Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 243−249
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Variation of soda content in fine alumina trihydrate by seeded precipitation

Gui-hua LIU, Peng WANG, Tian-gui QI, Xiao-bin LI, Lü TIAN, Qiu-sheng ZHOU, Zhi-hong PENG
School of Metallurgy and Environment, Central South University, Changsha 410083, China

Received 2 December 2012; accepted 26 April 2013

Abstract: High soda content in fine alumina trihydrate(ATH) limits its application and increases the soda consumption. The variation of soda content in the fine ATH by seeded precipitation was determined by detection of electric conductivity of solution, soda content in ATH, measurement of particle size distribution and microscopic analysis. The results show that high concentration of sodium aluminate solution, ground circulative seed, low temperature or fast initial precipitation rate increases the soda content in ATH. Soda mainly exists in lattice soda and less soda in desilication product (DSP) exists in the fine ATH precipitated from sodium aluminate solution with concentration of Al_2O_3 ($\rho_{Al_2O_3}$) more than 160 g/L and mass ratio of alumina to silica (μ_{SiO_2}) of 400, and lattice soda decreases with increasing initial precipitation temperature, aging seed, and low precipitation rate and precipitation time. Results also imply that $Na^+Al(OH)_4^-$ ion-pair influences lattice soda content in ATH on the basis of electric conductivity variation.
Key words: alumina trihydrate; seeded precipitation; soda content; lattice soda; sodium aluminate solution

1 Introduction

Fine alumina trihydrate (ATH) is not only used as the raw material of alumina-based ceramic and catalyst carrier, but also as the main filler of environmental friendly flame retardant, artificial agate and so on. Compared with neutralization and alkoxide hydrolysis for preparing fine ATH, the seeded precipitation from sodium aluminate solution has a lot of advantages, such as low cost, spent-liquor circulation and less pollution. But high soda (expressed in Na_2O) content in ATH from sodium aluminate solution limits its application. High concentration solution ($\rho(Na_2O)$>160 g/L), rather than low concentration solution, is often employed in seeded precipitation for digestion of diasporic bauxite in China [1], leading to high soda content (Na_2O 0.3%−0.7%) in ATH. So the variation of the soda content in ATH is essential for reducing the soda content of the fine ATH, and for understanding the mechanism of seeded precipitation in production of smelter grade alumina.

Soda in ATH exists in three forms: lattice soda (inserted in lattice), soda in DSP and adsorption soda (adsorbing on the surface of ATH), but only the third can be washed with boiling water. Diluting solution, elevating temperature, controlling seed coefficient φ (the mass ratio of alumina in seed to alumina in solution) or varying particle size of seeds can slightly reduce the soda content of the coarse ATH [2,3]. However, soda content in ATH is not clear so far for the co-existence of many kinds of soda in ATH from industrial aluminate solution. Many researches focus on the influence of cation on mechanism of particle growth and on particle agglomeration in preparation of coarse ATH. FLEMING et al [4] studied the structure of gibbsite and the occurrence of Na^+ and K^+ in crystals by computer modeling techniques, and suggested that cation incorporation benefited the elongation of the prismatic faces. FREIJ and PARKINSON [5] reported that Na^+ was located in (001) face between two layers of crystal during the crystallization process. LOH et al [6] and PRESTIDGE and AMEOV [7] reported that Na^+ benefited agglomeration while K^+ and Cs^+ improved nucleation. BLAGOJEVIĆ et al [8] found that Na^+ was adsorbed on the surface of the ATH and then inserted into particle during agglomeration process in the low concentration, and that soda content in ATH of particle size <45 μm is more than that of particle size of 45−63 μm, and that soda content reduced with addition of seeds due to the inhibition of agglomeration. GAN and

Foundation item: Project (51274242) supported by the National Natural Science Foundation of China
Corresponding author: Tian-gui QI; Tel: +86-731-88877830; E-mail: qitiangui@csu.edu.cn
DOI: 10.1016/S1003-6326(14)63053-3

FRANKS [9] found that the most active protons and oxygen atoms in crystal were located in (001) face, implying that the distribution of atoms on surface may affect the soda content in ATH. The above experiments were generally carried out under low concentration ($\rho(Na_2O)$<150 g/L) with either large seed coefficient or no seed. Researchers focused on the cation's behavior in growth and agglomeration rather than the variation of soda content in ATH.

This work mainly studied the variation of precipitation ratio, precipitation rate, particle size distribution (PSD) and soda content in the fine ATH from the high concentration solution, and discussed the dependence of lattice soda content on the precipitation ratio, precipitation rate, PSD, morphology of ATH and solution structure.

2 Experimental

2.1 Preparation of raw material

Sodium aluminate solution for seeded precipitation was made from industrial grade alumina trihydrate ($Al(OH)_3$>98% in mass fraction, CHALCOA) and spent liquor (from an alumina refinery in Henan province, China), and μ_{Si} (mass ratio of alumina to silica in solution) of pregnant liquor was 400±30 after desilication in sodium aluminate solution by adding lime in analytically pure grade (AR grade). Sodium aluminate solution for electrical conductivity measurement was made from alumina trihydrate (AR grade) and sodium hydroxide (AR grade). Seed was made from the reaction of sodium aluminate solution (ρ_{Na_2Ok}=165.26 g/L, $\rho_{Al_2O_3}$=177.08 g/L) with sulphuric acid (0.5 mol/L). Other reagents were in AR grade.

2.2 Analysis method

The concentrations of Na_2O and Al_2O_3 in solution were measured by titration, the concentration of SiO_2 was determined with SP−752 UV-V15 spectrophotometer (Spectrum Shanghai, Ltd), Na_2O content in ATH was detected by Flame Photometer (Shanghai AOPU Analytical Instr. Co., Ltd), electrical conductivity of solution was carried out with DDSJ−308A conductivity meter (Shanghai REX Instrument Factory) at 25 °C, PSD of ATH was finished on Mastersizer 2000 laser particle size analyzer (Malvern, British), and morphology of ATH was observed by JSM−6360V scanning electron microscope (JEOL , Japan).

2.3 Procedures

1000 mL pregnant liquor was transferred into a stainless steel tank with a volume of 1200 mL (Heating in water bath, temperature accuracy ±0.5 °C, stirring speed controlled by electric motor), and seed with φ=0.07−0.1 was then added. Sample was sucked from the tank by piette and then centrifuged. The concentrations of Na_2O_k, Al_2O_3 and SiO_2 in sodium aluminate solution were determined. The fine ATH was washed with boiling water until pH ~9 of washing water, and the washed ATH was then dried at 80 °C for PSD measurement and morphology observation.

3 Results and discussion

3.1 Influence of Al_2O_3 concentration of solution on soda content of ATH

Pregnant liquor with high concentration (ρ_{Na_2Ok}>160 g/L, $\rho_{Al_2O_3}$>170 g/L) is adopted in the treatment of diasporic bauxite in China, while their concentrations are low (ρ_{Na_2Ok}<145 g/L, $\rho_{Al_2O_3}$<155 g/L) in the treatment of gibbsite bauxite by Bayer process at abroad. Reaction behavior of aluminate anion in seeded precipitation process is influenced remarkably by the concentration of sodium aluminate solution. The effect of concentration of Al_2O_3 in solution on soda content of ATH is listed in Table 1.

Table 1 Effect of alumina concentration on PSD and soda content in ATH

Sample No.	Pregnant liquor concentration/ $(g\cdot L^{-1})$		PSD/μm			$\eta_{Al_2O_3}$/%	Na_2O content/%
	Al_2O_3	Na_2O	$d(0.1)$	$d(0.5)$	$d(0.9)$		
1	133.28	124.50	0.437	0.672	1.384	58.45	0.215
2	148.00	140.25	0.193	0.256	0.496	59.09	0.205
3	156.18	147.75	0.249	0.351	0.632	57.35	0.271
4	177.08	165.26	0.191	0.248	0.430	53.21	0.332

φ=0.07, temperature 45 °C, time 48 h, stirring rate 500 r/min

As shown in Table1, a decreasing precipitation ratio $\eta_{Al_2O_3}$, $\eta_{Al_2O_3}=(\rho_{init}-\rho_{end})/\rho_{init}$, where ρ_{init} and ρ_{end} are Al_2O_3 concentrations in pregnant liquor and spent liquor, respectively, can be observed with increasing Al_2O_3 concentration under the same experiment condition. And the soda content in the fine ATH rises with increasing Al_2O_3 concentration. For example, the soda content of ATH is 0.332% at $\rho_{Al_2O_3}$=177.80 g/L, while only 0.205% at $\rho_{Al_2O_3}$=148.00 g/L. Although the above variation of soda content in ATH is consistent with that in producing fine low soda ATH from the low concentration solution [10,11], it costs much by diluted aluminate solution in China due to the expensive evaporation of excess water and the low productivity of ATH per unit volume.

3.2 Influence of circulative seed on PSD and purity of alumina trihydrate

Circulative seed can prevent other impurities from