

ECONOMIC ANALYSIS OF PRODUCING ALUMINA WITH LOW-GRADE BAUXITE(RED MUD) BY CALCIFICATION-CARBONIZATION METHOD

ZHAO Qiuyue, ZHANG Zimu, ZHU Xiaofeng, LIU Yan, LV Guozhi, ZHANG Ting'an, WANG Shuchan

ZHAO Qiuyue, Associate Professor, E-mail: zhaogy@smm.neu.edu.cn, Liaoning 110819, China

ZHANG Zimu, Doctoral student, E-mail: zhangzimu111@sina.cn, Liaoning 110819, China

ZHU Xiaofeng, Doctoral student, E-mail: zhuxiaofeng1316@163.com, Liaoning 110819, China

LIU Yan, Professor, E-mail: liuyan@smm.neu.edu.cn, Liaoning 110819, China

LV Guo-zhi, Lecture, E-mail: lvgz@smm.neu.edu.cn, Shenyang, Liaoning 110819, China

ZHANG Ting-an, Professor, E-mail: zta2000@163.net, Shenyang, Liaoning 110819, China

WANG Shuchan, Doctoral student, E-mail: wangshuchan@sina.com, Liaoning 110819, China

Key Laboratory of Ecological Utilization of Multi-metal Intergrown Ores of Ministry of Education,
Northeastern University, Shenyang 110819, China

Keywords: low-grade bauxite, red mud, calcification-carbonization method, metsim software, economic analysis

Abstract

Calcification-carbonization is a new method of producing alumina with low-grade bauxite (red mud). Low-grade bauxite (red mud) are all converted into garnet hydration during calcification process, then garnet hydration are treated with CO₂ and the new structure red mud are gained by digestion. Main components of the new structure red mud are CaSiO₃ and CaCO₃, it can be used directly for cement industry and Bauxite resource recycling is carried out. A series of experiments were done by our team and confirmed that the new method was feasible, A/S of new structure red mud dropped to 0.21 and the content of sodium is under 0.2%. Process calculation software METSIM was used to design and simulate the new process of producing alumina with low-grade bauxite (red mud) by calcification-carbonization method, and its economic with series process and bayer process was analyzed.

Introduction

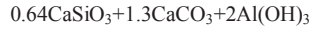
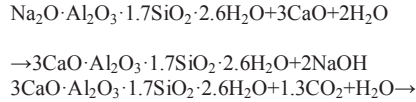
At present, Bayer process is widely adopted in the industry of producing alumina. By using the method of alumina production, there are two main problems. One is the low yield and low economic benefit in the process of producing alumina with alumina bauxite of low aluminum silicon ratio. Two is that a large amount of red mud which has high alkali content can not be directly used. Equilibrium phase of the leaching residue (red mud) in Bayer process is hydrated alumino silicate. In its production process, the loss of alumina and consumption of caustic alkali both increase with the higher silica content in minerals. The proportion of alumina and silica content loss relationship is 1:1, but the actual production is more than 1:1. Such as producing alumina with alumina bauxite of aluminum silicon ratio of 3, alumina theoretical maximum yield is only 66%, while the caustic consumption is up to more than 90 kg/t. Therefore, contradiction between low grade bauxite resources and production technology has become one of the main bottlenecks of China's alumina industry and Aluminum recycling economy development.

In Bayer process digestion of red mud dealcalization, from economic considerations, lime is a kind of effective removal of alkali additives. Aluminum industry in China has done a lot of research and practice of industrial production in the 70~80's in Lime-Bayer process [1-3]. But because equilibrium phase of digestion slag is hydrogarnet in the Lime-Bayer process, the A/S ratio is higher than that of acid sodium hydrated silicon aluminum, so the overall yield of the method is inferior to ordinary alumina Bayer process. At present, lime dosage is low in China's alumina production enterprises, at around 10%. Sodium alkali content in dissolving slag is up to more than 4%. The comprehensive utilization is difficult. In the Bayer de-alkali process, the lime is undoubtedly the most suitable additives. So as long as to find a simple and easy method of extracting alumina in the hydrate garnet, it can simultaneously reduce alumina alkali consumption of the red mud and improve overall yield, to achieve efficient resource recycling aluminum. After years of research, Northeastern University puts forward the calcification-carbonization method of processing low-grade bauxite (red mud) and other alumina materials [4-8]. In view of this new technology, this paper adopts METSIM flow calculation software to carry out the design and simulation, and compares it with series process and Bayer process on the economic benefits.

1. Technology fundamentals

This technology firstly converts bauxite or red mud into garnet hydration during calcification process, secondly treats garnet hydration with CO₂ to gain carbide slag which is mainly composed of calcium silicate, calcium carbonate and aluminum hydroxide during Carbonization process, and then obtains red mud of a new structure by low-temperature soluble aluminum. Main structure components of the new red mud are CaSiO₃ and CaCO₃, it can be used directly for cement industry and Bauxite resource recycling is carried out.

The calcification reaction and carbonization reaction are respectively shown in formula (1) and (2).



The dissolution reaction is shown in formula (3).
 $\text{Al}(\text{OH})_3 + \text{NaOH} \rightarrow \text{Na}_2\text{Al}_2\text{O}_4 + \text{H}_2\text{O}$
 Technological process of producing alumina with red mud by calcification-carbonization method is shown in figure 1.

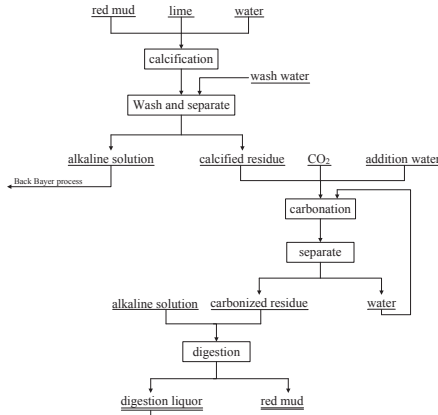


Figure 1 - Process flow diagram

2. METSIM Material Balance Calculation

2.1 Raw Database

According to the principle of calcification-carbonation reaction, composition of reactant and product were determined. In order to meet the needs of chemical reaction, the relevant elements and substances were selected in the METSIM database, which can provide physical, chemical and thermodynamic data. The operation interface was shown in figure 2.

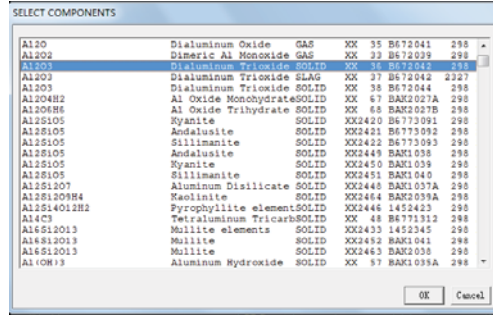


Figure 2 - Selection interface of compound component

2.2 Establishment of Material balance calculation flow diagram

According to the process flow diagram of producing red mud by calcification-carbonization method, the METSIM calculation of material balance was shown in figure 3.

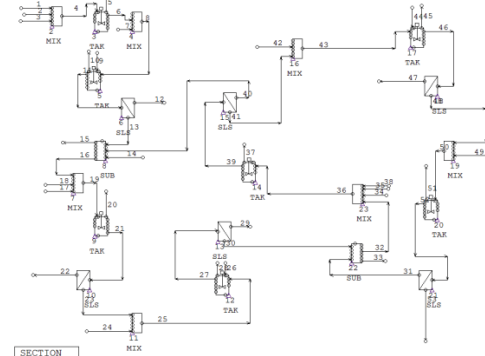


Figure 3 - METSIM material balance calculation process of producing red mud by calcification-carbonization method

The process includes the calcification process, three-stage carbonization process and the corresponding digestion process of carbide slag. In order to make the operation simple, the choices of equipments were mainly stirred tank, mixing tank solid-liquid separation equipment and so on.

The computation process of red mud in a place as raw material, and its main components were shown in table 1.

Table 1 - Composition of red mud

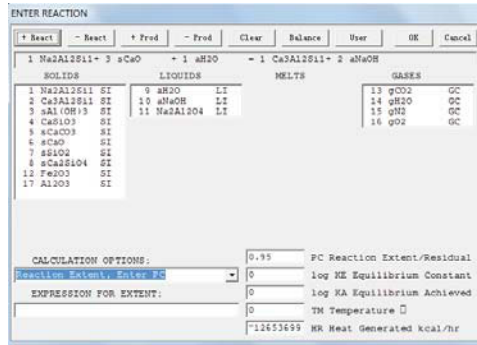
Composition	Al ₂ O ₃	SiO ₂	Na	Fe	L.O.I	A/S
Content (%)	20.3	33.82	7.53	16.41	9.7	0.6

Calcification conditions: liquid- solid ratio 4:1, calcium-silicon ratio 2.5:1 (mass) (CaO:SiO₂=2.5:1), the reaction rate was 95%, reaction temperature 120 °C, system pressure 3Mp, reaction time 30min. Carbonization conditions: liquid-solid ratio 10:1, reaction temperature 120 °C, system pressure 1.2 Mp, the single reaction rate was 20%, reaction time 120min. Dissolution conditions: if using lye, 100 g/L NaOH, liquid- solid ratio 10:1, reaction rate was 100%, reaction time 90min. After settling separation

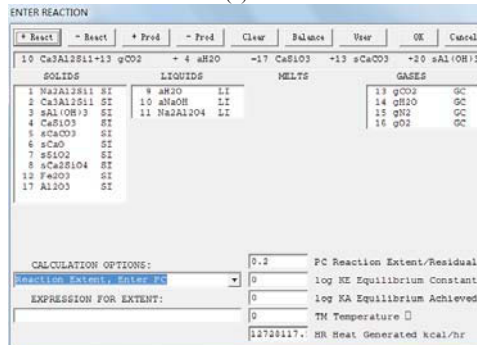
of each section, solids holdup underflow was 45%.

2.3 Input of Original Data

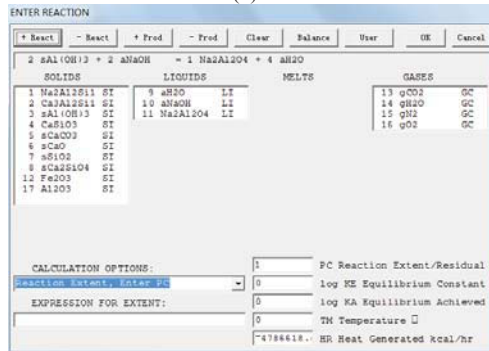
Based on the above established calcification-carbonation reaction process and the test results, reaction equation was input and all the reaction efficiency were set in the unit operation of calcification, carbonization and dissolution reaction, which were shown in figure 4.



(a)



(b)



(c)

Figure 4 - Input of reaction equation

3. Results and Discussion

In alumina plant with an annual output of 250000 tons dry red mud calculation, the results were as follows: water requirement in calcification process was 3511.24 Kg/min, CaO flow obtained by calcification reaction was 402.16 Kg/min, NaOH concentration in calcified slag was 16.12 g/l. The above results were in good agreement with the test results. According to the logistics calculation results, the economic benefit was analyzed, which was shown in table 3.

According to the factory annual emissions 250,000 tons of red mud, the economic benefits of this technology can reach more than 200 million yuan. If used for processing the existing red mud, economic benefits can be generated more than 40 billion yuan (by province stockpiles of 50 million tons of red mud calculation)

Conclusion

(1) Metsim software was successfully used in the process of producing alumina with low-grade bauxite (red mud) by calcification-carbonization method. The operation results had good agreement with the test results and it was reliable and accurate.

(2) Favorable economy benefit can be reached to treat low-grade bauxite (red mud) by using this method and it was better than the similar technology. Production cost was 2598 Yuan per ton alumina with alumina-silica ratio 3.29 and reduced by 400Yuan compared with traditional Bayer. Only core equipment for carbonization process was needed to add to Alumina production enterprises the method has vast extension prospect.

Table 2 - Reaction efficiency

Main reaction	Calcification	Primary carbonization	Secondary carbonization	Third carbonization	Dissolution
Efficiency%	95	20	20	20	100

Table 3 - Product value and consumption obtained with processing one ton Bayer red mud by Calcification-Carbonization Method

Products and consumption of raw materials	Additional product yield and consumables usage, tons of red mud	Unit price, RMB / t	Single products price, RMB / t
Products - caustic alkali	0.05	2450	122.5
Products - alumina	0.18	2600	468
Products - calcium silica slag	1.4	200	280
Reduce red mud maintenance costs	1	50	50
Lime consumption	0.8	300	-240
Total			880.5

Acknowledgement

This research was supported by the National 863 Plan (2010AA03A405, 2012AA062303), the National Natural Science Foundation of China (U1202274, 51004033, 51204040, 50974035), the National Science and Technology Support Program (2012BAE01B02) and Fundamental Research Funds for the Central Universities (N100302005).

Reference

1. CHENG Li, YUAN Hua-Jun, YANG Jing-chun, et al., "The Effect of Lime on Phase Changes of Red Mud During High Pressure Digestion of GuiZhou Bauxite", *Nonferrous Metals*, 37(1985), 83-91.
2. ZENG Xing-qing. "The Effect of Excessive Content of Lime on eliminating Sodium During Digestion", *Light Metals (China)*, 12(1983), 15-26.
3. YUAN Hua-jun, XIANG Yang, YUAN Yi. "The Relation Between the Added Quantity of Lime and the Leaching Rate of Alumina and The Consumption of Sodium Hydroxide in Bayer Process", *Journal of GuiZhou University of technology*, 27(1998), 67-76.
4. Zhang Ting'an, LV Guozhi, LIU Yan, et al. "A Method for digestion and save Bayer red mud". *Chinese patent*, 201110275030.X.
5. Zhang Ting'an, LV Guozhi, LIU Yan, et al. "Calcification- Carbonation Method for Alumina Production". *Chinese patent*, 201110275013.6.
6. LV Guozhi, ZHANG Ting'an, ZHU Xiaofeng, Pan Lu, Qin Mingxiao, Liu Yan, ZHAO Qiuyue, LI Yan. "Research on the Phase Transformation and Separation Performance in Calcification- Carbonation Method for Alumina Production". *Light Metals 2013*, TMS 2013 Annual Meeting and Exhibition, 245-250.
7. ZHU Xiaofeng, ZHANG Ting'an, LV Guozhi, LIU Yan, ZHAO Qiuyue, LI Yan, DOU Zhihe. "Basic Research on Calcification Transformation Process of Low Grade Bauxite". *Light Metals 2013*, TMS 2013 Annual Meeting and Exhibition, 2013: :239-244.
8. ZHANG Ting'an, ZHU Xiaofeng, LV Guozhi, PAN Lu, LIU Yan, ZHAO Qiuyue, LI Yan, HE Jicheng. "Calcification - carbonation Method for Alumina Production by Using Low-Grade Bauxite". *Light Metals 2013*, TMS 2013 Annual Meeting and Exhibition, 2013: :233-238.