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Short communication

Regulating the digestion of high silica bauxite with calcium ferrite addition

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ABSTRACT

The digestion reactions of diasporic bauxite with A/S* of 5.96 was studied by adding calcium ferrite. With increasing addition of calcium ferrite, A/S and N/S* in the red mud are reduced. Under the conditions of higher digestion temperature and longer time, A/S in the red mud is also reduced with lower bauxite addition and higher soda in the liquor. Larger-scale experiments have been done with adding calcium ferrite under the conditions of 250 °C, 60 min which results in A/S in the red mud = 0.69 and N/S = 0.21. The main silicon mineral of red mud is ferrite hydrogarnet through analysis of XRD and energy-dispersive XRF. The coefficient of SiO_2 approaches 1, Al_2O_3 0.22, and Fe_2O_3 0.73 in iron hydrogarnet. It is because the structure of the silicon mineral is changed that A/S and N/S in the red mud are greatly reduced.
*A/S: mass ratio of %Al_2O_3 and SiO_2 in the solid; N/S: mass ratio of %Na_2O and SiO_2 in the solid.

1. Introduction

The characteristics of Chinese bauxite are high alumina, high silica, low ferrite, and middle- and low-grade diasporic bauxite (Niu, 2003; Yang, 2006). Consequently a combination process (Gu, 2004; Ai and Cheng, 2002) is mainly used to produce alumina in China, in which the flow is complicated and the energy consumption is high. The Bayer process is an economical process with simple flows, low energy consumption and low operation cost. The silicon minerals of bauxite are changed into sodium alumino-silicate (typical formula $Na_2O \cdot Al_2O_3 \cdot 1.7SiO_2 \cdot nH_2O$), which consist in Bayer process red mud (Liu et al., 2006; Smith, 2009). The lowest A/S of the red mud in the Bayer process is only 1 in theory. However, if the bauxite grade is lower and the content of silicon minerals is higher, the loss of alumina and soda in the red mud will increase dramatically if the traditional Bayer process is applied.

The basis of the method for reducing desilication soda losses by the use of lime through the formation of calcium silicates may be traced to the pioneering work of Klan (1969). This process was developed and patented by Comalco (Cresswell and Milne, 1982, 1983, 1984). Similar processes were developed in Eastern Europe and Russia (Zoldi et al., 1987; Medvedev et al., 2003; Solymar et al., 1997). The use of lime with the specific intent of forming hydrogarnets has been further developed in China (Gu et al., 2002; Zhao et al., 2002); but in a "Lime Bayer" process, the A/S of the red mud is about 1.4 and the alumina recovery is only about 75%. So to get high alumina recovery and low soda loss, a combination process and other methods have to be used.

In a new Bayer process with hydrocalcium ferrite (Liu and Zhu, 2003; Li et al., 2005; Liu et al., 2003), the previously prepared hydrocalcium ferrite is added when the bauxite is processed. Some silicon minerals in the bauxite can be changed into iron hydrogarnet ($3CaO \cdot Fe_2O_3 \cdot nSiO_2 \cdot H_2O$) (Zoldi et al., 1987; Yang, 1982) which becomes the main composite of the red mud. Hence A/S and N/S of the red mud can be reduced (Li et al., 2006a,b, 2007). But the preparation and application of hydrocalcium ferrite are very complicated. Firstly iron ore and limestone are sintered together to get calcium ferrite. Secondly calcium ferrite needs to be hydrated with water and calcium oxide and then hydrocalcium ferrite can be obtained. Finally it is preprocessed with bauxite in caustic liquor and digested.

In this paper, the preparation of the additive is simplified and the step of hydrating calcium ferrite is omitted. Instead, calcium ferrite is preprocessed with bauxite in caustic liquor and then digested. Again the A/S and N/S of the red mud are reduced (Li et al., 2006b, 2007). In this paper the digesting rule for diasporic bauxite with A/S of 5.96 by adding calcium ferrite is examined. The effect of dosage of calcium ferrite, addition of bauxite, digestion time and temperature on the A/S and N/S in the red mud is reported. Larger-scale (10 L) experiments have been carried out at 250 °C for 60 min with addition of calcium ferrite (Li and Wang, 2005) which confirm that the A/S and N/S of the red mud can be greatly reduced by changing the structure of the silicon mineral. The main silicon mineral of red mud is iron hydrogarnet through analysis of XRD and energy-dispersive XRF.

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Table 1
Chemical and mineralogical composition of the bauxite (mass fraction %).

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI
58.16	9.76	12.44	3.21	1.68	0.34	0.13	1.47	13.28

Diaspore	Kaolinite	Ilinite	Hematite	Goethite	Anatase	Rutile	Calcite
58.6	10.0	11.0	7.0	5.8	2.1	1.0	2.8

2. Experimental

2.1. Materials from the plant

Ironstone: mainly magnetite, Fe_2O_3 98.5%.

Limestone: mainly calcite, CaO 53.2%.

Mixed and milled bauxite: chemical and mineralogical composition in Table 1.

Caustic aluminate liquor: adjusted with spent liquor taken from the plant. Its main composition is N_T 237 g/L, N_K 220 g/L, Al_2O_3 120.4 g/L.

2.2. Tests programme

To prepare calcium ferrite (C_2F), first iron ore and limestone were mixed in proportion to $CaO:Fe_2O_3 = 2:l$ (molar ratio) then made into small round balls and sintered. Digestion was done with 50 mL caustic aluminate liquor and the required bauxite and calcium ferrite in steel bombs placed in a molten salt bath. After a certain time, the digestion slurry was filtered and the filtrate was analyzed for Al_2O_3 and Na_2O. The filter cake red mud was washed with hot water, then dried and analyzed for Al_2O_3, SiO_2 and Na_2O so that A/S and N/S and alumina recovery could be calculated.

3. Results and discussion

3.1. The effects of C_2F addition to A/S and N/S of the red mud

The digestion tests were conducted at 260 °C for 60 min with different amounts of C_2F added to achieve a range of silica ratios in iron hydrogarnet ($3CaO \cdot Fe_2O_3 \cdot nSiO_2 \cdot (6\text{-}2n)H_2O$) where n 1.4, 1.6, 1.8, 2.0, 2.2. The "n" coefficient for SiO_2 is smaller with more addition of C_2F. The relationship between the "n" coefficient of SiO_2 and A/S and N/S in the red mud is shown in Fig. 1.

It can be seen from Fig. 1 that "n" is smaller, the A/S and N/S of the red mud are reduced to below 0.8 and 0.3, respectively. If too much of C_2F is added, it is difficult to accept in industry so the best "n" coefficient of SiO_2 is in range of 1.8–2.0.

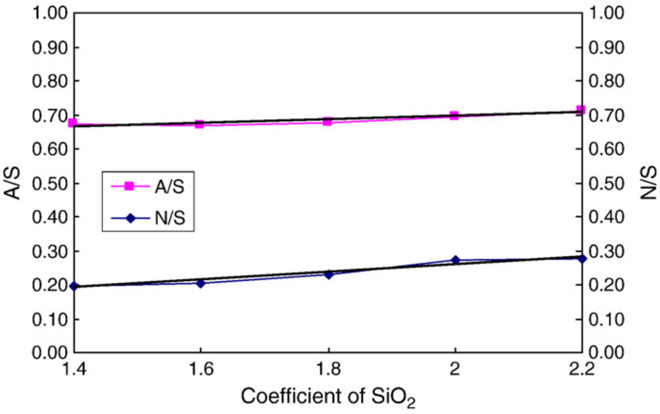

Fig. 1. Relation between coefficient of SiO_2 and A/S N/S in the red mud.

3.2. The effects of bauxite amount to A/S of the red mud

Digestion tests were carried out with different molar ratios of caustic Na_2O and Al_2O_3 in the liquor ("a_K") using bauxite addition to change the ratio in steps from 1.40 to 1.70. Therefore the molar ratio is presumed ("burden a_K") from the calculated amount of bauxite added. The conditions of the tests were 260 °C, 60 min, with C_2F addition to give the coefficient n for silica = 1.8.

The relationship between burden a_K and A/S in the red mud is shown in Fig. 2. Clearly, as less bauxite is added and burden a_K increases, the A/S of the red mud is reduced and remains steady around 0.75 when $a_K \geq 1.45$.

3.3. The effects of digestion temperature and time to A/S and N/S of the red mud

C_2F addition according to the coefficient of SiO_2 1.8, on the conditions of the results of different digestion temperatures ranging from 220 to 280 °C and different digestion times ranging from 15 to 150 min (with the same C_2F addition to give 1.8 silica in iron hydrogarnet) are shown in Table 2.

It can be seen from the table that increasing temperature or prolonged time, reduces the A/S of the red mud. But too low digestion temperatures, for example 220 °C slows the reaction too much and even after 150 min the A/S of the red mud is still above 1. At higher temperatures, the A/S of the red mud is lower and it takes a shorter time to get lower A/S values. The suitable digestion temperature is in range of 250–260 °C over a period of about 60 min.

3.4. Discussion of the mechanism

From the conclusions of the above test results, a larger-scale (10 L) test was carried out at 250 °C for 60 min with calcium ferrite addition to give $1.9SiO_2$ in hydrogarnet. This resulted in A/S = 0.69 and N/S = 0.21 in the red mud which is obviously lower than A/S = 1 and N/

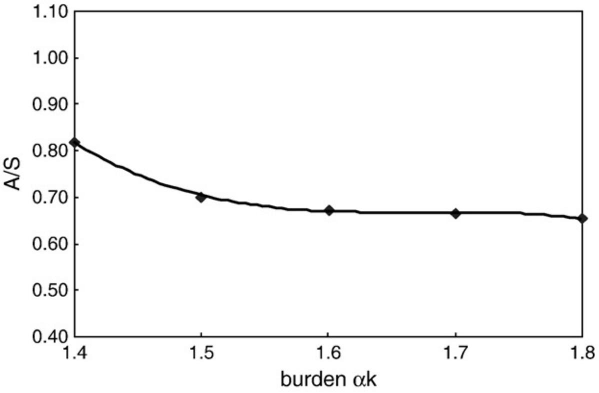

Fig. 2. Relation between burden a_K and A/S in the red mud.