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≫ 연구논문 ≪

수산화나트륨 침출용액으로부터 과산화수소에 의한 침전으로 알루미나 회수

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Recovery of Alumina from Sodium Hydroxide Leaching Solution by Precipitation with Hydrogen Peroxide

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요 약

블랙드로스로부터 순수한 알루미나를 회수하기 위해 기계적 처리한 블랙드로스의 수산화나트륨 침출용액을 대상으로 침전실험을 수행했다. 본 연구에서는 합성용액에 과산화수소를 침전제로 첨가했다. 실험변수중 과산화수소의 농도와 과산화수소와 용액의 부피비가 수산화알루미늄의 침전에 큰 영향을 미쳤다. 최적 조건에서 용액중 알루미네이트이온이 대부분 침전되었다. 수산화알루미늄을 1200 ℃에서 하소시켜 θ와 α상을 지닌 알루미나를 얻었고 제조한 알루미나의 특성은 XRD와 EDS로 측정했다. 알루미나 입자의 평균 입경은 3.73 μm 이었다.

주제어 : 블랙드로스, 알루미나, 수산화알루미늄, 침전, 과산화수소

Abstract

In order to recover pure alumina from balck dross, precipiatation experiments were done to the NaOH leaching solution of mechanically activated black dross. In this work, hydrogen peroxide was added to the synthic solution as a precipitating agent. Among some variables, the concentration of H_2O_2 and the volume ratio of H_2O_2 to solution showed a remarkable effect on the precipitation of aluminum hydroxide. At the optimum conditions, most of the aluminate was precipitated. Calcination of the aluminum hydroxide at 1200 ^oC led to the formation of θ and α-alumina. The charactistics of the synthesized activated alumina was measured by XRD and EDS. The average particles size of the alumina was 3.73 μm.

Key words : Black dross, Alumina, Aluminum Hydroxide, Precipitation, Hydrogen peroxide

1. Introduction

Aluminum dross contains alumina, metal oxides and nitrides and some salts[1]. Black dross results from the treatment to recover aluminum metal. Hydrometallurgical processes have been developed to recover alumina from black dross. Although alumina is amphoteric, alkaline leaching has a selectivity for the leaching of alumina

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and results in pure aluminate solution with a small amount of silicate[2,3].

In previous studies, a process consisting of ball milling followed by NaOH leaching was performed to selectively dissolve alumina from black dross[3]. The leaching behavior of the mechanically activated black dross was investigated as a function of NaOH concentration, leaching temperature, time and pulp density. Pulp density was found to have a remarkable effect on the dissolution of silica. As pulp density increased to higher than 100 g/L, only alumina and a small amount of silica were dissolved from the mechanically activated dross, leaving the other oxides in the residues. The purity of Al(III) in leaching solution was higher than 98% at the optimum conditions (5 M NaOH, 50 °C, 2 h, pulp density of 100 g/L). Although the purity is relatively high, around 150 ppm of silicate were still present in the solution[3]. Therefore, the removal of silicate by coagulation with PAM was investigated. In our previous work on the recovery of alumina from black dross, aluminate solution with purity higher than 99.9% was obtained from the synthetic leaching solution of mechanically activated black dross by removing most of the silicate with coagulation with PAM[4]. An important step in the production of alumina and compound from black dross by NaOH leaching is the crystallization of aluminum hydroxide from sodium aluminate solutions (leaching liquor). Aluminum hydroxide can be precipitated from sodium aluminate solution for the production of alumina[5]. This hydrate is then calcined to alumina for further processing. The conversion of hydrates to the oxide is complex and provides several low-temperature alumina such as ρ, χ, η, and γ [6]. These can in turn be converted to one or more of the following high-temperature transition alumina: δ, κ, and θ. The last stage in these transformations is α-Al_2O_3, which is thermodynamically the most stable[7].

Hydrogen peroxide has been utilized for the regeneration of sodium hydroxide from aluminum washed solution[8] and the synthesis of alumina particles with high surface area by precipitating boehmite from sodium aluminate solution[9]. The properties of the synthesized alumina depend on the initial conditions of solution (the concentration of NaOH and aluminate, temperature) and the method of addition of precipitating agents. The concentration of NaOH and aluminate in our previous work was 5 M NaOH and 13000 mg/L, respectively. Few works have been reported on the synthesis of alumina from this strong alkaline solution with high aluminate content. In this work, hydrogen peroxide was employed as an additive to synthesize aluminum hydroxide. Parameters affecting the crystallization from the solution such as H_2O_2 concentration, the volume ratio of H_2O_2 to leaching liquor, temperature and reaction time were investigated. Moreover, the effect of calcination conditions on the properties of activated alumina was also reported.

2. Experimental

The leaching liquor was prepared by dissolving extra pure sodium hydroxide (NaOH) (Duksan Co.) in doubly distilled water. And then, the alkaline solution was used to dissolve $AlCl_3$ (Daejung Chemicals and Metals Co., 95%). The concentration of Al(III) in the synthetic solution was fixed at 13000 mg/L in 5 M NaOH. The synthetic solution was prepared on the basis of the concentration of Al(III) and Si(IV) present in the real leaching solution. Hydrogen peroxide (Daejung Chemicals and Metals Co., 30%) solutions were prepared at varying concentrations by dilution (using deionized water).

For the aluminum hydroxide precipitation reactions, varying dosage of hydrogen peroxide (H_2O_2) was added to 20 mL of the synthetic solution in covered 100 mL beakers equipped with a magnetic stirrer bar in a heating mantle. The mixture was stirred at 400 rpm and at 20 ºC except for the effect of temperature. The slurry samples at desired time intervals were taken and filtered by using vacuum filtration. In each case, the aluminum hydroxide was separated by vacuum filtration, washed several times with warm deionized water, till the filtrate became neutral to litmus paper. The concentration of Al(III) in the solution was measured by inductively coupled plasma optical emission spectrometers ICP-OES (Spectro Arcos). Precipitation yield of $Al(OH)_3$ of the synthetic solutions was calculated as follows

$$Y = \frac{m_0 - m}{m_0} \times 100\% \quad (1)$$

where m_0 and m represent the concentration of Al(III) (mg/L) in the solution before and after precipitation, respectively.

For the production of activated alumina, precipitates were calcinated at 1200 °C for 5 hours in an SX-GD7123 muffle furnace. The structure and morphology of activated alumina was characterized by X-ray diffraction (XRD) (D8 Advance (Bruker AXS, Karlsruhe, Germany)) with Cu Ka (40 kV/40 mA, $\gamma = 0.15406$ nm) radiation and by Field Emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi, Tokyo, Japan). Image analysis is one of the best methods for measuring powder size distribution. Therefore, ImageJ software, which is freeware Java-based Image Processing software, was employed in this work for particle size distribution analysis of alumina for each specimen using the collected FE-SEM images. The chemical composition of the alumina powder was analyzed using EDS.

3. Results and Discussion

3.1. Precipitation of aluminum hydroxide from sodium aluminate solution by using hydrogen peroxide

3.1.1. Effect of H_2O_2 concentration

The effect of hydrogen peroxide concentration on the precipitation of aluminum hydroxide was investigated by varying H_2O_2 concentration from 5 to 30 wt%, the volume ratio of H_2O_2 to leaching liquor: 1, at 400 rpm for 3 hrs. The precipitation percentage of aluminum hydroxide increased to 99% as H_2O_2 concentration increased to 30% (see Fig. 1). In order to precipitate aluminum hydroxide, it is necessary to remove the hydroxide ion coordinated to aluminum ion. In most cases, the removal of coordinated hydroxide ions can occur by condensation reaction which releases water molecules. Therefore, it is necessary to provide hydrogen ions to react with the coordinated hydroxide ions. A possible mechanism for the precipitation of aluminum hydroxide can be explained as follows. In strong alkaline solution, metal ions may be entirely coordinated by hydroxide ligands, which can be represented as $[M(OH)_x]^{n-}$. When H_2O_2 is added to concentrated NaOH solution, H_2O_2 is decomposed to hydroperoxide ion (HO_2^-) and hydrogen ion (H^+) as Eq. (1)[10]. The hydroperoxide ion (HO_2^-) can disproportionate to hydroxide ion and oxygen gas as Eq. (2).

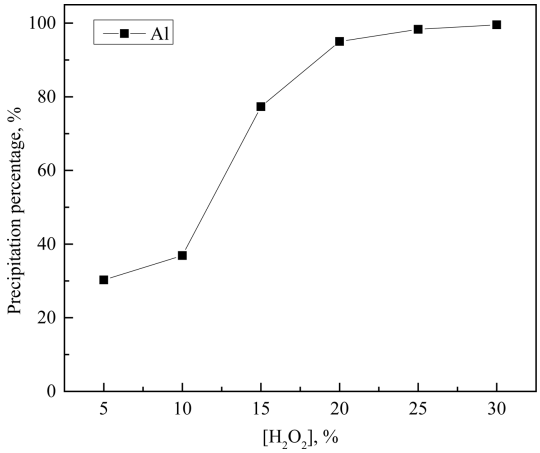


Fig. 1. Effect of H_2O_2 concentration on the precipitation of aluminum hydroxide from synthetic solution.

$$H_2O_2 = HO_2^- + H^+ \quad (1)$$

$$HO_2^- = OH^- + 1/2O_2 \quad (2)$$

This hydrogen ion can react with aluminate to precipitate either AlO(OH) or $Al(OH)_3$, depending on the concentration of NaOH in the solution. The precipitation reaction of aluminum hydroxide by H_2O_2 can be represented as Eq. (3)[11].

$$NaAlO_2 + H_2O_2 = AlO(OH) + NaOH + 1/2O_2 \quad (pH = 14) \quad (3)$$

Instead of adding acids as a hydrogen ion source, the addition of H_2O_2 can regulate the production rate of hydrogen ion and thus control the size of the precipitates. This method is a kind of homogenous precipitation.

3.1.2. Effect of H_2O_2 volume

The effect of the volume ratio of H_2O_2 to aluminate solution on the precipitation of aluminum hydroxide was

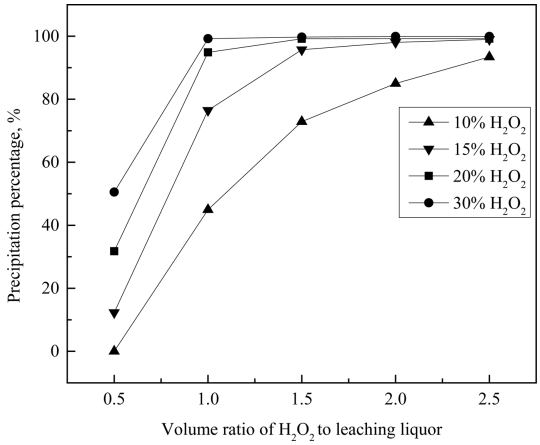


Fig. 2. Effect of the volume ratio of H_2O_2 to the leaching liquor on the precipitation of aluminum hydroxide from synthetic solution.

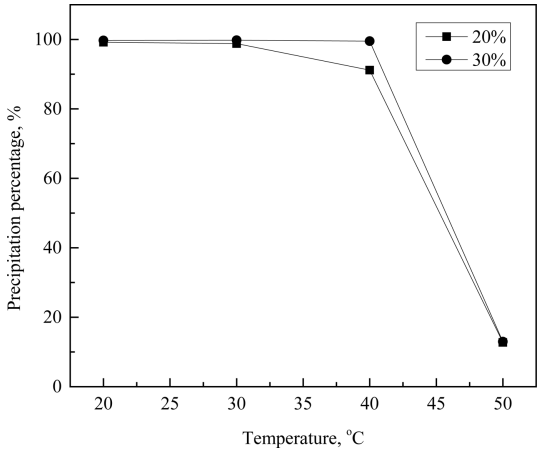


Fig. 3. Effect of temperature on the precipitation of aluminum hydroxide from synthetic solution.

investigated at 10%, 15%, 20%, 30%. In this work, the volume ratio of H_2O_2 to leaching liquor (V_1:V_2) was in the range from 0.5 to 2.5 and the corresponding results are shown in Fig. 2. Precipitation percentage of aluminum hydroxide was increasing with the increase in the volume ratio of H_2O_2. When the volume of ratio of H_2O_2 to the aluminate solution was less than 1.5, only a small amount of aluminum hydroxide precipitates was formed in these conditions. In contrast, as the volume ratio increased from 1.5 to 2.5, precipitation percentage of aluminum hydroxide rapidly increased, even in low hydrogen peroxide concentrations like 10%, 15%. Based on the stoichiometry of the precipitation equations (Eq. (3)), H_2O_2 ratio has a great influence on the precipitation of aluminum hydroxide. For a complete reaction to occur, the ratio of hydrogen peroxide and sodium aluminate must be greater than 1. This is consistent with the experimental results.

3.1.3. Effect of reaction temperature and time

The effect of reaction temperature was investigated at H_2O_2 concentrations of 20% and 30%. Most of aluminate ions were precipitated at both concentrations of H_2O_2 as long as reaction temperature was lower than 30 °C. The precipitation efficiency with H_2O_2 decreased when the temperature was raised above 40 °C (see Fig. 3). The standard enthalpy change of Eq. (3) is approximately −1032 kJ mol^{-1}, indicating that Eq. (3) is exothermic[12]. Therefore, the reaction degree of Eq. (3) should decrease as reaction temperature increases. Our results agree well with this trend.

The effect of reaction time was investigated at both conditions of H_2O_2 concentration (20% and 30%). Within our experimental range, reaction time did not show any significant effect on the precipitation of aluminum hydroxide in both concentrations of H_2O_2 (see Fig. 4). An optimum condition for the precipitation of aluminum hydroxide was obtained as follows: 20% H_2O_2, the volume ratio of H_2O_2 to solution: 1.5, 20 °C, 400 rpm,

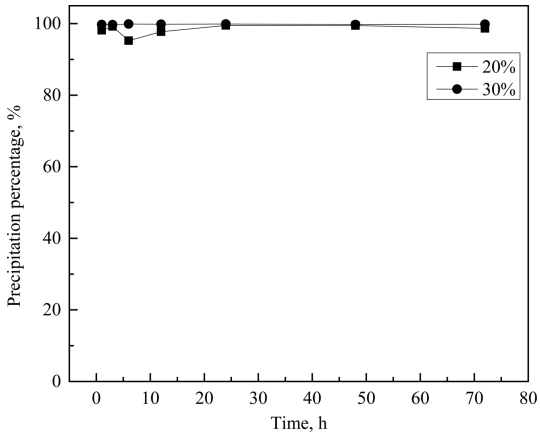


Fig. 4. Effect of reaction time on the precipitation of aluminum hydroxide from synthetic solution.

Table 1. Chemical reaction occurred at different temperature

Temperature/°C	Reaction
100 ~ 120	$2Al(OH)_3 = Al_2O_3 \cdot 3H_2O$
200 ~ 250	$Al_2O_3 \cdot 3H_2O = Al_2O_3 \cdot H_2O + 2H_2O$
700	$Al_2O_3 \cdot H_2O = \gamma\text{-}Al_2O_3 + H_2O$
900	$\gamma\text{-}Al_2O_3 = \theta\text{-}Al_2O_3$
1150 ~ 1200	$\theta\text{-}Al_2O_3 = \alpha\text{-}Al_2O_3$

and 3 hrs. At this condition, the precipitation percentage of aluminum hydroxide was 99%.

3.2. Production of activated alumina from aluminum hydroxide

The precipitated $Al(OH)_3$ was calcined at 1200 °C for 5 h and Al_2O_3 powders were obtained. The chemical reactions occurring during temperature increase are listed in Table 1. After calcination treatment, the $\alpha\text{-}Al_2O_3$ and $\theta\text{-}Al_2O_3$ powders were obtained. Their characteristics was measured by chemical analysis, XRD and SEM. From the XRD pattern in Fig. 5, the diffraction peaks of the powders agreed well with the standard diffraction peaks of $\alpha\text{-}Al_2O_3$ and $\theta\text{-}Al_2O_3$, indicating that the powders consist of $\alpha\text{-}Al_2O_3$ and $\theta\text{-}Al_2O_3$. EDS spectra of powders calcined at 1200 °C for 5 hrs is shown in Fig. 6. It is obvious from EDS results that the powders prepared at

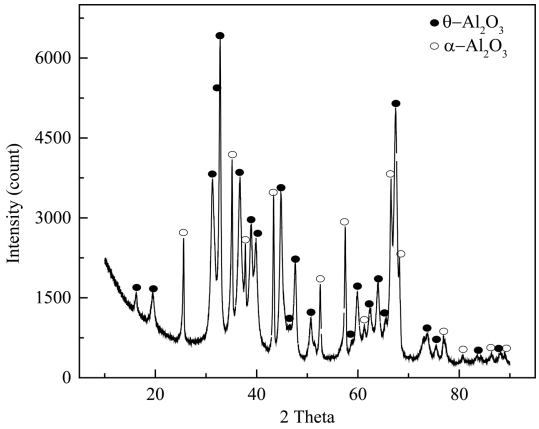
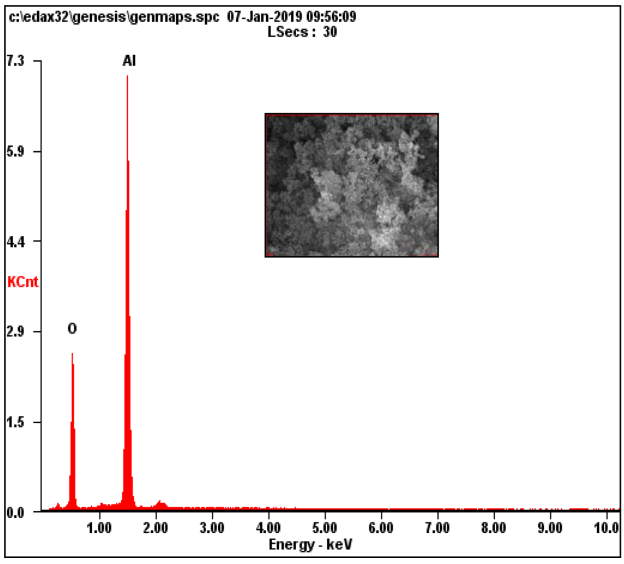


Fig. 5. The XRD pattern of the precipitates after calcined at 1200 °C for 5 hrs.

this condition are alumina particle (56.73% aluminum and 43.27% oxygen). Moreover, there are no trace of other impurities like sodium and chloride in the powder samples.

Fig. 7 depicts the FE-SEM micrograph of the alumina powders. The powders have a rounded-corner shape. A lot of tiny grains were attached on large ones and non-uniformly distributed. Moreover, well-structured meso-porous alumina with high surface area and narrow pore size distribution was obtained by calcination at 1200 °C



Element	*Wt%*	*At%*
OK	43.27	56.26
AlK	56.73	43.74
Matrix	Correction	ZAF

Fig. 6. Energy dispersive spectra of the activated alumina.

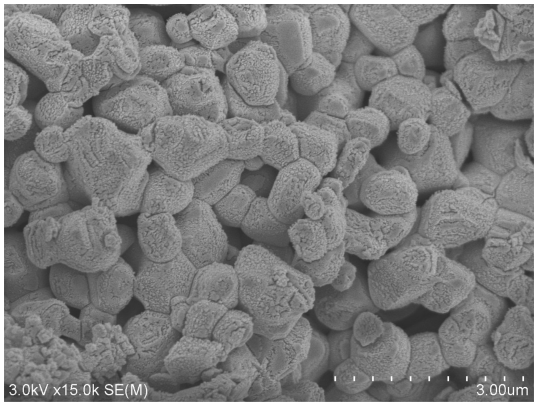


Fig. 7. SEM micrograph of alumina calcinated at 1200 °C for 5 hrs.

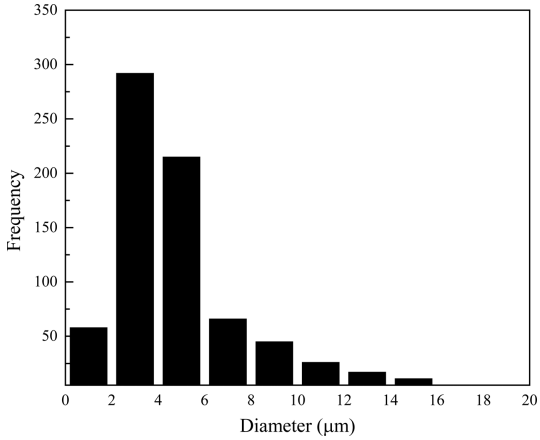


Fig. 8. Particle size distributions of the synthesized alumina powders.

for 5 hours. The particles size was found to be in the range of 0.5 μm to 15 μm (see Fig. 8). The particle size distribution of the powders were analyzed by using an ImageJ[13] and Origin Pro 9.0 software (Origin lab corporation, Northampton, MA, USA, 2012) based on the SEM morphology (Fig. 7). The surface area of the synthesized alumina powders calcined at 1200 °C for 5 hrs was found to be nearly 63.2 m^2/g (Table 2), which is equivalent to a median particle size of 3.73 μm.

Table 2. The surface area of activated alumina at 1200 °C for 5 hours

	Temperature (°C)	Time (hour)	BET Surface area (m^2/g)
Activated alumina	1200	5	63.1992

4. Conclusions

Black dross results from the re-melting of used aluminum cans and is a valuable resource containing alumina. NaOH leaching of mechanically activated aluminum black dross followed by the removal of dissolved silicate results in an aluminate solution with 99.9% purity. In order to recover activated alumina from the leaching solution, precipitation of aluminum hydroxide and subsequent calcination was investigated. In this work, H_2O_2 was selected as a precipitating agent and precipitation efficiency of aluminum hydroxide was investigated by varying conditions. Among the precipitation conditions, the concentration of H_2O_2 and the volume ratio of H_2O_2 to aluminate solution showed a remarkable effect on the precipitation of aluminum hydroxide. The precipitation of aluminum hydroxide increased as the concentration of H_2O_2 and the volume ratio of H_2O_2 to leaching liquor increased. At the optimum conditions (20% H_2O_2, the volume ratio of H_2O_2 to leaching liquor: 1.5, 20 °C, 3 hrs, 400 rpm), the precipitation percentage of aluminum hydroxide was higher than 99%. This hydrate was then calcined to activated alumina at 1200 °C. XRD and EDS analysis indicated that the product consisted of α-phase and θ-phase alumina (α-Al_2O_3, θ-Al_2O_3) with high surface area (63.2 m^2/g). The synthesized alumina powder had a median particle size of 3.73 μm. In this study, alumina with high purity was obtained from the synthetic leaching solution of mechanically activated black dross by precipitation of aluminum hydroxide with H_2O_2. Further work is necessary to verify the obtained results with the real leaching solution of mechanically activated black dross.

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