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Role of hydrazine and hydrogen peroxide in aluminium hydroxide precipitation from sodium aluminate solution

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Abstract: Aluminium hydroxide precipitation from synthetic sodium aluminate solution was studied in the presence of hydrazine or hydrogen peroxide. The addition of low concentration of hydrazine is found to be effective, while higher amount of hydrogen peroxide is required to generate similar effect. XRD data confirm the product phase to be gibbsitic by nature. The scanning electron micrographs (SEM) show that agglomerated products form in the presence of hydrazine while fine discrete particles are produced with hydrogen peroxide. The probable mechanism of precipitation in the presence of hydrazine and hydrogen peroxide is also discussed.

Key words: aluminium hydroxide; hydrazine; hydrogen peroxide; sodium aluminate; precipitation

1 Introduction

In the Bayer process, bauxite is digested with hot concentrated sodium hydroxide to produce supersaturated sodium aluminate [$\mathrm{NaAl(OH)_4}$] solution. Aluminium hydroxide, $\mathrm{Al(OH)_3(s)}$ (gibbsite), is obtained from the aluminate liquor by seeded precipitation method, and the spent caustic solution is recycled to the digestion process. The productivity of the plant depends upon the gibbsite yield which is low under typical plant operating conditions such as temperature from 60 to 75 °C, $m(\mathrm{Al_2O_3})$:$m(\mathrm{Na_2O})$ ratio of about 1.0, seed addition of 400 to 600 g/L and precipitation period of 48 to 72 h. The wide gap between the quantity of gibbsite precipitates and its equilibrium solubility at a specific precipitation temperature provides scope to enhance the gibbsite yield.

The decomposition of sodium aluminate to precipitate aluminium hydroxide is possible through either physical or chemical method. Seeding is a physical method by which the decomposition of $[\mathrm{Al(OH)_4^-}]$, takes place to form $\mathrm{Al(OH)_3(s)}$. Another means of decomposition of $[\mathrm{Al(OH)_4^-}]$ is by proton ($\mathrm{H^+}$) assisted precipitation such as acid neutralization. Carbonisation decomposition is another example of chemical decomposition process [1]. In the present work, the use of hydrazine as an additive was investigated to observe any effect if it can impact the decomposition of aluminate ions since it is a weak base in comparison to highly alkaline sodium aluminate solution. Studies so far reported for enhancing the aluminium hydroxide precipitation have dealt with either thermal or mechanical seed activation [2−6]. Use of additives, mainly organic polymers or surfactants, for promoting productivity, has also been investigated [6−15]. The incorporation of $\mathrm{H^+}$ ions in the form of EDTA has been demonstrated for improving the yield [12]. Although hydrogen peroxide has been utilized for regeneration of spent sodium hydroxide from aluminium washed solution [13] and for synthesis of high area alumina particles by precipitating boehmite from sodium aluminate solution [15], its use for precipitating aluminium tri-hydroxide in Bayer precipitation process

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has not been explored yet. Thus, hydrogen peroxide as an additive has also been studied for enhancing the aluminium hydroxide precipitation.

2 Experimental

2.1 Materials

The chemicals used in this work were analytical grade reagents and obtained from Merck, India. Hydrazine hydrate ($N_2H_4{\cdot}H_2O$) containing 64% N_2H_4 and hydrogen peroxide (H_2O_2) as 30% by volume of H_2O_2 in aqueous solution were used. Super saturated sodium aluminate solution was prepared by dissolving measured quantity of aluminium granules in concentrated sodium hydroxide solution. In all the experiments, $m(Al_2O_3):m(Na_2O)$ (A/C) ratio was maintained at either 0.95 or 1.0. The particle size of gibbsite seed was 62.2 μm (d_{50}).

The apparatus used in the precipitation studies was made up of 304 stainless steel of 500 mL capacity. The precipitator is fitted with a digital RPM controller. An anchor type impeller was used for the agitation of the solution. Rotation speed of (190±2) r/min was maintained throughout the time period. The temperature of the system was maintained through a constant thermostatic bath circulator (JULBO, Germany) via an inlet and an outlet port.

2.2 Method

All the experiments were conducted taking 250 mL solution with A/C ratio of 0.95 or 1.0, where caustic concentration was fixed at 150 g/L and Al_2O_3 concentration was fixed as per the A/C ratio. The temperature was maintained at about 75 °C else otherwise mentioned and the precipitation was continued for 8 or 24 h. The seed and other additions were made once the required temperature was attained. H_2O_2 was added after mixing it with few drops of NaOH solution to avoid addition of acidic H_2O_2. At the end of the precipitation period, the slurry was filtered and the residue was washed several times before drying in an oven overnight at 100 °C. The aluminium hydroxide precipitation yield was calculated as follows:

$$\eta = \frac{m_{\mathrm{p}} - m_{\mathrm{s}}}{V} \tag{1}$$

where η is the aluminium hydroxide precipitation yield, m_{p} is the mass of precipitate, m_{s} is the mass of seed, and V is the experimental volume of solution.

X-ray diffractograms were recorded for the aluminium hydroxide powders using PANalytical diffractometer (PW 1830, Philips, Japan) with Cu K_α radiation, λ=1.54056 Å. The scans were recorded in 2θ range of 5° to 65°. A scanning electron microscope (SEM) (JEOL JSM 6510, Japan) was used to examine the surface morphology of the precipitates.

In this work, two different precipitation ratios were analyzed and calculated as follows:

$$R_{\mathrm{E}} = \frac{\eta_{\mathrm{a}} - \eta_{\mathrm{b}}}{\eta_b},\quad R_{\mathrm{s}} = \frac{\eta}{\eta_s} \tag{2}$$

where R_{E} is the yield enhancement ratio, η_{a} is the yield with additive, η_{b} is the yield under blank, "blank" specifies the condition when precipitation was carried out in the absence of additives. It should be kept in mind that yield under blank condition changes with solution concentration, temperature, and A/C ratio. R_{s} is the precipitation ratio under available supersaturation, η is the yield, and η_{s} is the supersaturation level.

2.3 Equilibrium solubility

The equilibrium solubility of $Al(OH)_3$ is the saturation point of solution below which level precipitation is improbable at a particular temperature; only the available supersaturation can practically be precipitated at the most under standard seeded precipitation process. The equilibrium solubility of alumina in the sodium aluminate solution was measured using the well known Rosenberg-Healy [16] formula as follows:

$$A_{\mathrm{eqm}} = 0.96197C \times \left\{ 1 + 10^{\left[\frac{-9.2082\sqrt{I}}{1+\sqrt{I}} + (0.8743I) - (0.2149I^{3/2}) \right]} \Big/ \exp\left(\frac{\Delta G}{RT} \right) \right\}^{-1} \tag{3}$$

where ionic strength I=0.01887c+0.01937c_{s}; c and c_{s} are the caustic and carbonate concentrations in g/L, respectively; ΔG=−30.96 kJ/mol is Gibbs free energy of solid formation; R=8.3145 kJ/mol is the universal gas constant; T is the precipitation temperature, K. Using the above equation, the equilibrium solubility of alumina at 75 °C (A_{75}) was calculated. When the Na_2O concentration is 150 g/L, A_{75}=88 g/L. Therefore, for A/C=1.0, where Al_2O_3 concentration is 150 g/L and $\rho(Na_2O)$=150 g/L, the available supersaturation is 62 g/L as $\rho(Al_2O_3)$=95 g/L as aluminium hydroxide. Similarly, for A/C=0.95, where Al_2O_3 concentration is 142.5 g/L, the available supersaturation is 54.5 g/L as $\rho(Al_2O_3)$= 83.35 g/L as aluminium hydroxide.

3 Results and discussion

3.1 Effect of hydrazine

Figure 1 shows the effect of hydrazine concentration on the precipitation yield of aluminium hydroxide. It is observed that at an A/C ratio of 0.95 or 1.0, when hydrazine is added with small quantities, the yield is increased for both 8 h and 24 h precipitation