ROASTING PRETREATMENT OF HIGH-SULFUR BAUXITE WITH LOW-MEDIAN GRADE IN CHONGQING CHINA

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Keywords: High-sulfur bauxite, Desulfurization, Roasting, Desulfurization ratio, Residual sulfur

Abstract

High-sulfur bauxite is being paid more and more attention due to the decreasing grade for traditional ore in China. There is rich high-sulfur bauxite with low-median grade in Chongqing, which is being treated with Bayer process with dressing. But there still exist excess impurities of sulfur and iron in the alumina product. The effect of surface density, particle size, temperature and time on the roasting desulfurization process was studied. The optimized roasting conditions are as follows: 750 ℃, 60 minutes, the surface density of 7.6 kg / m^2 and the particle size from 147 μm to 177 μm for the ore. Under these conditions, residual sulfur in the roasted ore is lower than 0.4%, which can meet the requirements of alumina production. Meanwhile, the digestion performance of the roasted ore improves. Roasting desulfurization might be one of methods for treating high-sulfur bauxite with low-median grade, and better technical and economic results might be attained when it is used to treat high-sulfur bauxite with organic and / or goethite impurites.

Introduction

High-sulfur bauxite refers to the ore containing sulfur over 0.7% used for the alumina industry. There is about 0.56 billion tons of the ore in China, and reserves are still increasing with recent discoveries on the base of coal seam in Henan, Shanxi, and Guizhou, etc. The ore is seldom adopted or often abandoned because of the negative effect of the sulfur impurity on alumina production. With the rapid development of the alumina industry, Chinese bauxite supply is facing a serious challenge. So low-median grade bauxite even nontraditional bauxite ore, including high-sulfur bauxite, is being paid more and more attention by Chinese alumina producers and researchers [1-3].

The sulfur in the bauxite has negative effect on the alumina production process, it can cause the decrease of the digestibility of the alumina, the loss of caustic alkali, scaling for the evaporators and digesters, the corrosion of steel equipments, the rise of sulfur and iron impurities and the decrease of particle size for the alumina product [4]. So for high-sulfur bauxite, the sulfur must be removed to the content less than 0.4% or at least 0.7% before it is adopted in the Bayer process.

For lots of desulfurization methods of high-sulfur bauxite [5-7], they can be divided into two groups. One is pretreatment desulfurization, and the other is process desulfurization. The pretreatment desulfurization, removes the sulfur impurity before the Bayer process and has no negative effect on the alumina production, so it is usually a priority method. Among the pretreatment desulfurization methods, flotation, biological, ore-blending and roasting technologies are included. Flotation desulfurization has been applied to industry scale, but there still exist problems such as a complicated system of chemical reagents and operation, large dosage of chemicals, high water content in the concentrate, and low efficiency for dispersed pyrite, etc [8]. For biological desulfurization, the difficulties lie in screening of functional strain, decreasing production cost and increasing efficiency [9]. Ore-blending is only a passive and limited method, meanwhile, the sulfur of the blending ore will enter, cycle, accumulate in the process, and has a negative effect on the alumina production in the end.

Roasting desulfurization is based on treating the high-sulfur bauxite to a certain temperature, causing pyrite transform into sulfur dioxide which is lost and then the roasted bauxite ore can be used in the Bayer process. Pyrite in the bauxite will react as follows under the conditions of oxidation roasting [10]:

$$(1\text{-}x)FeS_2+(1\text{-}2x)O_2=Fe_{1\text{-}x}S+(1\text{-}2x)SO_2 \quad (1)$$

$$2Fe_{1\text{-}x}S+(3\text{-}x)O_2=2(1\text{-}x)FeO+2SO_2 \quad (2)$$

$$3FeO+1/2O_2=Fe_3O_4 \quad (3)$$

$$2FeS_2=2FeS+S_2 \quad (4)$$

$$S_2+2O_2=2SO_2 \quad (5)$$

$$4FeS+7O_2=2Fe_2O_3+4SO_2 \quad (6)$$

The total chemical reaction can be expressed as follows:

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2 \quad (7)$$

Roasting models [11-13], such as muffle furnace, rotary kiln, fluidized bed and microwave, have an effect on the desulfurization process for high-sulfur bauxite. Studies by Guozhi Lv et al [12] showed optimum conditions for a muffle furnace and rotary kiln were 750 ℃ and 30 minutes, yet those of fluidized bed were 800 ℃ and 10 minutes. Rui Zhu et al [14] thought that optimum conditions of microwave were power 4.5 kW and 15 minutes, where the sulfur decreased from 4.15% to 0.32% and the digestion ratio of alumina was more than 90%.

Previous researches mainly focused on high-sulfur of high grade ores, seldom on that of low-median grade. There is nearly half of high-sulfur bauxite with low-median grade in China [8]. There exists more than 0.1 billion tons of high-sulfur bauxite ore in Chongqing, with average alumina content over 65%, average sulfur content from 2.5% to 4% and average mass ratio of alumina to silica (A/S) 4.76 [15, 16]. The bauxite ore in Chongqing is being treated with Bayer process with dressing, but there still exist excess impurities of sulfur and iron in the alumina product. The effect of temperature, time, particle size and surface density on the roasting desulfurization process was investigated in the paper, and the results are expected to provide technical support for the development of high-sulfur bauxite with low-median grade in China, especially in Chongqing.

Experimental

<u>High-sulfur bauxite</u>

Experimental samples of high-sulfur bauxite were obtained from Chongqing China, and were treated successively by milling, screening, and drying. The main chemical compositions of the bauxite were shown in Table 1 analyzed by an XRF spectrometer. It can be seen that the total sulfur (S_T) of the bauxite is 2.7%, which is more than the upper limit (0.7%) needed for the Bayer process, so the bauxite must be treated by desulfurization before it is used in Bayer process. There also exist considerable amounts of silicon with the A/S of 5.0. So it can be concluded that the experimental ore belongs to high-sulfur bauxite with low-median grade.

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	P_2O_5	CaO	S_T	A/S
56.2%	11.2%	6.2%	2.3%	1.9%	0.3%	2.7%	5.0

Table 1 Chemical compositions of experimental bauxite

Roasting experiments

A Muffle furnace and corundum crucible were adopted in the roasting pretreatment experiments. The effect of surface density, particle size, temperature and time on the desulfurization process was studied, and the desulfurization ratio was calculated as follows:

$$\eta = \frac{m_1 \cdot x_1 - m_2 \cdot x_2}{m_1 \cdot x_1} \times 100\% \quad (8)$$

Where η is the desulfurization ratio, m_1 is the mass of bauxite before roasting, m_2 is the mass of bauxite after roasting, x_1 is the sulfur content of bauxite before roasting, and x_2 is the residual sulfur content of bauxite after roasting.

Analysis of main chemical compositions

The main chemical compositions of the bauxite before roasting, after roasting and red mud were analyzed by XRF spectrometer, model DF -1000, manufactured by Yantai Dongfang Analytical Instruments Co., Ltd, China.

Results and Discussion

Effect of surface density on the roasting process

Surface density refers to the mass per unit surface area, which is often used to characterise layered and powder materials. The high-sulfur bauxite samples of 5 g, 7.5 g, 10 g, 15 g, 20 g and 30 g were fed into corundum crucibles with the diameter of 50 mm, then the surface density of the bauxite in the crucibes are 2.5 kg / m^2, 3.8 kg / m^2, 5.1 kg / m^2, 7.6 kg / m^2, 10.2 kg / m^2 and 17.8 kg / m^2 respectively. The effect of surface density of the bauxite on the roasting process under the conditions of 700 ℃, 60 minutes and particle size from 125 μm to 177 μm was studied, which was shown in Fig.1. It shows that there is an optimum surface density for the roasting desulfurization process, in which the desulfurization ratio is maxium yet the residual sulfur is minimal. The surface density of 7.6 kg / m^2 is the optimum value in the experiments, where the desulfurization ratio is 86.46% yet the residual sulfur is only 0.4%.

When the surface density is low in the roasting desulfurization process under atmospheric conditions, pyrite in the bauxite might transform into intermediates such as ferric sulfate or ferrous sulfate [17], which might cause the decrease of desulfurization ratio and increase of residual sulfur. But if it is too much, it is also difficult for both contact between air and solid bauxite particles, and the emission of sulfur dioxide.

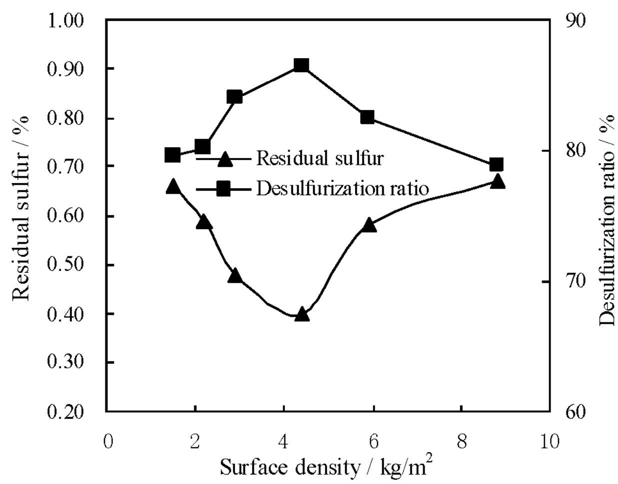

Fig. 1 Effect of surface density on the roasting process

Effect of particle size on the roasting process

Bauxite samples with different particle size were prepared by screening. The effect of particle size of the bauxite on the roasting process under the conditions of 750 ℃, 60 minutes and surface density of 7.6 kg / m^2 was investigated, and the result is shown in Fig.2.

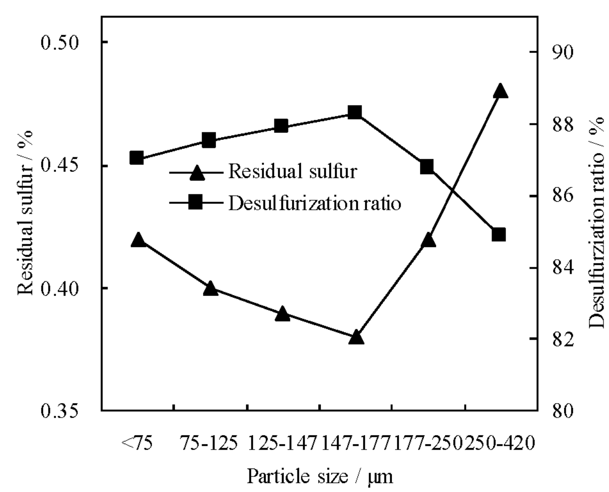

Fig.2 Effect of particle size on the desulfurziation process

As shown in Fig. 2, when the particle size increases, the desulfurization ratio increases gradually at first and then decreases obviously, yet the residual sulfur of the roasted bauxite decreases gradually at first and then clearly increases. For bauxite ore from 147 μm to 177 μm, the desulfurization ratio reaches 88.33% and the residual sulfur of the roasted bauxite is only 0.38%. Particle size from 75 μm to 177 μm (200 mesh to 80 mesh) is also suitable for this roasting desulfurization process with residual sulfur of the roasted bauxite less than 0.4%, which can meet the requirement of the Bayer process.

Thermochemical reactions of roasting high-sulfur bauxite are complicated, of which the main reaction can be expressed as follows:

$$4FeS_2(s)+11O_2(g)=2Fe_2O_3(s)+8SO_2(g)-Q \quad (9)$$

It can be learnt that the desulfurization efficiency is related to the gas diffusion and the interface between gases and solids. Smaller particles have a larger surface area, yet smaller gap among particles and vice versa. There might be an optimal particle size, which would be an optimum for both gas diffusion and the air/particle interface, and good desulfurization results would be attainted.

Effect of temperture on the roasting process

The effect of temperature on the roasting process was studied under the conditions of 60 minutes, surface density of 7.6 kg / m^2 and particle size from 125 μm to 177 μm, and the result was shown in Fig.3.

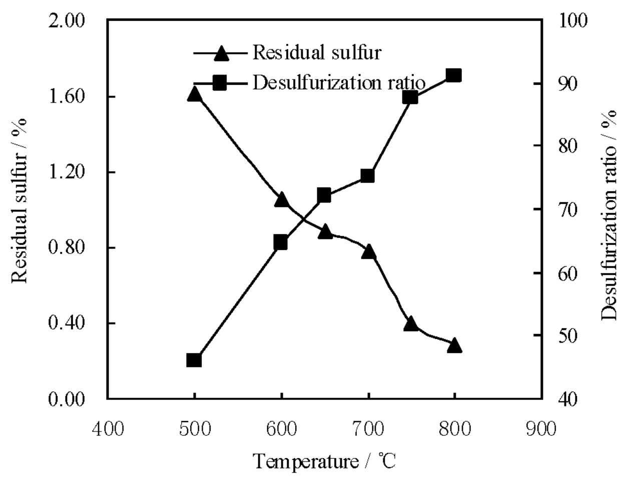

Fig. 3 Effect of temperture on the roasting process

It can be learnt that roasting temperature has a great effect on the desulfurization process. With increasing temperature, the desulfurziation ratio increases rapidly, while residual sulfur of the roasted bauxite decreases. When the temperature exceeds 750 ℃, the desulfurization ratio is more than 87.63%, yet the residual sulfur is less than 0.40%. Taking into account the energy consumption and desulfurziation efficiency, 750 ℃ will be an optimum roasting temperature.

If the high temperature of 750 ℃ is only used to remove sulfur, it might cause ecnomic problems for the process. It is well known that there may exist organic and / or goethite impurites for certain bauxite ores. These organics and / or goethite will also have negative effect on the alumina production. The organic impurities can be removed easily by roasting. Goethite can be transformed into hematie at 250 ℃, and particle size of the hematie increases with temperature [18]. So if the roasting method was used to pretreat bauxite containing goethite, it will be favorable for goethite transforming into hematie and improve the filtration performance of red muds. If roasting at 750 ℃ is used to pretreat high-sulfur bauxite containing organics and / or goethite, sulfur and organic impurities would be removed together, while the filtration performance of red muds would be improved too, and good technical and economic benefits could be attained.

Effect of time on the roasting process

The effect of time on the roasting process was studied under the conditions of 750 ℃, surface density of 7.6 kg / m^2 and particle size from 125 μm to 177 μm, and the result is shown in Fig.4.

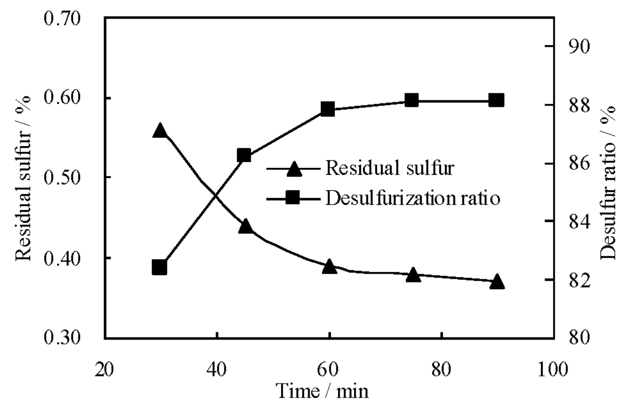

Fig. 4 Effect of time on the roasting process

It shows that, with the increase of time, the desulfurziation ratio increases gradually then reaches a stable value, yet the residual sulfur of the roasted bauxite decreases gradually then keeps stable too. When the time exceeds 60 minutes, the desulfurization ratio is more than 87.82%, yet the residual sulfur is less than 0.40%. Taking into account the desulfurziation efficiency, 60 minutes is an optium roasting time, in which residual sulfur of the roasted bauxite is 0.39%. The optimum roasting time is a little longer than that in the literature [12], which might due to the low-median grade bauxite ore adopted in the experiments.

3.5 Comprehensive experiments of roasting

Several comprehensive experiments were conducted under the optimum conditions of 750 ℃, 60 minutes, surface density of 7.6 kg / m^2 and particle size from 125 μm to 177 μm, and chemical components of the roasted bauxite were listed in Table 2.

Table 2 Chemical components of the roasted bauxite

No.	Al(%)	Si(%)	A/S	S_T(%)
1	56.33	11.25	5.01	0.38
2	56.41	11.34	4.98	0.38
3	56.46	11.23	5.02	0.39
4	56.19	11.16	5.03	0.38
5	56.38	11.25	5.01	0.38

It demonstrates that average residual sulfur is only 0.38%, which is satisfactory for the roasting desulfurization process.

Digestion experiments

The roasted bauxite was adopted in digestion experiments under the conditions of 205 ℃, 60 minutes, caustic concentration (C_{Na2Ok}) 250 g/L and lime dosage 5%. The A/S in red mud is 1.59, and the digestion ratio of alumina is 85.4%. But it is hard to digest untreated bauxite in Chongqing under the same conditions. So it might be concluded that the roasting pretreatment is advantagous for the digestion process. It might be due to the transformation of the diaspore to a highly active transition alumina during the roasting desulurization process [12].

Conclusion

The effect of temperature, time, surface density and particle size on the roasting desulfurization process of high sulfur bauxites was investigated, and conclusions were made as follows:
1) Temperature has greatest effect on the roasting desulfurization process, then time, surface density and particle size.
2) The optimum roasting conditions are 750 ℃, 60 minutes, surface density of 7.6 kg / m^2 and particle size from 125 μm to 177 μm. The roasted bauxite also has better digestion performance, which can be utilised in the Bayer process.
3) Roasting desulfurization might be one of the methods for treating high-sulfur bauxite with low-median grade, and better technical and economic results might be attained when it is used to treat high-sulfur bauxite with organic and / or goethite impurites.

Acknowledgement

This work was financially supported by National Natural Science Foundation of China No. 51204221, Chongqing Natural Science Foundation No. cstc2012jjA90010, Scientific and Technological Research Program of Chongqing Municipal Education Commission No. KJ131417, Research Foundation of Chongqing University of Science & Technology No. CK2010B20, and Science and Technology Innovation Foundation of Chongqing University of Science & Technology No. 2014023.

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