Original Article

Development of a hydrometallurgical process for the recovery of pure alumina from black dross and synthesis of magnesium spinel

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In order to recover pure alumina and synthesize magnesium spinel from black dross, a hydrometallurgical process was developed. This process consisted of 1) NaOH leaching of the mechanically activated black dross, 2) removal of silicate(IV) from the leaching solution by adsorption followed by coagulation, 3) precipitation of aluminum hydroxide from the purified leaching solution, 4) synthesis of magnesium spinel. Continuous experiments on the above-mentioned steps at optimum conditions were performed. Magnesium spinel was synthesized at 1000 °C for 5 hrs by the co-precipitation method. The purity of spinel was 99.99 % and its characteristics were analyzed by XRD and SEM. Mass balance of the whole process indicated that the recovery percentage of alumina from the black dross was only 34 % owing to low leaching percentage. Further work on the pretreatments of black dross to improve its dissolution behavior is needed.

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1. Introduction

Aluminum dross results from the re-melting of used aluminum cans and contains some aluminum metal together with other metal oxides. Treatment of aluminum dross to recover aluminum metal results in black dross, which consists of alumina, metal oxides and some kinds of salts [1]. Black dross is considered to be hazardous owing to the evolution of toxic gases when exposed to moisture. In general, hydrometallurgical and pyrometallurgical processes are extensively practiced to recover alumina from the black dross [2,3]. Pyrometallurgical processes have disadvantages like high energy consumption, while hydrometallurgical processes need the separation of aluminum ions from either alkaline or acidic leaching solutions of black dross [2,4,5]. Compared to acid leaching, alkaline leaching of black dross can lead to purer aluminate(III) solution [6,7].

In previous works, the effect of ball milling treatment on the leaching behavior of the oxides present in black dross was investigated by employing NaOH solution. Alumina together with some of silica was selectively dissolved in NaOH solution, while iron oxides and calcium and magnesium oxides were not dissolved [6,8]. It was found that ball milling treatment has a favorable effect on the selective dissolution of alumina from the black dross. Although the purity of aluminate(III) in the NaOH leaching solution of mechanically activated black dross was about 98 %, the leaching percentage of alumina was only 35 %, which should be improved [6]. During the recovery
of alumina from the NaOH leaching solution of mechanically activated black dross, silica is selectively precipitated from the leaching solution during the treatment with hydrogen peroxide. Therefore, it is necessary to remove silicate(IV) from the leaching solution in order to recover pure alumina.

Some methods such as nano-filtration, reverse osmosis, precipitation, coagulation, adsorption were employed to remove silicate(IV) [8–10]. However, the disadvantage of nano-filtration, reverse osmosis, precipitation lies in the fact that the separation of aluminate(III) and silicate(IV) from the leach solution is complicated because of the similarity in their predominant species in the aqueous solution. Unlike these methods, our results clearly indicated that adsorption and coagulation methods can be applied to selectively remove silicate(IV) over aluminate(III) from strong alkaline leaching solution of black dross [11,12].

Crystallization of aluminum hydroxide from the purified aluminate solution is an important step in the recovery of alumina from the black dross by the hydrometallurgical method. Aluminum hydroxide can be precipitated by reaction with hydrogen peroxide from the strong alkaline solution [13]. Spinel is represented as AB₂O₄ where A is a divalent ion and B is trivalent ion. Spinel derives its name from the mineral spinel, MgAl₂O₄. Compared to aluminum hydroxide or alumina, magnesium spinel has more economic value. The aluminum hydroxide obtained from the purified aluminate(III) solution can be employed as a starting material for the synthesis of spinel. Therefore, recovery of alumina from black dross and synthesis of magnesium spinel would improve the process economics.

Several literatures have reported that magnesium spinel powder can be synthesized by solid-state reaction [14], wet chemical methods [15], organic gel-assisted citrate method [16], the aerosol method [17], sol-gel of double or semi-alkoxides [18]. Some works have been done for the synthesis of spinel from black dross [19–21]. Namely, Hashshinshin et al. demonstrated that a magnesium/silicon aluminate spinel could be synthesized from aluminum dross using an induction synthesis method [21]. In this process, spinel was synthesized by first adding MgO to the alkaline leached residue and then sintering the mixture [22]. Spinel synthesis was investigated in detail using the traditional solid-phase sintering method [23,24]. However, most of the reported processes for the synthesis of spinel from black dross have several disadvantages, such as high calcination temperature, prolonged reaction time, and the low purity of the spinel due to the existence of impurities. This motivated us the idea of investigating the synthesis of pure spinel from black dross at lower temperatures.

In previous studies, we have reported the synthesis of magnesium spinel by both ball milling and co-precipitation methods [25]. Among the two methods, co-precipitation was found to be more efficient for the synthesis of magnesium spinel.

Our previous works were obtained from the synthetic solution of each step. The presence of minor elements in the real solution would have some effect on the purification of the leaching solution and the characteristics of the synthesized spinel. In developing a process, it is of immense importance to verify the process and report the process efficiency and mass balance of the important elements. Therefore, we conducted continuous experiments for the recovery of pure alumina from the black dross produced in a company. In each step, the optimum conditions which had been reported in the literature were applied. Finally, magnesium spinel was synthesized by using the recovered aluminum hydroxides and its characteristics were measured. Based on the results, a hydrometallurgical process was proposed to treat black dross and synthesize magnesium spinel.

2. Experimental

2.1. Materials

The black dross employed in this work was provided by a company in Korea. This black dross contained the oxides of Al, Ca, Fe, Mg, Si, and Ti together with some salts like KCl and NaCl. The salts present in black dross were dissolved in water at the following conditions: pulp density, 100 g/L; temperature, 90 °C and leaching time, 2 h. The residues were dried in an oven for 2 days and then milled at 400 rpm for 1 h. The XRD pattern of the black dross is shown in Fig. 1 with the possible phases present. The Field Emission scanning electron microscopy data (FE-SEM, S-4800, Hitachi, Tokyo, Japan) and particle size distribution of as-received and mechanically activated black dross are shown in Fig. 2. According to the distribution of particle size in SEM micrographs of as-received and mechanically activated black dross, mechanical activation of black dross by ball milling decreased the particle size of the treated black dross. The decrease in particle size of black dross results in a reduction in the thickness of the product layer. Moreover, an increase in the surface area (BET, TriStar II 3020, Micromeritics, Norcross, GA 30093-2901, USA) of the black dross before and after mechanical activation was observed from 86.43 m²/g to 162.18 m²/g. The chemical composition of the black dross after water leaching was determined by X-ray fluorescence spectrophotometry (XRF, Hitachi, Tokyo, Japan) and is shown in Table 1. Hydrocalumites (Ca₃Al(OH)₆Cl₂H₂O) were synthesized by the co-precipitation method [8]. Polyacrylamide ([(C₃H₅NO)n, molecular weight = 10,000 g/mol, Aldrich,
Milwaukee, WI), hydrogen peroxide (Daegung Chemicals and Metals Co., 30%), magnesium oxide powder (Daegung Chemicals and Metals Co., 96%), NaOH (Duksan Pure Chem. Co., Ltd., Ansan-si, Korea) were employed in the experiments.

2.2. Experimental procedure

2.2.1. Leaching experiment

After the black dross was treated with water, the residues were mechanically activated at 400 rpm for 1 h (Fritsch Pulverisette 7 BeadMill, Fritsch, Idar-Oberstein, Germany). This mechanically activated dross was dissolved in a 5 M NaOH solution at 50 °C for 2 h at a pulp density of 100 g/L. In the leaching experiments, the mechanically activated dross was put into the NaOH solution in 1000 mL three-neck flat bottom beaker on the hot plate. During all the experiments, the beaker was kept closed by the cover to prevent the loss of the solution, and mixed solution was stirred by the magnetic stirrer bar. After the required reaction period, the samples were obtained at desired time intervals and separated from the solution by using vacuum filtration.

2.2.2. Silicate(IV) removal and purification experiment

For the removal of silicate(IV) from the leaching solution, various dosage of hydrocalumite/polyacrylamide (PAM) was added to 50 mL of real leaching solution in covered 100 mL beakers. The experiments were done by employing heating mantle with a magnetic stirrer bar. The mixture of hydrocalumite/PAM and leaching solution was stirred at desired temperature. The residue was separated from solution by using vacuum filtration. The concentration of Si(IV) and Al(III) in the filtrate was measured by ICP-OES (inductively coupled plasma optical emission spectrometers, Spectro Arcos). The removal percentage of silicate (R, %) was calculated by using equation (1)

\[
R = \frac{(C_0 - C_f)}{C_0} \times 100\%
\]

where \(C_0\) and \(C_f\) represent the concentration (mg/L) of silicate ion in the solution before and after the experiment.

2.2.3. Synthesis of magnesium spinel

Aluminum hydroxides were obtained from the pure aluminate solution by reaction with hydrogen peroxide. The precipitated aluminum hydroxides were separated by vacuum filtration, washed several times with warm deionized water. Magnesium spinel was synthesized by co-precipitation method [25]. For the formation of magnesium spinel, precursors were calcined in an SX-GD7123 muffle furnace. The structure and morphology of aluminum hydroxide, magnesium spinel was characterized by High-resolution X-ray diffraction (HR-XRD) (PANalytical X’Pert-PRO, The Netherlands)) with Cu Ka (40 kV/40 mA, \(\gamma = 0.15406\) nm) radiation and by Field Emission scanning electron microscopy.

3. Results and discussion

3.1. The selective dissolution of alumina by sodium hydroxide leaching from the mechanically activated dross

In the leaching of the mechanically activated black dross with NaOH solution, only alumina and silica were dissolved, while other oxides were not dissolved [7]. The real leaching solution was obtained at the following optimum conditions: 5 M NaOH, reaction temperature of 50 °C, pulp density of 100 g/L, reaction time of 2 h, and stirring speed of 200 rpm. Under these conditions, the metal concentration in the leaching solution of mechanically activated black dross is shown in Table 1. Alumina exists as Al(OH)\(_4^-\) in the leaching solution, while silica...
exists as $H_2SiO_3^-$ ($\text{HO}_3\text{SiO}^-$) and $H_2SiO_4^{2-}$ ($\text{HO}_3\text{SiO}_2^{2-}$). The change in the speciation of silicate with solution pH can occur by detachment of the hydrogen ion from the silicate to the hydroxide ion and thus form water. The successive formation of ($\text{HO}_3\text{SiO}^-$ and ($\text{HO}_3\text{SiO}_2^{2-}$ can be represented as Eqs. (2) and (3) [26,27].

\[
\text{Si(OH)}_{\text{n(geo)}} + \text{OH}^- = (\text{HO})_3\text{SiO}^- + \text{H}_2\text{O} \tag{2}
\]

\[
(\text{HO})_3\text{SiO}^- + \text{OH}^- = (\text{HO})_3\text{SiO}_2^{2-} + \text{H}_2\text{O} \tag{3}
\]

### 3.2 Removal of silicate(IV) by hydrocalumite

#### 3.2.1 Effect of hydrocalumite dosage

In order to remove silicate(IV) from the real leaching solution of black dross, adsorption experiments were performed by varying the dosage of hydrocalumite from 10–90 g/L. Fig. 3 displays the influence of hydrocalumite dosage on the removal of silicate(IV). In these experiments, the reaction temperature and time was fixed at 50 °C and 2 h, respectively. The removal percentage of silicate(IV) increased with hydrocalumite dosage and 98 % removal percentage was obtained at 70 g/L. The adsorption reaction of silicate(IV) onto hydrocalumite can be represented as Eq. (4). The adsorbed silicates(IV) $H_2SiO_3^{2-}$ are then intercalated into the interlayer through exchange with the chloride ion in the interlayer, which is displayed in Fig. 4.

\[
2\text{Ca}_2\text{Al(OH)}_6(\text{H}_2\text{O})_2\cdot\text{Cl}[(\text{surface})]+\text{SiO}_2(\text{OH})_2^{2-}
= \text{Ca}_3\text{Al}_2(\text{OH})_{12}\cdot\text{SiO}_2+2\text{Cl}^- + \text{Ca(OH)}_2+4\text{H}_2\text{O} \tag{4}
\]

However, the removal percentage of aluminate(III) was very low when the hydrocalumite dosage was below 50 g/L, but nearly 20 % of aluminate was removed when hydrocalumite dosage was in the range from 70 to 90 g/L. The results indicate that the removal of silicate(IV) alone from the real leaching solution of black dross is possible by adjusting the adsorbent dosage. At 50 g/L dosage of hydrocalumite, the removal percentage of silicate(IV) was about 95 %, while that of aluminate(III) was nearly zero. Therefore, 50 g/L dosage of hydrocalumite will be employed in the following experiments.

#### 3.2.2 Effect of temperature

In adsorption, reaction temperature has a significant effect on the removal of silicate(IV) and thus the effect of temperature was investigated. In these experiments, the removal of silicate(IV) was carried out for 2 h at 400 rpm. The results show that reaction temperature greatly affected the adsorption efficiency of silicate, while that of aluminate(III) was not affected (see Fig. 5). As the reaction temperature increased to 70 °C, the adsorption efficiency of silicate(IV) was rapidly increased. However, further increase in reaction temperature to 90 °C showed negative effect on the removal of silicate(IV). This may
be ascribed to the instability of the hydrocalumite at 90 °C, resulting in the inactivation of hydrocalumite [28,29].

3.2.3. Effect of stirring speed

The stirring speed has an important role in promoting the adsorption of silicate(IV) onto hydrocalumite. In these experiments, stirring speed was varied from 200 to 800 rpm in order to evaluate the effect on adsorption efficiency. The effect of stirring speed was investigated using 50 g/L hydrocalumite at 60 °C for 2 h. As shown in Fig. 6, the removal percentage of silicate(IV) increased from 88 to 95 % as the stirring speed increased from 200 to 400 rpm and was nearly constant thereafter. This behavior might indicate that the adsorption of silicate(IV) reached equilibrium at this condition. In order to verify this, the effect of reaction time on the adsorption of silicate(IV) onto hydrocalumite was performed at a stirring speed of 400 rpm in further experiments.

3.2.4. Effect of reaction time

In order to find an optimum condition for the removal of silicate(IV), the effect of reaction time was investigated. The effect of reaction time was performed by varying reaction time from 2 to 8 h at 50 g/L hydrocalumite and 50 °C. Fig. 7 shows that the removal percentage of silicate(IV) decreased from 95 % to 83 % with increasing reaction time, while there was no change in the removal of aluminate(III). The results indicated that the removal of silicate(IV) by using hydrocalumite depends on the hydrocalumite dosage, reaction temperature and time. At this condition, the purity of the aluminate(III) solution after removal of silicate(IV) by hydrocalumite was higher than 99 %. The change in concentration of Al(III) and Si(IV) and the purity of Al(III) in the solution before and after adsorption are shown in Table 2.

3.3. Purification of real leaching solution by Polyacrylamide (PAM)

After removal of silicate(IV) by reaction with hydrocalumite, about 60 mg/L of silicate(IV) still remained in the leaching solution. This silicate(IV) would be co-precipitated into aluminum hydroxide, which decreases the purity of the recovered alumina. Therefore, further removal of silicate(IV) was investigated by employing coagulation with polyacrylamide (PAM). Fig. 8 shows that the removal percentage of silicate(IV) increased with PAM dosage and silicate(IV) was completely removed from the leaching solution when 3 g/L of PAM was added. In these experiments, the reaction temperature and
time were fixed at 50 °C and 3 hs, respectively. At this condition, the purity of the aluminate(III) solution after purification was higher than 99.99%. The composition of the real leaching solution and the purity of aluminate(III) after treatment with 3 g/L PAM are shown in Table 3.

In previous experiments on the removal of silicate by treatment with PAM and hydrocalumite, nearly complete removal of silicate(IV) was possible. However, it was difficult to remove silicate(IV) by either method from the real leaching solution. This might be due to the interference of other minor ingredients in the real leaching solution, which were not detected through ICP measurement. Therefore, it is necessary to employ consecutive steps to remove most of the silicate(IV) and other minor impurities from the real leaching solution of black dross.

### 3.4. Precipitation of aluminum hydroxide

An important step in the recovery of alumina and synthesis of some compounds from the NaOH leaching solution of black dross is the crystallization of aluminum hydroxide from the solution. Aluminum hydroxide can be precipitated from the sodium aluminate solution by reacting with hydrogen peroxide [30]. This hydrate is then calcined to alumina for further processing. We have reported the recovery of alumina from synthetic leaching solution of black dross [13]. The precipitation of aluminum hydroxide depends on the initial conditions of solution (the concentration of sodium hydroxide, aluminate and temperature) and the method of addition of precipitating agents. The concentration of NaOH and aluminate(III) in the purified real leaching solution was 5 M NaOH and 12627.4 mg/L, respectively. In this work, 20 % hydrogen peroxide was added to the solution at the following conditions: the volume ratio of H₂O₂ to leaching solution was 1.5, stirring speed of 400 rpm and room temperature.

In strong alkaline solution, metal ions may be entirely coordinated by hydroxide ions, like Al(OH)₄⁻. When H₂O₂ is added to concentrated NaOH solution, H₂O₂ is decomposed to hydroperoxide ion (HO₂⁻) and hydrogen ion (H⁺) as Eq. (5) [31]. The hydroperoxide ion (HO₂⁻) can disproportionate to hydroxide ion and oxygen gas as Eq. (6).

\[ \text{H}_2\text{O}_2 = \text{HO}_2^- + \text{H}^+ \]  \hspace{1cm} (5)

\[ \text{HO}_2^- = \text{OH}^- + \frac{1}{2}\text{O}_2 \]  \hspace{1cm} (6)

This hydrogen ion can react with aluminate(III) to precipitate aluminum hydroxide as shown in Eq. (7). The overall precipitation reaction of aluminum hydroxide by H₂O₂ can be represented as Eq. (8).

\[ \text{H}^+ + \text{Na}^+ + \text{Al(OH)}_4^- = \text{Al(OH)}_3 + \text{Na}^+ + \text{H}_2\text{O} \]  \hspace{1cm} (7)

\[ \text{Na}^+ + \text{Al(OH)}_4^- + \text{H}_2\text{O}_2 = \text{Al(OH)}_3 + \text{NaOH} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \]  \hspace{1cm} (8)

The precipitated aluminum hydroxides were separated by vacuum filtration, washed several times with warm deionized water, till the filtrate became neutral to litmus paper. The SEM image of the aluminum hydroxide powders obtained is shown in Fig. 9. The morphology of aluminum hydroxide was uniform and these powders were used as starting materials for the synthesis of magnesium spinel.

### 3.5. Synthesis of magnesium spinel

The optimum conditions obtained from the previous studies were employed to synthesize magnesium spinel [25]. First, aluminum hydroxide powders recovered from the purified leaching solution were dissolved in aqua regia and then the mixture was diluted 4 times with distilled water. After adding
MgO powder to this diluted aqua regia in a 2:1 molar ratio of Al to Mg, the mixture was kept for 6 h at 90 °C. Further refluxing was carried out for 2 h to make the mixed solution homogeneous. The co-precipitated spinel precursors were stirred at 25 °C and 300 rpm. Then, the pH of the solution was kept at 8.5 by adding 2 M NH₄OH solution. The precipitates were filtered off and washed with de-ionized water and dried at 70 °C for 48 h. Samples of the precursor were calcined at 1000 °C for 5 h and spinel powders were obtained. Their characteristics were measured by chemical analysis, XRD and SEM. From the XRD pattern shown in Fig. 10, the diffraction peaks of the powders agreed well with the standard diffraction peaks of magnesium spinel. For the precursor sample, it indicated that the aluminum hydroxide (Al(OH)₃), ammonium chloride (NH₄Cl), magnesium (2+) ion ammonium hexahydrate trichloride (MgCl₂NH₄Cl·6H₂O) crystallized during co-precipitation with NH₄OH. A sample of the precursor was calcined at 1000 °C for 5 h. The characteristic peaks of these compounds were observed in X-ray diffraction. The results indicated that impurities completely disappeared and a single-phase of magnesium spinel was obtained. The formation of a single spinel phase can be attributed to two main reasons. First, decomposition of salts (NH₄Cl, MgCl₂NH₄Cl·6H₂O) at high temperatures.

Secondly, the continuous stirring of the solution makes the distribution of Mg(II) and Al(III) uniform, which facilitates the co-precipitation of the spinel [32,33]. These reactions can be described as follows [34]

\[
\text{Mg}^{2+} + \text{Al}^{3+} + 5\text{OH}^- = \text{Mg(OH)}_2 + \text{Al(OH)}_3
\]  
\[
\text{1/2Mg(OH)}_2 + \text{Al(OH)}_3 = 1/2\text{MgO} + 1/2\text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}
\]  
\[
\text{MgO} + \text{Al}_2\text{O}_3 = \text{MgAl}_2\text{O}_4
\]

Fig. 11 depicts the FE-SEM micrograph of precursor and magnesium spinel powders. For the precursor sample, the structure is uniform in the form of hydroxide product. After calcination process, well-crystallized powders were obtained by heat treatment at 1000 °C. At this condition, the crystallite size of magnesium spinel was fine and the morphology was uniform having the average particle size of about 12 nm (see Fig. 12). The particle size distribution of the powders was estimated by employing an ImageJ [35] and Origin Pro 9.0 software on the basis of the SEM morphology (Fig. 11b).
4. Proposal of a process

A hydrometallurgical process has been developed for the recovery of pure alumina and synthesis of magnesium spinel from black dross (see Fig. 13). Table 4 shows the mass balance of components present in black dross in each step and the purity of the product. The real leaching solution of black dross was obtained by leaching with 5 M NaOH solution. Silicate(IV) is removed from the leaching solution by adsorption followed by coagulation. Aluminum hydroxide powders with high purity can be precipitated from the purified solution by reaction with H$_2$O$_2$. Finally, pure magnesium spinel (MgAl$_2$O$_4$) can be synthesized by employing the precipitated aluminum hydroxides. Since the leaching percentage of alumina from the mechanically activated black dross was 34%, the recovery percentage of alumina from the black dross was 34%. However, the purity of the synthesized spinel was 99.99%, indicating that this spinel can be employed for the manufacture of advanced materials. Besides that, some more works like bioleaching need to be done for recycling sodium hydroxide in the solution and for the recovery of some elements left in the alkaline leaching residues.

Compared to other processes developed to recover pure alumina from black dross, the advantage of our process lies in the fact that fewer steps are involved in the recovery of either alumina or spinel with purity higher than 99.99% and the process can be considered as an environmentally-friendly one.

5. Conclusions

In order to recover pure alumina and synthesize magnesium spinel, a hydrometallurgical process has been developed. For this purpose, real alkaline leaching solutions of black dross were employed in the experiments. First, silicate(IV) was removed from the leaching solution by adsorption onto hydrocalumite. Then the silicate(IV) remaining in the solution was successfully removed by coagulation with PAM. Aluminum hydroxides were precipitated from the purified

![Fig. 13 – Flowsheet for the production of magnesium spinel from black dross.](image-url)
leaching solution by adding hydrogen peroxide. These aluminum hydroxides were employed as starting materials for the synthesis of magnesium spinel by co-precipitation method. Analysis of the characteristics of the synthesized spinel verifies that pure magnesium spinel with high intensity was obtained at 1000 °C for 5 h. Mass balance of the continuous process indicated that magnesium spinel with 99.99 % purity was obtained from the black dross. However, the recovery percentage of alumina was only 34 %. Therefore, further work is necessary to improve the leaching percentage of black dross.

Conflicts of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the article.

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