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Ball Milling Treatment of Black Dross for Selective Dissolution of Alumina in Sodium Hydroxide Leaching

Thi Thuy Nhi Nguyen [1], Man Seung Lee [1,*] and Thi Hong Nguyen [1,2]

[1] Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Jeollanamdo 534-729, Korea; thuynhi1828@gmail.com (T.T.N.N.); nthong43@ctu.edu.vn (T.H.N.)

[2] College of Natural Sciences, Can Tho University, Can Tho City 900000, Viet Nam

* Correspondence: mslee@mokpo.ac.kr; Tel.: +82-61-450-2492

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Abstract: A process consisting of ball milling followed by NaOH leaching was developed to selectively dissolve alumina from black dross. From the ball milling treatment, it was found that milling speed greatly affected the leaching behavior of silica and the oxides of Ca, Fe, Mg, and Ti present in dross. The leaching behavior of the mechanically activated dross was investigated by varying NaOH concentration, leaching temperature and time, and pulp density. In most of the leaching conditions, only alumina and silica were dissolved, while the leaching percentage of other oxides was negligible. The leaching percentage of silica decreased rapidly to nearly zero as pulp density increased to 100 g/L. At the optimum leaching conditions (5 M NaOH, 50 °C, 2 h, pulp density of 100 g/L), the purity of Al in the leaching solution was higher than 98%, but the leaching percentage of alumina was only 35%.

Keywords: black dross; ball milling; leaching; NaOH solution; aluminum

1. Introduction

Aluminum is lightweight, high specific strength, and high corrosion resistance. Aluminum metals are produced from ores such as bauxite and other secondary resources [1]. However, more than 95% of energy can be saved by recycling secondary resources instead of producing Al metal from ores [2]. Aluminum dross is produced by treating secondary resources containing Al metal. This dross consists of a mixture of free Al metal and nonmetallic substances such as aluminum oxide, nitride, carbide, salts, metal oxides, and other elements [3]. In general, the small amount of Al metal present in dross is recovered and black dross results from this treatment. Since toxic gases can be produced during the treatment of black dross, black dross is regarded as hazardous waste. However, some Al metal and oxides of several metals are still present in black dross. Therefore, the recovery of valuable components in black dross is important in light of environmental concerns.

Pyrometallurgical and hydrometallurgical processes have been developed to recover aluminum, silica, and other components from black dross [4,5]. Both processes have advantages and disadvantages [4,6–8]. In the hydrometallurgical treatment of black dross, either acidic or alkaline solutions are employed to selectively dissolve components from black dross [9,10]. In one study, over 80% of alumina was dissolved from black dross in both HCl and NaOH solutions, and the leaching percentage of silica was 40 and 68% in the HCl and NaOH solutions, respectively [11]. Since some oxides in black dross are dissolved together with alumina, HCl leaching should not be used to recover pure alumina [12]. Although the leaching percentage of alumina via NaOH solutions is not as high as that via HCl solutions, an alkaline leaching solution has some selectivity for alumina because

the oxides of Ca, Fe, and Mg will not dissolve in this medium [8]. Furthermore, pure aluminum hydroxide can be recovered from an alkaline leaching solution of black dross via crystallization or precipitation, which is considered economical and environmentally friendly [5,13].

Several processes have been reported on the recovery of alumina from black dross by alkaline leaching followed by the precipitation of aluminum hydroxide [14–16]. In most of the reported works on the employment of NaOH, the leaching percentage of alumina from the dross is less than 50% at atmospheric pressure. Moreover, some of the other oxides are dissolved. In one study, from an alkaline leaching solution, aluminum hydroxide was recovered by precipitation with NH_4HCO_3 and carbonation with CO_2 gas [14].

Ball milling treatment can change the physicochemical properties of the components of black dross by providing mechanical energy to them. However, few works on the ball milling treatment of black dross have been reported. In this work, the effect of ball milling treatment on the leaching behavior of certain oxides in black dross was investigated by employing an NaOH solution. For this purpose, ball milling time and speed were varied in the mechanical activation of the black dross after water treatment. The ball-mill-treated black dross was dissolved in an NaOH solution by varying such leaching conditions as NaOH concentration, pulp density, and leaching time and temperature. Alumina was selectively dissolved in NaOH solution from the mechanically activated dross, which resulted in the recovery of pure alumina from black dross. The optimum conditions for ball milling and leaching were obtained in this work.

2. Materials and Methods

2.1. Material

The salts present in black dross were dissolved in water at 90 °C. After the residues dried in an oven, the dried residues with an average particle size <150 μm were collected for experiments. The chemical composition of the black dross after water leaching was analyzed using X-ray fluorescence spectrophotometry (XRF, Hitachi, Tokyo, Japan) and is represented in Table 1. The leaching solution was prepared by dissolving sodium hydroxide (Duksan Co., 93%) in doubly distilled water.

Table 1. The chemical composition of black dross after water leaching. (unit: wt %).

Element	Al	Ca	Fe	Mg	Si	Ti
Residue after water leaching	40.52	3.55	8.34	2.86	15.13	12.01

2.2. Ball Milling Treatment

A vertical planetary ball mill (Fritsch Pulverisette 7 Bead Mill, Fritsch, Idar-Oberstein, Germany) with a rotation speed up to 800 rpm was employed in the mechanical activation of black dross. Mechanically activated samples were prepared as follows: the black dross after water leaching (8 g) was added into a vessel with 40 g agate balls (a ball of 6 mm in diameter) with the weight ratio of ball/black dross of 5:1 and were then milled for 1, 3, 5, 7, and 10 h at 400 rpm. In the case of the effect of ball mill speed, the samples were milled at 250, 400, 550, and 700 rpm for 1 h at the ball to a powder weight ratio of 5:1. The structure and morphology of the ball-mill-treated black dross was characterized by X-ray diffraction (XRD) (D8 Advance (Bruker AXS, Karlsruhe, Germany)) with Cu Ka (40 kV/40 mA, γ = 0.15406 nm) radiation and by scanning electron microscopy (SEM) (SU-70, Hitachi, Tokyo, Japan). The crystal size was determined by the full width at half maximum (FWHM) of peaks in XRD samples. The FWHM can be applied to bell-shaped curves such as those of Gaussian and Lorentzian functions using Origin Pro 9.0 software (Originlab corporation, Northampton, MA, USA, 2012).

2.3. NaOH Leaching

Each leaching experiment of the ball-milled black dross in the NaOH solution was carried out in a 250 mL three-neck round bottom flask equipped with a magnetic stirrer bar in a heating mantle. Teflon tape was used to seal the outside joints of the glassware to avoid evaporation loss. The slurry sample with specific pulp density was stirred at 200 rpm at 50 °C. The slurry samples at desired time intervals were obtained and filtered using vacuum filtration. The concentration of metals in the leachates was analyzed with inductively coupled plasma optical emission spectrometers (ICP-OES) (PerkinElmer Inc., Wellesley, MA, USA).

3. Results and Discussion

3.1. Change in Crystallite Size and Structure of Mechanically Activated Black Dross

The XRD patterns of as-received and mechanically activated black dross are shown in Figure 1. No new crystalline phase was observed from the mechanically activated samples. However, the diffraction peaks of Al_2O_3 were broadened and its intensity increased as mechanical activation time increased. The ball milling treatment resulted in a significant change in the morphology of dross owing to severe plastic deformation of the particles during the milling process [17]. Ball milling treatment reduced the crystallite size of the dross. The average crystallite size (d) of the ball mill treated was estimated by using Equation (1) [18].

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the radiation wavelength, β is the full width at half maximum value in radian, and θ is Bragg's angle in radian. It was found that ball milling time has some effect on the reactivity of the black dross. The full width at half maximum of the different patterns at 2θ = 65.189 were from 0.2651 to 0.3240 in the case of the ball mill treated for 1–10 h, and the determined values are shown in Table 2. It is seen that the average crystallite size reduced from 52 to 43 nm as ball milling time increased from 1 to 10 h.

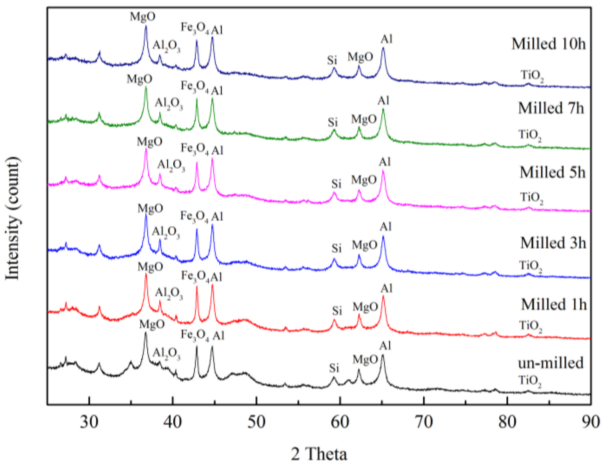


Figure 1. XRD pattern of mechanically activated back dross at different ball milling times.

Table 2. Variation in the average crystallite size of mechanically activated black dross with ball milling time.

Milling Time (Hour)	Average Crystallite Size (nm)
1	52.6
3	50.6
5	45.0

Table 2. *Cont.*

Milling Time (Hour)	Average Crystallite Size (nm)
7	44.0
10	43.0

The SEM micrographs of as-received and mechanically activated black dross are shown in Figure 2. The black dross initially contained angular particles with different sizes and were broken into much smaller particles after mechanical activation. Large clusters with a typical size of several micrometers were observed due to the aggregation of smaller nanoparticles [19].

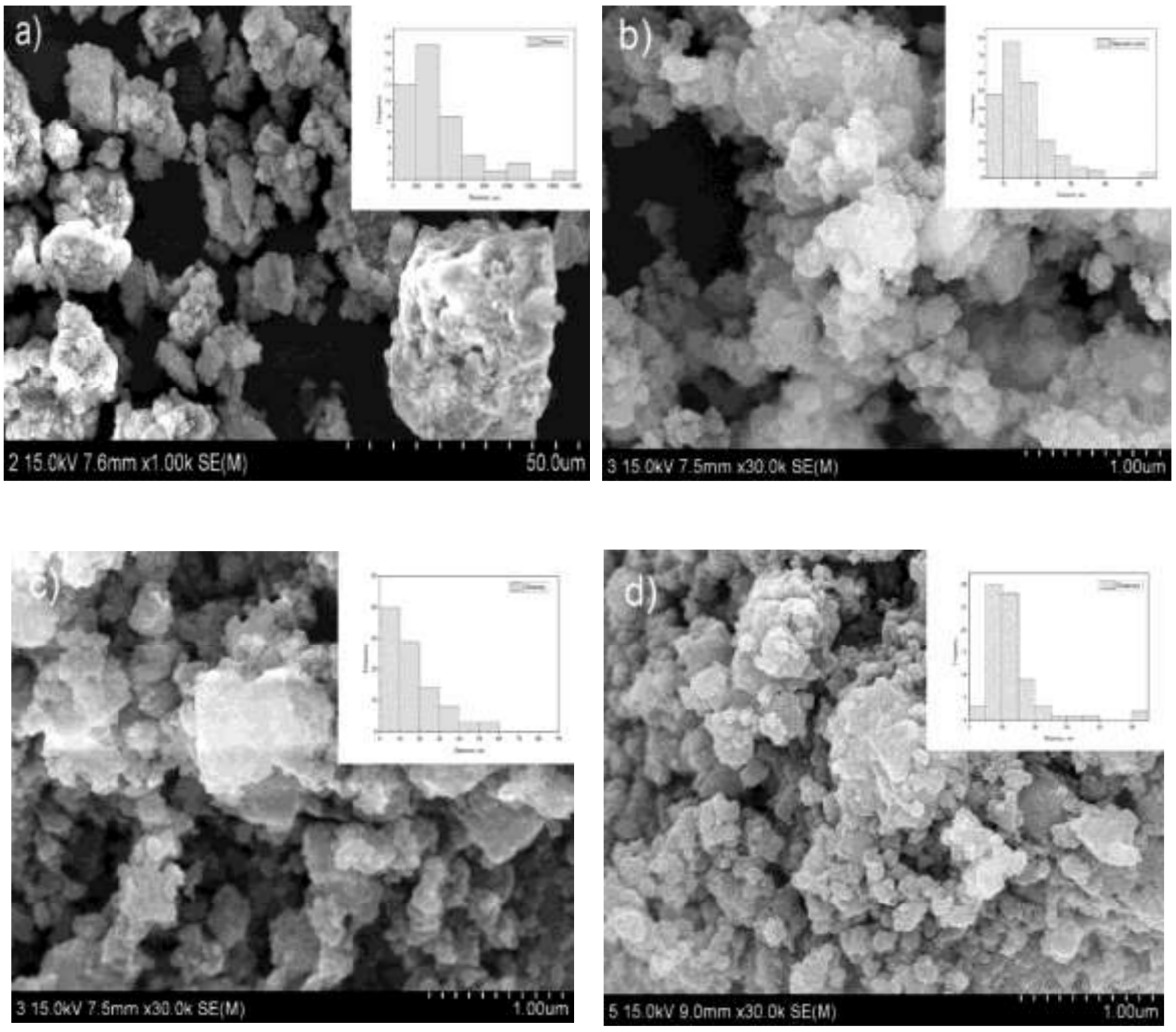


Figure 2. SEM images of mechanically activated black dross: (**a**) as-received; (**b**) milled for 1 h; (**c**) milled for 3 h; (**d**) milled for 7 h. (Milling speed: 400 rpm).

3.2. Leaching of the Mechanically Activated Dross in NaOH Solution

3.2.1. The Effect of Milling Time and Speed

The structure of mechanically activated black dross affects the leaching behavior of the oxides in dross. In ball milling treatment, milling time and milling speed are two parameters that lead to a change in structure of the mechanically activated materials. Therefore, the milling time effect was investigated. After the black dross was water-leached, the residues were mechanically activated at

400 rpm by increasing the milling time from 1 to 10 h. This mechanically activated dross was leached in a 5 M NaOH solution at 50 °C for 2 h at a pulp density of 20 g/L and a stirring speed of 200 rpm. Figure 3 shows that only alumina and silica were dissolved into the 5 M NaOH solution, while the other oxides were not. The leaching percentages of alumina and silica were 50% and 30%, respectively, and were rather constant, irrespective of the ball milling time.

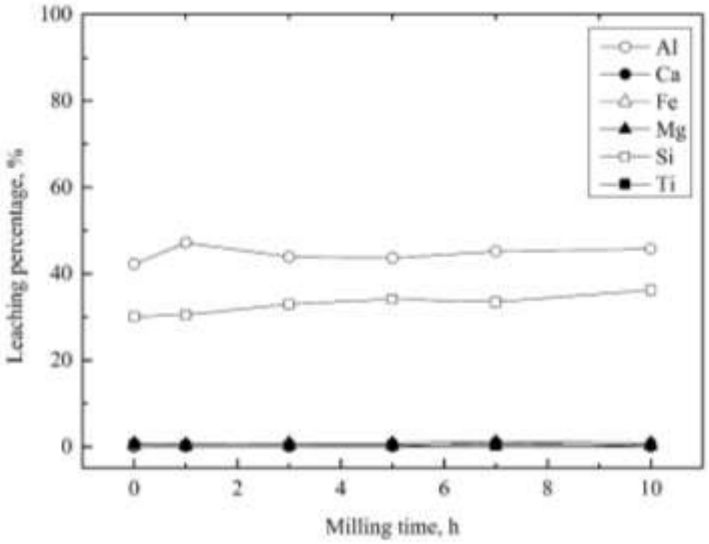


Figure 3. The effect of milling time on the leaching of the oxides from the mechanically activated dross in a 5 M NaOH solution at 50 °C. (stirring speed: 200 rpm, pulp density: 20 g/L).

Table 2 shows that average crystallite size decreased rapidly from 52.6 to 45.0 nm as milling time increased to 5 h, but the decrease in crystallite size was diminished with the further increase in milling time from 5 to 10 h. The variation in the crystallite size together with the change in morphology of the mechanically activated dross with milling time agrees well with the leaching data shown in Figure 3 [20].

In order to investigate the effect of milling speed on the leaching behavior of the dross, the dross was mechanically activated by varying milling speed from 250 to 700 rpm. These mechanically activated dross was leached using a 5 M NaOH solution at a pulp density of 20 g/L, 50 °C for 2 h. The leaching percentage of alumina and silica was about 45 and 25%, respectively, in the milling speed range of 250–500 rpm, while other oxides were not dissolved (see Figure 4). As milling speed increased from 550 to 700 rpm, a remarkable change in the leaching behavior of the oxides, except alumina, was observed. The leaching percentage of silica decreased from 25 to 5% with an increase in milling speed from 550 to 700 rpm, while that of Ca, Fe, Mg, and Ti oxides was slightly increased.

High milling speed causes defects and a decrease in diffusion length in the microstructure of mechanically activated samples, which enhances the diffusivity of the components [21]. This might be the reason why the leaching percentages of Ca, Fe, Mg, and Ti oxides were increased with the increase in milling speed from 550 to 700 rpm. The constant leaching percentage of alumina with milling speed might be related to the formation of large clusters, which prevents the movement of the NaOH solution into smaller nanoparticles containing alumina. Figure 5 shows the SEM images of the dross before ball milling and ball milling at 400 and 700 rpm. It can be seen that the mechanically activated dross at high milling speed became agglomerated. Namely, fine particles with extremely high surface energy tend to be agglomerated to reduce their surface area [22]. This led to a decrease in the leaching percentage of silica as the milling speed increased from 500 to 700 rpm. The optimum rotation speed for the selective dissolution of alumina from the mechanically activated dross was found to be 400 rpm in terms of the negligible dissolution of impurities such as Ca, Fe, Mg, and Ti oxides and the filtration problem.

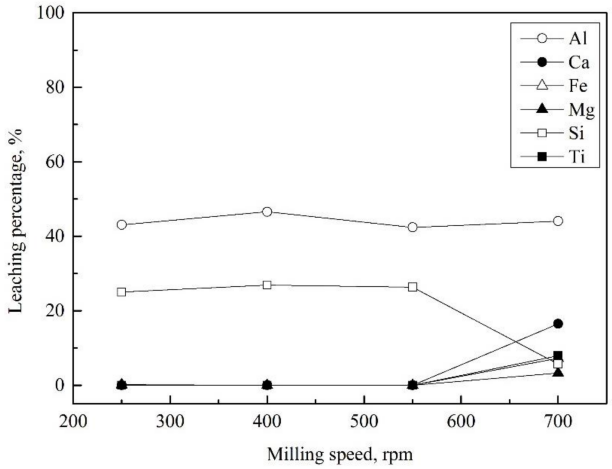


Figure 4. The effect of milling speed on the leaching of the oxides from the mechanically activated dross in a 5 M NaOH solution at 50 °C. (reaction time: 2 h, pulp density: 20 g/L).

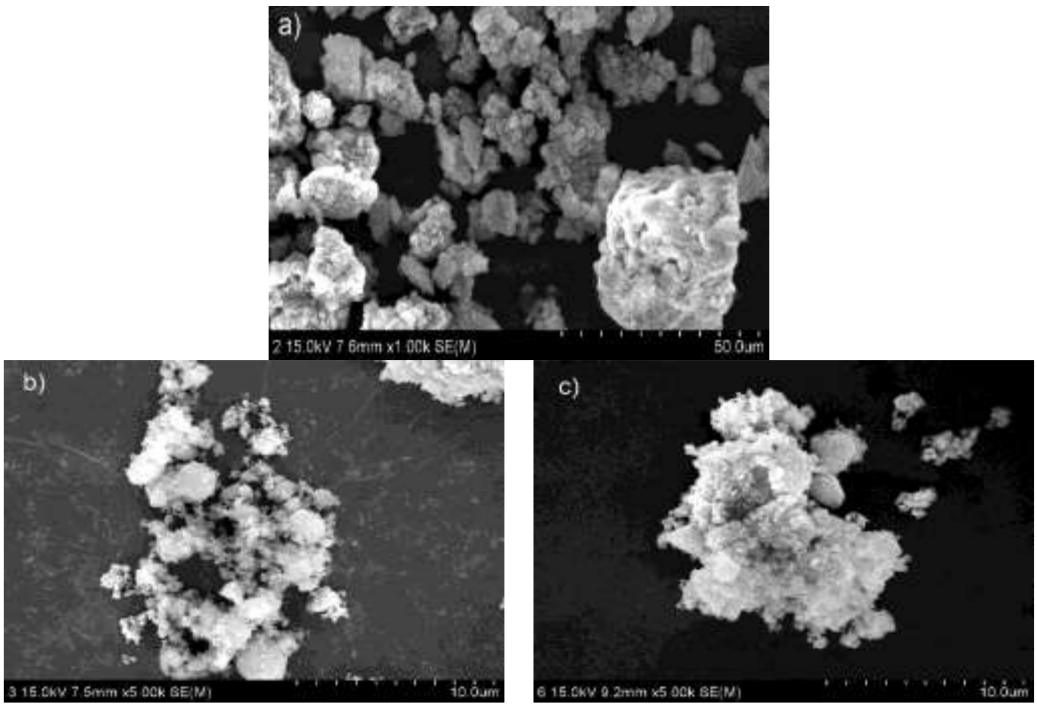
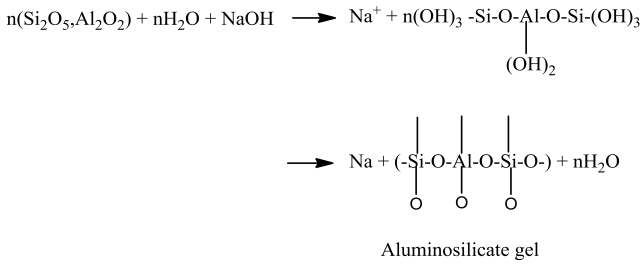


Figure 5. SEM images of the dross before and after ball milling: (**a**) as-received; (**b**) milled at 400 rpm, (**c**) milled at 700 rpm.

3.2.2. The Effect of NaOH Concentration

The effect of NaOH concentration on leaching behavior of mechanically activated dross was investigated by varying NaOH concentration from 1 to 7 M at 50 °C for 2 h. For this purpose, the dross was mechanically activated at 400 rpm for 1 h. Figure 6 displays the variation in leaching percentage of the components in dross with NaOH concentration. The leaching percentage of alumina and silica rose from 36 and 8% to 46 and 27%, respectively, as NaOH concentration increased up to 5 M and then slightly decreased with the further increase in NaOH concentration. It has been reported that a 5 M NaOH solution is the best condition to dissolve alumina from the dross without mechanical activation [11]. No oxides of Ca, Fe, Mg, and Ti were dissolved at any NaOH concentration range studied. A low NaOH concentration is not enough to drive the leaching reaction to its maximum,

while a high NaOH concentration leads to the alkaline hydrolysis of the issolved alumina and silica [23]. In addition, a small amount of dissolved alumina might react with silica to



(2)

form precipitates of sodium alumina silicate at high NaOH concentrations [24]. The formation of sodium alumina silicate can be schematically described as Equation (2) [25].

Thus, the leaching percentage of alumina and silica slightly decreased when NaOH concentration was in 5–7 M. Since the highest leaching percentage of alumina was obtained at 5 M NaOH, further leaching experiments were conducted using a 5 M NaOH solution.

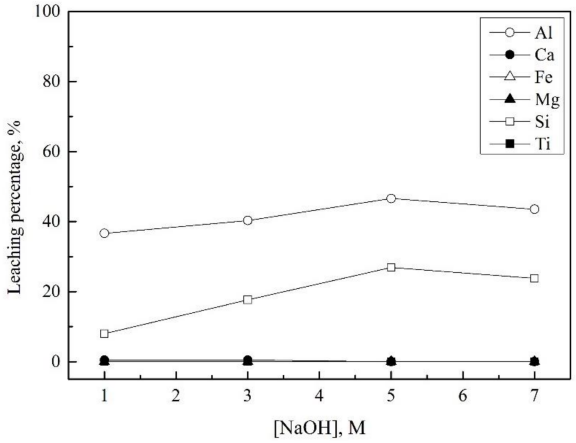


Figure 6. The effect of NaOH concentration on the leaching of the oxides from the mechanically activated dross at 50 °C. (reaction time: 2 h, stirring speed: 200 rpm, pulp density: 20 g/L).

3.2.3. The Effect of Temperature

In order to investigate the effect of temperature on the dissolution of oxides in dross, the dross mechanically activated at 400 rpm for 1 h was leached by varying temperature from 30 to 100 °C for 2 h. In these experiments, a 5 M NaOH solution was used, and the pulp density was kept at 20 g/L. The leaching percentage of alumina and silica increased from 40 and 19% to 47 and 37%, respectively, as temperature increased from 30 to 100 °C, while that of other oxides was negligible (see Figure 7). The enhancement in leaching percentage of alumina and silica at high temperatures is related to the increase in the energy available for atomic and molecular collisions, which accelerate the interaction between hydroxyl ions with alumina and silica [26].

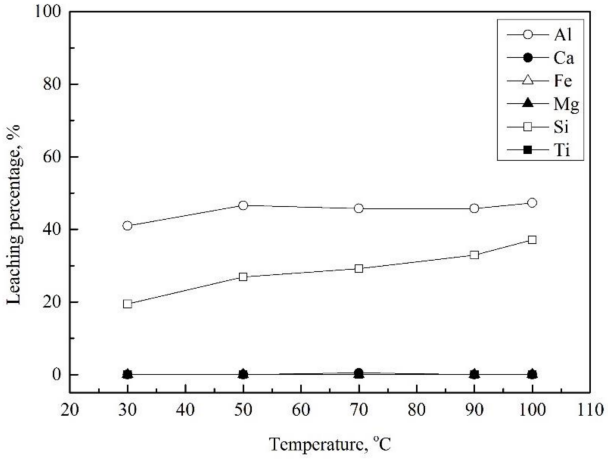


Figure 7. The effect of reaction temperature on the leaching of the oxides from the mechanically activated dross in a 5 M NaOH solution. (reaction time: 2 h, stirring speed: 200 rpm, pulp density: 20 g/L).

3.2.4. The Effect of Pulp Density

In the leaching process, pulp density generally affects productivity. Therefore, the effect of pulp density on the leaching behavior of the dross mechanically activated at 400 rpm for 1 h was investigated by varying pulp density from 20 to 120 g/L. In these experiments, the mechanically activated dross was leached using a 5 M NaOH solution with a reaction time of 2 h at 50 °C. As the pulp density increased from 20 to 120 g/L, the leaching percentage of alumina slightly decreased (see Figure 8). The leaching percentage of silica decreased rapidly with the increase in pulp density, and no silica was dissolved when pulp density was higher than 100 g/L. Moreover, the oxides of Ca, Mg, Fe, and Ti were not dissolved in the whole range, so pure alumina solution was obtained by adjusting the pulp density.

As pulp density increases, the mass of NaOH available for the leaching reaction becomes reduced and the solution becomes more viscous, which results in an increase in the mass transfer resistance at the liquid–solid interface [8]. Therefore, it is expected that the leaching percentage of alumina and silica would be decreased with the increase in pulp density. The leaching behavior of alumina agrees well with this trend. The rapid decrease in the leaching percentage of silica might be related to the precipitation of the dissolved silica by reaction with both caustic soda and dissolved alumina, the reaction steps of which are shown below [27–29]:

$$Al_2O_3 \cdot SiO_2 \cdot 2H_2O_{(s)} + 6NaOH_{(aq)} = 2Na_2SiO_{3(aq)} + 2NaAlO_{2(aq)} + 5H_2O \quad (3)$$

$$6Na_2SiO_{3(aq)} + 6NaAlO_{2(aq)} + Na_2X_{(aq)} + 12H_2O = 3(Na_2O.Al_2O_3.2SiO_2.nH_2O).Na_2X_{(s)} + 12NaOH_{(aq)} \quad (4)$$

where X represents anions like CO_3^{2-}, SO_4^{2-}, $Al\ O_2^{-}$, $2OH^{-}$, and $2Cl^{-}$.

Figure 8 indicates that selective leaching of alumina over other oxides from the mechanically activated dross is possible by adjusting the pulp density in a 5 M NaOH solution. Therefore, the pulp density of 100 g/L was suggested as the best condition for selective leaching of alumina in terms of the highest purity of alumina in the leaching solution.

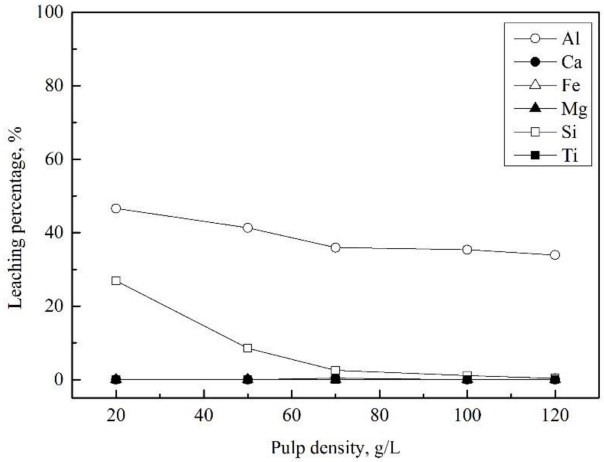


Figure 8. The effect of pulp density on the leaching of the oxides from the mechanically activated dross in a 5 M NaOH solution at 50 °C. (reaction time: 2 h, stirring speed: 200 rpm).

3.2.5. The Effect of Leaching Time

The effect of leaching time was investigated using a 5 M NaOH at a pulp density of 100 g/L and 50 °C. In these experiments, the dross mechanically activated at 400 rpm for 1 h was leached by varying leaching time from 2 to 10 h. Within our experimental range, the leaching time did not show any effect on the leaching behavior of the oxides in the mechanically activated dross (see Figure 9). The leaching percentage of alumina was about 35%, while that of other oxides was nearly zero at any leaching time. The purity of Al in the leaching solution was 98.8% at the leaching time of 2 h. The composition of the leaching solution and purity of Al in the solution after NaOH leaching is shown in Table 3.

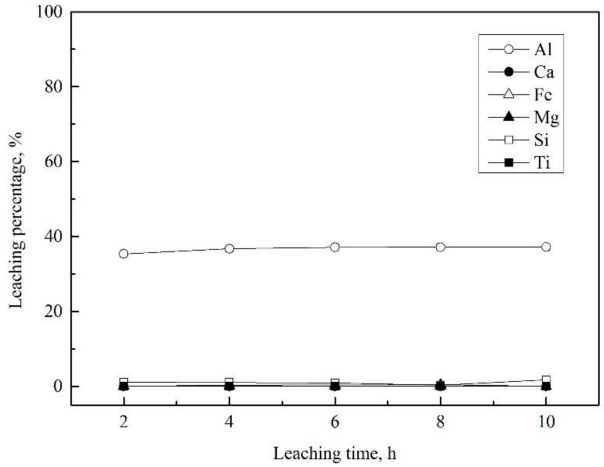


Figure 9. The effect of reaction time on the leaching of the oxides from the mechanically activated dross in a 5 M NaOH solution at 50 °C. (stirring speed: 200 rpm, pulp density: 20 g/L).

Table 3. The composition of the leaching solution and the purity of Al in the solution after NaOH leaching of the mechanically activated dross at the optimum condition.

Composition	Al	Si	Purity of Al (%)
Concentration (ppm)	12,726.0	149.0	98.8

4. Conclusions

In order to recover pure alumina from black dross, a process consisting of ball milling treatment followed by NaOH leaching was developed. First, the salts present in the black dross were removed

by water leaching at 90 °C. The effect of ball milling time on the crystallite size and the change in the morphology of the mechanically activated dross was analyzed via XRD and SEM images, respectively. Milling speed had a profound effect on the leaching behavior of silica and the oxides of Ca, Fe, Mg, and Ti. The optimum milling speed and time for the selective dissolution of alumina from the mechanically activated dross were found to be 400 rpm for 1 h from the leaching experiments on the basis of the negligible dissolution of impurities such as Ca, Fe, Mg, and Ti oxides. The leaching behavior of the mechanically activated dross was investigated as a function of NaOH concentration, leaching time and temperature, and pulp density. In most of the leaching conditions, both alumina and silica were dissolved, but the oxides of Ca, Fe, Mg, and Ti were not. Among the leaching variables, pulp density showed a remarkable effect on the leaching of silica, so only alumina was dissolved as the pulp density increased. At the optimum leaching conditions (5 M NaOH, 50 °C, 2 h, pulp density of 100 g/L) for the selective dissolution of the mechanically activated dross, the purity of Al in the leaching solution was higher than 98%. However, the leaching percentage of alumina at these conditions was only around 35%, so further work is needed to improve the leaching of alumina from the mechanically activated dross.

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Author Contributions: Man Seung Lee designed the research and helped analyze data. Thi Thuy Nhi Nguyen performed experiments and wrote the paper. Thi Hong Nguyen participated in the discussion of the results.

Conflicts of Interest: The authors declare no conflict of interest.

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