polyacrylamide) and seeds with flocculent on the rate of sedimentation of magnesium hydroxide obtained from brine (bittern) was investigated. The experiments showed that the rate of sedimentation of magnesium hydroxide generally increased after the addition of seeds, flocculent, and seed with flocculent. Hence, the capacity of the thickener was also increased. The rate of sedimentation increases with increasing seed concentration up to an optimum concentration (20 wt.% seed) after that the sedimentation rate decreases with further increase in seed concentration. After addition of flocculent, the sedimentation rate increases with increasing flocculent concentration up to a concentration of 30 ml/L. Beyond that, increasing the flocculent concentration have no significant effect on the sedimentation rate. The concentration of 20 wt.% seed and 30 ml/L of flocculent gave the maximum sedimentation rate.

INTRODUCTION

The precipitation of magnesium hydroxide is of great interest as an intermediate step in the production of magnesium oxide from inland brine (bittern) or seawater containing magnesium chloride using calcium hydroxide or hydrate dolime [$Ca(OH)_2.Mg(OH)_2$] as the precipitant[1].

In this process, the magnesium hydroxide is precipitated from previous reaction and recycled as a seed from a settling tank to the reaction vessel[2]. Gilpin[3] was the first to apply this process in the late 1950s when the water containing convertible Mg salt is treated in the reaction vessel with powder burnt lime or dolime. The liquid containing precipitated magnesium hydroxide in suspension is transferred to a settling vessel. Seed crystals of magnesium hydroxide are then returned to the first reaction vessel until the weight is about 10-15 times the magnesium hydroxide precipitated.

Liu and Nancollas[4] studied the growth of magnesium hydroxide crystals in supersaturated solution over a range of concentrations of magnesium and hydroxide ion. A surface diffusion process is proposed as the controlling step in the crystallization process. Magnesium hydroxide in this study was prepared from magnesium chloride reacted with sodium hydroxide. Magnesium hydroxide exists in two modifications, the labile form, which is obtained by precipitation of magnesium salt with base, always has a high solubility value. The stable form resulting from the recrystallization of the labile form somewhat has lower solubility. The growth of magnesium hydroxide in supersaturation may be expresses as:

$$-\frac{d[Mg^{+2}]}{dt} = k_c S\left[([Mg^{+2}][OH^-]^2)^{1/3} - \left(\frac{k_{sp}}{f_1^2 f_2}\right)^{1/3}\right]^{n_1} \quad (1)$$

It can be seen that the initial surge has an effective order ni=14 followed by a slower normal growth n_1~l corresponding to a rate of growth which is proportional to the first power of the relative supersaturation. Although, there is a general increase in $k_c.S$ with increasing amount of seed crystals, the increase is not in direct proportion to the latter.

Klein *et al.*[5] studied the rate of homogeneous nucleation of magnesium hydroxide as a function of the solution concentration. The nucleation rate becomes measurable at supersaturating ratio of about 4 and may be written as:

$$\frac{dN}{dt} = k(IP)^{n_z} \qquad (2)$$

where N, t, IP, and nz are the number of nuclei formed, time, ion product, and number of $Mg(OH)_2$ units in the nucleus (=33).

Flocculation[6]

The tendency of the particulate phase of colloidal dispersion to aggregate is an important physical property, which find practical application in solid-liquid separation processes such as sedimentation and filtration. The aggregation of colloids is known as coagulation, or flocculauon.

In flocculated (or coagulated) suspension of fine particles or floes are the basic structural units and in a low shear rate process, such as gravity sedimentation, their settling rate and sediment volume depend largely on volumetric concentration of floe and on interparticle forces. The type of settling behavior exhibited by flocculated suspension depends largely on the initial solid concentration and chemical environment; two types of batch settling curves. are frequently seen. At low initial solids concentration, the floes may be regarded as discrete unit consisting of particles and immobilized fluid. The floes settle initially at a constant settling rate but as they accumulate on the bottom of the vessel they deform under the weight of the overlying floes.

When me solid concentration is very high, the maximum settling rate is not immediately reached and may increase which increasing initial weight of suspension. Such behavior appears to be characteristic of structural flocculation associated with a continuous network of floes extending to the walls of the vessel,

The purpose of this study is to increase the rare of sedimentation of magnesium hydroxide, thus increasing the capacity of the thickener and hence the production rate. To achieve this purpose: three methods were employed: (i) the addition of seeds (magnesium hydroxide previously formed as a seed recycled from thickener to reactor), (ii) addition of flocculent (polyacrylamides), and (iii) addition or both seeds and flocculent.

EXPERIEMNTAL WORK

Materials

The brine bittern used for precipitating magnesium hydroxide in this study was prepared from analar chemicals and has a composition of: 118.79 g/L $MgCl_2$, 118.34 g/L NaCl, 4.46 g/L $CaCl_2$, 36.51 g/L KCl and density of 1150 g/L.

Calcium hydroxide produced by the Nowra Factory, Karbula-Iraq was used. The molecular weight of calcium hydroxide is 74.1 g/gmol. Appropriate quantities of solid $Ca(OH)_2$ were mixed with water to make up a suspension containing 24 wt.% $Ca(OH)_2$.

Polyacrylamide is a non-ionic polymer. The polyacrylamide used in the present work has a molecular weight of approximately 180000 g/gmol supplied by American Cyanamid Company. Appropriate quantities of solid polyacrylamide were dissolved in distilled water accompanied with mixing and gentle heating to make up the concentration of polyacrylamide to be 7.14 g/L.

Description of Equipment

Experiments were carried out in a cylindrical Perspex reactor supplied with four equally spaced baffles (the reason for using Perspex reactor is to allow visual observations). The diameter of the reactor is 10.0 cm and the height is 12.6 cm. the width of baffles is 1/10 of the reactor diameter. The mixer consists of a stainless steel shaft with 0.5 cm diameter, which is screwed with four pitched turbine blades impeller, the diameter of the impeller is 5.0 cm. The impeller is mounted on a central vertical shaft by means of nuts. The outer end of the shaft is coupled to an AC motor by means of a stainless steel coupling. The motor is connected in series with a variance to give the desired speed of impeller (maximum 600 rpm).

Experimental Procedure

Hydrated lime. suspension of concentration 24 wt.% Ca(OH)2 and volume 218 ml was added to 567 ml of prepared brine (bittern) with an appropriate quantities of magnesium hydroxide seeds. The suspension was agitated for 90 minutes with reaction temperature fixed at 30°C by means of a water bath. The suspension was then poured into 1000 ml graduated glass cylinder. The amount deposition of the precipitate was then measured at different time intervals.

The same procedure was repeated but using flocculent alone and using seed with flocculent. A schematic diagram of the procedure is shown in Fig. (1).

The conversion of magnesium chloride to magnesium hydroxide is monitored by ultraviolet visible recorder spectrophotometer (type Shimadza UV160A) at the absorption spectrum λ_{max}=285.2 nm. To calibrate the UV spectrophotometer, samples at different concentrations were prepared, and then the absorption spectra was measured.

To determine the concentration of magnesium hydroxide produced, the product was analyzed for magnesium content by means of atomic absorption spectrophotometer at the State Company for Geological Survey. The average percentage was found to be equal to 36.3 wt.%.

The particle size of magnesium hydroxide product was measured by means of a scanning electron microscopy (JEOL: Japanese Electro Optical Lamp Type 6400) at Al-Majed Company.

RESULTS AND DISCUSSION

The rate of sedimentation of magnesium hydroxide obtained from the reaction between brine (bittern) and milk of lime at stoichiometric ratio is studied. The rate of sedimentation is measured by visual observation of the height of precipitate with time.

Effect of seed concentration on reaction time

The reaction time of unseeded and seeded (best concentration 20 wt.% seed) is shown in Fig. (2). From this figure, it can be seen that the reaction time for the best seeded concentration is shorter by 17% than unseeded reaction. This can be interpreted as, that for unseeded reaction the growth begin after initial *induction period* or *time lag* (the time interval between mixing and appearance of crystal is known as induction period) during which there is a negligible change in the bulk solute concentration. This effect has been observed in the precipitation of many slightly soluble salts. For seeded reaction where sufficient seed is initially available for growth, no induction is needed. Indeed, induction period in seeded system is known to be due to surface contamination only[7,8].

Effect of seed concentration on sedimentation rate

The effect of seed concentration on sedimentation rate is shown in Fig. (3). From this figure, it can be seen that increasing the seeds concentration cause an increase in sedimentation rate up to a value of 20 wt.°o. This can be discussed as follows: increasing of seed concentration can be attributed to the increase in the mean grain size until a maximum mean size is reached at optimum seed concentration. After that, an increase in the concentration of seeds lead to a relative decrease in the mean grain size. This decrease in mean grain size (as indicated by sedimentation rate) is due to the deposition of the same mass of magnesium hydroxide produced on the relatively greater number of seed crystal and hence the produced grain size has a reduced mean grain size and the sedimentation rate is lowered[1 J]. Or, for heterogeneous nucleation the growth rate increases as the crystalline surface area increases, and then decreases because of the greater effect of the lowered supersaturation[1].

The seed concentration of magnesium hydroxide obtained from seawater had beed studied[13,] previously and the best seeds concentration for maximum sedimentation rate was obtained at the concentration of Mg between 12.55 and 17.3 g/L.

Effect of stirrer speed

The effect of stirrer speed on sedimentation rate at different concentration of seed is shown in Fig. (4). The agitation speeds considered were 200, 350, and 500 rpm. For agitation in laboratory experiments, a minimum agitator speed level (200 rpm). was determined from visual observation (minimum agitation speed is the point at which the slurry is completely suspended[10]). The increase in agitation speed causes a limited decrease of sedimentation rate within the range of speeds employed. This is due to the fact that since crystal size is a function of srirrer speed, i.e., the higher the speed the faster is the decay (as indicated by sedimentation rate). Thus, a lower sedimentation rate was obtained at the higher speeds.

Similar observations have been reported in the earlier study[11], even though for magnesium hydroxide concentration of 0.7-2.9 g/L as compared to that used in the present work for magnesium hydroxide concentration of 57.8-64.1 g/L.

Effect of seed concentration on particle size

The use of seeded solution is a useful method for controlling the particle size distribution of crystallization process. Particles of magnesium hydroxide when observed by a scanning electron microscope had mean particle sizes of approximately 1.5 u.m for the unseeded reaction, and approximately 4 u.m for the seeded reaction (20 wt.% seed).

A similar study^ showed that the particle size obtained was between 0.03 and 4 urn for magnesium hydroxide concentration 201.7 g/L.

Effect of flocculent concentration on sedimentation rate

The effect of flocculent (polyacrylamide) concentration on sedimentation rate is shown in Fig. (5). From this figure, it can be seen that increasing the flocculent concentration leads to an increase in the sedimentation rate up to a concentration of 30 ml/L 9each ml contains 7.14 x 10^{-3} g polyacrylamide). Beyond that, increasing the flocculent concentration have no significant effect on the sedimentation rate. This can be interpreted as follows: solid magnesium hydroxide in a colloidal suspension normally exhibits a net electrical surface charge within the hydrodynamic boundary layer around each particle. The charge of these particles is the same for all the particles in the suspension, which causes them to repel each other and remain in stable and unsettelable conditions. Colloidal destabilization by chemical treatment (addition of polyacrylamide) has been to the extent that individual particles can approach each other close enough for Van der Waals and/or chemical forces to cause the particles to aggregate into agglomerates, which facilitates their removal thus increasing sedimentation rate.

In earlier studies^[12,13], similar observations were made using magnesium hydroxide from seawater at a concentration of 5.75 g/L and flocculent concentration of 3.5 ml/g as compared with the present work when magnesium hydroxide concentration was 50.9 g/L and flocculent concentration of 30 ml/L.

Effect of stirring time on the sedimentation rate

The effects of stirring time on the sedimentation rate at the best concentration (see above) of flocculent are shown in Fig. (6). From this figure, it can be seen that increasing stirring time result in decreasing the sedimentation rate. This is due to the fact that increasing the stirring time leads to break up (disintegration) of the formed agglomerate. This leads to a reduction in the size of particles agglomerated (as indicated by the sedimentation rate), thus resulting in a lowered sedimentation rate.

When the agglomerates are formed naturally or originate as a chemical precipitate, they tend to reform after shear. Those that are formed by the addition of organic polyelectrolytes rarely reformed: and if reformation occur, the agglomerate exhibits significant differences from the original structure.

The effect of stirring time in the presence of a flocculent has been the subject of the smdy by Petric and Petric[12,13]. They concluded that a shorter time is more effective on sedimentation rate of magnesium hydroxide.

Effect of seed with flocculent on sedimentation rate

The effect of using both seeds and flocculent on the sedimentation rate of magnesium hydroxide at different concenirations of flocculent for the best seed concentration of 20 wt.% are given in Fig. (7). From this figure, it can be seen that increasing :he seed concentration at constant concentration of flocculent leads to an increase in sedimentation race more man that for seed alone. Also, increasing the flocculent concentration at constant seed concentration leads to an increase in the sedimentation rate more than for flocculent alone.

Thus, we see that the combined effect of using both seed and flocculent is more effective than using the seed or flocculent alone. The sedimentation rate of magnesium hydroxide using both seeds and flocculent are not reported in the literature.

CONCLUSIONS

1. The sedimentation rate of magnesium hydroxide under seeding conditions: (a) increases with increasing seed concentration until an optimum seed concentration (20 wt.% seed) after that the sedimentation rate decreases with further increase in seed concentration, (b) ..decreases with increasing srirrer speed. .
2. The sedimentation rate of magnesium hydroxide using flocculent: (a) increase with increasing flocculent concentration uo to 30 ml/L. At concentration higher than 30 ml/L, the increase in sedimentation rate is not significant, (b) decreases with increasing stirring time up to the point at which the flocculent becomes completely mixed with suspension (best stirring time in the present work is 1 minute).
3. The sedimentation rate of magnesium hydroxide using both seeds and flocculent: (a) increases with increasing flocculent concentration at constant seed concentration, (b) the concentration of 20 wt.% seed and 30 ml/L of flocculent gave the maximum sedimentation rate.
4. Seed concentration of 20 wt.% gave a reaction time shorter by 17% than unseeded reaction.

NOMENCLATURE

d	Diameter of particles	m
f_x	Activity coefficient of ion of charge x	-
g	Acceleration of gravity	m/s^2
k	Constant	-
K_1	Constant	-
k_c	Rate constant of $Mg(OH)_2$ crystal growth	-
k_{sp}	Thermodynamic stability of $Mg(OH)_2$	$Mole^3$
N	Number of nucleus formed	-
n_2	Number of $Mg(OH)_2$ units in the nucleus	-
IP	Ion product	-
S	Number of seed crystal added	-
t	Time	s
μ	Viscosity of fluid	$N.s.m^{-2}$
ρ	Density of fluid	Kg/m^3
ρ_3	Density of particles	Kg/m^3

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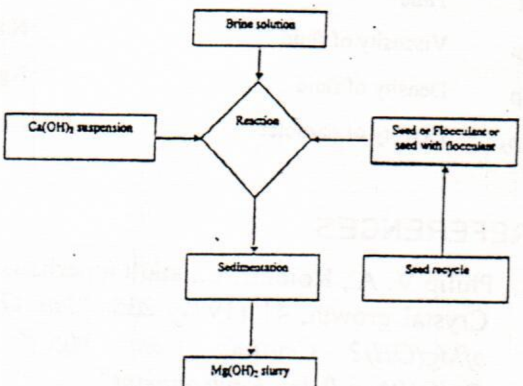

Fig. (1) Schematic diagram of experimental procedure

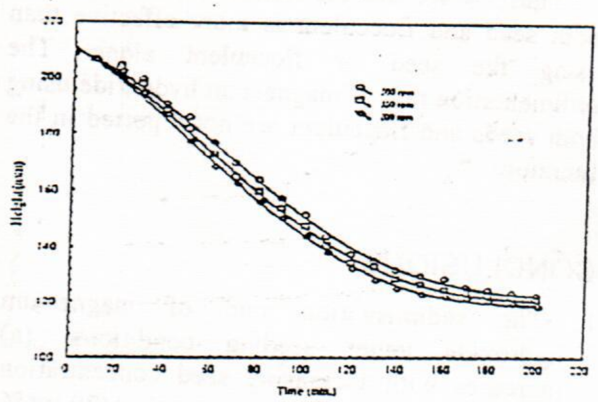

Fig. (4) Effect of rpm on settling curve at 20% seed

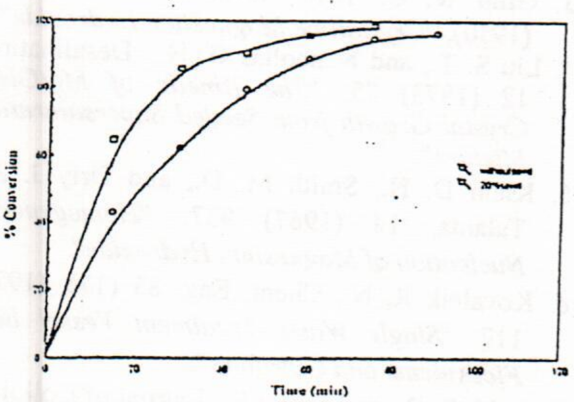

Fig. (2) Relation between conversion and time

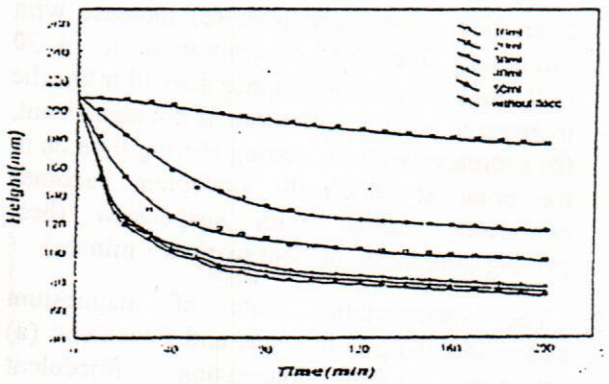

Fig. (5) Effect of flocculent concentration on settling curve

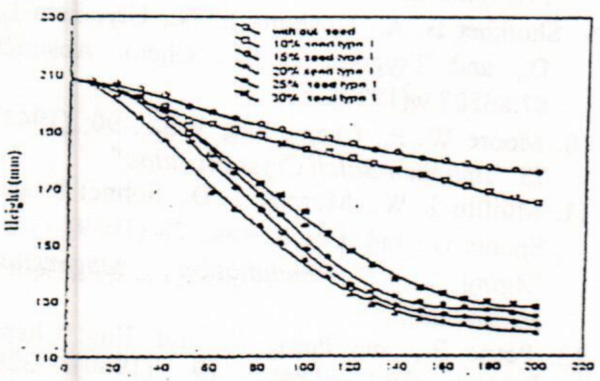

Fig. (3) Effect of seed concentration on settling curve

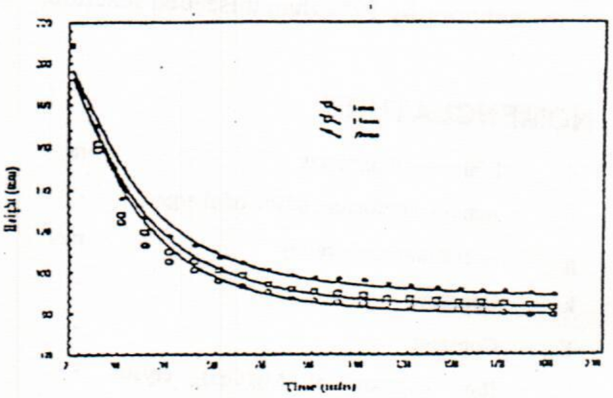

Fig. (6) Effect of stirring time on settling curve with 30 ml flocculent

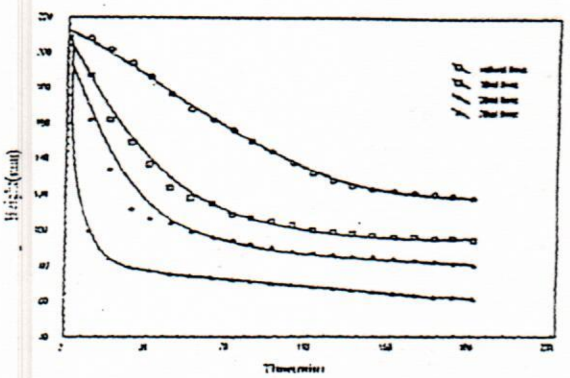

Fig. (7) Effect of flocculent on settling curve with 20% seed