

CAUSTIC AND ALUMINA RECOVERY FROM BAYER RESIDUES

Gu Songqing

Science & Technology Division of Chalco, No.62 Xizhimenbei Street, Beijing China

Keywords: Bayer residue, Sintering process, Flotation-Bayer process, Lime-Bayer process, Hydro-process, DSP, Hydrogarnet

Abstract

The Bayer process is not suitable for alumina production from high silica bauxites due to the high caustic and alumina loss into the Bayer residue. In this study, caustic and alumina recovery from the Bayer residue by various processes, such as sintering, lime treatment and hydro-processing etc, is analyzed and compared theoretically. The most important target to treat Bayer residue for the recovery of these products is to find an efficient Desilication Product (DSP) containing less alumina and caustic soda by some suitable and efficient processes.

Introduction

The biggest challenge for the Chinese alumina industry is the bauxite supply shortage and the reduction of the grade of the available resource, including the ratio of alumina to silica (A/S) and the alumina content in these bauxites. The bauxite A/S supplied to some Chinese refineries has continuously been reducing from 12 to less than 6 in the past 8 years and even to 5.3 last year, which brings a major negative impact on alumina production cost. The bauxite grade change trend is shown in Fig. 1.

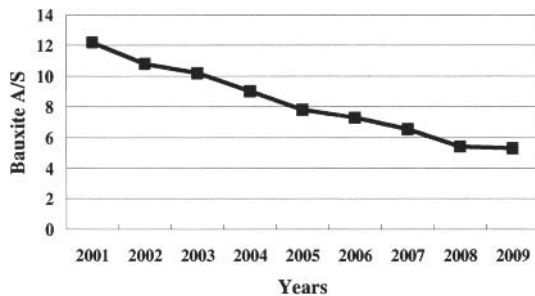


Fig. 1 Bauxite grade reduction for some Chinese refineries

Table 1 The Grade Distribution of Chinese Bauxites

| Bauxite grade | low grade | | middle grade | | high grade | |
|---------------|-----------|-----|--------------|-----|------------|-----|
| A/S | 3-4 | 4-6 | 6-7 | 7-9 | 9-10 | >10 |
| % | ~8 | ~49 | ~11 | ~15 | ~12 | ~5 |

Table 2 The Characteristics of Chinese Bauxite Reserves

| Bauxite | Reserve | Reserve Base | Reserve/Population | A/S | Mine Size | Bauxite Types | Silica Minerals Types |
|---------|----------|--------------|--------------------|-------|---------------------|----------------------|-----------------------------------|
| World | 23 B t | 35 B t | 4 t | > 10 | Large > 0.1 B t | Gibbsite Boehmite | Simple Kaolinite, Quartz |
| China | 0.54 B t | 0.72 B t | 0.4 t | 4 - 7 | Small < 0.03 B t | Diaspore | Complex Kaolinite, Illite etc. |

* B t—billion tons

Even though China is rich in bauxite resources, only about 20 % of bauxite reserves are of sufficient quality for Bayer processing as shown in Table 1, while bauxites of A/S 4-6 make up about 60% of total reserves.

Most of Chinese bauxite is diasporic with both high alumina & silica content and has very complex silicate mineral composition. However the bauxite reserves per capita are only 10 % of the world average. Furthermore the bauxite mines are usually small in size, and there are lots of underground bauxite reserves in China, which brings about bauxite mining difficulties and higher mining cost. See Table 2.

Based on the situation mentioned above, the Chinese alumina industry has to face serious raw materials issues and is forced to put great effort into R&D of new efficient processes to deal with lower grade bauxites.

Too low a grade of bauxite means higher silica and reduced alumina content, which greatly impacts the cycling efficiency and productivity. The DSP produced in the Bayer process will carry more caustic and alumina to the residues increasing red mud disposal. Consequently, caustic consumption and alumina loss will increase and the operational cost grows quickly.

Comparison of various processes to treat low grade bauxites

There are many studies looking for new, high efficient processes for the low grade bauxite.

The invention of the Flotation – Bayer process in the last decade, tries to pretreat low grade bauxite for silica minerals removal before introduction to the Bayer process. It was a success and applied in some Chinese refineries. But the alumina recovery is too low due to two stage losses in both the flotation and Bayer processes, and the organic substances entering the Bayer process might lead to some behavior changes of desilication and precipitation.

The Lime-Bayer process was developed to reduce caustic consumption by adding more lime to substitute some caustic from the residues. The Lime-Bayer process is simple and easy to apply.

But too low an alumina recovery and high lime additions makes the production cost increase and the amount of residue increase, as well due to its lower desilication efficiency.

The “Bayer-Sintering in Series” process is being tested in some Chinese refineries. The core concept for this process is to recover caustic and alumina from Bayer residue by sintering to form calcium silicates as the DSP. It seems that only a small part of the energy can be recovered and the energy consumption is still very high in the “Bayer-Sintering in Series” process compared with the original “Bayer-Sintering Combined” process.

The high pressure hydro-process invented by former Russia scientists is a complete hydrometallurgical process without any pyro-process, and offers high alumina recovery and less caustic loss. The major concept is to recover caustic and alumina from Bayer residue by hydro-processing to form calcium sodium silicates as DSP. But this process is too complex and the evaporation is too large for production of a high concentration liquor and sodium aluminate precipitation, and again this process features high energy consumption.

According to the process review above there is no highly efficient and energy saving process at present to deal with low grade bauxites. A comprehensive summary of the advantages and disadvantages of all the processes and theoretical investigation of the process reactions and products will provide the opportunity to develop new and efficient processes.

DSP analysis for the existing processes to treat low grade bauxite

Fig 2 and Table 3 show the major DSP in the residues for existing processes.

To improve the desilication efficiency in caustic alumina production, the most important factor is to get suitable DSP with low A/S, N/S and C/S, that is, the less Al_2O_3 and Na_2O content in the residues and the less lime addition, the more efficient for the process.

This is the goal of looking for a targeted DSP. The DSP from the sintering process contains no Al_2O_3 and Na_2O so that it is high efficient for silica removal and is energy intensive as well. The DSP from the Bayer process has the biggest N/S so it could not be used for high silica bauxites. The DSP from lime-Bayer process contains much Al_2O_3 and CaO , but no Na_2O at all, so the process can only be used in the refineries with access to cheap lime and bauxite.

Key technical concepts to develop high efficient alumina production

For more economical recovery of caustic and alumina from Bayer residues, it is essential to find an efficient DSP and to apply energy saving processes. The alumina production efficiency can be improved by higher desilication efficiency.

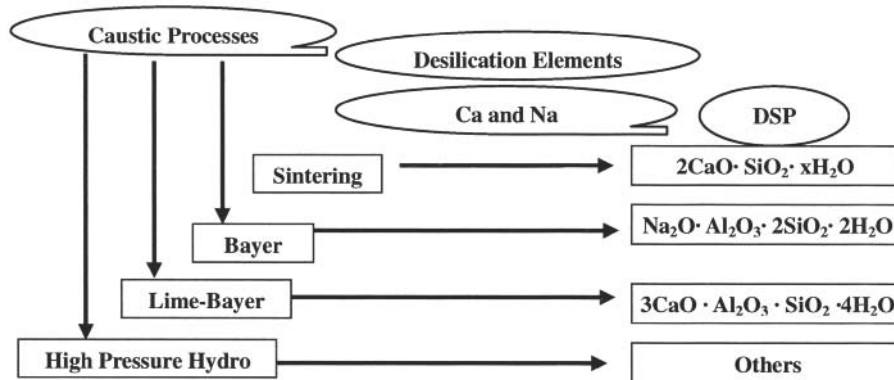


Fig 2 DSP analysis for the residue from different processes

Table 3 The chemical compositions of the various DSP

| Processes | DSP in residues | A/S | N/S | C/S |
|------------|---|---------|------|--------|
| Sintering | $2CaO \cdot SiO_2 \cdot xH_2O$ | 0 | 0 | 1.87 |
| Bayer | $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$ | 0.85 | 0.52 | 0 |
| Lime-Bayer | $3CaO \cdot Al_2O_3 \cdot nSiO_2 \cdot xH_2O (n:0.2-1)$ | 8 ~ 1.7 | 0 | 14 ~ 3 |

A/S—ratio of Al_2O_3 to SiO_2 content; N/S—ratio of Na_2O to SiO_2 content;

C/S-- ratio of CaO to SiO_2 content

The new highly efficient process to be found must be producing the DSP with relatively lower ratios of A/S, N/S and C/S so as to greatly reduce consumptions of bauxite, caustic soda and lime addition.

Another criteria for any suitable process is that it should be as energy efficient as possible, by adopting hydrometallurgical processing instead of pyrometallurgical processing to save energy.

Calcium compounds are much cheaper than other possible elements to replace Na₂O. But the multi elements compounds containing CaO are very complex and form at quite variety of reaction conditions. So the key solution to get the most efficient DSP will be based on the tests results at various conditions to find suitable compounds.

There are numerous compounds produced from Al₂O₃, SiO₂, Fe₂O₃ and TiO₂ (existing in bauxite) and Na₂O, CaO and MgO (added into the processes) etc, which can be found from X-ray diffraction tables and the phase diagrams. The most possible DSP in the processes to treat Bayer residues can be seen in Table 4. In this Table, the desilication efficiency increases from top to bottom.

Table 4 Possible DSP in Bayer residue treatment

| DSP in residues | A/S | N/S | C/S |
|---|------|------|------|
| Na ₂ O·2CaO·2SiO ₂ ·xH ₂ O | 0 | 0.52 | 0.94 |
| CaO·2Al ₂ O ₃ ·2SiO ₂ ·H ₂ O | 1.7 | 0 | 0.47 |
| 3CaO·Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O | 0.85 | 0 | 1.4 |
| 3CaO·Fe ₂ O ₃ ·2SiO ₂ ·2H ₂ O | 0 | 0 | 1.4 |
| 3CaO·2SiO ₂ ·mH ₂ O | 0 | 0 | 1.4 |
| CaO·SiO ₂ ·xH ₂ O | 0 | 0 | 0.94 |

It is found from Table 4 that the DSP from CaO and SiO₂ is the most efficient because there are no Al₂O₃ and Na₂O losses. Also, the higher the SiO₂ coefficient in the DSP, the higher the desilication efficiency.

Laboratory tests show that the DSP from both CaO and SiO₂ usually form at very high temperatures, or in the pyrometallurgical processes.

Hydrogarnet is a series of compounds containing CaO, SiO₂ and the oxides of other elements, such as Al₂O₃, MgO, Fe₂O₃ and TiO₂ etc. Usually CaO in the hydrogarnet like structured DSP can be replaced by Na₂O, MgO and K₂O, while Al₂O₃ in the DSP can be replaced by Fe₂O₃ and TiO₂.

The minerals containing Fe₂O₃ and TiO₂ are commonly found in bauxites and will take part in the reactions during the residue treatment so the study on the replacement of Fe₂O₃ and TiO₂ to Al₂O₃ should be carefully monitored to reduce Al₂O₃ content in the final hydrogarnet like structured products.

It seems that the hydrometallurgical process is the first choice for getting an efficient DSP since the pyrometallurgical processes such as the sintering process will consume too much energy without much better waste heat recovery.

The only way to greatly reduce energy consumption in the sintering process is by recovering as much energy from sintering as possible, and to enhance the process efficiency so that the total cost of sintering process can be competitive with the Bayer process.

Conclusions

- (1) The bauxite A/S for some Chinese refineries has continuously been reducing, which greatly impacts on the technical and economical performance and production cost.
- (2) The advantages and disadvantages of various existing processes to treat the low grade bauxite are analyzed according to their desilication efficiency and energy consumption.
- (3) A theoretical study has been carried out by comparison of the chemical compositions of the DSP from the different existing processes.
- (4) The key technical concepts to develop new and efficient processes for low grade bauxite are summarized. The most important is to produce a DSP with low A/S, N/S and C/S in a hydro-process.
- (5) It is possible to develop a process to form hydrogarnet structured compounds, which may indeed be the most efficient DSP.

References

- [1] Gu Songqing, Wu Lichun, Liu Fengqin et al., *Progresses of Nonferrous Metals in China (in chinese)*, (Changsha, China, Central South University Publishing House, 2007)
- [2] Bi Shiwen, Yu Haiyan, *Alumina Production Processes (in chinese)*, (Beijing China, Chemical Industry Press, 2006)
- [3] Gu Songqing. "Chinese bauxite and its influences on alumina production in China". *Light Metals 2008*, 79-83
- [4] Claudia Brunori et al., "Reuse of a treated red mud bauxite waste", *Journal of Hazardous Materials*, B117, (2005), 55-63
- [5] Ma Shuhua, et al., "Recovery of soda and alumina from red mud", *Multipurpose Utilization of Mineral Resources (in chinese)*, No.1 (2008), 27-30