RESOURCE UTILIZATION OF HIGH-SULFUR BAUXITE OF LOW-MEDIAN GRADE IN CHONGQING CHINA

Jianguo Yin, Wentang Xia, Mingrong Han
Chongqing University of Science & Technology, Chongqing 401331, PR China

Keywords: High-sulfur bauxite, Resource utilization, Low-median grade, Desulfurization

Abstract

Resource utilization of high-sulfur bauxite is one of the technical problems for alumina refineries in China. There are rich high-sulfur bauxite ores of low-median grade in Chongqing China, which haven't been utilized until now. Sulfur in bauxite will cause many negative effects on alumina production. There are still some disadvantages for current desulfurization technologies and it is difficult to make a breakthrough progress only from the view of application of these desulfurization technologies. So it is necessary to undertake fundamental theoretical studies on the occurrence of sulfur in high-sulfur bauxites, the reaction behavior and the impact of sulfur in the production process. Combining theoretical research with experiments, it is possible to develop a feasible desulfurization process. This will provide technical support and theoretical guidance for the utilization of high-sulfur bauxites in Chongqing, and is also advantageous for prolonging bauxite resource security for the Chinese alumina industry.

Introduction

The alumina industry in China has developed quickly in recent years. Output of alumina in the year of 2009 was up to 24 million tons, and production capacity reached 33 million tons. It may be above 40 million tons in the following 2 or 3 years. This brings serious supply problems for bauxite resources as the production capacity of alumina expands so rapidly in China. From the view of the world, the service life of bauxite ore reserves is more than 100 years based on an annual output of 80 million tons of alumina and annual consumption of 2.5 billion tons bauxite. But from the view of China, the service life is no more than 15 years, based on an annual output of 20 million tons of alumina, even if the prospective reserves are considered (1). For Chinese bauxite ores, quality will decrease rapidly or even to exhaustion in the traditional mining areas. So it is necessary for the Chinese alumina industry to cope with this serious resource problem in order to ensure the alumina industry develops continuously, stably and healthily.

There are some bauxite resources which are difficult to be utilized until now in the main mining areas, which include high-sulfur bauxite ores. There are 11% or so of these high-sulfur bauxite ores and about 5.6 billion tons reserves in China. With the further survey of bauxite ore under the coal seams, the portion of the ore may rise. There are rich high-sulfur reserves in Nanchuan Chongqing China, the proven reserves are more than one billion tons and the prospective reserves are about 3 billion tons. Bauxite ores of Chongqing have their own characteristics, which belong to high-sulfur diaspore bauxite of low-median grade and very different from those of Guizhou. The average quality index of the bauxite ores are as follows: Al_2O_3 44.26%-71.39%, SiO_2 9.54%-19.16%, Fe_2O_3 0.80%-20.27%, S 0.16%-2.19%, A / S (the mass ratio of alumina to silica) 3.68-7.54 (2).

It is generally thought that bauxite ores containing sulfur over 0.7% cannot be used directly to produce alumina. So high-sulfur bauxite ore has been basically abandoned, or has had a little utilization mixed into other resources until now. If a process using high-sulfur bauxite to produce a suitable quality alumina can be successfully developed, the resource life of Chinese bauxite ores will be prolonged by about 10 years. So for resource utilization of high-sulfur bauxite, it is very important not only for the development of the regional economy in Chongqing but also for the China alumina industry.

Negative effect of sulfur on the alumina production

Sulfur in the bauxite ores will cause a lot negative effects on the alumina production. It will increase the soda consumption and decrease the digestion ratio of alumina. Sulfur in the form of the anions S^{2-} and $S_2O_3^{2-}$ in the liquors will erode the steel and iron of the pipes and equipment, and increase the iron content in the liquors and the products, which will cause negative effects on the quality of alumina product and in the subsequent aluminum electrolysis. When sulfur accumulates to a certain concentration, it will be precipitated in certain forms and cause scaling of the spent liquor evaporator and slurry digester, which will decrease the heat transfer coefficient of these devices or even make them not work (3). So it is necessary to desulfurize in the process of alumina production from such ores.

Previous desulfurization technologies

Desulfurization technologies for high-sulfur bauxite ores have been studied a lot at home and abroad, and can be divided into flotation desulfurization, roasting desulfurization and wet desulfurization. Classification of desulfurization technologies is shown is Fig.1.

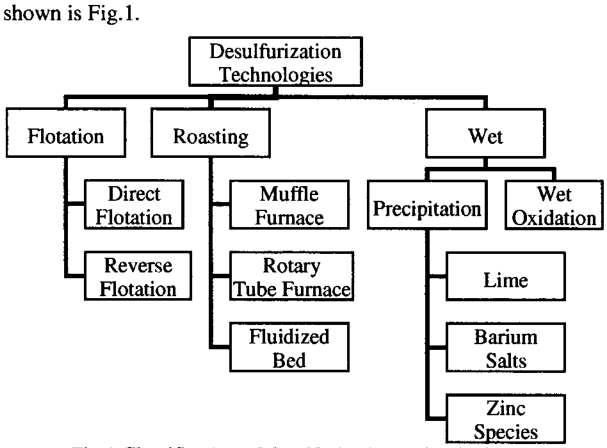

Fig.1 Classification of desulfurization technologies

Flotation desulfurization

Through differences in the physicochemical properties of mineral surfaces, the minerals can be beneficiated, and the differences can be enlarged by adding flotation reagents and manually modified, which makes the flotation method very adaptable. Moreover the flotation method has high separating efficiency, so it is one of the most extensively adopted beneficiation methods. Sulfur in the bauxite ore mainly exist in the form of pyrite. Pyrite can be floated easily by xanthate collectors, but ores containing aluminum are hydrophilic and not easy to collect. So xanthate collectors can realize the separation pyrite from the ores easily and then decreases the sulfur content of the ores. Flotation desulfurization was firstly used by the Ural Engineering Institute of the former Soviet Union. Technologies of one-roughing, two-cleaning and two-scavenging stages were adopted to treat bauxite ore containing 2% sulfur and the concentrate contains sulfur less than 0.41%. But this flotation desulfurization process is too complicated. Flotation desulfurization by potential control was reported, but it was too hard to realize on production scale (3).

Xiaomin Wang et al. studied desulfurization by reversed flotation using ethyl xanthogenate, and attainted optimum conditions as follows: pH value 12, flotation reagent dosage 0.4 kg / t, agitation time 15 minutes, the content of ore slurry 10% and particle size of ore less than 0.09 mm. Under these conditions, the sulfur content of bauxite ore can be reduced from 2.08% to 0.65%, and recovery ratio of alumina reaches 91.46%, which is suitable for alumina production (4). Using butyl xanthogenate as a reversed flotation regent, good desulfurization results can also be attained (5). Using soda as pH modifier, sodium hexametahposphate as an inhibitor, sodium sulfide and copper sulfate as activators, ethyl xanthogenates and butyl xanthogenate as collectors, Wenmi Chen treated high-sulfur bauxite in Guizhou China by reversed flotation. For the concentrate, the sulfur content is 0.44% and the recovery ratio of alumina is 96% (6). Adopting a one-stage flotation process to treat high-sulfur bauxite ore in Guizhou, the concentrate contains 0.15% sulfur and alumina losses are only 6.3% (7).

From the view of the technology itself flotation desulfurization is matured, but from the view of alumina production it brings some negative effects as the concentrate contains water and flotation reagents. At the same time, the process needs to treat large amount of bauxite ores, waste water and tails, and add a lot of reagents and fresh water (8).

Roasting desulfurization

A lot of research has focused on roasting desulfurization (9-13). Muffle furnaces, rotary tube furnaces and fluidized beds were used to pretreat high-sulfur bauxite ore. Optimum roasting conditions for muffle furnace and rotary tube furnace are a temperature of 750 centigrade and time of 30 minutes. Those for fluidized bed are temperature 800 and time 10 minutes. The digestion performance of the pretreated ore from the fluidized bed is the best, with the digestion ratio of alumina reaching 93.7% under the digestion conditions of temperature 220, molecular ratio of the proportioning 1.3 and caustic concentration 220 g / L (14-17). Sulfur is removed in the form of gas, and the roasted bauxite ore has better digestion performance. It is found that roasting makes the red mud loose and porous, and converts goethite to hydrophobic hematite, which improves the settling performance. But if the roasted ore is too loose, it will cause red mud fines and seriously decrease its settling performance. Compared to that roasted in a muffle furnace, the ore from the rotary tube furnace has better settling performance (18). High-sulfur bauxite ore in Henan province was investigated by Xiaolian Hu et al. with lime roasting in a muffle furnace. It shows that sulfur in the form of sulfide decreases after roasting. Lime roasting has better result for sulfur-fixation, and it decreases the content of sulfur dioxide emitted into the air. In the roasting process, pyrite is converted to hematite. After treatment, the bauxite ore decreases the sulfide content of the digestion liquor and improves its digestion performance. The optimum roasting temperature is 600. When adding 1% lime and roasting, the comparative digestion ratio is 95.35 % and sulfide in the liquor is 0.16 g / L (19). In the process of lime sintering, sulfur is removed by adding anthracite. But the desulfurizing efficiency is low (20). Improving the adding way of coal can increase desulfurizing efficiency (21).

It can be concluded that roasting desulfurization is relatively simpler, however, it increases the energy consumption and pollutes the environment.

Wet desulfurization

1. Desulfurization by wet oxidation
Desulfurization by wet oxidation involves pumping in air to oxidize sulfur into sodium sulfate which precipitates in the evaporation process of the spent liquor (22). But increasing the sodium sulfate in the spent liquors will lead to the double salt of burkeite precipitating in the evaporation process, which accelerates the evaporator scaling and effects its operation. So the formation of the thiosulfate anion needs to be prevented, lest it hastens the corrosion of the equipment. In addition, desulfurization by wet oxidation is a little dangerous.

2. Desulfurization by precipitation
Lime is commonly used as a desulfurization reagent by precipitation. Jun Lan investigated desulfurization by precipitation for a high-sulfur bauxite ore of high grade in Maochang Guizhou China. The effects of lime dosage, alkali concentration, digestion temperature and time on the desulfurization efficiency were investigated. The results show that optimum conditions are as follows: lime dosage 10%, digestion temperature 245, desulfurization time 70 minutes and alkali concentration 240 g / L. Under these conditions, the digestion ratio of sulfur is only 31.3% and that of alumina is over 81% (23). Adopting the same technology, Runde He thought the optimum conditions are as follows: lime dosage 12%, digestion temperature 260, desulfurization time 50 minutes and alkali concentration 195 g / L. Under these conditions, the digestion ratio of sulfur is only 13% and that of alumina is over 88% (24, 25).

Barium salts are another desulfurization reagents utilizing precipitation. Barium oxide and barium hydroxide were chosen to purify industrial sodium aluminate liquors (26). Desulfurization efficiency of barium salts is satisfying, and can reach 99%. But when the contents of silicate and carbonate in the liquors are high, the consumptions of barium salts will increase. As these two salts are expensive, it will increase desulfurization expense. Adopting cheap bauxite ore of high grade, and barium carbonate to generate a desulfurization reagent of barium aluminate, the desulfurizing result is similar to those of the two barium salts, but the desulfurization expense can be greatly reduced (27, 28). Desulfurization ratio reaches 94.5 % when barium aluminate is adopted to purify washing water of red mud (29). It is thought that washing water of red mud is suitable to be desulfurized and purified (30). Fanghai Lu thought that spent liquors and the first washing water of aluminum hydroxide are suitable to be desulfurized (31).

Zinc oxide has also been used as a desulfurization reagent, which makes sulfur precipitate in the form of zinc sulfide, and iron was removed at the same time. But zinc species are expensive, which will increase the cost of desulfurization. Adding zinc species will also influence the quality of the products.

Wet desulfurization has the advantage of high desulfurization efficiency. The key is to choose a cheap desulfurization reagent in order to decrease the total cost of the process.

Our suggestion

From the above discussion, for previous desulfurization technologies for high-sulfur bauxite, there are some disadvantages such as the negative effects on alumina products, increasing material or energy consumption, polluting the environment, increasing the expense or hard to realize in the production environment etc. Under the current circumstance, it seems hard to make a breakthrough progress only from the view of the desulfurization technology itself. More importantly, previous studies focused on desulfurization only for high-sulfur bauxite ore of high grade, there is little research on bauxite ore of low-median grade. In order to deal with resource utilization of the high-sulfur bauxite of low-median grade in Chongqing China, it is necessary to have fundamental theoretical studies on the occurrence of sulfur in high-sulfur bauxites, its speciation, reaction behavior and the impact of sulfur in the production process.

Combining modern instrumental analysis with chemical phase analysis, it is possible to fully investigate the occurrence of sulfur in the bauxite ore first, which will guide the following work. Then simulated study of the reaction behavior of different compounds containing sulfur in the alkali liquors can be undertaken, according to this information. Investigations of the sulfur chemical species, reaction behavior and its effect on the digestion ratio of alumina in the digestion process will follow along with a study of the digestion ratio of sulfur under the conditions of controlled digestion. On the basis of previous work, combining physicochemical properties with theoretical analysis results, and controlling the chemical reaction in the whole process, a suitable way of desulfurization for high-sulfur bauxite ore of low-median grade might be attained.

It is founded that total sulfur of high-sulfur bauxite in Nanchuan Chongqing is about 1.4%. Most of this exists in the form of pyrite constituting about 1%. Other forms exist such as marcasite, melnikovite or gypsum, which are disseminated through the ore deposit and hard to separate only by flotation. Because of the diversity of sulfur species for high-sulfur bauxite ores in Nanchuan Chongqing, it is hard to get good desulfurization results by only applying a single desulfurization technology. So it is necessary to undertake some fundamental studies in order to utilize high-sulfur bauxite ores of low-median grade in Chongqing China to produce alumina of metallurgic grade.

Conclusion

There are rich high-sulfur bauxite ores of low-median grade in Chongqing China, which are characteristic of the region and have not been utilized till now. It is necessary to undertake fundamental theoretical studies on the occurrence of sulfur in high-sulfur bauxites of low-median grade, occurrence, reaction behavior and the impact of sulfur in the production process. Combining theoretical research with experiments, it is possible to develop a feasible desulfurization process. This will provide technical support and theoretical guidance for the utilization of high-sulfur bauxites in Chongqing, and is also advantageous for prolonging bauxite resource security for the Chinese alumina industry.

References

1. Qiuxia Wang, Keren Zhang, Junwei Zhao, et al., Status, problems and countermeasures of development and utilization of bauxite resources in China, Conservation and Utilization of Mineral Resources, 5(2008), 46-50.
2. Yang Sun, Fuchun Zhou. Study on processing industry of superior mineral resource in Chongqing, Mining Safety and Environment Protection, 32(2)(2005), 27-30,54
3. Wenmi Chen, Qiaoling Xie, Xiaolian Hu, et al., Research on reverse flotation for desulfurizing of high grade bauxite containing sulfur and producing qualified alumina products, Light Metals of China, 9(2008), 8-12.
4. Xiaomin Wang, Tingan Zhang, Guozhi LV, et al., Flotation process for desulfurization of high-sulfur bauxite, Chinese Journal of Rare Metal, 33(5)(2009), 728-732.
5. Xiaomin Wang, Tingan Zhang, Guozhi LV, et al., Flotation desulfurization of high-sulfur bauxite with butyl xanthate as collector, The Chinese Journal of Process Engineering, 9(3)(2009), 498-502.
6. Wenmi Chen, Qiaoling Xie, Xiaolian Hu, et al., Experimental study on reverse flotation technique for desulfurizing of high-sulfur bauxite, Mining and Metallurgical Engineering, 28(3)(2008), 34-37.
7. Fangyin Niu, Qin Zhang, Jie Zhang, Orthogonal test research on flotation desulfurization of high-sulfur bauxite, Acta Mineralogica Sinica, 27(3/4)(2007), 393-395.
8. Runde He, Si chun Hu, Zhiying Li, et al., Discussion on the method of hydrometallurgical desulfurizing during producing alumina with high grade bauxite containing sulfur, Hydrometallurgy of China, 23(2)(2004), 66-68.
9. Chongyu Yang, Technology of alumina production (Beijing: Metallurgical Industry Press, 1993), 133-140.
10. Yiyong Wang, Tingan Zhang, Xia Chen, et al., Effects of microwave roasting on leaching behavior of diaspore ore, The Chinese Journal of Process Engineering, 7(2)(2007), 317-321.
11. Hengqin Zhao, Chongyu Yang, Hangbo Liu, Investigation on kinetics of bauxite's digestion improved by preroasting process, 6(3)(1998), 28-32.
12. A. R. Padill, D. Vega, M. C. Ruiz, Pressure leaching of sulfidized chalcopyrite in sulfuric acid-oxygen media, Hydrometallurgy, 6(1/2)(2008), 80-88.
13. Pi Liu, Zijian Lv, Zhongling Han, Analysis of effect of China bauxite ore preroasting on the Bayer process and its industrial application, Light Metals of China, 4(1997), 15-18.
14. Guozhi Lv, Tingan Zhang, Li Bao, et al., Desulfurizatin of high-sulphur bauxite by fluosolid roasting and its effect on the

digestion performance, Ming and Metallurgical Engineering, 28(6)(2008), 58-61.
15. Guozhi Lv, Tingan Zhang, Li Bao, et al., Roasting pretreatment of high-sulfur bauxite, The Chinese Journal of Process Engineering, 8(5)(2008), 892-896.
16. Guozhi Lv, Tingan Zhang, Li Bao, et al., Roasting pretreatment and digestion performance of high sulfur bauxite, The Chinese Journal of Process Engineering, 9(Supplement 1)(2009), 71-75.
17. Guozhi Lv, Tingan Zhang, Li Bao, Roasting pretreatment of high-sulfur bauxite and digestion performance of roasted ore, The Chinese Journal of Nonferrous Metals, 19(9)(2009), 1684-1689.
18. Guozhi Lv, Tingan Zhang, Li Bao, et al., On the settling performance of red mud from preroasted high-sulfur bauxite, Journal of Northeastern University (Natural Science), 30(2)(2009), 242-245.
19. Xiaolian Hu, Wenmi Chen, Qiaoling Xie, Study on desulfurization of high-sulfur bauxite by calcium oxide roasting, Light Metals of China, 1(2010), 9-14.
20. Shiwen Bi, Alumina production technology (Beijing: Chemistry Industry Press, 2006), 120-122.
21. Yucheng Feng, Jinglian Zhang, Strengthened reduction and sulfur-removal with high temperature coaling for alumina clinker sintering, Light Metals of China, 1(1990), 16-19.
22. C. И. Кузнецов, Desulfurization of sodium aluminate liquors with furnace ash, Techniques of Light Metals, 1(1974), 10-14.
23. Jun Lan, Xianxi Wu, Yuancheng Xie, Research of desulfurization in the course of disposing of high grade bauxite containing sulfur, Applied Chemical Industry, 37(8)(2008): 886-890.
24. Ting He, Zhiying Li, Optimal condition analysis of Guizhou high-sulfur bauxite leaching process, Nonferrous Metals, 60(2)(2008), 68-70.
25. Runde He, Zhiying Li, Nianbing Zhang, et al., Research on leaching function of Guizhou high-sulfur bauxite, Journal of Guizhou University of Technology (Natural Science Edition), 34(3)(2005), 4-7.
26. Huajun Yuan, Qinqin Li, Technological choose of Barium oxide purifying industrial sodium aluminate liquors, Light Metals of China, 4(1995), 13-17.
27. Sichun Hu, Min Guo, Hengqin Zhao, et al., Study on desulfurizing from sodium aluminate Liquors with barium aluminate, Nonferrous Metals (Extractive Metallurgy), 1(2007), 11-13.
28. Runde He, Nianbing Zhang, Sichun Hu, et al., Barium aluminate's combinative study with high grade bauxite instead of aluminum hydroxide, Light Metals of China, 4(2005), 13-17.
29. Runde He, Xifa Tan, Nianbing Zhang, et al., Barium aluminate-purifing Bayer red mud lotion desulfurization experiment, Journal of Guizhou University of Technology (Natural Science Edition), 35(3)(2006), 29-31.
30. Zhiying Li, Nianbing Zhang, Runde He, et al., Research on the new method of desulphurizing in producing alumina with exploitable sulfur-containing and high grade bauxite, Journal of Guizhou University of Technology (Natural Science Edition), 36(2)(2007), 29-31.
31. Fanghai Lu, Discussion on the desulfurizing technique of high grade bauxite containing sulfur in Maochang, Light Metals of China, 9(2008), 17-20.