



Extraction of aluminium as aluminium sulphate from thermal power plant fly ashes

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Abstract: Valuable metal extraction technology from thermal power plant fly ash is limited. In the present study, aluminium is extracted from fly ash as highly pure aluminium sulphate (>99.0%) by leaching with sulphuric acid, followed by pre-concentration and successive crystallization. Two types of fly ashes from different sources, i.e., Talcher Thermal Power Station (TTPS) and Vedanta Aluminium Company Limited (VAL) were chosen for comparative study on the extraction of aluminium as aluminium sulphate. The product is characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Purity of aluminium sulphate was also investigated by inductively coupled plasma–optical emission spectrometry (ICP–OES). The extraction efficiency of aluminium depends on the varied solid-to-liquid ratio (fly ash : 18 mol/L H_2SO_4 , g/mL) and particle size of fly ashes. Physico-chemical analysis indicates that the obtained product is $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, having low iron content (0.08%).

Key words: fly ash; sulphuric acid; aluminium sulphate; leaching; solid-to-liquid ratio; particle size

1 Introduction

Thermal power plant fly ash linked to various environmental problems, particularly its accumulation posed a great threat to air, water and soil pollution. Besides bulk utilization like the brick, cement and non-cement uses, high-value utilization of fly ash is also essential to conserve the natural resources. Fly ash contains major components such as silica (around 60%), alumina (around 30%) and iron oxides (4%–20%) along with various other impurities such as calcium oxides (1%–12%), magnesium oxides (1%–2%), titanium oxides, sodium oxides and potassium oxides. The extraction of aluminium and other strategic metals has specific relevance in view of safe disposal and residue utilization. The recovery of aluminium is amenable through metallurgical processes such as direct acid leaching or soda–lime sinter processes. Although a large number of processes have been developed for gainful utilization and safe management of fly ashes [1–5], constraints still persist for the high-value applications (metal recovery) due to process difficulty. Several methods for the recovery of aluminium from coal fly

ashes have been proposed [6–20], but a definite process has not been established for its commercialization. The obvious reason is that the physical properties and precise composition of fly ashes vary depending on the source of the coal being burned, type and uniformity of the coal, the operating parameters of the power plant and the collection methods employed to separate the ashes.

Nitric acid and hydrochloric acid leaching processes for the recovery of alumina and other minerals have little practical applications due to low recovery. Low cost and stability have prompted sulphuric acid as lixiviant by several investigators for the recovery of alumina [21,22]. According to MATJIE et al [22], the aluminium extraction efficiency of 85% was achieved when the sintered pellets of fly ash, mixed with calcium oxides, were leached with sulphuric acid using an acid concentration of 6.12 mol/L at 80 °C for 4 h. Many researchers have reported about the extraction of aluminium from ores of clay, shale and aluminosilicate by using H_2SO_4 as leachant at different temperatures for different leaching time [23,24]. HUANG [25] investigated the potential of hydrofluoric acid (HF) in the extraction of aluminium by treating coal ash with 52% HF at 25 °C for 1 h. In another process, a coarse

γ - Al_2O_3 powder was prepared by acid leaching, and the extraction rate of Al_2O_3 was found to be 87% [26]. Pressure acid leaching method achieved 82.4% extraction efficiency by using 74 μm particle size of coal fly ash with 50% sulphuric acid in a pressure reaction kettle at 180 °C for 4 h [8]. The extraction of alumina from coal fly ash using an acid leach–sinter–acid leach technique has been proposed by SHEMI et al [27], based on the dissimilar response characteristics of the amorphous and mullite–alumina phases present in coal fly ash. The reaction behaviour of Al_2O_3 and SiO_2 in high alumina coal fly ash under various alkali hydrothermal conditions was explored by JIANG et al [28]. The results showed that the Al_2O_3 and SiO_2 leaching efficiencies of coal fly ash were dependent on the dissolution of glass phase and the precipitation of zeolite phase. DING et al [29] has extracted alumina from high alumina pulverised coal by using high alkali sodium aluminate solution through a reactor in two stages. Alumina extraction efficiency of 96.03% has been achieved. SIBANDA et al [30] have reviewed the hydro-metallurgical extraction processes of different workers to assess the available opportunity and prospects of commercial exploitation of the aluminium extraction from coal fly ash.

All of the above studies aimed at finding alternate routes to produce smelter grade alumina, but these processes have their own engineering difficulty for commercial viability. The present investigation is an attempt to convert a considerable amount of aluminium into environment friendly material for industrial uses. In the proposed process, selective recovery of aluminium has been tried in the form of aluminium sulphate from the leach liquor with acceptable iron and other impurities. To make the process more economical, direct acid leaching method has been employed with the commercial grade sulphuric acid and moreover, as-received fly ash samples have been used in leaching without further being subjected to energy intensive grinding, size classification or sintering.

2 Experimental

2.1 Leaching of fly ash

Coal fly ash (CFA) samples were collected from two different thermal power stations, viz., Talcher Thermal Power Station (TTPS) and Vedanta Aluminium Company Limited (VAL). Both the samples were subjected to particle size, chemical and mineralogical analyses [31,32]. In continuation to our earlier reported works [15,33,34], leaching study of both the fly ashes has been undertaken systematically with varying solid-to-liquid ratio (1:1, 1:2, 1:3 and 1:4) to investigate the extent of aluminium extraction from the as-received

coal fly ashes without further grinding and size reduction. Representative fly ash samples (100 g) from each TTPS and VAL were mixed separately with a specific volume of 18 mol/L H_2SO_4 to produce suspensions with varying solid-to-liquid ratio (1:1, 1:2, 1:3 and 1:4). The resulting suspensions were heated up to 200 °C for 4 h at normal atmospheric pressure with the evolution of white fumes. The fly ash residues were filtered from the leached liquor by using G3 Buchner funnel followed by washing with hot water. The extraction efficiency of aluminium is determined using the following formula [35]:

$$E = \frac{C_{bl}(\text{Al}) - C_{al}(\text{Al})}{C_{bl}(\text{Al})} \times 100\% \quad (1)$$

where E is the extraction efficiency, and $C_{bl}(\text{Al})$ and $C_{al}(\text{Al})$ are the concentrations of aluminium present in fly ash before and after acid leaching, respectively.

2.2 Precipitation of aluminium sulphate

The leached liquor obtained after filtration and washing was evaporated by using hot water bath. The liquor got concentrated on slow evaporation to a point where aluminium sulphate started precipitating. Then, the concentrated liquor was kept overnight at 8 °C in a cooling incubator. White coloured aluminium sulphate (gel) precipitated out, it was filtered in cold condition using G1 Buchner funnel. The same procedure was repeated for complete crystallization of aluminium sulphate. Since aluminium sulphate is almost insoluble in acetone, the precipitate obtained was washed with acetone and further dried by vacuum desiccation. As aluminium sulphate is highly hygroscopic, it was dried at 60 °C followed by keeping it in a desiccator and then subjected to physico-chemical analysis.

2.3 Sample characterization

The elemental compositions of the aluminium sulphate, recovered from both fly ashes, were determined by ICP-OES (Perkin Elmer Optima 2100 DV) and the thermal behaviour of both samples was examined by means of TG/DTA (METTLER STAR[®] SW 9.01). The crystalline phases were characterized by powder X-ray diffraction (XRD) (Phillips diffractometer, PW-1710) using Cu K_α radiation. The FTIR spectra of the samples were taken with FTIR spectrophotometer (IR Prestige-21, Shimadzu) in the range of 400–4000 cm^{-1} . The particle size analysis of fly ash residues was carried out by MALVERN particle size analyzer (UK, Model-3600).

3 Results and discussion

The TTPS and VAL fly ashes were characterized chemically and mineralogically to understand the chemical composition, phase mineralogy and particle

size [34,36]. A representative sample of TTPS fly ash contained Al_2O_3 (29.09%), SiO_2 (59.49%), CaO (0.99%), Fe_2O_3 (3.90%), TiO_2 (1.90%), K_2O (0.72%), MgO (0.33%), Na_2O (0.13%) and LOI (2.58%), whereas VAL fly ash contained Al_2O_3 (27.64%), SiO_2 (65.12%), CaO (1.35%), Fe_2O_3 (4.69%), TiO_2 (0.81%), K_2O (0.12%), MgO (0.61%), Na_2O (0.16%) and LOI (0.98%).

3.1 Acid leaching of fly ash

Fly ash samples from two different thermal power plants, without further grinding and size classification, were digested at boiling temperature with H_2SO_4 for 4 h. The aluminium oxide (Al_2O_3) present in the amorphous and crystalline (mullite) phases gets dissolved in the sulphuric acid. As per the speciation of aluminium, crystalline mullite and quartz phases accounted for 38%, and amorphous glass phase contained the remaining aluminium. Exhaustive leaching studies of both the fly ashes, i.e., TTPS and VAL, with sulphuric acid predict that the extraction efficiency of aluminium along with other metals increases with increase in acid concentration due to the increase in fly ash to sulphuric acid ratio (Fig. 1). As observed in Fig. 1, there is an appreciable increase in the aluminium extraction efficiency from 1:1 to 1:2 for TTPS fly ash and from 1:1 to 1:3 for VAL fly ash. The maximum aluminium extraction efficiency is obtained at solid-to-liquid ratio of 1:2 for TTPS (84.19%) and at solid-to-liquid ratio of 1:3 the aluminium extraction efficiency of VAL fly ash is 68.69%. When the solid-to-liquid efficiency increases to 1:4, the extraction rate slightly decreases for both the fly ashes. The increase in solid-to-liquid ratio involves an increase in the volume of acid, keeping constant the amount of fly ash. The increase of acid volume causes more solid and liquid contacts, resulting enhancement of reaction rate and dissolution of aluminium [37]. In both cases, after attaining the maximum extraction efficiency, the percentage of extraction of aluminium decreases. The presence of sulphate ions in the leach liquor triggers the

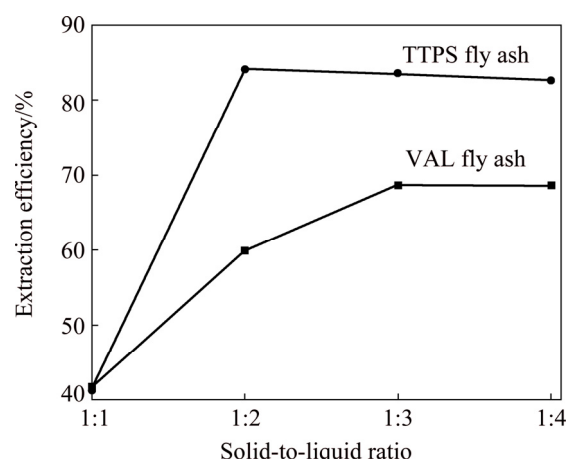


Fig. 1 Extraction efficiency of aluminium in TTPS and VAL fly ashes at different solid-to-liquid ratios

generation of calcium sulphate, which forms a surface coating onto the unreactive mullite and quartz fractions, thus inhibiting aluminium dissolution [38].

3.2 Effect of particle size on aluminium extraction

Leaching studies show that the extraction efficiency of aluminium is more in TTPS than in VAL fly ash. Particle size analysis reveals that TTPS fly ash has smaller particles than VAL, therefore, having more specific surface area per volume as listed in Table 1. Hence, the available surface area is more for acid attack, thus causing more extraction in TTPS compared to VAL fly ash. Moreover, the smaller particle size is advantageous for chemical reactivity due to better surface contact between coal fly ash and sulphuric acid [26]. Further, higher SPAN value (2.88) (SPAN, which is calculated as $(D_{90}-D_{10})/D_{50}$, is a useful parameter for determining the usability of an ash) of VAL fly ash with very high D_{90} (151.54 μm) and D_{50} (50.68 μm) indicates the presence of considerable amount of coarser particles which tend to reduce the leachability of aluminium [39]. On one hand, a large

Table 1 Particle size distribution of pre- and post-leached TTPS and VAL fly ashes

Fly ash	Solid-to-liquid ratio	$D_{90}/\mu\text{m}$	$D_{50}/\mu\text{m}$	$D_{10}/\mu\text{m}$	Specific surface area/($\text{m}^2\cdot\text{g}^{-1}$)	SPAN value
TTPS	Pre-leached fly ash	58.68	19.84	5.89	0.5509	2.66
	1:1	43.84	11.32	3.21	0.8297	3.58
	1:2	46.89	9.73	5.89	0.9119	4.49
	1:3	69.31	14.54	3.77	0.6550	4.24
	1:4	64.80	14.12	3.83	0.6560	4.31
VAL	Pre-leached fly ash	151.54	50.68	5.27	0.389	2.88
	1:1	130.53	32.38	3.44	0.579	3.92
	1:2	108.09	26.57	3.59	0.581	3.93
	1:3	96.98	23.76	3.51	0.608	3.93
	1:4	106.82	25.04	3.33	0.630	4.13

SPAN value may be due to one or more of the following items: 1) very high D_{90} and very small D_{10} , 2) moderate D_{90} and D_{10} but very small D_{50} . On the other hand, a small SPAN value may result from moderate D_{90} , D_{50} and small D_{10} . A very high SPAN value with a very high D_{90} indicates the presence of a considerably high percentage of coarser particles. Post-leached samples have decreased particle size with increasing specific surface area per volume. This observation is due to the elimination of appreciable amount of amorphous phases that surround insoluble crystals of mullite and quartz during acid leaching, thus exposing of high surface area [15].

3.3 Recovery of aluminium sulphate from leached liquor

The recoveries of aluminium as aluminium sulphate in leached liquors of TTPS and VAL fly ashes are presented in Table 2. Since various metals present in fly ash, which have a tendency to leach out with the increased concentration of acids, several other metals like Si, Ca, Mg, Na and K are leached out along with aluminium into the solution [40]. Hence, a controlled precipitation method is employed to avoid contamination of the extracted product by other impurities [41]. The maximum content of aluminium sulphate recovered from TTPS was 79.97%, which is considerably higher compared to VAL leached liquor (63.96 %) (Table 2). The solubility of aluminium sulphate increases with the increase in temperature. Aluminium sulphate can occur as both anhydrous and hydrated forms. Most commonly, it crystallizes from aqueous solution as hydrated form and contains 18, 16, 10 and 6 mol of water [42], among which the common form of aluminium sulphate is $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. It is noted that aluminium sulphate solution can be super cooled easily at 10 °C, i.e., more below the saturation point. It is observed that during leach liquor concentration on evaporation, crystallization starts at a certain point with the formation of white crystals. On gentle agitation, clear supersaturated

solutions exhibit the onset of nucleation by the appearance of silky, curling streamers of microscopic nuclei [41]. Once nucleation begins the cooling effect of the crystallizing salt leads to an accelerated crystallization and the super saturation sets up rapidly into a mushy, immobile mass.

The recovered aluminium sulphates from the leached liquor of both fly ashes are analyzed separately for their purity and the analysis data are presented in Table 3. The recovered aluminium sulphate from TTPS fly ash is found to be 99.80% pure, whereas the purity in VAL fly ash is 82.42%. The impurities found in TTPS fly ash are mainly iron (0.08 %) and minor quantities of Ti, Na, K, Ca and Fe. Similarly, the aluminium sulphate recovered from VAL fly ash consists of impurities such as iron (0.124%) and other metals as shown in Table 3. The investigation by using analytical techniques such as XRD, FTIR and TG/DTA shows that the extracted salt is the basic aluminium sulphate, considered to be $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

3.4 Characterization of aluminium sulphate

The aluminium sulphate obtained from the leached liquors of both the fly ashes (TTPS and VAL) was dried at 60 °C for 24 h and then subjected to X-ray diffraction (XRD) analysis. The XRD patterns of the aluminium sulphate recovered from TTPS and VAL fly ashes are shown in Fig. 2. The XRD result shows that both of the samples match with the XRD pattern of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and have a characteristic peak around a 2θ value of 20° [43]. The reorientation or segregation of the crystals may happen, which may cause the presence of different peak intensities at the same position obtained for the samples. However, due to the presence of impurities in minor concentration, different peaks other than $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ are also observed.

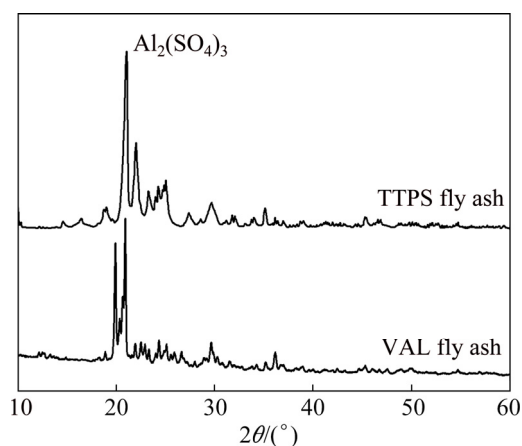
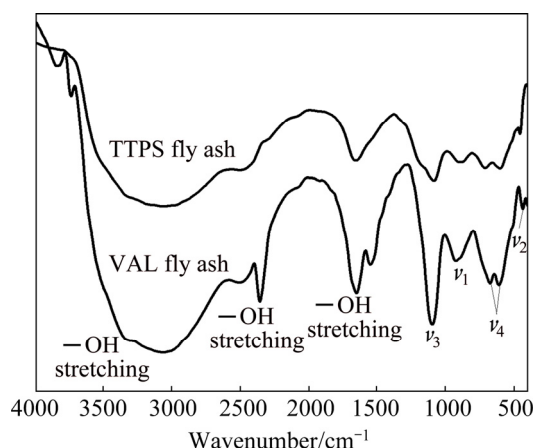
FTIR spectra of recovered aluminium sulphates from both of the fly ashes are shown in Fig. 3. The identified bands of aluminium sulphate are similar to those reported in literatures [44,45]. Differences are

Table 2 Aluminium concentration (CFA), extraction efficiency and recovery of aluminium sulphate in TTPS and VAL fly ashes

Fly ash	Solid-to-liquid ratio	Al content in fly ash (before leaching)/%	Al content in leached liquor (after leaching)/%	Extraction efficiency of Al/%	$\text{Al}_2(\text{SO}_4)_3$ content recovered from leach liquor/%
TTPS	1:1	15.404	6.42	41.67	31.65
	1:2	15.404	12.97	84.19	79.97
	1:3	15.404	12.72	82.57	71.01
	1:4	15.404	12.68	82.32	68.02
VAL	1:1	14.63	6.10	41.69	35.83
	1:2	14.63	8.76	59.87	63.96
	1:3	14.63	10.05	68.69	47.97
	1:4	14.63	10.03	68.55	60.52

Table 3 Impurities present in aluminium sulphate recovered from TTPS and VAL fly ashes

Composition	Al ₂ (SO ₄) ₃ content	Al ₂ (SO ₄) ₃ content
	from TTPS fly ash/%	from VAL fly ash/%
Al ₂ (SO ₄) ₃ ·18H ₂ O	99.80	82.42
Si	0	0.0062
Fe	0.080	0.124
Ti	0.029	6×10 ⁻⁵
Ca	0.0184	0.3899
Mg	0	0.0276
Na	1.6×10 ⁻⁴	0.130
K	2.37×10 ⁻⁴	0.140

**Fig. 2** XRD patterns of aluminium sulphate recovered from TTPS and VAL fly ashes**Fig. 3** FTIR spectra of aluminium sulphate recovered from TTPS and VAL fly ashes

observed in relative intensities and small shifts in peak positions, due to the impurities in the extracted sample. Early infrared spectroscopic studies have revealed that the free sulphate anion (SO_4^{2-}) has four infrared absorption peaks at ~ 1100 , ~ 1000 , ~ 600 , and ~ 450 cm^{-1} (namely the asymmetric stretching (ν_3), symmetric

stretching (ν_1), asymmetric bending (ν_4) and symmetric bending (ν_2), respectively) [46,47] among which ν_3 and ν_4 are infrared active. However, these vibrational frequencies could be modified when the sulphate anion is present in a solid or crystalline environment with a repeating molecular order, which results in appearance of all four sulphate vibrational modes in the spectrum [48]. In TTPS fly ash, ν_3 of SO_4^{2-} is found to be at 1085 cm^{-1} and ν_4 at 710 and 603 cm^{-1} . However, for VAL fly ash, the ν_3 appears at 1098 cm^{-1} and ν_4 at 673 and 610 cm^{-1} . In addition to strong absorption peaks at 1085 cm^{-1} (TTPS) and 1098 cm^{-1} (VAL), the ν_3 vibrational frequency of both of the recovered aluminium sulphates shows shoulder around 1190 cm^{-1} . It is of interest to note that, when SO_4^{2-} is bound to any metal, the symmetry can be either C_{3v} or C_{2v} . For C_{3v} symmetry ν_3 splits into two peaks and for C_{2v} symmetry ν_3 splits into three peaks [44,49]. As depicted from the IR spectra (Fig. 3), the presence of two peaks for ν_3 regions of both the recovered aluminium sulphates suggests the symmetry of the sulphate ion to be C_{3v} . Since the aluminium sulphate recovered from TTPS fly ash is purer in comparison to VAL fly ash, the bands observed in IR spectra of TTPS are more defined than that observed in spectra of $\text{Al}_2(\text{SO}_4)_3$ recovered from VAL. The broad bands at 3066 and 3069 cm^{-1} for TTPS and VAL fly ashes, respectively confirm the presence of $-\text{OH}$ group in aluminium sulphate. The bands at 1660 and 1650 cm^{-1} match with the bending peaks of H_2O for both TTPS and VAL fly ashes respectively, showing the existence of water molecules [50].

The TGA profiles of aluminium sulphate for two different fly ashes were obtained in a temperature range of 28 to 1000 $^\circ\text{C}$. Pure $\gamma\text{-Al}_2\text{O}_3$ was used as a blank reference. Both of the samples of aluminium sulphate recovered from TTPS and VAL fly ashes start decomposing at very low temperature (~ 32 $^\circ\text{C}$ and 28 $^\circ\text{C}$, respectively) in a step wise manner with the loss of coordinated water molecule, giving rise to one or more intermediate products (Figs. 4(a) and (b)). The resultant intermediate products are assigned from the estimated mass loss and they seem to be stoichiometric. The thermal study of aluminium sulphate [42] obtained from TTPS fly ash predicted that the dehydration proceeded in four different stages. Two molecules of water were lost at 73 $^\circ\text{C}$, 11 molecules of water at 169 $^\circ\text{C}$, 16 molecules of water at 350 $^\circ\text{C}$ and 17 molecules of water at 390 $^\circ\text{C}$. The last molecule of water started decomposing after 390 $^\circ\text{C}$, thus forming anhydrous $\text{Al}_2(\text{SO}_4)_3$, which is observed to be stable up to 719 $^\circ\text{C}$, as seen in Fig. 4(a). The presence of endothermic peaks at 73 , 120 , 349 and 844 $^\circ\text{C}$ in DTA curve confirms the decomposition of water molecules in aluminium sulphate. The majority of the sulphates were decomposed in the temperature range

719–844 °C. A sharp endothermic peak at 844 °C provides additional evidence for the decomposition of sulphates as SO_2 and SO_3 until the formation of Al_2O_3 .

Similarly, aluminium sulphate of VAL fly ash started decomposing at 70 °C and reached a steady state at over 870 °C (Fig. 4(b)). The dehydration of water molecules took place in four different stages. One molecule of water was lost at 70 °C, seven molecules of water at 163 °C, 12 molecules of water at 220 °C and then 17 molecules of water at 340 °C. The last molecule of water started decomposing after 340 °C, thus forming anhydrous $\text{Al}_2(\text{SO}_4)_3$, which is observed to be stable up to 665 °C, as seen in Fig. 4(b). It has been observed that the mass loss of around 50% is due to dehydration occurring during heating to around 400 °C and on further heating to 870 °C the decomposition of anhydrous aluminium sulphate caused an additional loss of about 36%. The complete decomposition of sulphates took place around 875 °C, leading to the formation of Al_2O_3 .

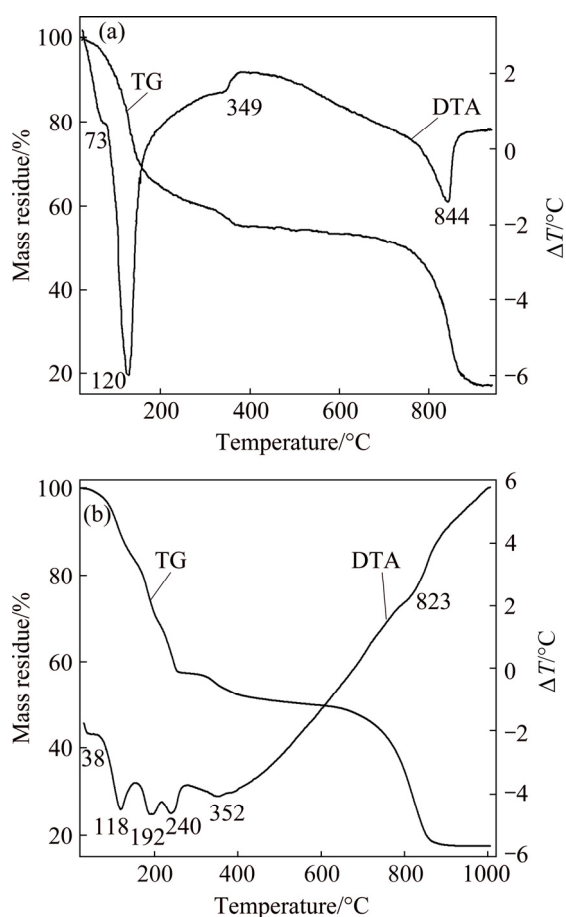


Fig. 4 TG/DTA curves of aluminium sulphate recovered from TTPS (a) and VAL (b) fly ashes

4 Conclusions

This study predicts that highly pure $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ could be prepared by the reaction of coal fly ash with sulphuric acid followed by successive

crystallization. Several metal values are found to be present in the leached liquor and hence, the purification of leach liquor to obtain industrial grade aluminium sulphate poses a great concern. Although agglomeration of some iron oxides with alumina and silica made it difficult to completely separate the iron from the fly ash, this has been overcome by separating $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ effectively from the potential contaminants, such as iron, titanium and several other metals by recrystallization process. Compared with VAL fly ash, the recovered aluminium sulphate from TTPS fly ash is pure (>99.0%) and of industrial grade having low iron content (0.080%). The important advantage of the process is that the digestion of fly ash with H_2SO_4 in mild operating condition avoids the conventional energy intensive methods. The process does not involve any grinding, sieving and size classification of fly ash. The commercial grade H_2SO_4 is used as leachant, which could be recovered and recycled in the process. Although the leaching behaviour follows a general trend irrespective of different ashes from different sources, the association of mineral matters and size fractions plays a vital role in determining the extraction efficiency of the desired element. Considering the rising cost of landfill and community opposition to toxic waste dumps, this process could be a viable method for providing an alternate aluminium source. Hence, the problem of generation of fly ash can be solved by looking at it as a resource or by-product rather than waste.

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References

- [1] BLISSETT R S, ROWSON N A. A review of the multi-component utilisation of coal fly ash [J]. *Fuel*, 2012, 97: 1–23.
- [2] DUTTA B K, KHANRA S, MALLICK D. Leaching of elements from coal fly ash: Assessment of its potential for use in filling abandon coal mines [J]. *Fuel*, 2009, 88: 1314–1323.
- [3] ZHOU C, LIU G, WU S, PAUL P K. The environmental characteristics of usage of coal gangue in brick-making: A case study at Huainan, China [J]. *Chemosphere*, 2014, 95: 274–280.
- [4] YANG M, GUO Z, DENG Y, XING X, QIU K, LONG J, LI J. Preparation of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass ceramics from coal gangue [J]. *International Journal of Mineral Processing*, 2012, 102: 112–115.
- [5] YAO Z T, JI X S, SARKER P K, TANG J H, GE L Q, XIA M S, XI Y Q. A comprehensive review on the applications of coal fly ash [J]. *Earth-Science Reviews*, 2015, 141: 105–121.
- [6] PARK H C, PARK Y J, STEVENS R. Synthesis of alumina from high purity alum derived from coal fly ash [J]. *Materials Science and Engineering A*, 2004, 367: 166–170.

- [7] SHEMI A, MPANA R N, NDLOVU S, van DYK L D, SIBANDA V, SEEPE L. Alternative techniques for extracting alumina from coal fly ash [J]. *Minerals Engineering*, 2012, 34: 30–37.
- [8] WU Cheng-you, YU Hong-fa, ZHANG Hui-fang. Extraction of aluminium by pressure acid-leaching method from coal fly ash [J]. *Transactions of Nonferrous Metals Society of China*, 2012, 22: 2282–2288.
- [9] MEAWAD A S, BOJINOVA D Y, PELOVSKI Y G. An overview of metals recovery from thermal power plant solid wastes [J]. *Waste Management*, 2010, 30: 2548–2559.
- [10] IZQUIERDO M, QUEROL X. Leaching behaviour of elements from coal combustion fly ash: An overview [J]. *International Journal of Coal Geology*, 2012, 94: 64–66.
- [11] YAO Z, XIA M S, SARKER P K, CHEN T. A review of the alumina recovery from coal fly ash, with a focus in China [J]. *Fuel*, 2014, 120: 74–85.
- [12] MEHTAP P, MERYEM S, GUL A A, SANDSTROM A, MICHEL L S, JAN P. Acid leaching of ash and coal: Time dependence and trace element occurrences [J]. *International Journal of Mineral Processing*, 2006, 79: 27–41.
- [13] MERYEM S, MEHTAP P, AKE S, DYK L D, SIBANDA V, SEEPE L. Acid leaching of coal and coal-ashes [J]. *Fuel*, 2003, 82: 1721–1734.
- [14] LI J, GAN J, LI X. Leaching of aluminium and iron from boiler slag generated from a typical Chinese steel plant [J]. *Journal of Hazardous Materials*, 2009, 166: 1096–1101.
- [15] NAYAK N, PANDA C R. Aluminium extraction and leaching characteristics of Talcher thermal power station fly ash with sulphuric acid [J]. *Fuel*, 2010, 89: 53–58.
- [16] BAI Guang-hui, TENG Wei, WANG Xiang-gang, QIN Jin-guo, XU Peng, LI Peng-cheng. Alkali desilicated coal fly ash as substitute of bauxite in lime-soda sintering process for aluminum production [J]. *Transactions of Nonferrous Metals Society of China*, 2010, 20(S1): s169–s175.
- [17] WANG Ruo-chao, ZHAI Yu-chun, WU Xiao-wei, NING Zhi-qiang, MA Pei-hua. Extraction of alumina from fly ash by ammonium hydrogen sulfate roasting technology [J]. *Transactions of Nonferrous Metals Society of China*, 2014, 24(5): 1596–1603.
- [18] YANG Quan-chen, MA Shu-hua, ZHENG Shi-li, ZHANG Ran. Recovery of alumina from circulating fluidized bed combustion Al-rich fly ash using mild hydrochemical process [J]. *Transactions of Nonferrous Metals Society of China*, 2014, 24(5): 1187–1195.
- [19] DOUCET F J, MERWE E M V, NEYT N, PRINSLOO L C. Extraction of aluminium and other strategic metals from coal fly ash using a novel process and low cost recoverable reagent [C]//*Proceedings of World of Coal Ash Conference (WCOA) 2015*. Nashville, Tennessee, USA: Ash Library Press, 2015: 1–10.
- [20] LIU N, PENG J, ZHANG L, WANG S, HUANG S, HE S. Extraction of aluminium from coal fly ash by alkali activation with microwave heating [J]. *Journal of Residual Sciences & Technology*, 2016, 13(S): s181–s187.
- [21] FREEMAN M J. The manufacture of alumina in south Africa: Mintek Report No. M376 D [R]. 200 Hans Srijdom Drive, Randburg, South Africa, 1993.
- [22] MATJIE R H, BUNT J R, van HEERDEN J H P. Extraction of alumina from coal fly ash generated from a selected low rank bituminous South African coal [J]. *Minerals Engineering*, 2005, 18: 299–310.
- [23] BALASIEWICZ M, MICHALOWSKI S, POROWSKI J, MORKOWSKA E. Alumina from non-bauxite ores by the Bretznajder sulphuric acid method [M]. Columbus, Ohio: Trav Com Int Etude Bauxites, Alumine Alum, 1982: 11–18.
- [24] LIVESEY-GOLDBLATL E, NAGY I F, TUNLEY T H. Aluminium and uranium recovery: South Africa, ZA 8105294 [P]. 1983.
- [25] HUANG W H. New extraction technique for alumina from coal ash [C]//*Proceedings of the 4th International Congress for the Study of Bauxites*. Athens, Greece: The Clay Mineral Society, 1978: 117–125.
- [26] LI Lai-shi, WU Yu-sheng, LIU Ying-ying, ZHAI Yu-chun. Extraction of alumina from coal fly ash with sulfuric acid leaching method [J]. *The Chinese Journal of Process Engineering*, 2011, 11: 254–258. (in Chinese)
- [27] SHEMI A, NDLOVU S, SIBANDA V, van DYK L D. Extraction of alumina from coal fly ash using an acid leach–sinter–acid leach technique [J]. *Hydrometallurgy*, 2015, 157: 348–355.
- [28] JIANG Zhou-qing, YANG Jing, MA Hong-wen, WANG Le, MA Xi. Reaction behaviour of Al_2O_3 and SiO_2 in high alumina coal fly ash during alkali hydrothermal process [J]. *Transactions of Nonferrous Metals Society of China*, 2015, 25: 2065–2072.
- [29] DING J, MA S, ZHENG S, ZHANG Y, XIE Z, SHEN S, LIU Z. Study of extracting alumina from high-alumina PC fly ash by a hydro-chemical process [J]. *Hydrometallurgy*, 2016, 161: 58–64.
- [30] SIBANDA V, NDLOVU S, DOMBO G, SHEMI A, RAMPOU M. Towards the utilization of fly ash as a feedstock for smelter grade alumina production: A review of the developments [J]. *Journal of Sustainable Metallurgy*, 2016, 2: 167–184.
- [31] WARREN C J, DUDAS M J. Weathering processes in relation to leachate properties of alkaline fly ash [J]. *Journal of Environmental Quality*, 1984, 13: 530–538.
- [32] WARREN C J, DUDAS M J. Formation of secondary minerals in artificially weathered fly ash [J]. *Journal of Environmental Quality*, 1985, 14: 405–410.
- [33] NAYAK N. Leaching behaviour of fly ash from Talcher thermal power station with mineral acids [J]. *Applied Science and Advanced Materials International*, 2015, 1(4–5): 126–132.
- [34] SANGITA S, PANDA C R. Acid leaching technique for the possible recovery of aluminium and other metal values from coal fly ash [J]. *Journal of Indian Chemical Society*, 2016, 93: 1–7.
- [35] XIAO J, LI F, ZHONG Q, BAO H, WANG B, HUANG J, ZHANG Y. Separation of aluminium and silica from coal gangue by elevated temperature acid leaching for the preparation of alumina and SiC [J]. *Hydrometallurgy*, 2015, 155: 118–124.
- [36] NAYAK N, PANDA C R. Some characteristics of Orissa fly ash with reference to mineral recovery [J]. *Journal of Indian Chemical Society*, 2007, 84: 603–608.
- [37] BAI G, QIAO Y, SHEN B, CHEN S. Thermal decomposition of coal fly ash by concentrated sulfuric acid and alumina extraction process based on it [J]. *Fuel Processing Technology*, 2011, 92: 1213–1219.
- [38] SEIDEL A, ZIMMELS Y. Mechanism and kinetics of aluminium and iron leaching from coal fly ash by sulphuric acid [J]. *Chemical Engineering Science*, 1998, 53(22): 3835–3852.
- [39] SARKARA A, RANO R, MISHRA K K, SINHA I N. Particle size distribution profile of some Indian fly ash—A comparative study to assess their possible uses [J]. *Fuel Processing Technology*, 2005, 86: 1221–1238.
- [40] BERRY E E, HEMMINGS R T. Enhanced resource recovery by beneficiation and direct acid leaching of fly ash [C]//*Symposium Proceedings of Materials Research Society*. Cambridge: Cambridge University Press, 1987: 365–380.
- [41] DARRAGH K V. Aluminium sulphate and alums [M]. 3rd ed. New York: Wiley, 1978: 246.
- [42] OTTO H, HUDSON L K, MISHRA C, WEFERS K, HANS S, DANNER M. Aluminium compounds [M]. Weinheim: Wiley-VCH Publishers, 1985: 527.
- [43] MATORI K A, WAH L C, HASHIM M, ISMAIL I, ZAID M H M. Phase transformations of α -alumina made from waste aluminum via a precipitation technique [J]. *International Journal of Molecular Science*, 2012, 13: 16812–16821.

- [44] NAKAMOTO K. Infrared and Raman spectra of inorganic and coordination compounds [M]. 4th ed. New York: Wiley, 1986: 103–110.
- [45] MOENKE H. Mineralspektren (I) [M]. Berlin: Akademie-Verlag, 1962: 40.
- [46] HERZBERG G. Molecular spectra and molecular structure II [M]. New York: Van Nostrand Company, 1945.
- [47] HUG S J. In situ Fourier transform infrared measurements of sulfate adsorbed on hematite in aqueous solutions [J]. Journal of Colloid and Interface Science, 1997, 188: 415–422.
- [48] LANE M D. Mid-infrared emission spectroscopy of sulfate and sulfate-bearing minerals [J]. American Mineralogist, 2007, 92: 1–18.
- [49] ROSS S D. Infra red spectra of minerals [M]. London: Mineralogical Society, 1974: 430–439.
- [50] GADSDEN J A. Infrared spectra of minerals and related inorganic compounds [M]. London: Butterworth Group, 1975: 46.

从热电厂粉煤灰中提取铝生产硫酸铝

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摘 要: 目前从热电厂粉煤灰中提取有价金属的方法存在一定的局限性。研究用硫酸从热电厂粉煤灰中提取铝制备高纯硫酸铝(>99.0%)。以硫酸为萃取剂分别提取 Talcher 热电站和 Vedanta 铝业有限公司的粉煤灰中的铝制备硫酸铝。采用 X 射线衍射谱、傅里叶红外光谱和热重分析等手段对硫酸铝产品进行表征, 用电感耦合等离子-光学发射光谱测量硫酸铝产品的纯度。结果表明, 粉煤灰的浸出率取决于粉煤灰与硫酸的固液比以及粉煤灰的颗粒尺寸。物化分析结果表明, 所得产品为 $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 其铁含量较低, 仅为 0.08%(质量分数)。

关键词: 粉煤灰; 硫酸; 硫酸铝; 浸取; 固液比; 颗粒尺寸

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