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Removal of carbonate and oxalate pollutants in the Bayer process using thermal and chemical techniques

Mostafa Mahmoudian [a,b], Ahad Ghaemi [c,*], Shahrokh Shahhosseini [c]

[a] Iran Alumina Complex, P.O. Box 94415_1135, Jajarm, Iran
[b] Department of Chemical Engineering, Islamic Azad University, Shahrood Branch, Shahrood, Iran
[c] Department of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

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ABSTRACT

In the Bayer process, diasporic bauxite is dissolved in a caustic soda solution in the presence of lime at high temperature. During this process, concentration of carbonate and oxalate gradually increases causing problems in the alumina refining process. In this work, removal efficiency of the carbonate and oxalate pollutants from sodium aluminate solution has been increased using thermal and chemical techniques. The pollution of sodium aluminate solution has been reduced by heating the bauxite and removing the carbonate and oxalate by applying a chemical method. Bauxite heating leads to the organic compounds and carbonates in magnesite and calcite minerals exit as CO_2, preventing addition of these substances into the sodium aluminate solution. In the method of chemical removal of the carbonate and oxalate soluble in sodium aluminate liquor, barium aluminate with structures of $Ba_2Al_2O_5$, $Ba_2Al_4(OH)_{16}$ and $BaAl_2O_4$, calcium aluminate ($Ca_3Al_2(OH)_{12}$) and sodium phosphate (Na_3PO_4)–lime were separately used. As a result, these substances were sedimented as carbonate or barium oxalate, calcium and apatite. The results also showed that soda was retrieved as sodium aluminate or sodium hydroxide. Investigating the effect of temperature, time, concentration of caustic soda, Al_2O_3 and sodium carbonate revealed that using $Ba_2Al_4(OH)_{16}$ and the heating methods are the most efficient technique to remove the carbonate and oxalate, respectively.

1. Introduction

The Bayer process is known as extracting alumina from bauxite ore (Sonthalia et al., 2013; Xiao et al., 2007a,b). In this process, bauxite is mixed with lime and concentrated caustic soda solution at high temperature to dissolve alumina in caustic liquor. Then, the insoluble substances, named red mud, are separated from the sodium aluminate solution and disposed into special ponds. Sodium aluminate solution is sent to the precipitation stage. Then after cooling and adding seed, aluminum hydroxide, which is a white powder, is separated (Technoexport Praha., 1997). The process stages are given in Fig. 1.

The bauxite is the main source of organics in the Bayer process (Xiao et al., 2007a,b; Ellis et al., 2002; McSweeney et al., 2011). In addition to organic compounds, there are inorganic materials such as sodium carbonate and sulfate, which are formed during the digestion either by dissolution of the salts or minerals or from degradation of the organic compounds containing sulfur or nitrogen (Power and Loh, 2010). Bauxite and lime used in the process contain carbonate salts and organic compounds. These materials are entered into the sodium aluminate solution and produce carbonate and oxalate pollutions and over time, their concentration in the solution is increased in a cyclic trend (Pulpeiro et al., 1998; Machold et al., 2011).

Carbonate and oxalate pollutants enter into the Bayer process through bauxite, lime and sodium hydroxide solution and cause a number of problems in the alumina production cycle (Sonthalia et al., 2013; Pulpeiro et al., 1998; Whelan et al., 2003; Ellis et al., 2002; Pearson and The, 1985). Impurities in the solution can considerably affect crystal nucleation and growth (Cao et al., 2009). Oxalate reduces production of alumina, increases density, viscosity, specific heat and boiling point of the sodium aluminate solution (Hind et al., 1999; The, 1980; Soucy et al., 2013). It also increases production of fine-seed alumina and impurities in alumina (Hind et al., 1999; Atkins and Grocott, 1988; Shin et al., 2004; Zhang et al., 2008). In addition, oxalate leads to the loss of caustic soda (Armstrong et al., 1993; Power et al., 2012), co-precipitation of sodium oxalate along with aluminum hydroxide (Hind et al., 1999), produces foam at Bayer solution and sedimentation in equipment (Soucy et al., 2013). Furthermore, oxalate decreases settling rate of the red mud (Soucy et al., 2013; Jones et al., 1998), dying the sodium aluminate solution and aluminum hydroxide (Hind et al., 1999; Shin et al., 2004) and reduces efficiency of aluminum hydroxide precipitation (Shin et al., 2004; Strominger and Malito, 1994; Loh et al., 2008; Power and Tichbon, 1990). The other troublemaker, sodium carbonate,

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* Corresponding author.
E-mail address: aghaemi@iust.ac.ir (A. Ghaemi).

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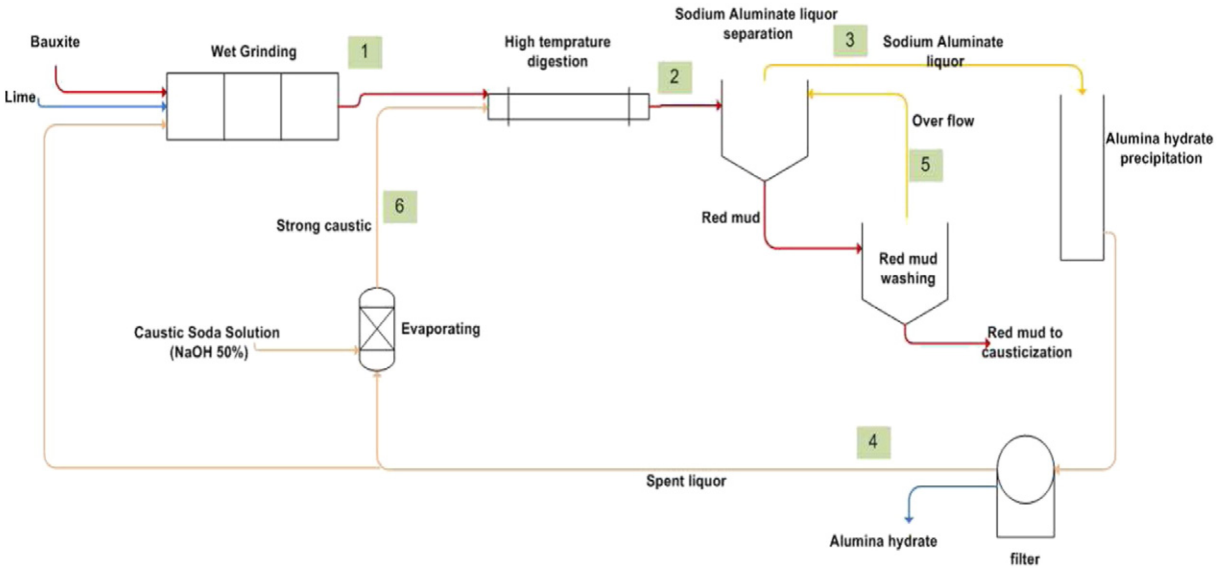

Fig. 1. Diagram of the process of alumina production from bauxite.

causes to increase density, viscosity and boiling temperature of sodium aluminate solution (Shin et al., 2004). It increases sedimentation on the equipment (Shin et al., 2004; Brady, 2011), and loss of the caustic soda (Armstrong et al., 1993; Grocott and Rosenberg, 1998). It also increases chlorine in the sodium aluminate solution (Hind et al., 1999) in the process of alumina production. Therefore, development of new techniques for removing these impurities from Bayer liquor is of great interest to the alumina refining industry (Dong et al., 2011). Several methods have been presented to remove carbonate and oxalate pollutions. Selecting an appropriate method depends on various parameters including operational and economic conditions. Several researches have been conducted on wet oxidation methods using oxygenated compounds such as air oxygen and ozone (Malito, 2006; Loh et al., 2010, Dong et al., 2010), filtration, ultrafiltration and reverse osmosis (Mueller and Green, 2000; Marciano et al., 2006), adsorption by resin, active carbon, alumina collected by an electrostatic precipitator (Williams, 1998), washing alumina hydrate (Yamada et al., 1980), evaporation, condensation and precipitation (Conroy and Gloster, 1979), evaporation using spray (Carruthers et al., 1977), calcinations of solution (Soucy et al., 2004; Machold et al., 2009), using lime (Matyasi et al., 1982), flocculation by additives such as polydadmac (poly diallyl dimethyl ammonium chloride) and acrylic polymer (Sommese and Mahoney, 1955), precipitation by germination (sodium oxalate, sodium aluminate, lime, etc.) (Gnyra, 1981), liquid–liquid extraction (Bush and The, 1985), photocausticization of Bayer liquor (Pareek et al., 2003), increasing soda concentration (Donaldson et al., 1984; Akihisa et al., 1972), oxidative photocatalytic degradation (Wang and Adesina, 1997) and using a source of phosphate in the presence of lime (Gerald. Dunstan et al., 2006).

Reviewing the conducted studies indicates that some reported methods resulted in low efficiency of the Bayer process. In addition, some other methods are carried out in undesirable operational conditions including temperature, pressure and concentration of the pollutants in the solution leading to incapability of some of these methods to be applied. Among these, using the method of chemical elimination by the use of additive compounds to remove carbonate and oxalate impurities from the Bayer process solution has more efficiency and flexibility due to the conditions governing the alumina refining process.

The aim of this work was to increase the removal efficiency of the pollutants for the Bayer process using simultaneous chemical and heating methods. Bauxite heating and removing method has been applied using phosphate–lime, calcium aluminate with the structure of $Ca_3Al_2(OH)_{12}$ and barium aluminate with the structures of $BaAl_2O_4$, $Ba_2Al_2O_5$ and $Ba_2Al_4(OH)_{16}$. In addition, experimental data were obtained from Iran Alumina Company in different operational conditions. The experiments were carried out on sodium aluminate solution in different units of this company. We tried to find a workable, effortless, capable and accessible method with minimal adverse side effects and good efficiency in accordance with the terms governing the Bayer process.

2. Material and compound analysis

An electric furnace (Carbolite-RW1400, England), a dryer (Ecocell, England) and a heater equipped with temperature control and magnetic stirrer were used to perform the experiments. The quantitative analyses of the compounds in the bauxite and red mud were performed using XRF (Siemens-SRS3000, Germany) and AAS (Unicam, England) devices. XRD (Siemens-D5000, Germany) was used to qualitatively analyze bauxite, red mud, final sediments of the tests and the prepared required materials (such as calcium aluminate and barium) and with the aim of identifying the nature and type of the combinations. The chemical analysis of the solution phase was done before and after the experiments. During the experiment, the values of Na_2O_c, Na_2O_t, Na_2O_u, Al_2O_3 and oxalate were measured. The values of phosphate and SiO_2 of the sodium aluminate solution were also measured using a UV–visible spectrometer (Unicam, England).

The required bauxite and lime have been used from mine and lime kilns located in Jajarm Alumina Company. The required barium aluminate was prepared and produced using barium chloride, barium carbonate and barium oxide from Merck Company, and alumina and sodium aluminate solution produced in Jajarm alumina company. The applied calcium aluminate was prepared and used by lime milk and sodium aluminate solution. Phosphate and sodium carbonate used in the experiments were obtained from Merck Company. Table 1 indicates the solubility of the prepared additives and precipitation products. These data indicate that sodium carbonate and sodium oxalate as Bayer process pollutants have good solubility. The pollutants were sediment as insoluble material like carbonate or barium oxalate, calcium and apatite.

The XRD diffraction patterns of different barium aluminate forms including $BaAl_2O_4$, $Ba_2Al_4(OH)_{16}$ and $Ca_3Al_2(OH)_{12}$ samples are shown in