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Technical note

The effect of iron sources on caustic and alumina recovery from synthetic bayer DSP (sodalite)

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ABSTRACT

The formation of desilication product (DSP) in the processing of high silica bauxite is both a significant cost to production and a potential threat to the environment due to the high level of caustic soda it contains. Hydrothermal reprocessing of DSP to recover caustic is a promising solution to the problem. The basis of this technology is the formation of iron-rich hydrogarnet and calcium silicate by redigesting DSP in caustic solution with lime and an "active" iron source. This paper highlights the influence of iron sources on phase formation during re-processing of synthetic DSP (sodalite) as well as the efficiency of soda and alumina extraction and lime consumption. Sodium ferrite, ferric nitrate, ferric chloride and hematite were chosen as iron sources for this study.

Different iron sources significantly affected the mineralogical composition of the reprocessed residues and the efficiency of the process. Under conditions of relatively low temperatures (200-230°C), digestion time of 10 to 40 min and lime charge of molar CaO/SiO_2 ratio ~1-2, ferrite and sodalite readily reacted to an iron-rich hydrogarnet. Ferric nitrate and chloride also produced hydrogarnet which has less iron incorporation because of competing reactions to form hematite. This drawback was minimized by separate injections of lime and ~ neutral salt solutions into digestion. Hematite did not react with lime and iron hydrogarnets did not form. Instead tobermorite formed as the dominant calcium-containing phase which is more efficient in lime consumption (molar $CaO/NaOH \sim < 1$) and soda extraction, and equally good in alumina extraction.

1. Introduction

Desilication product (DSP) formed in the processing of high silica bauxite in the Bayer process represents a significant cost to the production of alumina due to the high level of caustic soda losses in the form of sodalite. It also presents a potential threat to the environment because of the slow release of this soda from residue impoundment areas. Many methods have been investigated to recover the soda and alumina from DSP (Smith, 2009; Xu et al. 2009, 2010a, 2010b) including hydrothermal reprocessing of the DSP. The basis of this latter technology is the formation of iron rich hydrogarnet and calcium silicate hydrate by re-digesting DSP in caustic solution with lime in the presence of a suitable iron source. Cresswell and Milne (1982, 1984) digested Bayer residues and lime at 260 - 300 °C for ~20 min in high caustic but low aluminium solution to form calcium silicates. Zoldi et al. (1987) and Solymar et al. (1997) also applied a hydrothermal method to recover soda and alumina through the formation of iron-rich hydrogarnet utilizing the high iron content in residues under similar high temperature and high free caustic conditions thought to solubilise some of the iron present in the residue. Although these hydrothermal methods can recover >90% of soda and >70% of alumina from the mud, they are difficult and expensive to integrate to the Bayer process, and the high temperature and high free caustic conditions required increase corrosion of plant equipment.

Hydrothermal methods for processing red mud at lower temperatures have been investigated by others. Zhong et al. (2009) developed a two-step digestion process to extract alumina and soda from mud. In the first step, alumina was leached at 210 °C for 3.5 hr in the presence of lime. The residue of the leach process was separated and re-digested at 170 °C for further 2 hr to recover soda, giving a final residue consisting mainly of calcium silicate and iron hydrogarnet. The iron in these compounds was from the original mud. They claimed that ~87% of alumina and ~96% of Na_2O were recovered from mud. However, the rate of the extraction process was slow. Another promising hydrothermal method to process Bayer red mud using lime and sodium ferrite in high caustic solution has been reported (Medvedev et al., 2003). It was claimed that iron hydrogarnet formed ($Ca_3Fe_2(SiO_4)_2(OH)_4$) at temperatures as low as 235 °C and its rate was faster due to its favourable formation enthalpy. Na_2O/SiO_2

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molar ratio in processed residues was reported to be less than 0.1 and high recovery of soda and alumina from mud was apparently achieved. However, some information was not described.

It appears from the literature that the formation rate of iron hydrogarnet is related to the iron source activity. Here we report the results of our recent study on the effect of iron sources/activity on phase formation in the re-digestion of synthetic DSP in caustic solution with lime under non-optimized conditions. The extraction efficiencies of caustic soda and alumina as well as lime consumption are discussed.

In this paper standard North American Bayer notation is employed unless otherwise specified: A = g/L Al_2O_3, C = g/L of sodium hydroxide and sodium aluminate and S = C + sodium carbonate (C and S both expressed as equivalent g/L Na_2CO_3).

2. Experimental

2.1. Sodalite

Sodalite ($Na_6(AlSiO_4)_6 \cdot 2NaOH$) was prepared by digestion of pure kaolinite (Eckalite A, ECC International) at 150°C for 30 min in synthetic liquor (starting C ~ 250 g/L, A/C ~ 0.58 and C/S = 0.89). The exit slurry was pressure filtered and the residue cake was washed three times using aliquots of deionised water (last filtrate pH = 10.6). The washed residue was then dried at 110°C overnight. Starting and exit liquors were analysed for alumina, caustic and carbonate content by industry standard gluconate titration (Connop, 1996). A sub-sample of the residue was analysed by XRF and XRD. The XRD trace showed the main phases to be hydroxy-sodalite and sodalite (not shown).

2.2. Iron sources

Synthetic sodium ferrite and commercial laboratory grade ferric nitrate, ferric chloride, and hematite were chosen for this study. Sodium ferrite ($NaFeO_2$), as an important reactant in this work, was synthesized by roasting stoichiometric charge of sodium carbonate (A.R grade) and hematite (industrial grade hematite) at 800 °C for 8 hr in a muffle furnace. Under these conditions, particulate rather than clinker form of ferrite formed. The final product was allowed to cool to room temperature and then ground using a mortar and pestle. A sub sample of the product was examined by XRD (not shown), which indicated that the hematite was fully converted to sodium ferrite.

The nominal iron source charge was at a molar Fe/Si ratio of 1 to encourage the formation of ideal iron hydrogarnet $Ca_3Fe_2(SiO_4)_2(OH)_4$:

$$\begin{aligned}&Na_6(AlSiO_4)_6 \cdot 2NaOH + 9Ca(OH)_2 + 6NaFeO_2 \\ &\quad + 12H_2O \rightarrow 3Ca_3Fe_2(SiO_4)_2(OH)_4 + 6NaAl(OH)_4 + 8NaOH\end{aligned} \tag{1}$$

The actual charge of iron source was restricted by the injection method (see Section 2.4) and determined by XRF on dry residues.

2.3. Lime

Laboratory grade lime ($Ca(OH)_2$) was charged at nominal molar CaO/SiO_2 ratio 1.5-3. Actual lime charge was restricted by the injection method to a molar ratio of ~0.9-1.9 determined by XRF on final dry reprocessed residues. Lime and iron were first made into slurry with either caustic solution or de-ionised water and then injected into autoclave (see Section 2.4) when reaction temperature reached its preset value.

2.4. Digestion tests

All digestion tests were conducted using a PARR autoclave (~2 L capacity). Sodalite was directly charged at ~20 g/L to the autoclave together with caustic solution (C – 200 g/L) before the autoclave was sealed. The autoclave was heated to its preset temperature and the DSP slurry digested at temperature for up to 20 min. Lime and iron source were then injected together into the autoclave. Reaction time was deemed to commence at this point, maintained at temperature for 20 min then quenched. At the end of each run, solids and liquids were treated in the same way as described in the sodalite preparation section.

3. Results and discussion

3.1. Phase evolution

Fig. 1 shows the effect of iron sources on phase evolution in digesting of sodalite at comparable lime and (active) iron sources charges. When sodium ferrite was used, iron hydrogarnet (a variant of hibschite) was the main product, with trace amount of cancrinite. The same products but with higher level of cancrinite were observed when ferric nitrate was charged. In addition, a small amount of hematite also formed due to rapid dissociation and hydrolysis of ferric nitrate. In the presence of ferric chloride, iron hydrogarnet also formed. The original hydroxy-sodalite disappeared but sodium aluminium silicate chloride (a different type of sodalite) became one of the major phases. It is not clear whether this latter sodalite was formed through direct incorporation of Cl^- into the original sodalite or was the product of dissolution and re-precipitation of the original sodalite. Trace amount of hematite formed as well.

For hematite as iron source, no hydrogarnet formed, instead tobermorite ($Ca_5(OH)_2Si_6O_{16} \cdot 4H_2O$) was the main product. The lack of reactivity was probably due to higher stability of hematite at the reaction temperature (200-230 °C). Hematite is still the dominant phase in the digested residue.

XRD traces of samples with higher lime charges are not shown. These indicate the presence of trace amounts of tri-calcium aluminate – (silicate) (TCA, TCA-S) and un-reacted lime.

3.2. Caustic soda reduction in re-processed residues

The soda level in the redigested residues was significantly reduced due to the formation of iron hydrogarnet and other calcium silicate compounds. Fig. 2 shows the plot of molar Na_2O/SiO_2 ratio against molar CaO/SiO_2 ratio in the residues for all the four iron sources. It is clear that the soda level in all the residues declines with increasing lime charge within the current range and is much lower than the molar Na_2O/SiO_2 ratio (0.67, not shown) in the original DSP. For sodium ferrite, because of the wider lime charge used and more data points available, a linear inverse relation between lime charge and soda level can be drawn. For other iron sources, no such relation can be established due to insufficient data points.

Nevertheless, comparison of soda level can be made between the residues generated using these iron sources. The residues produced using hematite as iron source have the lowest soda level owing to the favourable chemical composition of tobermorite. The next lowest soda level is in the residues produced by the reaction of sodium ferrite because of the formation of substantial iron hydrogarnet. Relatively higher soda levels are observed in the residues formed in the presence of ferric chloride and nitrate because of the competitive formation of hematite as a consequence of hydrolysis. Suppression of the hydrolysis can improve the efficiency in soda reduction. For example, the data point of ferric nitrate (labelled as “nitrate 2”) on the regression line of ferrite was achieved by separate injection of