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Aluminium recovery from NALCO fly ash by acid digestion in thepresence of fluoride ion

[1]SUDEEP KUMAR SINGH,
Gandhi Institute of Excellent Technocrats, Bhubaneswar, India
[2]SOUMYA PRIYADARSINI DHIR,
Adarsha College of Engineering, Angul, Odisha, India

a b s t r a c t

The safe disposal and utilisation of coal fly ash (CFA) for value addition are still major problems worldwide. Al_2O_3 is a major valued material associated with it. Till date no methods are available to treat CFA for recovering its valued materials. Leaching of alumina from CFA in an economical way is very difficult, which either requires higher chemical consumption or application of stringent reaction conditions such as high temperature and pressure. In this paper a simple alternative method has been attempted to dissolve alumina from CFA. Addition of fluoride ion as HF improved the acid leaching performance of fly ash to a large extent. XRD data showed mullite, the alumina bearing phase, as the major phase which gets dissolved during leaching operation. A standard procedure for the precipitation of alumina can be employed after the leached solution is obtained.

1. Introduction

The power generation in India is around 2,00,000 MW at present and is going to be enhanced to 3,00,000 MW in near future. The coal is a major source of such power in India and going to be so as abundant coal is available. Indian coal contains higher amounts of ash (35–45%) thereby generating huge quantity of fly ash. The average quantity of fly ash generated in India at present is about 130 million tons (Emanul Haque, 2013). Coal fly ash is an incombustible residue produced by burning coal in thermal power plants. The nature of the coal decides the composition of fly ash. The silico-aluminous fly ash contains various valuable minerals such as mullite, quartz, hematite, magnetite, alpha-alumina, CaO, and TiO_2 in a matrix of aluminosilicate glass. Alumina, the major valued material is getting wasted due to unavailability of suitable processing options. The presence of high level (~65%) of silica poses serious problem in processing the fly ash for the recovery of alumina value through the Bayer method or through other conventional methods. Alternatively, the disposal of such huge quantity of fly ash also poses environmental problem due to the leaching of toxic elements to the biosphere which will pose serious problem in future. Although fly ash is being used for making roads, bricks, etc., the rate of production of fly ash is much higher than the rate of consumption. Disposal of unused fly ash is a huge problem due to limited availability of landfill sites and strict regulations. Geo-polymerisation of fly ash is one approach to immobilise the toxic elements. However, the widespread use of geo-polymers is currently restricted due to the lack of long term durability studies. One aspect of long term durability of geo-polymers is to study the leaching behaviour in aqueous medium. The alkalies used for geo-polymerisation are the major leachable entities in geo-polymers (Ly et al., 2007; Izquierdo et al.) making the process not 100% safe and thus, warrants further investigation. Therefore, the authors feel that some alternate work needs to be conducted for value added utilisation of fly ash.

In the United States, 25% of the fly ash is used as construction material and 75% as landfill (Tyson and Blackstock, 1996). The situation in India is not encouraging, about 15% is used for construction and other purposes and the rest is for landfill (Yao et al., 2014). It is very important to note that in India around 30 to 35 million tons of alumina is lost every year in fly ash. The greatest difficulty in fly ash processing is its high silica (~ 65%) content. The main alumina bearing mineral is mullite, therefore, unless mullite structure is broken, alumina recovery is impracticable.

Alumina extraction from fly ash as a source has been tried through different methods such as lime stone sintering (Matjie et al., 2005; Zhang and Zhou, 2007), soda lime sintering (Bai et al., 2010), calsinter process (Goodboy, 1976; Seeley et al., 1981), ammonium sulphate sintering process (Li et al., 2012) and acid leaching processes (Li et al., 2011; Wu et al., 2012). A number of disadvantages are associated with these processes. Sintering process produces huge quantity of residue which is 8-10 times higher than the original fly ash. In ammonium

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Table 1
Average elemental analysis of NALCO fly ash.

Sample	Al_2O_3, %	SiO_2, %	Fe_2O_3, %	CaO, %	TiO_2, %
Fly ash	23–25	60–62	3–4	~0.6	1–2

sulphate process the requirement of ammonium sulphate is huge (almost 10 times of the mass of alumina present in fly ash). The sulphuric acid method requires temperature of about 200–210 °C and higher concentration of acid (volumetric ratio of acid to CFA is 5:1) for achieving extraction efficiency of 85%.

In the present study, acid leaching process was used to solubilise alumina values from coal fly ash. Different inorganic acids such as sulphuric and hydrochloric acids were tried as lixiviants. The addition of fluoride ions in the form of hydrofluoric acid to the leaching medium was carried out to study the extent of impact of fluoride ions on the solubilisation of alumina at a lower temperature such as 90 °C. This process has got added advantage for aluminium recovery if there is enough aluminium in the fly ash.

2. Experimental

Coal fly ash (CFA) was obtained from the thermal power plant of National Aluminium Company, Bhubaneswar, India. The as received material is having average particle size of 36.8 μm (d_{50}) and d_{90} of about 117.8 μm. This material was ground to an average size of 4.4 μm (d_{50}) using a steel ball mill. All the particles were in the range of 0.5 μm to 100 μm. D_{90} was measured to be 14.46 μm. The particle size was scaled down to 8 times compared to that of original size during ball milling. The particle size was measured in a Malvern Master sizer (model 2000E, Ver. 5.6). d_{50} is the size of 50% particles passing through a particular size, similarly d_{90} is the size of 90% particles passing through a particular size. All the chemicals used are of analytical grade and purchased from Merck, India. Characterisation work was carried out using Philips X-ray diffractometer (PW 1710), Scanning Electron microscope (SEM, Jeol, JSM-6510), and optical microscope (Leice Orthoplan). Table 1. shows the percentage composition of NALCO fly ash indicating the major elements present in it.

3. Methodology

All the leaching experiments were carried out in batches using a standard double walled borosilicate glass reactor of 250 mL capacity. The temperature of the solution was controlled by a circulating thermostatic water bath through an inlet and an outlet port of the reactor. In each experiment 100 mL solution was taken at a 10% solid concentration. Concentration of acids (H_2SO_4 and HCL) was varied between 10 and 25% (v/v). Initially the required quantity of acid solution was introduced in to the reactor and the temperature of the solution was maintained. In all the experiments, temperature was maintained at 90 °C. The reactor was kept on a magnetic stirrer and agitation was made with the help of a magnetic paddle. Once the desired temperature was attained the required amount of fly ash sample was added into the solution with agitation. The reaction time period in each leaching experiment was 3 h. After the reaction was over the slurry was filtered and the residue was washed thoroughly. The filtrate obtained was then analysed for aluminium value and the recovery percent (amount of alumina leached/amount of alumina originally in fly ash, in percentage) was calculated. The sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and hydrofluoric acid (HF) used for leaching studies were procured from Merck, India with the purity of 98, 35 and 48% respectively.

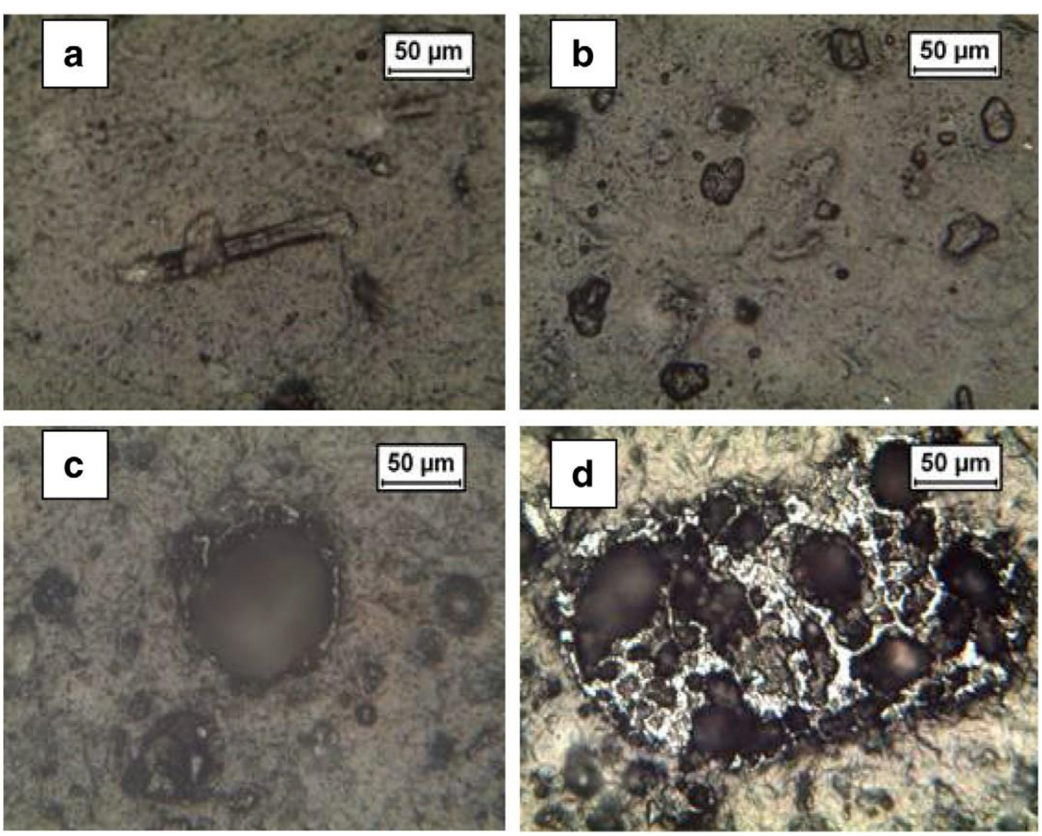

Fig. 1. Optical micrograph of fly ash sample showing different minerals. a. Needle shaped mullite grain. b. Small irregular grains of mullite. c. A large quartz grain. d. Intergrowth of hematite with quartz.

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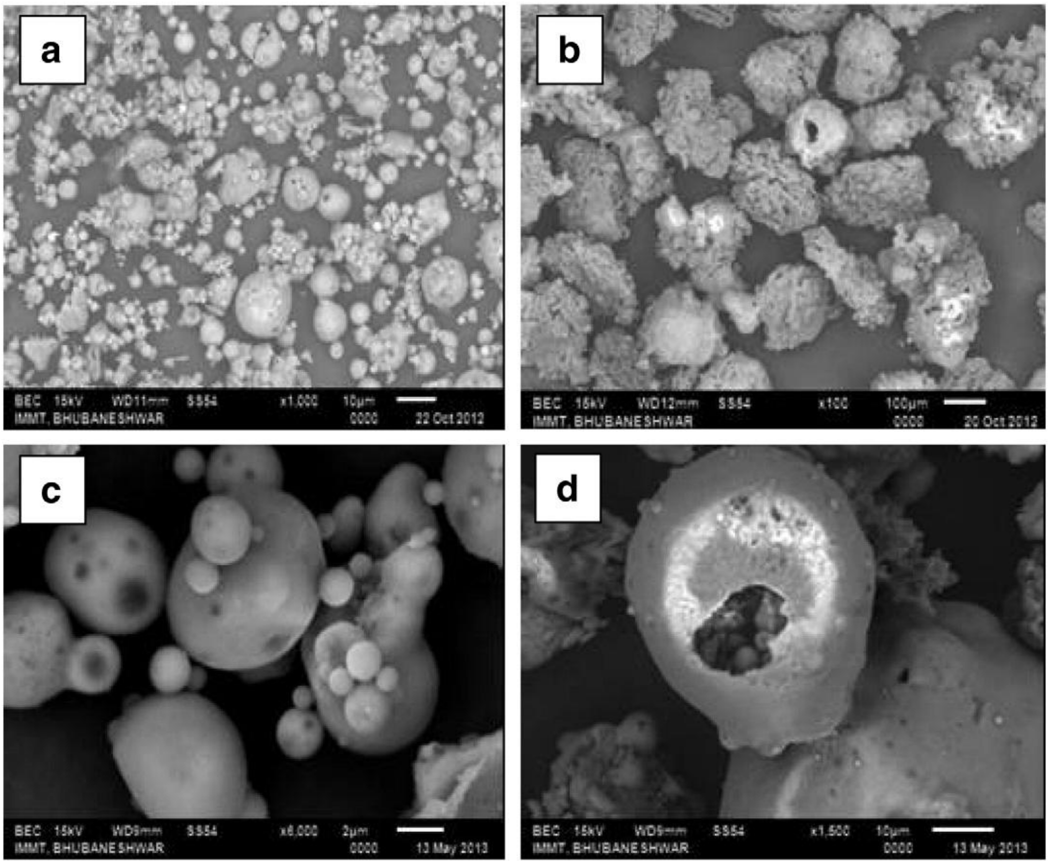

Fig. 2. Electron micrograph of fly ash sample showing different grains. a. Cenospheres and ferrospheres. b. Concretionary grains. c. Ceno-spheres. d. Small cenospheres within a cavity.

4. Results and discussions

Characterisation

The bulk fly ash samples were examined under optical microscope. Fig. 1 illustrates the silicate minerals such as quartz and mullite present in the NALCO fly ash. Needle shaped (Fig. 1a) and small irregular grains (Fig. 1b) of mullite are seen. A large grain of quartz (Fig. 1c) as well as intergrowth of hematite with quartz (Fig. 1d) are also seen. Mullite in the fly ash contains more than 90% alumina. Thus for alumina recovery mullite dissolution is very much essential. Micromorphology of fly ash particles was examined under scanning electron microscope. Fig. 2. shows the different sizes of cenosphere and ferrospheres (Fig. 2a) with some concretionary grains (Fig. 2b). Ferrospheres are brighter (Fe rich) while concretionary types are fine irregular grain look mostly sintered type and are porous. Micron sized cenospheres (Fig. 2c) welded over relatively larger one are commonly observed. Sometimes it was

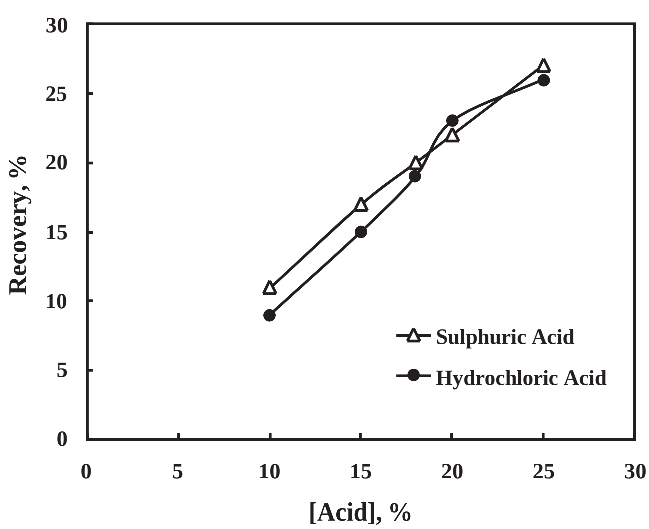

Fig. 3. Percentage recovery of alumina during leaching with H_2SO_4 and HCl. Solution quantity: 100 mL, fly ash: 10 g, temperature: 90 °C.

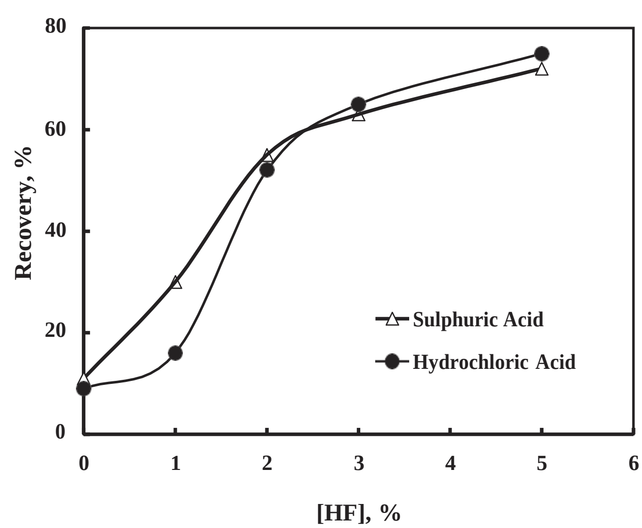

Fig. 4. Effect of hydrofluoric acid on percentage recovery of alumina during leaching with lower concentration of H_2SO_4 and HCl. Solution quantity: 100 mL, Fly ash: 10 g, temperature: 90 °C H_2SO_4 and HCl — 10% each.

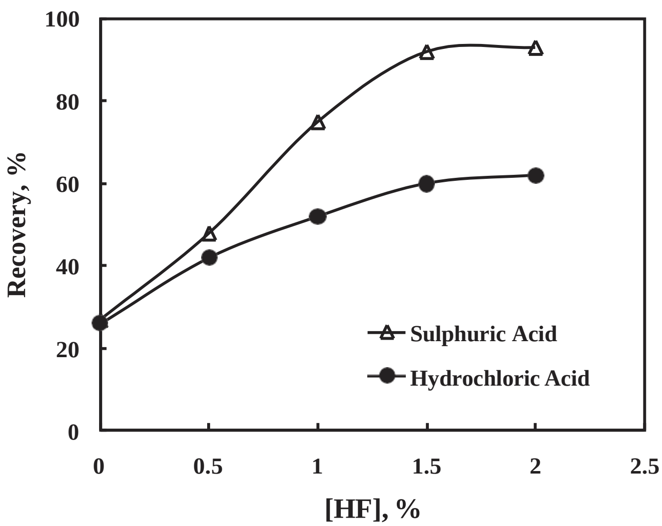

Fig. 5. Effect of hydrofluoric acid on percentage recovery of alumina during leaching with higher concentration of H_2SO_4 and HCl. Solution quantity: 100 mL, Fly ash: 10 g, Temperature; 90 °C H_2SO_4 and HCl: 25% each.

found that small sized cenospheres and concretionary grains were embedded within the cavities of large cenospheres (Fig. 2d).

Leaching

Leaching studies were carried out to dissolve the alumina value present in the fly ash. The alumina bearing solutions are generally treated for further downstream operations to obtain solid alumina powder. In this study, work is restricted to dissolution of alumina only because leaching of alumina in fly ash is the main bottleneck in fly ash processing. Mullite, where most of the alumina is associated, is a very hard material and requires stringent conditions for any kind of solubilisation operation. It requires very high concentration of acid and a very high temperature (N 200 °C) for its dissolution. Attempt was made to treat the NALCO fly ash with 10% H_2SO_4, which showed 10% aluminium recovery (Fig. 3). Increasing the acid amount to 25%, the recovery was enhanced to 25% only. Similar recoveries were also obtained with HCl (Fig. 3). Thus it was observed that treatment of the NALCO fly ash with either H_2SO_4 or HCL even at very high concentration (25%) was also not suitable and the recoveries were still quite low. Similar observations were also made by Kelmers et al. (1982) and Shemi and Zimmels (1998). Wu et al. (2012) could able to leach ~ 82% aluminium using pressure acid leaching method, where they used 50% sulphuric acid and temperature of 180 °C with reaction time of 4 h.

Gajam and Raghvan (1985) have reported that the presence of fluoride ions enhances the leaching rate of clays to extract aluminium. Thus in the present study attempts were made to use hydro fluoric acid as a source of fluoride ion to see its effect on the leaching behaviour of

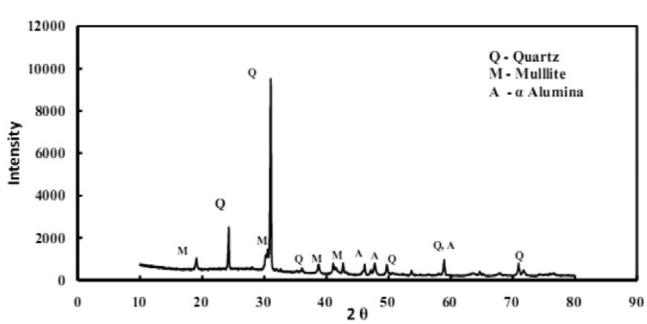

Fig. 6. X-ray diffraction pattern of ball milled fly ash.

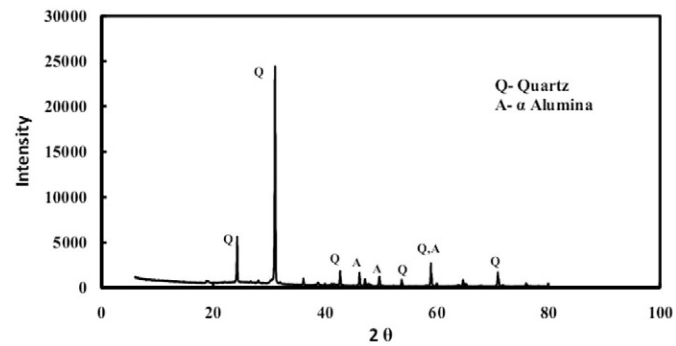

Fig. 7. X-ray diffraction pattern of leached residue of 25% H_2SO_4 + 1.5% HF treated ground fly ash.

NALCO fly ash. Fig. 4 shows the percentage recovery of alumina when H_2SO_4 and HCl concentrations were kept at 10% level, with the addition of different amounts of HF. When 1% HF was added the recoveries were increased to 30% and 15% in cases of H_2SO_4 and HCl respectively. It was observed that with the increase in the concentration of HF, leaching efficiency increased. Thus, when HF addition was increased to 5%, the recoveries in both the cases were about 70%. It should be noted that when 15% H_2SO_4 or 15% HCl was used, only 15% alumina recovery was obtained but the addition of 5% HF to them separately enhanced the recovery by 4–5 fold in each case. This clearly indicates that the addition of fluoride to the leaching medium has solubilised the Mullite portion of fly ash liberating the alumina values.

It was also observed that when the concentration of H_2SO_4 for leaching was increased to 25%, addition of 1.5% of HF was sufficient for enhancing the recovery of alumina to ~92%, however, with 25% HCl, the recovery was limited to only 60% (Fig. 5). This reveals that, although, alumina recovery with HCl increases in the presence of HF, the improvement in leaching efficiency is not significant enough when compared with that of H_2SO_4. This may be due to the fact that, although the percentage of acids (H_2SO_4 and HCl) taken for leaching studies was same (25%), the actual concentration of sulphuric acid was higher than that of hydrochloric acid due to the difference in their purities (98 and 35% respectively).

Further, when leaching studies were carried out with 25% sulphuric acid in the presence of 1.5% HCl, no improvement in alumina recovery was observed, which indicated that the presence of chloride ion does not have any added advantage on the leaching behaviour of fly ash in H_2SO_4 medium. Apparently, it was clear that fluoride ion was very effective to break the mullite grain to release the alumina values. This observation was also supported by XRD data. The X-ray diffractogram of the original ground fly ash (Fig. 6) shows the peaks of mullite and quartz, however the X-ray diffractogram (Fig. 7) of the leach residue obtained after leaching the fly ash with H_2SO_4 and HF showed the absence of mullite peaks indicating complete dissolution of mullite phase in the presence of fluoride ion. This leaching condition is also suitable for proceeding to any downstream operation to obtain alumina value precipitated out.

5. Conclusions

Following conclusions were made from the above studies:

1. NALCO fly ash contains mullite, quartz, hematite along with small quantities of CaO and TiO_2. Mullite being the main phase bearing maximum alumina requires a stringent condition to be leached out.
2. The fly ash contains different sizes of cenospheres with concretionary grains. Sulphuric acid leaching in the presence of HF showed improvement in alumina leaching up to ~92%.
3. The XRD data showed the dissolution of mullite grains during leaching.

4. The leaching condition is suitable for downstream operations to acquire alumina value precipitated out.

References

Bai, G.H., Teng, W., Wang, X.G., Qin, J.g., Xu, P., Li, P.C., 2010. Alkali desilicated coal fly ash as substitute of bauxite in lime-soda sintering process for aluminium production. Trans. Nonferrous Met. Soc. China 20, s 169-s 175.

Emanul Haque, Md., 2013. Indian fly ash — production and consumption scenario. Int. J. Waste Resour. 3 (1), 22-25.

Gajam, S.Y., Raghvan, S., 1985. A kinetic model for the hydrochloric acid leaching of kaolinite clay in the presence of fluoride ion. Hydrometallurgy 15, 143-158.

Goodboy, K.P., 1976. Investigation of a sinter process for extraction of Al_2O_3 from coal wastes. Metall. Mater. Trans. B 7, 175-184.

Izquierdo, M., Querol, X., Phillipart, C., Antenucci, D., 2009. Influence of curing conditions on geopolymer leaching. World of Coal Ash (WOCA) Conference - May 4-7. Lexington, KY, USA, 1-7.

Kelmers, A.D., Canon, R.M., Egan, B.Z., Felker, L.K., Gilliam, T.M., Jones, G., 1982. Chemistry of direct acid leach, calsinter, and pressure digestion-acid leach methods for recovery of aluminium from fly ash. Resour. Conserv. 9, 271-279.

Li, Lai-shi, Wu, Yu-sheng, Liu, Ying-ying, Zhai, Yu-chun, 2011. Extraction of alumina from coal fly ash with sulphuric acid leaching method. Chin. J. Process. Eng. 11 (2) (Apr.).

Li, Lai-shi, Liao, Xin-qin, Wu, Yu-sheng, Liu, Ying-ying, 2012. Extracting alumina from coal fly ash with ammonium sulphate sintering process, Light Metals 2012, Edited by Carlos E. Suarez, TMS, The Minerals, Metals Society.

Ly, L., Vance, E.R., Perera, D.S., Aly, Z., Oulfson, K., 2007. Leaching of geopolymers in deionised water. AZo J. Mater. Online 3 (5), 1-14.

Matjie, R.H., Bunt, J.R., Van, H., 2005. Extraction of alumina from coal fly ash generated from a selected low rank bituminous South African coal. Miner. Eng. 18 (3), 299-310.

Seeley, F.G., McDowell, W.J., Felker, L.K., Kelmers, A.D., Egan, B.Z., 1981. Determination of extraction equillibria for several metals in the development of a process designed to recover aluminium and other metals from coal combustion ash. Hydrometallurgy 6, 277-290.

Shemi, A., Zimmels, Y., 1998. Mechanism and kinetics of aluminium and iron leaching from coal fly ash by sulphuric acid. Chem. Eng. Sci. 53, 3835-3852.

Tyson, S.S., Blackstock, T., 1996. Coal combustion fly ash — overview of applications and opportunities in the USA. Proceedings of 211 ACS National Meeting (New Orleans, LA), pp. 587-591.

Wu, Cheng-you, Yu, Hong-fa, Zhang, Hui-fang, 2012. Extraction of aluminium by pressure acid leaching method from coal fly ash. Trans. Nonferrous Met. Soc. China 22 (9), 2282-22 (Sept.).

Yao, Z.T., Xia, M.S., Sarker, P.K., Chen, T., 2014. A review of the recovery from coal fly ash, with a focus in China. Fuel 120, 74-85.

Zhang, B.Y., Zhou, F.L., 2007. The limestone sintering process to produce alumina with fly ash. Light Met. (6), 17-18 (27 (in Chinese)).