

MULTI-STEPS CARBONATION TREATMENT OF CALCIFIED SLAG OF RED MUD

LV Guozhi, ZHU Xiaofeng, ZHANG Ting'an, GUO Fangfang, PAN Lu, LIU Yan
ZHAO Qiuyue, LI Yan, JIANG Xiaoli, HE Jicheng

LV Guo-zhi, Lecture, E-mail: lvgz@smm.neu.edu.cn, Shenyang, Liaoning 110819, China
ZHU Xiaofeng, Doctoral student, E-mail: zhuxiaofeng1316@163.com, Liaoning 110819, China
ZHANG Ting-an, Professor, E-mail: zta2000@163.net, Shenyang, Liaoning 110819, China

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

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Abstract

Aluminum industry is one of the most important industries in China's nonferrous metallurgy industry. With the development of China's alumina output, red mud emission get 50 million ton at 2011. Under this condition, "Calcification-Carbonation Method" was put forward to deal with red mud by Northeastern University, the main purpose of this method is to change the balance phase of red mud into $2\text{CaO}\cdot\text{SiO}_2$ and CaCO_3 with hydrometallurgical process. This paper mainly research on the effect of carbonation conditions and steps on alumina extraction and dealkalize efficiency. The results indicate that: through multi-steps carbonation treatment of calcified slag by the new method, A/S of the new structure red mud lowed below to 0.24 and the Na_2O content lowed below to 0.26% at carbonation temperature 120°C , CO_2 pressure of 1.2MPa with 5-steps carbonation treatment. The new structure red mud could be used in cement industry directly.

1. Introduction

Red mud is a kind of solid waste produced after the process of extracting alumina from bauxite. It's mainly composed of alumina, silica, iron oxides, sodium (calcium)aluminosilicate hydrate, titania and other minor valuable constituents[1,2], and with characteristics of 20-30% solid holdup and high alkaline(pH10-12.5). Depending on the quality of bauxite and digestion conditions, between 1 to 1.25 tones of red mud are generated per tone of alumina produced [3,4]. As the global demand for alumina and aluminum, it is estimated that 2.7 billion tones of red mud generated as by-product after alumina extraction from bauxite. This amount is currently increasing approximately 120 million tones per year [5]. So much quantity of red mud highlights the urgency to develop and implement improved methods of storage and remediation, and to pursue large scale utilization options of this alkali waste.

At present, several attempts have been made for the effective utilization of red mud in many fields, some of these are: as construction materials like cement and bricks additive; land fill; adsorbents for removal of heavy metal and metalloid ions [6]; catalysts [7]; CO_2 sequestration [8]; and recovery of valuable metals [9]. For now, the main obstacle which restricts comprehensive utilization of red mud is its alkaline component. Therefore, it is important to removal sodium alkali in red mud, implement red mud in some non-hazardous form. Furthermore, there are considerable amount of other composition such alumina, iron oxides in red mud, extraction and recovery these valuable metals will promote red mud utilized more economically.

Most alkali lost in red mud during the Bayer digestion process as combine with the silicon in bauxite to form desilication product (DSP), this is, sodium aluminosilicate hydrate which is the main phase of the Bayer process red mud. Its formula approximately as $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 1.7\text{SiO}_2\cdot n\text{H}_2\text{O}$. Alumina also lost as generate DSP. Many literatures on recovery alumina and alkali from DSP have been reported. Zhong et al.[1] proposed a mild hydro-chemical process to extraction of alumina and sodium oxide from red mud, under the optimum conditions as leaching in 45% NaOH solution with CaO-to-red mud mass ratio of 0.25, 0.8Mpa at 200°C for 3.5h, 87.8% of Al_2O_3 and 96.4% of Na_2O were extracted from red mud. Although good results, however, the management of sodium concentrations as high as 45% NaOH solution. Zhang et al.[10,14,15] investigated recovery of alumina and alkali in Bayer red mud by the formation of andradite-grossularite hydrogarnet in hydrothermal process. In their study, the red mud reacted with sodium-aluminate solution in the presence of CaO and ferric oxide (hydroxide), the product is $\text{Ca}_3[\text{Al}, \text{Fe}]_2(\text{SiO}_4)_{3-x}(\text{O}_4\text{H}_4)_x$, a kind of hydrogarnet which occurs with the isomorphous substitution of Al and Fe. Under optimal

conditions, 0.5 wt% and A/S of 0.3 in leached residue could be achieved with Fe-rich red mud.

In this paper, our group put forward a new process to recovery alumina and alkali from Bayer process red mud and takes red mud in non-hazardous form at the same time. This new process called “Calcification-Carbonation Method” [11-13]. Firstly, red mud reacts with lime in hydrothermal process at 80 ~ 160°C, which is calcification process, It changes the DSP in red mud to calcium aluminosilicate hydrate, namely calcium hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot (6-2x)\text{H}_2\text{O}$). The alkali in DSP can be recovered in solution. The second step uses CO_2 gas for carbonation decomposition of hydrogarnet. The phases of decomposition products are mainly composed of calcium silicate, calcium carbonate and aluminum hydroxide. Then alumina is extracted by the alkaline solution at low temperature. Main compositions in the new structure red mud is calcium silicate and calcium carbonate.

2. Experimental

Experimental materials

The red mud used in the experiments, provided by an alumina production company in Shandong Province, China, was generated by the Bayer process for leaching of gibbsite. The chemical and phase analysis results of the red mud are shown in Table 1 and Fig.1, respectively. Phase analysis of the red mud (Fig.1) was performed on the PW3040/60 X-ray diffractometer. As shown in Table 1, the red mud is mainly composed of Al_2O_3 , SiO_2 , Fe_2O_3 and Na_2O with A/S of 0.6. According to the XRD pattern shown in Fig. 1, the identified mineral phases in the red mud are hematite (Fe_2O_3), quartz (SiO_2), sodium aluminosilicate hydrate ($1.08\text{NaO} \cdot \text{Al}_2\text{O}_3 \cdot 1.68\text{SiO}_2 \cdot 1.8\text{H}_2\text{O}$) and nordstrandite (Al_2O_3).

Sodium hydroxide (NaOH) and calcium oxide (CaO) used in this study was of analytical grade and was purchased. Research grade CO_2 (concentration of >99% was used without further purification) gas cylinder was also purchased.

Table 1 Chemical composition of red mud

Chemical composition	Al_2O_3	SiO_2	Fe	Na	L.O.I
Content, wt %	20.3	33.82	16.41	7.53	9.70

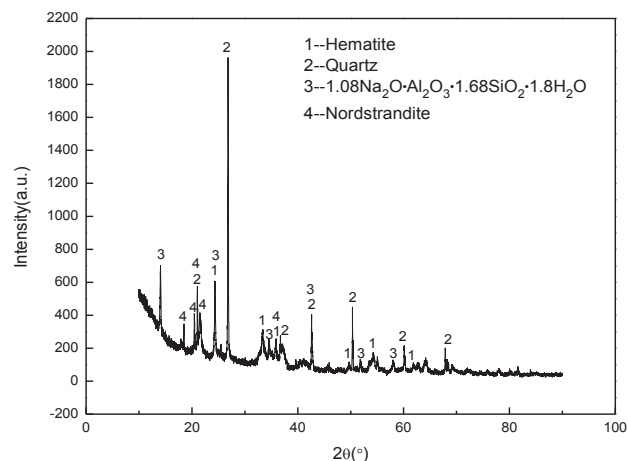


Fig.1. XRD patterns of red mud

Experimental method

a. Calcification experiment

The calcification experiment was carried out in a WHFS-1 autoclave, the water, lime (CaO) and red mud were put into the autoclave together, and the temperature of the autoclave was raised to the predetermined value then holding for 1 hour. After digestion, the temperature of autoclave was lowered to below 60°C, the digested slurry was separated into the solution and calcified slag by filtration.

b. Carbonation experiment

The carbonation experiment was also carried out in the WHFS-1 autoclave, the calcified slag was mixed with water, the temperature of autoclave was raised to the predetermined value, then pumped in CO_2 holding for 2 hours. After digestion, the digested slurry was separated into the solution and carbonated slag by filtration.

c. Alumina dissolving experiment

The alumina dissolving experiment was conducted in the constant temperature water bath, the carbonated slag was digested with alkali solution for $\text{Al}(\text{OH})_3$ recovery. The concentrations of Al_2O_3 and Na_2O (concentration of caustic soda) in solution and the content of Al_2O_3 and SiO_2 in the new type red mud were determined by ICP Prodigy xp and chemical titration.

The recovery rate of Al_2O_3 is expressed as:

$$\eta = \frac{(A/S)_O - (A/S)_F}{(A/S)_O} \times 100\% \quad (1)$$

Where $(A/S)_O$ and $(A/S)_F$ are the ratio of alumina to silica in original red mud and the new type red mud respectively. Then made the new type red mud carbonated five times to make sure

that the calcified slag was disposed completely.

3. Results and discussion

The calcification experiment was conducted in the conditions that 130 °C, liquid-solid ratio 4:1, holding time 1h, the ratio of CaO to SiO₂ ranges from 3.3 to 1.0; The carbonation experiment was conducted in the conditions that 120 °C, 1.2 MPa, liquid-solid ratio 10:1, holding time 2h; The alumina dissolving conditions is 60 °C, liquid-solid ratio 10:1, holding time 90min and 100g/L NaOH solution.

Once Carbonation

Fig.2 shows effect of CaO addition on Na₂O content in calcified residue. The general trend of Na₂O content decreased as CaO addition increases, as a result of excess CaO will promote the transformation of Na₂O·Al₂O₃·1.7SiO₂·nH₂O to 3CaO·Al₂O₃·xSiO₂·(6-2x)H₂O. When mass ratio of CaO to SiO₂ is 3.3, Na₂O content is 0.84 in residue, the recovery rate of Na₂O has reached 91.7%, however, the mass ratio of CaO to red mud has reached 1.1, its undesirable from an economic standpoint.

Fig.3 shows effect of CaO addition on A/S in red mud through once carbonation and extraction ratio of alumina. The general trend of CaO addition effect on extraction ratio of alumina is inconspicuous, and with low recovery rate of alumina. The lowest A/S (Al₂O₃ to SiO₂) in red mud is 0.47, corresponding recovery rate is about 20%. This may be due to the hydrogarnet has considerable stability, it is not easy to be decomposed by CO₂ through only once carbonation.

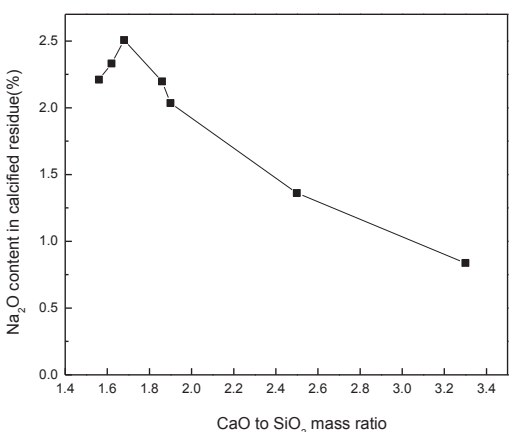


Fig. 2. Effect of CaO addition on Na₂O content in calcified residue

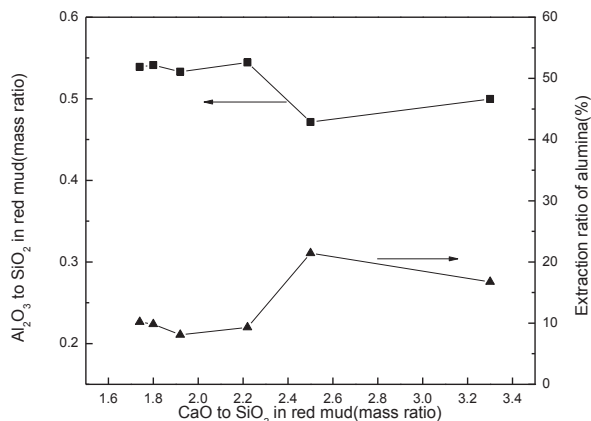


Fig.3. Effect of CaO addition on A/S in red mud through once carbonation and extraction ratio of alumina

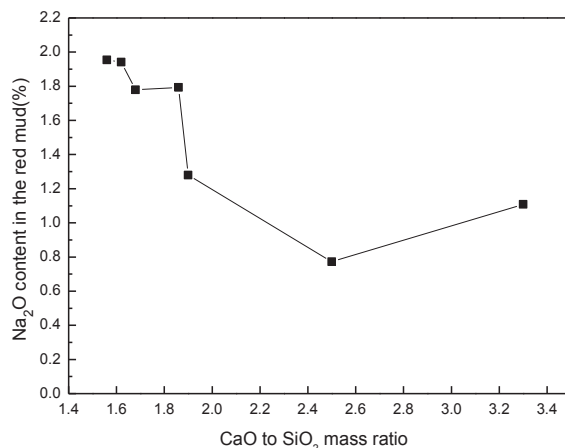


Fig. 4. Effect of CaO addition on Na₂O content in red mud through once carbonation

Multi-steps carbonation

Once carbonation did not acquired good results, therefore, we studied the multi-steps carbonation. Carbonation and alkali soluble processes were repeated several times. Fig. 5 and Fig. 6 show effect of CaO addition on A/S and extraction ratio of alumina in red mud through 5 times carbonation. Fig. 5 indicates A/S decreased as carbonation frequency increases, at the same time, more CaO addition gets lower A/S. When CaO/SiO₂ is 2.5 and 1.0, recovery rate of alumina is 63.2% and 51.1% respectively. The CaO addition amount increased 150% from CaO/SiO₂ 1.0 to 2.5, however, the recovery rate of alumina increased only approximately 20%, and it indicates excess CaO can not increase the recovery rate of alumina.

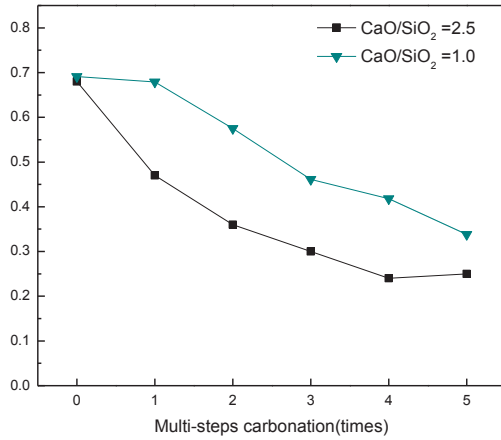


Fig. 5. Effect of CaO addition on A/S in red mud through 5 times carbonation

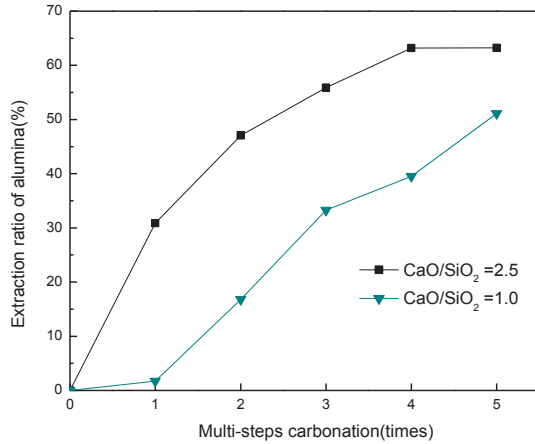


Fig. 6. Effect of CaO addition on extraction ratio of alumina through 5 times carbonation

As Fig. 7 shows, Na₂O content in red mud decreased as

carbonation times increased, more CaO addition amount gets lower Na₂O content in red mud, the Na₂O content reach 0.26% through 5 times carbonation when the CaO/SiO₂ is 2.5, but they remain 1.2% when CaO/SiO₂ is 1.0, this indicates increase CaO addition amount take advantage of Na₂O recovery.

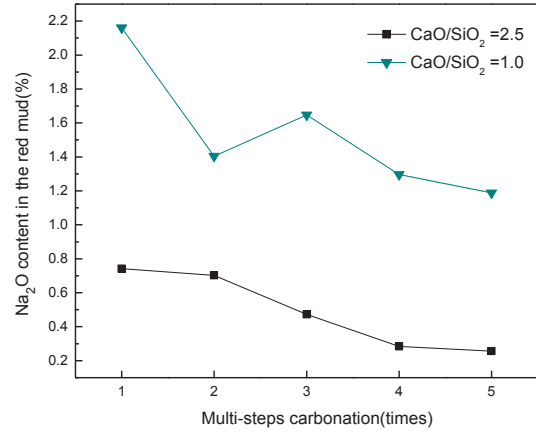


Fig. 7. Na₂O content in red mud through 5 times carbonation

3.3 X-ray diffraction study

Fig. 7 shows XRD patterns of residues after different process. The katoite, a kind of hydrogarnet generated after calcification reaction, Ca(OH)₂ also appears in the calcified residue as excess addition of CaO in the calcification reaction. The main phase in carbonized residue is CaCO₃ and Ca₃Fe₂(SiO₄)₃, no calcium silicate phase in the carbonized residue may be as its low degree of crystallinity in hydrothermal process. After alkali soluble, the phase of carbonized residue was almost invariant.

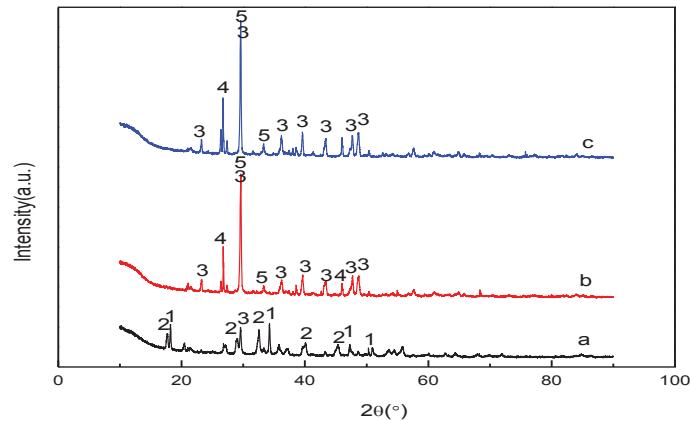


Fig.8. XRD patterns of red mud after different processes: (a) calcified residue, (b) carbonized residue, (c) alkali soluble residue.

1. Ca(OH)₂, 2. katoite(Ca_{2.93}Al_{1.97}Si_{0.64}O_{2.56}(OH)_{9.44}), 3. CaCO₃, 4. SiO₂, 5. Ca₃Fe₂(SiO₄)₃

Conclusions

The Calcification-Carbonation Method is feasible when dealing with red mud. When mass ratio of CaO to SiO₂ is 3.3, the recovery rate of Na₂O has reached 91.7%, Na₂O content in red mud decreased as CaO addition increases. The recovery rate of Al₂O₃ is about 20% through once carbonation. After multi-steps carbonation process, the recovery rate of Na₂O and Al₂O₃ reached 97.4% and 63.2%; A/S in red mud decreased as carbonation frequency increases, and more CaO addition gets lower A/S in the red mud.

The XRD patterns show that calcification reaction mainly generated kotoite, Ca(OH)₂ also appears in the calcified residue as excess addition of CaO. The main phase in carbonized residue are CaCO₃ and Ca₃Fe₂(SiO₄)₃. The phase of carbonized residue was almost invariant after alkali soluble.

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References

- 1 Li Zhong, Yifei Zhang, Yi Zhang, "Extraction of alumina and sodium oxide from red mud by a mild hydro-chemical process", *Journal of Hazardous Materials*, 172(2009), 1629-1634.
- 2 LI Xiao-bin, XIAO Wei, LIU Wei, LIU Gui-hua, PENG Zhi-hong, ZHOU Qiu-sheng, QI Tian-gui. "Recovery of alumina and ferric oxide from Bayer red mud rich in iron by reduction sintering", *Trans. Nonferrous Met. Soc. China*. 19(2009) 1342-1347.
- 3 Q.D. Nguyen, D.V. Boger. "Application of rheology to solving tailings disposal problems", *Int. J. Miner. Process*, 54 (1998) 217-233.
- 4 I. Paspaliaris, A. Karalis, "The effect of various additives on diasporic bauxite leaching by the Bayer process", *Light Met.* (1993) 35-39.
- 5 G. Power, M. Gräfe, C. Klauber. "Bauxite residue issues: I. Current management, disposal and storage practices",

Hydrometallurgy, 108(2011) 33-45.

- 6 Indrani Ghosh, Saumyen Guha, R. Balasubramaniam, A.V. Ramesh Kumar. "Leaching of metals from fresh and sintered red mud". *Journal of Hazardous Materials*, 185(2011) 662-668.
- 7 S. Ordonez, H. Sastre, F.V. Diez, "Catalytic hydrodechlorination of tetra-chloroethylene over red mud", *J. Hazard. Mater.* 81 (2001) 103-114
- 8 Vishwajeet S. Yadav, Murari Prasad, Jeeshan Khan, S.S. Amritphale, M. Singh, C.B. Raju. "Sequestration of carbon dioxide (CO₂) using red mud", *Journal of Hazardous Materials* 176 (2010) 1044-1050.
- 9 Y. Cengeloglu, E. Kir, M. Ersoz, T. Buyukerkek, S. Gezgin, "Recovery and concentration of metals from red mud by Donnan dialysis", *Colloids Surf. A* 223 (2003)95-101.
- 10 Ran Zhanga, Shili Zheng, Shuhua Maa, Yi Zhang. "Recovery of alumina and alkali in Bayer red mud by the formation of andradite-grossular hydrogarnet in hydrothermal process", *Journal of Hazardous Materials*, 189(2011), 827-835.
- 11 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.
- 12 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.
- 13 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.
- 14 Zhang Ting'an, LV Guozhi, LIU Yan, et al. "Calcification-Carbonation Method for Alumina Production". Chinese patent, 201110275013.6.
- 15 Zhang Ting'an, LV Guozhi, LIU Yan, et al. "A Method for digestion and save Bayer red mud". Chinese patent, 201110275030.X.