J. of Korean Inst. of Resources Recycling
Vol. 26, No. 3, 2017, 53-60
https://doi.org/10.7844/kirr.2017.26.3.53
pISSN : 1225-8326 eISSN : 2287-4380

≫ 연구논문 ≪

물과 수산화나트륨용액에 의한 블랙 드로스의 처리

행위동* · 안병두 · §이만승***

*목포대학교 신소재공학과, **㈜디에스리퀴드

Treatment of Black Dross with Water and NaOH Solution

Wei Dong Xing*, Byung Doo Ahn and §Man Seung Lee***

**Department of Advanced Material Science & Engineering, Institute of Rare Metal,*
Mokpo National University, Chonnam 534-729, Republic of Korea
***DSLiquid Co., Ltd*

요 약

블랙드로스에는 금속 알루미늄, 알루미나, 실리카, 산화마그네슘, 가용성 염 및 미량 성분이 함유되어 있다. 블랙드로스를 사용가능한 재료로 전환시키기 위해서는 실리카의 양을 조절하는 것이 중요하다. 먼저 가용성 염인 염화나트륨과 염화칼륨은 50°C에서 물에 용해되었다. 물세척 후 잔사에 함유된 실리카, 알루미나, 산화마그네슘 및 산화타이타늄의 침출거동을 NaOH의 농도와 반응온도를 변화시키며 조사하였다. 반응온도 25~95°C에서 알루미나의 침출율은 온도에 비례하나 실리카의 침출의 경우에는 최적 온도가 존재하였다. 한편 2~6 M의 NaOH용액에 산화마그네슘은 전혀 용해되지 않았다. 5 M의 NaOH와 95°C에서 알루미나와 실리카의 침출율은 각각 80과 68%이었다.

주제어 : 블랙드로스, 알루미나, 실리카, 침출, 수산화나트륨

Abstract

Black dross contains metallic aluminium, alumina, silica, MgO, soluble salts together with minor ingredients. Control of silica in black dross is important in transforming the black dross into usable materials. First, most of the soluble salts (KCl and NaCl) in black dross were dissolved in water at reaction temperature of 50°C. Leaching behavior of silica, alumina, MgO and TiO_2 from the residue after water treatment was investigated by varying NaOH concentration and reaction temperature. Reaction temperature (25~95 °C) was favorable to the leaching of alumina but an optimum temperature existed for silica. MgO was not dissolved at all in the NaOH concentration range from 2 to 6 M. At the leaching condition of 5 M NaOH and reaction temperature of 95°C, approximately 80% of alumina and 68% of silica was dissolved.

Key words : alumina, silica, black dross, leaching, NaOH

· Received : May 8, 2017 · Revised : May 19, 2017 · Accepted : May 26, 2017
§ Corresponding Author : Man-Seung Lee (E-mail : mslee@mokpo.ac.kr)
Department of Advanced Materials Science & Engineering, Mokpo National University, 1666 Yeongsan-ro, Cheonggye-myeon, Muan-gun, Chonnam, 58554, Korea

1. Introduction

Aluminum dross is a name for the mixtures of aluminum metal and aluminum oxide together with other components. Three kinds of drosses (white dross, black dross and slat) are produced during the melting of aluminum scraps and used beverage cans owing to oxidation of aluminum. The approximate composition of metallic Al, Al_2O_3 and salt in each dross is listed in Table 1[1-3]. The salt generally consists of chlorides. The disposal of black dross results in several toxic gases such as hydrogen and ammonia and thus in serious pollution of the environment[4].

In general, black dross is produced from the melting of white dross to recover the aluminum metal in white dross. Since there are some aluminum metals in the black dross, lots of work has been done to recover the aluminum metal from the black dross. Moreover, many methods were investigated to transform the hazardous materials in black dross into green materials for the use in construction by adding some agents[5-8]. Table 2 represents several methods with the advantages and disadvantages to treat the black dross. Among the methods listed in Table 2, aqueous chemical processing method can recover aluminum metal and aluminum oxide. Since black dross contains alumina and silica together with other minor ingredients, control of the amount of silica and minor oxides is important in recovering some materials from the black dross.

Table 1. Approximate composition of Aluminum by-products

	% metallic Al	% Aluminum oxide	% salt
White dross	15-80	20-85	0-1
Black dross	7-35	30-50	30-50
Salt cake	3-10	20-60	20-80

Silica and alumina can form various aluminosilicates in presence of potassium and sodium ions and thus the structure and chemical properties of the silica and alumina in black dross depend on the melting conditions and the treatment methods. For example, thermal treatment prior to leaching can improve the dissolution of alumina owing to the destruction of crystalline mullite phase ($3Al_2O_3 \cdot 2SiO_2$) releasing Al_2O_3 to be easily leached[9,10].

In leaching, increase of the reaction temperature is efficient in promoting the dissolution of Al and Si contained in the materials. Chengyou Wu et al.[11] reported that leaching percentage of Al from coal fly ash with sulfuric acid under the pressure at 180°C for 4 h was around 80% and pure alumina was recovered from the leaching solution. A. Shemi et al.[12] obtained 64% and 85% of aluminum are leached using sulfuric acid solution and acetylacetone, respectively after almost 8 h leaching. Some researchers[13-15] reported the use of strong sulfuric acid to dissolve around 90% of Al from aluminum dross. However, gelatinous silica can be formed from the dissolution of silicates with strong acidic solution, which makes the filtration after leaching troublesome during the leaching treatment of black dross[16].

In contrast, the use of alkaline solution can circumvent the formation of gelatinous silica during the treatment of black dross at high temperatures. P. E. Tsakiridis et al.[17] reported that 57% of Al was recovered from black dross by alkaline pressure leaching at 240°C followed by water washing. Furthermore, some salts such as $Ca(OH)_2$, $NaAl(OH)_4$ and $(NH_4)_2SO_4$ were added to improve the dissolution of Al at high reaction temperature. The disadvantage of employing strong alkaline solution at high temperature is the corrosion of reaction

Table 2. Advantages and disadvantages of the processes for the treatment of Aluminum dross

	Advantages	Disadvantages
Melting Crushing/grinding	– Avoidance of thermal or chemical processing	– Creation of dusts – Production of a reactive material
Aqueous chemical processing	– Energy saving	– Difficulty in controlling the quality of final product – Treatment of off-gas – Process complexity

vessel at these severe conditions[10,18,19].

The present work investigated the possibility of controlling the amount of silica in black dross by aqueous treatment method. Since there are some salts in black dross, the black dross was first treated by water to recover the salts. After the dissolution of salts by water, the leaching percentage of silica, alumina and other minor ingredients in black dross was investigated by varying both the reaction temperature and NaOH concentration.

2. Experimental

2.1. Materials

The black dross employed in this work was supplied from a company in Korea. The major components of the black dross were Al_2O_3, MgO, NaCl and KCl. In addition, there were some base metallic elements such as Al and Mg, the presence of which was manifested in the x-ray diffraction (XRD) patterns in Fig. 1. Since the weight of Mg metal in the black dross is generally very small, it is very difficult to determine the existence of metallic Mg in the residue by XRD. Table 3 shows the main chemical composition of the black dross determined by inductively coupled plasma-optical emission spectrometer OPTIMA 8300 (ICP-AES, Perkin Elmer, USA).

2.2. Experimental Procedure

The black dross was put into the leaching solution

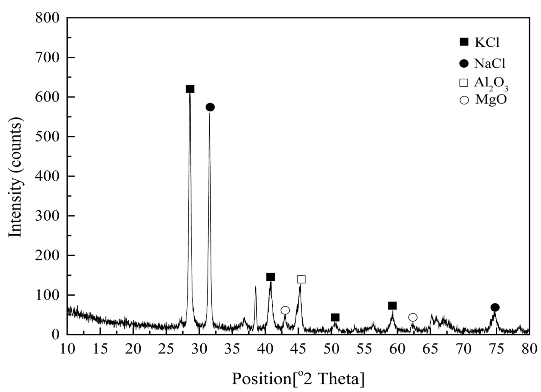

Fig. 1. XRD pattern of the black dross provided by a company in Korea.

Table 3. The chemical composition of Al dross provided by a company in Korea (wt%)

Element	Fe	Ca	Al	Mg	Na	K	Si	Ti
Contents	0.31	0.10	5.42	1.10	3.84	8.72	6.89	0.63

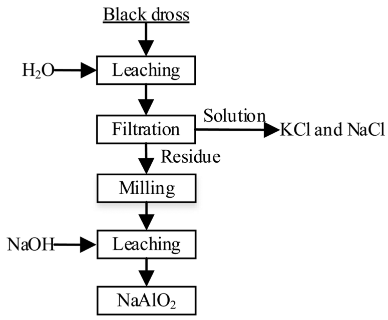

Fig. 2. The experimental procedure for the treatment of the black dross.

in a 250 ml three-neck flat bottom beaker on the hot plate. During all the experiments, the experimental setting was kept closed by the covers to prevent the loss of the solution, and the mixed solution was stirred well by magnetic stirrer bar. After the leaching experiments, the residue was separated from the solution with the Bucher filter and then dried in the oven. The leaching percentage of component A was calculated by using Eq. (1).

$$\text{Leaching percentage of A} = \frac{W_{A,\,initial} - W_{A,\,residue}}{W_{A.initial}} \times 100\% \quad (1)$$

where $W_{A,\,initial}$ and $W_{A,\,residue}$ represent the weight of A in the materials before and after the leaching experiments.

Fig. 2 shows the experimental procedure employed in this work to investigate the leaching behavior of the components in the black dross.

3. Results and Discussion

3.1. Pretreatment of Al black dross by water

There are large amounts of soluble salts in the black dross. These salts should be recovered for further use in the treatment of the black dross. Therefore, the black

Table 4. The change in the mass of the components in the black dross during the treatment with H_2O

Temperature, °C	30	50			70	90
Material, g	80.00	80.15	80.15	80.00	80.00	80.00
Residue, g	46.00	50.09	49.78	49.82	49.79	49.00
Dissolution percentage (%)	57.5	62.5	62.1	62.3	62.2	61.3

dross was first pretreated by distilled water to recover most of soluble KCl and NaCl and thus to lessen the consumption of leaching reagents[13].

The effect of reaction temperature on the dissolution of soluble salts is shown in Table 4. The experimental conditions were set as follows, reaction time, 2 h; stirring speed, 200 rpm; pulp density, 100 g/L. It is seen in Table 4 that the increase in reaction temperature had a slight effect on the dissolution of NaCl and KCl. Table 4 indicates that the dissolution percentage of soluble salts was almost constant in the temperature range from 50 to 90°C and thus it is better to do the pretreatment at temperatures lower than 50°C. Many bubbles were produced during the treatment with distilled water. The production of the bubbles may be related to the dissolution of Mg in water, producing hydrogen gas (Eq. (2)) together with some other gases due to the high temperature solution[4]. Eq. (2) represents the dissolution of Mg in water which does not contain dissolved oxygen.

$$Mg + H_2O = Mg(OH)_{2,solid} + H_{2(g)} \quad (2)$$

After the treatment of the black dross with water, the residue was crushed for further leaching experiments with NaOH solution. Compared to the composition of black dross (Table 3), 95% of K and 86% Na were dissolved from the dross by water treatment. From the XRD patterns of residue (see Fig. 3), the main ingredients of the residue after water treatment were found to be Al_2O_3 and MgO. Table 5 shows the chemical composition of the residue with different particle size. Generally, the small particles have larger specific surface area and are favorable for the dissolution of black dross. Therefore, the residues with particle size less than 100 μm were employed in the NaOH leaching experiments.

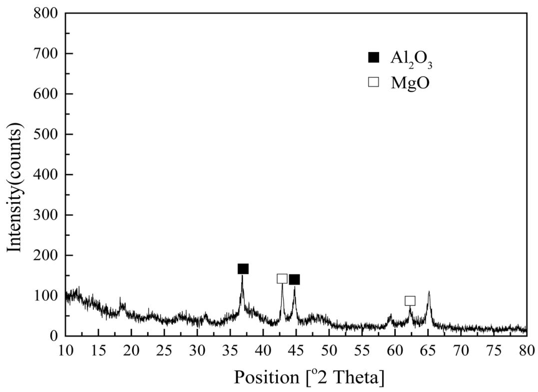

Fig. 3. The XRD pattern of black dross after water treatment.

Table 5. The chemical composition of black dross after water leaching (Unit: wt.%)

Element	Fe	Ca	Al	Mg	Na	K	Si	Ti
< 100 μm	0.42	0.21	13.0	0.60	0.21	0.41	0.42	1.16
100~200 μm	0.27	0.01	8.05	0.04	0.16	0.26	0.62	1.18
200~300 μm	0.24	0.07	7.03	0.06	0.48	0.34	1.43	0.96
300~500 μm	0.39	0.04	24.7	0.05	0.38	0.12	1.52	0.61
750 μm	0.27	0	34.7	0	0.19	0.11	5.76	0.04

3.2. Leaching of the residue with NaOH solution

Generally, increasing the reaction temperature and solution concentration could increase the activity of the reactants and thus facilitate the reaction. For this reason, effect of reaction temperature on the leaching of the ingredients in the residue was investigated by varying NaOH concentration from 2 to 6 M and the results are shown in Figs. 4 to 8. In these experiments, the reaction time, stirring speed and pulp density were 2 h, 200 rpm and 120 g/L, respectively.

Fig. 4 shows that the leaching percentage of alumina increased a little as reaction temperature increased from 25 to 65°C and then was almost constant at 80% with further increase of temperature. Nevertheless, the leaching percentage of silica decreased slowly and remained at 60% in the reaction temperature employed in this work. Therefore, it is known that reaction temperature had not a remarkable effect on the dissolution of silica and alumina from the residue. Although, there was some fluctuation in the leaching percentage of TiO_2, no Mg

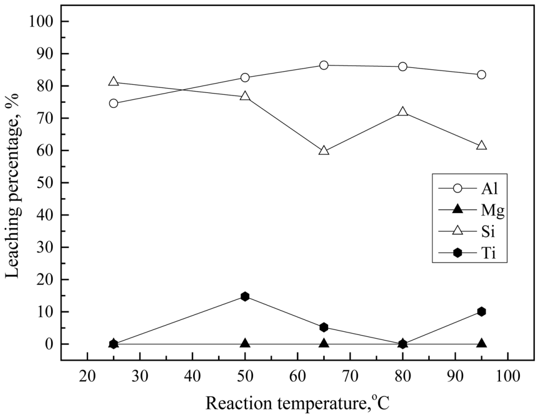

Fig. 4. The effect of reaction temperature on the leaching percentage of the components in black dross by 2 M NaOH solution. (reaction time, 2 h; stirring speed, 200 rpm; pulp density, 120 g/L)

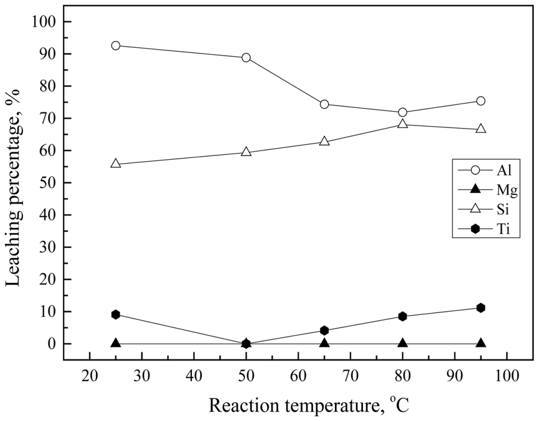

Fig. 6. The effect of reaction temperature on the leaching percentage of the components in black dross by 4 M NaOH solution. (reaction time, 2 h; stirring speed, 200 rpm; pulp density, 120 g/L)

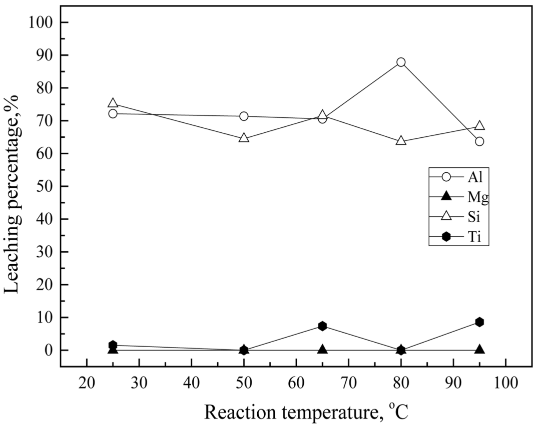

Fig. 5. The effect of reaction temperature on the leaching percentage of the components in black dross by 3 M NaOH solution. (reaction time, 2 h; stirring speed, 200 rpm; pulp density, 120 g/L)

was dissolved from the MgO in the balck dross. The formation of insoluble $Mg(OH)_2$ in alkaline solution is the cause of negligible dissolution of MgO from the balck dross.

Fig. 5 is the leaching results with 3 M NaOH solution. Compared to 2 M NaOH solution, the leaching percentage of silica increased a little to 70%. In the case of alumina, its leaching percentage decreased a little, which might be ascribed to the interaction between SiO_3^{2-} and $Al(OH)_4^-$ [20,21]. The leaching behavior of TiO_2 and MgO at this condition was similar to that at 2 M NaOH solution.

When 4 M NaOH solution (see Fig. 6) was employed, as the reaction temperature increased, the leaching percentage of alumina decreased from 90% to 75% and then remained constant at 65°C. The leaching percentage of silica increased a little as the reaction temperature increased to 95°C. However, with the further increase of NaOH concentration, the leaching percentage of silica decreased little owing to the interaction of dissolved silica with either $Al(OH)_4^-$ [22] or other metal ions, such as Ca^{2+}, Mg^{2+}, Na^+ and thus left in the residues. At this leaching condition, the formation of gelatinous silica was observed, which might be ascribed to the reaction between $Si(OH)_4$ and $Al(OH)_3$. The solution was viscous, which had negative effect on the leaching of the ingredients in the black dross owing to the decreased mass transfer coefficients[6,23].

Fig. 7 displays the effect of reaction temperature on the leaching of alumina and silica with 5 M NaOH solution. The leaching percentage of alumina increased a little as the temperature increased and remained constant from 65°C. However, 65% of silica was dissolved into the solution and kept a constant at all conditions. When the NaOH concentration was increased to 6 M (see Fig. 8), the leaching percentage of alumina was 80% and

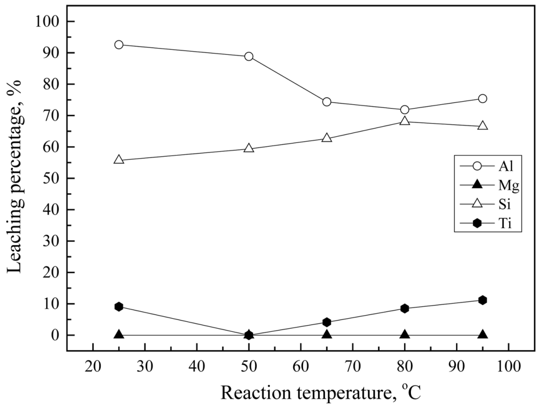

Fig. 7. The effect of reaction temperature on the leaching percentage of the components in black dross by 5 M NaOH solution. (reaction time, 2 h; stirring speed, 200 rpm; pulp density, 120 g/L)

kept a constant as the temperature increased. Nevertheless, the leaching percentage of silica decreased steadily. In strong NaOH solution, complex hydrated silicates could be formed and precipitated, which would have negative effect on the leaching of silica from the black dross[16].

From the leaching experiments of the residue by varying the concentration of NaOH and reaction temperature, it was found that the formation of aluminosilicate glass and zeolite affected the leaching of silica and alumina from the residue[22]. Moreover, the presence of Na^+ and K^+ in the leaching solution would facilitate the crystallization of zeolite in the NaOH solution and thus lower the leaching percentage[20]. Therefore, it is very important to recover the salt in the black dross by water washing.

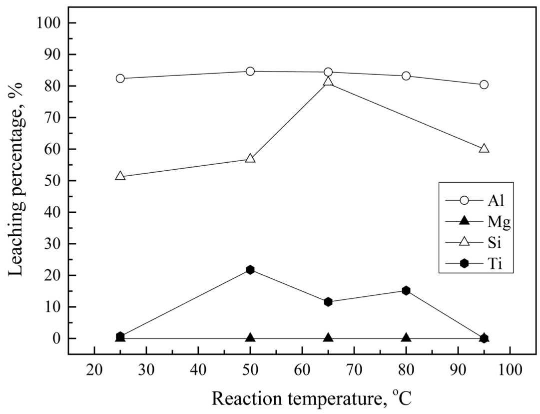

Fig. 8. The effect of reaction temperature on the leaching percentage of the components in black dross by 6 M NaOH solution. (reaction time, 2 h; stirring speed, 200 rpm; pulp density, 120 g/L)

Meanwhile, at all the experimental conditions of NaOH concentration (2 to 6 M), all the Mg was not dissolved and left in the residue. Although there was not distinct relation between reaction conditions and the leaching percentage of TiO_2, some Ti was dissolved into the solution. The adherence of some TiO_2 to the black dross may cause the fluctuations in the leaching percentage of TiO_2 with reaction temperature.

4. Conclusions

In order to control the amount of silica in the black dross, leaching experiments were performed with the residue which was obtained by washing treatment with water. In the treatment of the black dross with water, most of the salts (NaCl and KCl) were dissolved at temperatures lower than 50°C. The effect of reaction temperature and NaOH concentration on the dissolution of alumina, silica, MgO and TiO_2 in the residue was investigated. MgO was not dissolved at all in the experimental conditions tested in this work. Alumina and silica were dissolved into NaOH solution. The leaching percentage of alumina was proportional to reaction temperature but there was an optimum reaction temperature for the dissolution of silica. At the optimum condition of 5 M NaOH solution and reaction temperature of 95°C, the leaching percentage of alumina and silica was around 80% and 68%, respectively.

Acknowledgements

This work was supported by the Global Excellent Technology Innovation of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry &Energy, Republic of Korea (No. 20165010100880).

References

1. Shinzato, M. C. and Hypolito, R., 2005 : Solid waste

from aluminum recycling process: characterization and reuse of its economically valuable constituents. Waste Management, 25(1), pp. 37-46.

2. Scharf, Christiane and Ditze, André, 2015 : Recycling of black dross containing rare earths originating from melting and recycling of magnesium alloys. Hydrometallurgy, 157, pp. 140-148.
3. Hwang, J. Y., Huang, X., and Xu, Z., 2006 : Recovery of metals from aluminum dross and saltcake. Journal of Minerals & Materials Characterization & Engineering, 5(1), pp. 47-62.
4. Tsakiridis, P. E., 2012 : Aluminium salt slag characterization and utilization--a review. Journal of hazardous materials, 217-218, pp. 1-10.
5. Yoshimura, H. N., Abreu, A. P., Molisani, A. L., Camargo, A. C. de, Portela, J. C. S., and Narita, N. E., 2008 : Evaluation of aluminum dross waste as raw material for refractories. Ceramics International, 34(3), pp. 581-591.
6. Rattanasak, Ubolluk, and Chindaprasirt, Prinya, 2009: Influence of NaOH solution on the synthesis of fly ash geopolymer. Minerals Engineering, 22(12), pp. 1073-1078.
7. David, E. and Kopac, J., 2012 : Hydrolysis of aluminum dross material to achieve zero hazardous waste. Journal of hazardous materials, 209-210, pp. 501-509.
8. Somna, Kiatsuda, Jaturapitakkul, Chai, Kajitvichyanukul, Puangrat, and Chindaprasirt, Prinya, 2011 : NaOH-activated ground fly ash geopolymer cured at ambient temperature. Fuel, 90(6), pp. 2118-2124.
9. Li, Jinping, Gan, Jinhua, and Li, Xianwang, 2009 : Leaching of aluminum and iron from boiler slag generated from a typical Chinese Steel Plant. Journal of hazardous materials, 166(2-3), pp. 1096-1101.
10. Doucet, Frédéric J., Mohamed, Sameera, Neyt, Nicole, Castleman, Barbara A., and Merwe, Elizabet M. van der, 2016 : Thermochemical processing of a South African ultrafine coal fly ash using ammonium sulphate as extracting agent for aluminium extraction. Hydrometallurgy, 166, pp. 174-184.
11. Wu, Chengyou, Yu, Hongfa, and Zhang, Hui-fang, 2012 : Extraction of aluminum by pressure acid-leaching method from coal fly ash. Transactions of Nonferrous Metals Society of China, 22(9), pp. 2282-2288.
12. Shemi, A., Mpana, R. N., Ndlovu, S., Dyk, L. D. van, Sibanda, V., and Seepe, L., 2012 : Alternative techniques for extracting alumina from coal fly ash. Minerals Engineering, 34, pp. 30-37.
13. Dash, B., Das, B. R., Tripathy, B. C., Bhattacharya, I. N., and Das, S. C., 2008 : Acid dissolution of alumina from waste aluminium dross. Hydrometallurgy, 92(1-2), pp. 48-53.
14. Verbaan, B. and Louw, G. K. E., 1989 : A mass and energy balance model for the leaching of a pulverised fuel ash in concentrated sulphuric acid, Hydrometallurgy, 21, pp. 305-317.
15. Xiao, Jin, Li, Fachuang, Zhong, Qifan, Bao, Hongguang, Wang, Bingjie, Zhang, and Jindi Huang Yanbing, 2015 : Separation of aluminum and silica from coal gangue by elevated temperature acid leaching for the preparation of alumina and SiC. Hydrometallurgy, 155, pp. 118-124.
16. Habashi, Fathi, A Textbook of Hydrometallurgy. Metallurgie Extractive Quebec: 1993.
17. Tsakiridis, P. E., P. Vest, M. Schuster, and Agatzini-Leonardou, S., 2013 : Aluminium recovery during black dross hydrothermal treatment. Journal of Environmental Chemical Engineering, 1(1-2), pp. 23-32.
18. Li, Huiquan, Hui, Junbo, Wang, Chenye, Bao, Weijun, and Sun, Zhenhua, 2014 : Extraction of alumina from coal fly ash by mixed-alkaline hydrothermal method. Hydrometallurgy, 147-148, pp. 183-187.
19. Ma, Jiayu, Li, Zhibao, and Xiao, Qinggui, 2012 : A new process for Al_2O_3 production from low-grade diasporic bauxite based on reactive silica dissolution and stabilization in NaOH-NaAl$(OH)_4$ media. American Institute of Chemical Engineers, 58(7), pp. 2180-2191.
20. Murayama, Norihiro, Yamamoto, Hideki, and Shibata, Junji, 2002 : Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. Int. J. Miner. Process., 65, pp. 1-17.
21. Inada, Miki, Eguchi, Yukari, Enomoto, Naoya, and Hojo, Junichi, 2005: Synthesis of zeolite from coal fly ashes with different silica–alumina composition. Fuel, 84(2-3), pp. 299-304.
22. Jiang, Zhouqing, Yang, Jing, Ma, Hongwen, Wang, Le, and Ma, Xi, 2015 : Reaction behaviour of Al_2O_3 and SiO_2 in high alumina coal fly ash during alkali hydrothermal process. Transactions of Nonferrous Metals Society of China, 25(6), pp. 2065-2072.
23. Weng, L. and Sagoe-Crentsil, K., 2007 : Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part I – Low Si/Al ratio systems. Journal of Materials Science, 42(9), pp. 2997-3006.

행 위 동

- 2014 중국 Kunming Institute of Precious Metals 석사
- 현재 목포대학교 신소재공학과 박사과정

안 병 두

- 경희경학교 화학과 공학석사
- 현재 ㈜디에스리퀴드 부설연구소 소장

이 만 승

- 현재 목포대학교 신소재공학과 교수
- 당 학회지 제11권 1호 참조

회비 납부 안내

▣ 항상 본 학회에 관심을 가져 주신데 대해 진심으로 감사드립니다.

▣ 당 학회의 이사회 및 편집위원회를 통하여 학회운영의 어려움을 해결하는 방안으로 회비가 여러 해 미납된 회원을 분류해서 관리하는 것으로 논의가 되었으며, 학회지 지면을 통하여 회원여러분께 알려드리게 되었습니다.

▣ 정회원, 학생회원 중에 회비가 여러 해 미납된 회원께서는 8월 20일까지 회비를 꼭 납부해 주시기 바라며, 향후 년회비를 2년 이상 미납한 회원에게는 학회운영상 부득이 회지우송 및 기타 소식 관련 서비스도 중단할 것이오니 조속히 회비를 납부하여 주시기 바랍니다.

▣ **납부일** : 2017년 8월 20일(학회지 26권 4호(2017년 8월호) 부터 발송중지 예정)

▣ **납부방법** : 계좌이체 또는 지로입금(지로번호 7609637)
우리은행 : 1005 - 301 - 118587 예금주 : (사)한국자원리싸이클링학회

▣ 연락처 : 한국자원리싸이클링학회 사무국
전화 02-3453-3541~2, 팩스 3453-3540, E-mail : kirr@kirr.or.kr, http://www.kirr.or.kr