Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) s165−s168
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Alumina recovery from spent Bayer liquor by methanol

ZHANG Ying(张 盈)[1, 2], ZHENG Shi-li(郑诗礼)[1], DU Hao(杜 浩)[1],
WANG Shao-na(王少娜)[1], PENG Ying(彭 鹰)[3], ZHANG Yi(张 懿)[1]

1. National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China;
2. Graduate University of Chinese Academy of Sciences, Beijing 100049, China;
3. Beijing Tungsten and Molybdenum Material Factory, Beijing General Research Institute, Beijing 102206, China

Received 6 July 2009; accepted 30 December 2009

Abstract: Decomposition of sodium aluminate solution is the key step for alumina production; however, approximately only 55% alumina yield is obtained by seeded precipitation. So, it is difficult to obtain sodium aluminate solution with high caustic ratio. In this study, a method was explored to recover alumina from spent Bayer liquor by deep decomposition with methanol. A variety of conditions, including reaction temperature, reaction time, methanol amount and seed coefficient were elaborately investigated. The results showed that the appropriate conditions were 1:1 in volume ratio of methanol to spent Bayer liquor, more than 1.0 seed coefficient and in a 40 ℃ water bath for 24 h. By characterizing through XRD, the crystal products were found to be $Al(OH)_3$. With this method, the molar ratio of Na_2O to Al_2O_3 of the spent liquor can be increased from about 3.0 to 10.0 due to the recovery of alumina, which is beneficial for the treatment of red mud.

Key words: spent Bayer liquor; methanol; alumina; decomposition

1 Introduction

Aluminum hydroxide, 90% of which is refined by Bayer process, has a wide application in many contemporary technical domains[1−2]. About 90% of aluminum hydroxide is calcined and electrolyzed to produce aluminum[3]. The production of alumina increases rapidly in recent years, reaching 19.45 million tons in 2007 and 22.78 million tons in 2008. It is expected that the productivity would increase to 35 million tons in 2010. However, with the fast development, the production of red mud becomes a significant problem. 1.0−1.3 t of red mud will be output when 1 t Al_2O_3 is produced, which contains more than 20% of alumina and 8% of sodium oxide by mass fraction, respectively[4]. The release of red mud not only causes environmental pollution, but also leads to alumina resource waste.

A great number of researches on Al_2O_3 and Na_2O recycling from red mud have been done worldwide, among which hydrothermal treatment is considered to be the most promising way. KLAN[5] pointed out that, with the condition of high caustic ratio (10−11) (MR, the molar ratio of Na_2O to Al_2O_3) of spent Bayer liquor, hydrothermal treatment could be used to treat red mud by Bayer process. According to research results from Zhengzhou Research Institute of Chalco[6], a recycle ratio of 50%−70% of Al_2O_3 and 90% of Na_2O can be realized by using caustic liquor with MR higher than 8. Even though hydrothermal method is effective in Al_2O_3 and Na_2O recycling, it has not been applied widely in industries because of the difficulty to obtain sodium aluminate solutions with MR higher than 8. In Bayer process, the highest MR obtained is only about 3.2 from the spent Bayer liquor.

Currently, there are mainly three ways to prepare high MR caustic liquor. One is sodium aluminate crystallization method[7]. This method requires vaporization of the spent Bayer liquor to an alkaline

Foundation item: Project(50874099) supported by the National Natural Science Foundation of China; Project(2006AA06Z129) supported by the National Hi-tech Research and Development Program of China; Projects(2009CB219901, 2007CB613501) supported by the National Basic Research Program of China; Project(KGCX2-YW-321-2) supported by Knowledge Innovation Program of Chinese Academy of Sciences; Project supported by the Scientific Research Foundation of State Education Ministry for the Returned Overseas Chinese Scholars, China

Corresponding author: ZHENG Shi-li; Tel: +86-10-62520910; E-mail: slzheng@home.ipe.ac.cn

concentration of above 500 g/L, followed by crystallization of sodium aluminate, and a caustic liquor with high MR is obtained consequently. But this process has the disadvantage of large amount of water vaporization (12 t water per ton alumina) and high energy consumption. Another one is calcium aluminate hydrate method, which is adding lime into the sodium aluminate solution, synthesizing calcium aluminate and simultaneously obtaining the needed caustic liquor. But this method could only be used to treat low concentration caustic solutions. The third, extraction treatment[8], is an immature method that uses extractant to capture sodium ions and eventually separates sodium ions from the sodium aluminate solution. But high phase ratio, excessive extraction stages and complicated operation limit its application.

According to WANG et al[9−10] and ZHANG et al[11], the introduction of methanol can break the equilibrium of seeded precipitation, lead to a significant increase in the driving force for crystallization, and in the end, obtain high MR caustic solution. Further, methanol can be efficiently recycled by distillation. In this work, the deep decomposition of spent Bayer liquor with methanol is systematically studied. The effects of reaction temperature, reaction time, methanol amount and seed amount on the final MR are investigated.

2 Experimental

2.1 Materials

All reagents, including methanol (99.5%, manufactured by Beijing Chemical Works), sodium hydroxide (96%, from Beijing Chemical Reagents Company), aluminum hydroxide (with water content between 32.0% and 35.0%, produced by Beijing Chemical Reagents Company), were of analytical purity. High-purity Milli-Q water, with a resistivity of above 18.2 MΩ·cm at ambient temperature, was used in all experiments. The $Al(OH)_3$ seeds, with an average diameter of 29.6 μm, were produced using methanol decomposition method.

2.2 Preparation of spent Bayer liquor

The spent Bayer liquor with Na_2O concentration of 175.0 g/L and MR of 3.0 was prepared by dissolving a certain amount of $Al(OH)_3$ into hot sodium hydroxide solution in a polytetrafluorethylene vessel. The solution was filtered twice and reserved for use in an oven at a constant temperature of 80 ℃.

2.3 Precipitation reactor and procedure

Fig.1 illustrates the experimental apparatus used in this work. The batch reactor used was a three-neck flask. A two-blade mechanical stirrer was used to stir the solution and a liquid feed pump was used to add methanol. The reactor was heated by a thermostatic water bath with a precision of ±0.1 ℃, and a condenser was used to condense the liquid.

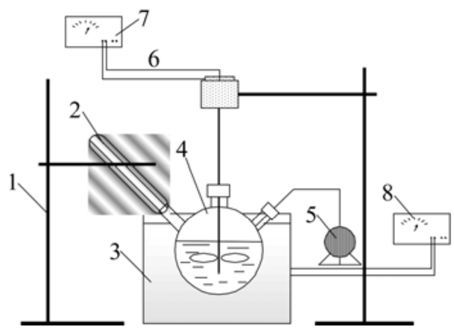

Fig.1 Schematic diagram of experimental installation: 1 Fastening stand; 2 Condenser; 3 Thermostat water bath; 4 Flask reactor; 5 Feed dosing pump; 6 DC electromotor; 7 Voltage regulator; 8 Digital multimeter

After the temperature reached the pre-set value, the spent Bayer liquor mixed with a certain amount of seeds were poured into the precipitation reactor. Then, a certain amount of methanol (V_{methanol}:V_{solution}) at the same temperature was added into the solution. The solution was kept stirring with a speed of 300 r/min under atmospheric pressure. At appropriate time intervals during a run, 5 mL of the filtrate was taken out and diluted to determine the concentrations of Na_2O and Al_2O_3 by ICP-OES.

The precipitation ratio (η) was calculated from the increase of *MR* according to Eq.(1)[3]:

$$\eta = \frac{R_a - R_0}{R_a} \tag{1}$$

where R_0 denotes the caustic ratio of initial solution and R_a denotes the caustic ratio of the solution after decomposition.

3 Results and discussion

3.1 Effect of reaction temperature

The solubility of alumina in sodium hydroxide solution greatly depends on temperature. The effect of temperature on R_a was investigated in this research. The experiments were performed with V_{methanol}:V_{solution} of 1:1 and a seed coefficient of 2.0. The temperatures were controlled to be below the boiling point of methanol. The results are shown in Fig.2 and Fig.3.

It can be seen from Fig.2 that MR increases sharply with the decrease of the temperature. Large gap exists between 40 ℃ and 50 ℃, and MR is 11.7 for 40 ℃ and 8.3 for 50 ℃ after 24 h, respectively. The distinction between 40 ℃ and 50 ℃ could be the co- effects of supersaturation degree which favors $Al(OH)_3$ precipitation

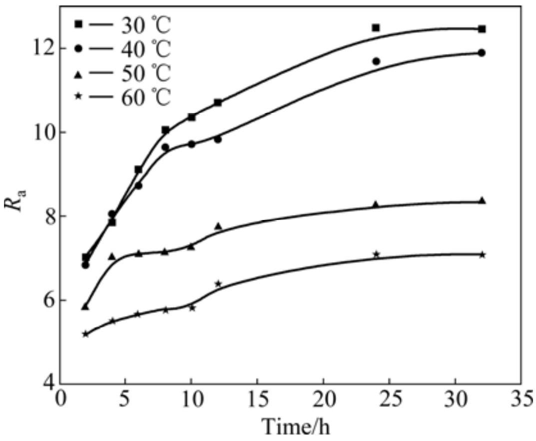

Fig.2 Effects of temperature on R_a

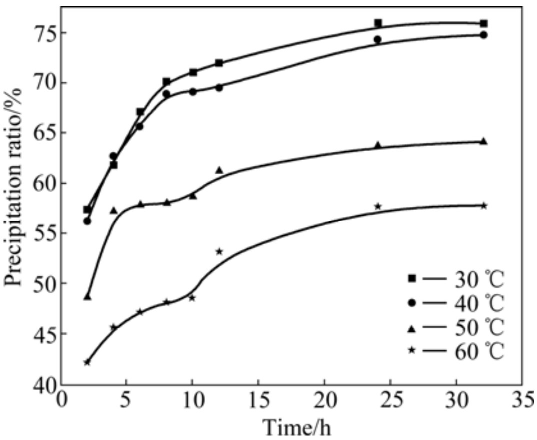

Fig.3 Effects of temperature on precipitation ratio

at low temperature and mass transfer which favors $Al(OH)_3$ precipitation at high temperature. It appears that supersaturation plays more significant role than mass transfer. MR gradually increases as temperature increases, and reaches platforms after 24 h. The highest MR is 12.5 at 30 ℃ and the lowest MR is 7.1 at 60 ℃. Correspondingly, the solution reaches the highest precipitation ratio of 76% at 30 ℃ and lowest precipitation ratio of 58% at 60 ℃. From these results, it is clear that in order to obtain a caustic solution with MR higher than 10, the temperature should not be higher than 40 ℃. In the following experiments, the temperature was fixed at 40 ℃ and the reaction time was 24 h.

3.2 Effect of volume ratio of methanol to spent Bayer liquor

Due to the difference in physicochemical property and ability to dissolve Na_2O and Al_2O_3 between water and methanol[12], the volume ratio of methanol to water is an important factor. In this work, the volume ratio of methanol to spent Bayer liquor (V_1:V_2) was in the range from 0.5:1 to 2.0:1 and the corresponding results are shown in Table 1. The seed coefficient in these experiments was 2.0.

Table 1 Effects of volume ratio of methanol to spent Bayer liquor on R_a

V_1:V_2	R_a (12 h)	R_a (24 h)
0.5:1	3.92	4.07
1:1	9.86	11.69
1.5:1	11.45	12.98
2.0:1	11.59	13.59

It can be seen from Table 1 that, MR is greatly dependent on the amount of methanol and it is remarkably increased with the increase of V_1:V_2, especially when the ratio is lower than 1.0. MR values are all above 10 when V_1:V_2 is not less than 1:1 after 24 h. When the volume ratio is higher than 1:1, further increase of MR becomes less appreciable. There is no much difference between 1.5:1 and 2:1. The most probable explanation for this observation is that the increase of methanol not only intensifies the dilution effect, which leads to the decrease of the amount of water molecules per unit volume, but also increases the binding of solvent molecules, which decreases the amount of free water molecules used to dissolve Na_2O and Al_2O_3[13]. They both promote the precipitation of $Al(OH)_3$. Undoubtedly, a higher MR must be weighed against a higher cost of raw materials and higher energy consumption for recycling methanol. With a comprehensive consideration, a volume ratio of methanol to spent Bayer liquor of 1:1 was selected.

3.3 Effect of seed coefficients

In the seeded precipitation process of supersaturated sodium aluminate solution, a large amount of seeds were added, which can reach a seed coefficient of 2.0. This means that double amount of $Al(OH)_3$ by mass is circled in this process. The effect of seed coefficients which is in the range from 0.5 to 3.0 is also investigated in this study. Other conditions are V_1:V_2=1:1, temperature of 40 ℃ and reaction time of 24 h. The corresponding results are shown in Table 2.

Table 2 Effects of seed coefficients on R_a

Seed coefficient	R_a (12 h)	R_a (24 h)
0.5	7.31	7.83
1.0	9.73	10.62
2.0	9.86	11.69
3.0	12.40	12.96

It can be concluded from Table 2 that seed coefficient greatly affects the MR and precipitation ratio. With a seed coefficient no less than 1.0, the ultimate R_a can be higher than 10. It has been known that fragments produced by micro-abrasion on seed surface is the origin for the secondary crystal nuclei. Consequently, seeds reduce the resistance of crystal formation and shorten the induction period. Because more seeds mean larger surface area, higher seed coefficient leads to higher eventual *MR*.

4 Product characteristics

From the above mentioned experiments, the optimum condition to recover alumina from spent Bayer liquor by methanol was mixing the spent Bayer liquor (175.0 g/L Na_2O, MR 30, and seed coefficient 1.0) with methanol of the same volume at 40 ℃ for 24 h.

The precipitated product was characterized by means of XRD. The XRD result exhibits a typical Bayerite type of aluminum hydroxide, as shown in Fig.4.

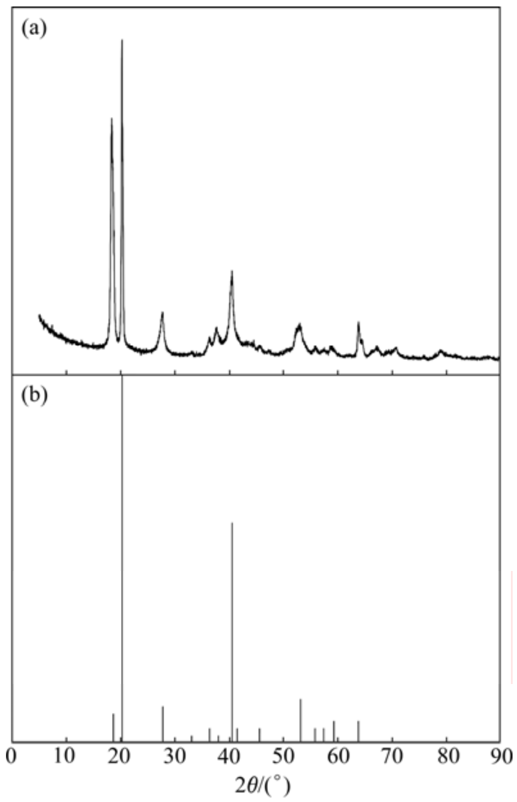

Fig.4 XRD spectra of Bayerite standard and product prepared at optimum condition: (a) Product; (b) Bayerite standard

5 Conclusions

The addition of methanol deepens the crystallization of spent Bayer liquor, which has the potential to obtain high MR (>10) caustic solution. Methanol can be readily distilled from the liquor and recycled whilst the caustic liquor with high MR can be used to treat red mud.

The experiments have shown that many factors, including the reaction temperature, time, methanol amount and seed coefficient influence the final caustic ratio. The optimum conditions are: an equal volume of methanol to spent Bayer liquor, 1.0 seed coefficient, 40 ℃ and 24 h. Under these conditions, the final MR can reach a value higher than 10. XRD spectra indicate that the precipitate is Bayerite type of aluminum hydroxide.

References

[1] WANG Er-xing, LIU Jiao-ping, WU Fu-yun. The application of $Al(OH)_3$ in papermaking and organic material fields [J]. Non-Metallic Mines, 1999, 22(5): 27−29. (in Chinese)

[2] SLEPPY W C, PEARSON A, MISRA C, MACZURA G. Non-metallurgical use of alumina and bauxite [J]. Light Metals, 1991: 117−124.

[3] BI Shi-wen. The alumina production process [M]. Beijing: Chemical Industry Press, 2006. (in Chinese)

[4] LIU Wan-chao, YANG Jia-kuan, XIAO Bo. Recovering iron and preparing building material with residues from Bayer red mud [J]. The Chinese Journal of Nonferrous Metals, 2008, 18(1): 187−192. (in Chinese)

[5] KLAN P. JCSOBA [R]. 1971, 3: 163−173.

[6] ZHOU Jie-fang, CHEN Wan-kun, GU Song-qing, YIN Zhong-lin, YANG Tian-xi. Hydrothermal treatment of Bayer red mud from Guangxi Filiale of CHALCO [R]. Guangxi Filiale of CHALCO, 1989. (in Chinese)

[7] SHAREN B C. The crystallization of sodium aluminate [C]// LIU Wen-qi. Chemistry and Process of Alumina. Beijing: China Industry Press, 1964: 48−54.

[8] GU Song-qing, YIN Zhong-lin, BAI Wan-quan, QI Li-juan, HAN Dong-zhan. A method of Bayer mother liquor extraction: China, 200610140858.3 [P]. 2006−10−13. (in Chinese)

[9] WANG Xue, ZHENG Shi-li, ZHANG Yi. Decomposing sodium aluminate by solventing-out process to prepare aluminium hydroxide [J]. Nonferrous Metals (Extractive Metallurgy), 2008(1): 18−21. (in Chinese)

[10] WANG Xue, ZHENG Shi-li, ZHANG Yi. Preparation of aluminum hydroxide with dissolution of sodium aluminate in methanol-water solvent [J]. Chinese Journal of Process Engineering, 2008, 8(1): 72−77. (in Chinese)

[11] ZHANG Ying, ZHENG Shi-li, DU Hao, XU Hong-bin, WANG Shao-na, ZHANG Yi. Improved precipitation of gibbsite from sodium aluminate solution by adding methanol [J]. Hydrometallurgy, 2009, 98(1/2): 38−44.

[12] WILLIAM F L. Solubilities [M]. Stamford: American Chemical Society, 1965.

[13] BORISSOVA A, DASHOVA Z, LAI X, ROBERTS K J. Examination of the semi-batch crystallization of benzophenone from saturated methanol solution via aqueous antisolvent drowning-out as monitored in-process using ATR FTIR spectroscopy [J]. Crystal Growth and Design, 2004, 4(5): 1053−1060.

(Edited by FANG Jing-hua)