

## Acid leaching technique for the possible recovery of aluminium and other metal values from coal fly ashes

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**Abstract :** The present study examines the rate of extraction of metals mainly aluminium and iron from coal fly ash collected from the captive power plant of Vedanta Aluminum Limited, Jharsuguda, Odisha by direct acid leaching method. The effect of different mineral acids, acid concentrations and solid : liquid ratios on rate of extraction of aluminium and iron have also been studied. The results presented in this paper shows sulphuric acid is the best leachant in comparison to other mineral acids. Aluminium extraction efficiency of 68.68% was achieved with sulphuric acid as leachant at 220 °C and at 1 : 3 solid to liquid ratios. It is also evident that extraction efficiency of aluminium and iron increases significantly with increasing concentration of acids and with solid : liquid ratio variation. The pre-leached and post-leached fly ash samples were analyzed for observing the morphological and mineralogical changes. Morphological and X-ray diffraction (XRD) analysis of post-leached residues indicated that the mullite inside fly ash was thermally decomposed during leaching with sulphuric acid due to the transformation of alumina and mullite into aluminium sulphate.

**Keywords :** VAL fly ash, acid leaching, aluminium extraction, post-leached ash characterizations.

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### Introduction

Fly ashes are the major combustion residues generated during the combustion of pulverized coal in thermoelectric power stations and collected by the electrostatic precipitators<sup>1</sup>. The generation of fly ash in India has increased from 68.88 million tonnes (1996-97) to 163.56 million tonnes (2012-13), of which only 100.37 million tonnes were utilized in low value applications<sup>2</sup>. At present, a small percentage of fly ash finds application in mine and landfills, cement and non-cement uses as well as in developing construction materials<sup>3,4</sup>. Hence, the large amounts of coal fly ashes that accumulate at thermal plants need greater attention to study their possible reuse, dispersion and mobilisation of toxic elements. A great deal of investigations has been carried out towards disposal management and gainful utilization of fly ash. However, the low percentage of utilization of fly ash in India is reflected in the low and medium value applications like bricks, cement and non-cement uses<sup>4-6</sup>.

Indian coal fly ash contains significant amounts of alumina, typically about 25–30%, which opens up an exciting new alternative source of alumina other than bauxite.

Alumina is present in these ashes as the second major constituent after silica and is, therefore, amenable to metallurgical and chemical processes of recovery<sup>7</sup>. Hence, extraction and production of aluminium from coal fly ash is a significant way of developing a new aluminum source than disposing the waste materials<sup>8</sup>. The recovery of minerals from solid waste is related to several factors including specific element solubility and availability potential. There are several processes for the recovery of alumina from clays and other alumina bearing minerals (other than bauxite) have been proposed by several workers<sup>9-15</sup>.

The objective of current study is to find out a suitable method and to establish an appropriate leaching condition for the extraction of various strategic metals especially aluminium from fly ash collected from captive power plant of Vedanta Aluminum Limited, Odisha. Fly ash characterization and systematic leaching behaviour will provide an insight towards identifying suitable rehabilitation methods, environmental assessment and utilisation opportunities<sup>16</sup>.

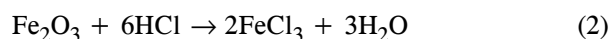
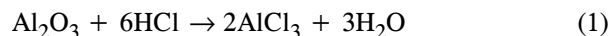
### Results and discussion

*Fly ash characterizations :* The chemical composition

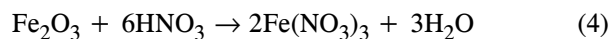
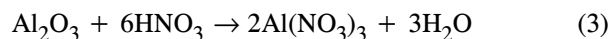
of coal ash is influenced to a great extent by the geological and geographical characteristics of the coal deposit and the combustion conditions<sup>17</sup>. The major inorganic oxides found in VAL fly ash are silica (65.12%), alumina (27.64%), iron oxide (4.69%), titanium oxide (0.81%), calcium oxide (1.35%), magnesium oxide (0.61%), sodium oxide (0.16%) and potassium oxide (0.04%) as presented in Table 1. The loss on ignition (LOI) value of fly ash (0.98%) indicates carbon content in the combustion residue. The concentration of trace elements analysed by open acid digestion method is given in Table 1. The morphology of fly ash sample reveals that it consists of mostly spherical particles and the spherical ash particles with much brighter surface are identified as cenospheres. The XRD pattern of the VAL fly ash shows the presence of predominant mineral phases such as quartz (q), mullite (m), silimanite (s), magnetite (ma) and hematite (h) which occur in crystalline form<sup>18,19</sup>. Quartz is considered as the primary mineral present in fly ash and indicated by sharp peaks in diffraction patterns. The XRD analysis of fly ash

shows that quartz, mullite, magnetite and hematite peaks are observed at  $2\theta$  values of 26.73 ( $d = 3.33$ ), 26.07 ( $d = 3.41$ ), 33.28 ( $d = 2.68$ ) and 35.34 ( $d = 2.53$ ), respectively. The particle size analysis of VAL fly ash shows greater value of  $D_{10}$  (5.276  $\mu\text{m}$ ),  $D_{50}$  (50.68  $\mu\text{m}$ ) and  $D_{90}$  (151.54  $\mu\text{m}$ ) with lower specific surface area (0.389  $\text{m}^2/\text{cc}$ ). This indicates the presence of coarser particles with irregular in shape and size<sup>20</sup>. SPAN, which is calculated as  $(D_{90} - D_{10})/D_{50}$ , is a helpful parameter in determining the usability of an ash. Usually VAL fly ash shows a small SPAN value (2.886) with smaller  $D_{10}$ , moderate  $D_{50}$  and comparatively higher value of  $D_{90}$ .

*Effect of acid concentrations on metal extraction* : The effect of concentrations of various mineral acid such as hydrochloric acid, nitric acid, phosphoric acid and sulphuric acid on metal extraction during the process of leaching has been studied. During leaching study with hydrochloric acid at 110 °C, it is noticed that aluminum extraction increases from 3.71 to 5.78% with increasing concentrations of HCl i.e. from 2 to 11.3 N and the same is also observed for iron extraction (46.12–73.95%) with varied concentrations of HCl as shown in Figs. 1a and 1b. The reaction mechanism given by the Livingston *et al.*<sup>21</sup> for the dissolution of Al and Fe in the fly ash with concentrated HCl is given below :



Leaching with nitric acid at 120 °C shows an increase in aluminum dissolution with increasing concentrations of  $\text{HNO}_3$  (2.78–4.37%), whereas iron extraction is found to be quite considerable with increasing concentration from 2 N (12.57%) to 14 N  $\text{HNO}_3$  (54.99%) as shown in Figs. 1a and 1b. The reaction mechanism for the dissolution of Al and Fe in the fly ash with concentrated  $\text{HNO}_3$  is given below :

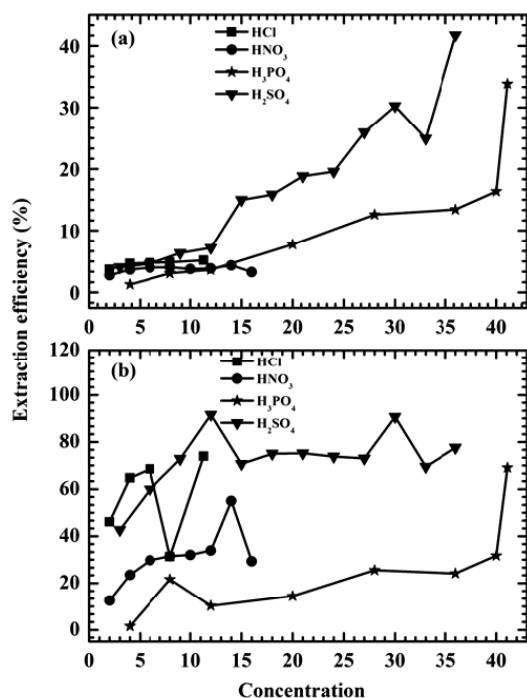


The leaching experiment with phosphoric acid has been carried out at 150 °C. It is observed that the rate of extraction of aluminum increases from 1.29 to 33.84% with increasing concentration of phosphoric acid (4 to 41.1 N) as shown in Fig. 1a. Also a substantial amount of iron was leached along with aluminium, i.e. 1.57% (4 N) to 69.04% (41.1 N) as depicted in Fig. 1b. The reaction

**Table 1.** Chemical compositions of VAL fly ash

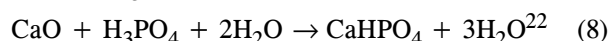
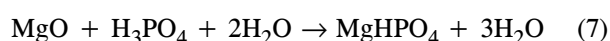
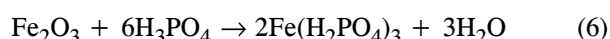
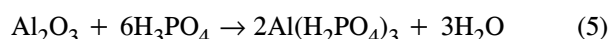
Major elements in fly ash (wt %)	
SiO <sub>2</sub>	65.12
Al <sub>2</sub> O <sub>3</sub>	27.64
Fe <sub>2</sub> O <sub>3</sub>	4.69
TiO <sub>2</sub>	0.81
CaO	1.35
MgO	0.61
Na <sub>2</sub> O	0.164
K <sub>2</sub> O	0.048
LOI	0.98
Total Organic Carbon	0.197
Trace elements in fly ash (mg/kg)	
Vanadium	119.29
Chromium	113.12
Manganese	200.93
Cobalt	22.65
Nickel	41.98
Copper	50.14
Zinc	60.97
Strontium	7.66
Lead	24.65

Notes : (a) SiO<sub>2</sub> - Silica; (b) Al<sub>2</sub>O<sub>3</sub> - Alumina; (c) Fe<sub>2</sub>O<sub>3</sub> - Iron oxide; (d) TiO<sub>2</sub> - Titanium oxide; (e) CaO - Calcium oxide; (f) MgO - Magnesium oxide; (g) Na<sub>2</sub>O - Sodium oxide; (h) K<sub>2</sub>O - Potassium oxide; (i) LOI - Loss on ignition.



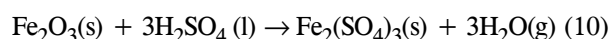
**Fig. 1.** (a) Extraction efficiency (%) of Al, (b) extraction efficiency (%) of Fe in varied concentrations of mineral acids : HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>.

mechanisms involved in the phosphoric acid leaching with metal oxides are given in the eqs. (5), (6), (7) and (8).



The effect of different concentrations of sulphuric acid on metal extraction has been studied at the temperature 220 °C. In case of sulphuric acid the extraction efficiency of various metals increase with increasing concentrations of the acid. There is a steady increase in aluminium extraction from 4.08 to 41.71% and from 42.7 to 91.67% for iron, when the acid concentration varied from 3 N to 36 N H<sub>2</sub>SO<sub>4</sub> (Figs. 1a and 1b). The other metals like Ca, Mg, Na, K and Ti are also co-dissolved along with aluminium and iron because of the increasing hydronium ion concentration. Similar trend was not observed in iron dissolution as iron extraction decreases at higher concentration due to simultaneous precipitation of calcium sulphate, which hinders the mass transfer rates of reactants and products in the slurry mixture<sup>23</sup>. The reaction mechanisms

involved in the H<sub>2</sub>SO<sub>4</sub> leaching with metal oxides are as per Lai-shi *et al.*<sup>24</sup> are given in eqs. (9), (10), (11) and (12).



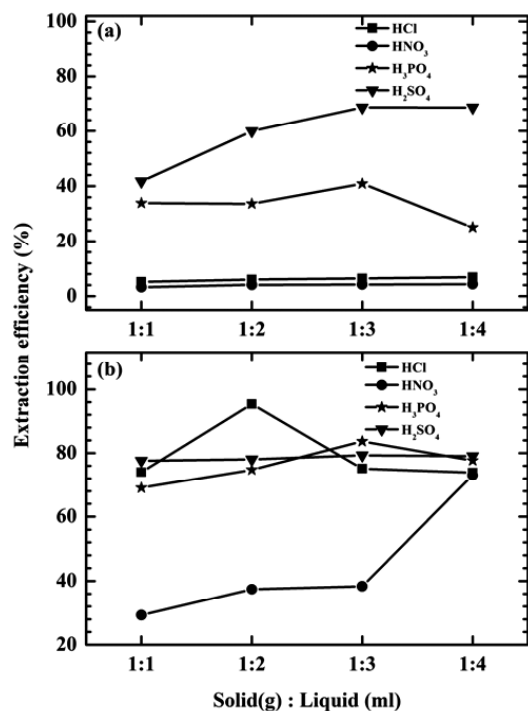
*Effect of solid : liquid ratios on metal extraction :*

With the variation of solid to liquid ratio it is observed that aluminium extraction is not significant during hydrochloric acid leaching, i.e. the maximum extraction reaches at 6.88% with 1 : 4 solid : liquid ratio, whereas the iron extraction (73.95–95.38%) is significant at 1 : 2 solid : liquid ratio as shown in Figs. 2a and 2b. It has been observed that the iron was extracted at a considerably faster rate than aluminium as shown in same figure, because the iron present in the coal ash is predominantly in the form of Fe<sub>2</sub>O<sub>3</sub>, produced by the oxidation of pyrite and siderite during the combustion process, whereas the aluminium is present in crystalline phases causing slow dissolution in concentrated HCl<sup>21</sup>.

In case of nitric acid the rate of Al extraction is found to be insignificant (3.27–4.38%) in comparison to the iron extraction (29.31–73.03%) with maximum extraction obtained at 1 : 4 solid : liquid ratio as shown in Figs. 2a and 2b. Extraction of Fe is more in comparison to aluminium, because of the fact that the iron oxide is present on the upper surface and not in the inner matrix of fly ash, whereas Al is present in the crystal phase (Fig. 2). The dissolution of Al and Fe using nitric acid are considerably lower than that of HCl<sup>5</sup>.

The effect of solid : liquid ratio on iron extraction using phosphoric acid is quite effective in comparison to the Al extraction. The extraction maxima for iron reaches at 83.67% at a solid : liquid ratio of 1 : 3, whereas the aluminium extraction maxima (40.90%) reaches at 1 : 3 and further decreases at 1 : 4 solid : liquid ratios (Figs. 2a and 2b). But in comparison to the HCl and HNO<sub>3</sub>, phosphoric acid is a good leachant for the extraction of elements, which enters into the matrix of aluminium silicate.

During sulphuric acid leaching, there is a gradual increase in aluminium concentration in the leachate from 41.71 to 68.68% with increasing solid : liquid ratio from 1 : 1 to 1 : 4 (Fig. 2a). The increase in solid : liquid ratios



**Fig. 2.** (a) Extraction efficiency (%) of Al, (b) extraction efficiency (%) of Fe in different ratio of fly ash and mineral acids : 11.3 N HCl, 16 N HNO<sub>3</sub>, 41.1 N H<sub>3</sub>PO<sub>4</sub>, 36 N H<sub>2</sub>SO<sub>4</sub>.

imply an increase in acid volume while the amount of solids remains constant. So it creates a less dense slurry mixture, frees up ash particles and makes available larger ash particle surface areas for contact between reactants which leads to higher reaction rates. Thus the increase in ash particle surface contact with the hydronium ion enhances the dissolution of aluminium. The highest extraction of aluminium (68.68%) is obtained at 1 : 3 solid :

liquid ratio. But further, at 1 : 4, the metal extraction becomes stable due to the surface coating of fly ash. Generation of sulphate ions and calcium ions in the leached liquor intensify the formation of calcium sulphate precipitates, which hinder mass transfer across the fly ash particle, thus slowing down the rate of reaction, inhibiting aluminium dissolution and consequently causing lower extraction<sup>23</sup>. Similar tendency is also obtained in the extraction of iron in the same concentration profile for different solid : liquid ratio. However, the iron extraction is found to be more in comparison to aluminium (Fig. 2b). Hence, from the above study it has been found that sulphuric acid is a good leachant for the extraction of Al along with other elements from fly ash by direct acid leaching method in comparison to HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>.

*Post-leached ash study :*

The leaching of various metals from the coal fly ash has been further confirmed by characterizing the post-leached ash residues.

*Particle size analysis :* The particle size and specific surface area values of the pre-leached and post-leached ash with different acids at a fly ash : acid ratio (1 : 1) is presented in Table 2. The specific surface area and mean particle diameter value (D<sub>50</sub>) of the pre-leached fly ash is 0.389 m<sup>2</sup>/gm and 50.68 μm, respectively. The particle size of post-leached ashes is less than parent fly ash and the specific surface area is more than parent fly ash. This observation is because of the elimination of appreciable amount of amorphous phases that surround insoluble crystals of mullite and quartz during acid leaching, thus ex-

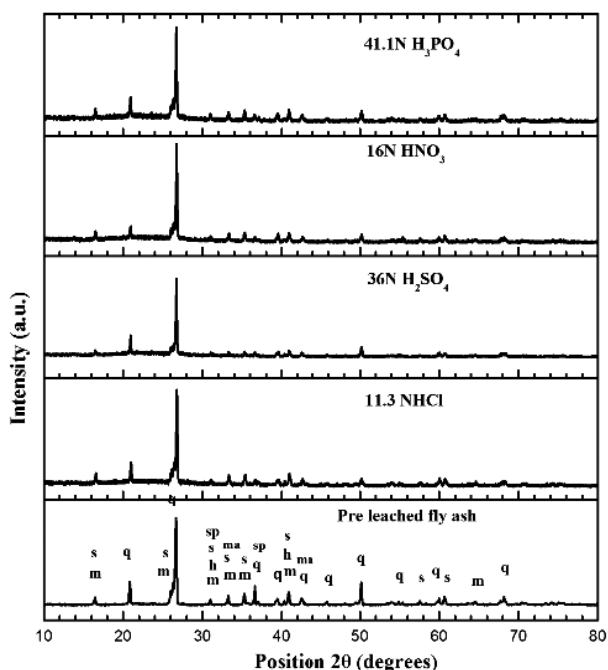
**Table 2.** Particle size distribution of pre- and post-leached VAL fly ash

Particle size characteristics	Pre-leached VAL fly ash	Post-leached VAL fly ash			
		Fly ash in g : Acid concentrations in N			
		Fly ash in g : 11.3 N HCl (1 : 1)	Fly ash in g : 16 N HNO <sub>3</sub> (1 : 1)	Fly ash in g : 36 N H <sub>2</sub> SO <sub>4</sub> (1 : 1)	Fly ash in g : 41.1 N H <sub>3</sub> PO <sub>4</sub> (1 : 1)
D <sub>50</sub> (μm)	50.68	31.44	47.85	32.38	46.29
D <sub>90</sub> (μm)	151.54	144.50	135.38	130.53	144.23
D <sub>10</sub> (μm)	5.276	3.44	4.26	3.44	4.30
SPAN	2.886	4.486	2.740	3.924	3.022
Specific surface area (m <sup>2</sup> /cc)	0.389	0.592	0.455	0.579	0.450

Notes : (a) D<sub>50</sub> : 50% of the particles are smaller than this diameter (μm); (b) D<sub>90</sub> : 90% of the particles are smaller than this diameter (μm); (c) D<sub>10</sub> : 10% of the particles are smaller than this diameter (μm); (d) SPAN = (D<sub>90</sub> - D<sub>10</sub>)/D<sub>50</sub>.

posing of high surface area<sup>5</sup>. It is being observed that fly ash, leached with sulphuric acid, has smaller particle size (32.38  $\mu\text{m}$ ,  $D_{50}$ ) in comparison to pre-leached and post-leached ashes of other acids. Since maximum dissolution of aluminium and other metals occur in sulphuric acid medium, the post-leached fly ash shows increase in specific surface area per volume with decreasing particle size.

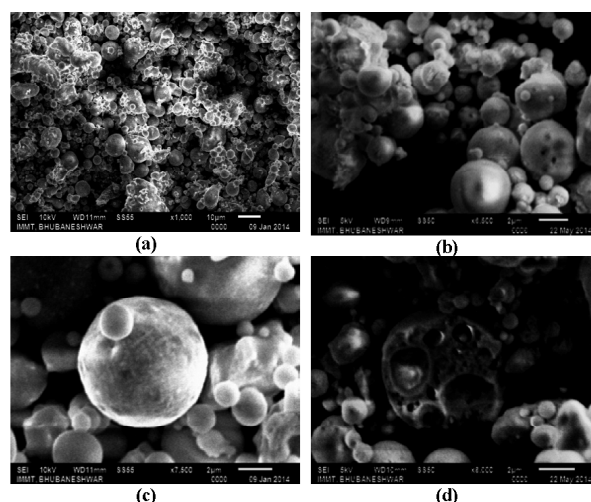
**Mineralogical and morphological studies :** XRD of pre-leached ash samples confirms the presence of quartz, mullite, hematite and magnetite as the dominant phases. It is being noticed that the quartz, mullite, magnetite and hematite peaks observed in pre-leached fly ash at  $2\theta$  values of 26.73 ( $d = 3.33$ ), 26.07 ( $d = 3.41$ ), 33.28 ( $d = 2.68$ ) and 35.34 ( $d = 2.53$ ), respectively are differing from each other in post-leached fly ash (Fig. 3). The intensities of mullite peaks which were very strong in the pre-leached fly ash were significantly reduced in the post-leached fly ash due to the acid attack on aluminosilicate phase, resulting in the formation of weak mullite peak and broad quartz peak<sup>25,26</sup>. But the shrinkage of aluminium peaks in sulphuric acid leached ash was a consequence of removal of aluminium sulfate by dissolution operation and hence the peak intensity of silicon dioxide becomes higher



**Fig. 3.** X-Ray diffraction peak of pre-leached and post-leached VAL fly ash with 11.3 N HCl, 36 N H<sub>2</sub>SO<sub>4</sub>, 16 N HNO<sub>3</sub>, 41.1 N H<sub>3</sub>PO<sub>4</sub>; (q = quartz, m = mullite, s = sillimanite, ma = magnetite, h = hematite).

due to its enrichment in the post-leached samples<sup>27</sup>. However, there is no such peak change was observed in HCl and HNO<sub>3</sub> leached fly ash. So the mineralogical structures of leached coal fly ash are in accord with the statement that sulphuric acid is a good leachant for aluminium extraction in comparison to other acids.

The scanning electron micrographs (SEM) of the pre-leached and post-leached fly ashes are presented in Fig. 4. The photomicrographs of pre-leached fly ash illustrate a smooth surface with collection of hollow spherical particles of different sizes as well as particles of irregular shape which are known as silica embedded in the surfaces. Due to presence of hollow spheres, a considerable amount of alumina was enclosed inside these spheres<sup>27</sup> (Fig. 4a). It has been seen from the photomicrographs that, pre-leached fly ash spheres were observed to be possessing relatively smooth surfaces compared to the post-leached fly ash spheres<sup>26</sup>. Also the SEM pictures of fly ash leached with H<sub>2</sub>SO<sub>4</sub> shows the presence of pitted, etched and corroded surface. This change in surface morphology of ash spheres is due to the acid attack on the smooth surface during leaching. Since the aluminium silicate matrix, which is also called mullite existed on the surface of the ash spheres, it must have been partially dissolved by the acid. The attack of H<sub>2</sub>SO<sub>4</sub> on the aluminium-silicate matrix is prominent as shown in Fig. 4d. The SEM photomicrographs (Fig. 4d) of fly ash leached with H<sub>2</sub>SO<sub>4</sub> at 1 : 4 solid : liquid ratio shows the most



**Fig. 4.** Scanning electron micrographs of fly ash sample : (a) pre-leached, (b) post-leached, (c) single particle pre-leached fly ash, (d) single particle leached fly ash with 36 N H<sub>2</sub>SO<sub>4</sub> (1 : 4).

corroded surface which indicates that a large amount of alumina present in the amorphous phase of fly ash is being removed by acid attack.

**FTIR studies :** The IR spectra of the pre- and post-leached fly ashes are presented in Fig. 5. The parent fly ash shows strong absorption bands at 1087.85, 794.67, 443.63  $\text{cm}^{-1}$  for quartz due to Si-O-Si asymmetric stretching frequency<sup>28</sup>. A weak and small peak at 840 and 734  $\text{cm}^{-1}$  shows the existence of  $\gamma$  alumina and a peak at 690.52  $\text{cm}^{-1}$  confirm the occurrence of mullite. A peak at 559  $\text{cm}^{-1}$  has been assigned for hematite as reported by Nayak<sup>29</sup>. The post-leached ash shows sharp bands at 1100.41, 930.67, 799.51, 695.35 and 456.17  $\text{cm}^{-1}$ , which matches with the quartz peak<sup>30</sup>. The dearth of absorption band for alumina in the post-leached residue confirms the leaching of aluminium oxide. The presence of prominent quartz peaks in the post-leached residue proves the decomposition of aluminium silicon glass and mullite in coal fly ash with increasing acid concentration. However certain broad peaks observed at 2352.23 and 1610.59  $\text{cm}^{-1}$  are due to the presence of adsorbed water molecule.

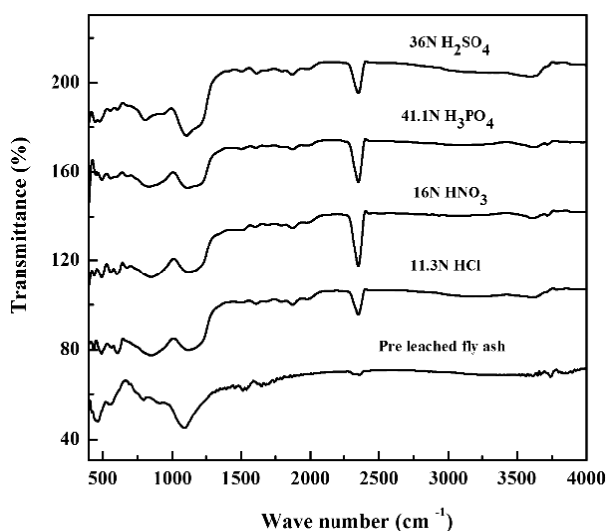


Fig. 5. Infrared spectra of pre-leached and post-leached fly ash.

## Conclusion

The direct acid leaching method was used to extract aluminum from coal fly ash and the effects of different acid concentrations and solid : liquid (fly ash : acid) ratios on extraction efficiency of aluminum was investigated. Different concentration of acids was used to break the crystalline mullite phase rendering free alumina for leach-

ing. It was observed that percentage extraction of aluminium and other metals increased with increasing concentration of acids and solid : liquid ratio. The rate of extraction of aluminum is quite lower using concentrated hydrochloric acid and nitric acid in comparison to sulphuric acid as leachant. The extraction efficiency of metals depends on the nature of leaching medium, acid concentrations, solid : liquid ratio, temperature and leaching time. From the above study, an aluminium extraction efficiency of maximum 68.68% was achieved with sulphuric acid at 220 °C and 1 : 3 solid to liquid ratio. This is further confirmed by the mineralogical and morphological composition of acid leached ash residue. This indicates the thermal decomposition of mullite in the CFA matrix and finally the mullite was transformed into aluminium sulphate during leaching with acid.

## Experimental

### Materials :

The fly ash sample is collected from the electrostatic precipitator of captive power plant of Vedanta Aluminum Limited (VAL) at Jharsuguda, Odisha. The as-received sample with no further grinding and size classification are characterized chemically and mineralogically.

### Characterization :

The chemical compositions such as major, minor and trace elements of VAL fly ash were analysed by means of Inductively coupled plasma optical emission spectrophotometer, Perkin-Elmer Model Optima 2100 DV (ICP-OES). The particle size distribution of fly ash was determined by means of laser diffraction particle size analyser (Model-Hydro 2000MU) with the wet dispersion method in water. The mineral composition of fly ash was determined by X-Ray Diffraction (XRD) using a Phillips diffractometer, PW-1710 and  $\text{CuK}\alpha$  radiation. The particle morphology is studied from the micrographs obtained with a JEOL JSM-6510 Scanning Electron Microscope (SEM). The particle shape is quantified by using image analysis and documented with micrographs. The Fourier transform infrared spectra (FTIR) of the sample obtained at room temperature by using Shimadzu model IR Prestige-21 spectrometer in the range 4000–400  $\text{cm}^{-1}$ .

### Experimental details :

Leaching experiments were conducted with various mineral acids, hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ),

phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) of varying concentrations. A set of experiments was carried out by treating fly ash samples (100 g) with a constant volume (100 ml) of acids. The mixture was boiled with constant stirring at boiling temperatures of different acids, i.e. 110 °C for HCl, 120 °C for HNO<sub>3</sub>, 150 °C for H<sub>3</sub>PO<sub>4</sub> and 220 °C for H<sub>2</sub>SO<sub>4</sub> with the evolution of white fumes. Boiling was continued up to four hours with time-to-time addition of appropriate amount of respective acids in order to retain the desired solid : liquid ratio. Then the mixture was extracted with 500 ml hot distilled water, filtered through a G3 Buchner funnel, followed by repeated washing (two times) with hot water. The leach liquor and washings were mixed and evaporated to a known volume before analysis for various elements like aluminium, iron, titanium, calcium, magnesium, sodium and potassium. Few more experiments were conducted with solid : liquid variation (1 : 1, 1 : 2, 1 : 3 and 1 : 4). Similarly, the leachates were analysed for various metals. Residues obtained during the leaching experiments were washed several times till neutral, dried at 110 °C and are subjected to various physico-chemical analysis.

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#### References

1. S. V. Vassilev and C. G. Vassileva, *Energy & Fuels*, 2005, **19**, 1084.
2. Z. T. Yao, X. S. Ji, P. K. Sarker, J. H. Tang, L. Q. Ge, M. S. Xia and Y. Q. Xi, *Earth-Science Reviews*, 2015, **141**, 105.
3. U. Bhattacharjee and T. C. Kandpal, *Energy*, 2002, **27**, 151.
4. S. Sushil and V. S. Batra, *Fuel*, 2006, **85**, 2676.
5. N. Nayak and C. R. Panda, *Fuel*, 2010, **89**, 53.
6. R. S. Iyer and J. A. Scott, *Resources, Conservation and Recycling*, 2001, **31**, 217.
7. R. S. Blissett and N. A. Rowson, *Fuel*, 2012, **97**, 1.
8. Wu Cheng-you, Yu Hong-fa and Zhang Hui-fang, *Transaction of Nonferrous Metal Society of China*, 2012, **22**, 2282.
9. P. Christie and R. Derry, Warren Spring Report, Report No. LR (219) ME, 1976.
10. C. A. Hamer, CANMET Report, 1977, Vol. 77, 54.
11. C. V. Phillips and K. J. Wills, *Hydrometallurgy*, 1982, **9**, 15.
12. M. R. Martinez-Tarazona and D. A. Spears, *Fuel Process. Technol.*, 1996, **47**, 79.
13. X. Querol, J. C. Umana, A. Alastuey, C. Ayora, A. Lopez-Soler and F. Plana, *Fuel*, 2001, **80**, 801.
14. R. H. Matjie, J. R. Bunt and J. H. P. Van Heerden, *Minerals Engineering*, 2005, **18**, 299.
15. Z. T. Yao, M. S. Xia, P. K. Sarker and T. Chen, *Fuel*, 2014, **120**, 74.
16. M. Ahmaruzzaman, *Progress in Energy and Combustion Science*, 2010, **36**, 327.
17. A. Sarkar, R. Rano, G. Udaybhanu and A. K. Basu, *Fuel Process. Technol.*, 2006, **87**, 259.
18. H. Shao, K. Liang, F. Zhou, G. Wang and F. Peng, *J. Non-Cryst. Solids*, 2004, **337**, 157.
19. D. P. Mishra and S. K. Das, *Material Characterizations*, 2010, **61**, 1252.
20. A. Sarkar, R. Rano, K. K. Mishra and I. N. Sinha, *Fuel Process. Technol.*, 2005, **86**, 1221.
21. W. R. Livingston, D. A. Rogers, R. J. Champman and N. T. Bailey, *Hydrometallurgy*, 1985, **13**, 283.
22. A. S. Wagh and S. Y. Jeong, *J. Am. Ceram. Soc.*, 2003, **86**, 1838.
23. A. Shemi, R. N. Mpana, S. Ndlovu, L. D. van Dyk, V. Sibanda and L. Seepe, *Minerals Engineering*, 2012, **34**, 30.
24. Li Lai-shi, Wu Yu-sheng, Liu Ying-ying and Zhai Yu-chun, *The Chinese J. Process Eng.*, 2011, **11**, 254.
25. S. B. Kanungo and R. Mohapatra, *J. Environ. Qual.*, 2000, **29**, 188.
26. T. Praharaj, M. A. Powell, B. R. Hart and S. Tripathy, *Environ. Int.*, 2002, **27**, 609.
27. G. Bai, Y. Qiao, B. Shen and S. Chen, *Fuel Process. Technol.*, 2011, **92**, 1213.
28. O. Celik, E. Danci and S. Piskin, *Indian Journal of Engineering & Material Science*, 2008, **15**, 433.
29. N. Nayak and C. R. Panda, *J. Indian Chem. Soc.*, 2007, **84**, 603.
30. J. A. Gadsden, "Infrared Spectra of Minerals and Related Inorganic Compound", Butterworth Group, UK, 1975, 46.

