Processing of Coal Fly Ash as an Alternate Resource for Alumina Ensuing Acid Leaching Route

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Abstract

Considering the depletion of Bauxite, the extraction of alumina has been experimented using alternate source material, coal fly ash. The process of recovering alumina from coal fly ash (CFA) is quite complex requiring the application of stringent reaction conditions such as high temperature and pressure including high inventory of chemicals. In order to simplify the leaching conditions the effect of fluoride ion on sulphuric acid leaching of coal fly ash has been tested. The addition of fluoride ions such as HF and NaF improved the acid leaching performance to a great extent when partial desilicated ash was used. The partial desilication was carried out through an alkali treatment of CFA. The use of desilicated CFA reduced the requirement of fluoride ion and sulphuric acid concentrations as compared to the original CFA treatment in the extraction of alumina. It has been observed that the HF is more reactive than the NaF. It was noted that extracting more than 90 % of alumina from the CFA requires one-third amount of HF than NaF while keeping the sulphuric acid quantity the same. The sodium silicate formed during the desilication process was treated with lime to produce calcium silicate as a by-product and sodium hydroxide regenerated is recycled back for subsequent alkali treatment of fly ash. The reactions mechanism and an overall flow sheet for the treatment of CFA have been described. The preliminary cost economics for extraction of alumina following the above process has also been worked out.

Keywords: Coal fly ash, Alumina, Sulphuric acid, Leaching, Fluoride ion.

1. Introduction

The world's annual generation of coal fly ash (CFA) is nearly about 800 million tonnes out of which India alone produces more than 180 million tonnes. The CFA contains different valuable minerals such as mullite, quartz, hematite, magnetite, α-alumina, calcium oxide, titanium dioxide, etc. Mullite is the main alumina bearing silicate phase. In India, nearly 30 million tonnes of alumina, the major value material, which is present in fly ash is getting wasted due to the unavailability of suitable technologies. Extraction of alumina from CFA has been tried in various places through different methods such as limestone sintering [1,2], soda-lime sintering [3], calsinter process [4,5], ammonium sulphate sintering process [6] and acid leaching processes [7,8]. However, these processes are associated with a number of disadvantages. The sintering

process produces a huge quantity of residue which is a few times higher than the original ash. In the ammonium sulphate process the requirement for ammonium sulphate is huge (10:1, ammonium sulphate: alumina). The sulphuric acid method requires a higher temperature of 200–210 ℃, at a ratio of acid to fly ash as 5:1 (v/v) with an extraction efficiency of 85 %.

Mullite is the major alumina bearing material in CFA. More than 90 % of alumina available in fly ash is associated with 8-10 % of silica in the form of mullite. Mullite, the aluminosilicate phase is a very stable refractory material. Due to its refractoriness, it is hard to dissociate into its constituent components for further processing through conventional pyro or hydrometallurgical routes. Mullite morphology is also important as there are two common morphologies for mullite. One is a platelet-shaped with low aspect ratio and the second is a needle-shaped with high aspect ratio. Needle shaped mullite forms have high mechanical strength and thermal shock resistance as the needles interlock. This type of mullite morphology is a major hindrance to its disintegration during leaching. Fly ash contains both needles as well as platelet types. Therefore, rigorous treatments are needed for processing the fly ash at high temperature or pressure conditions. In the present study, hydrometallurgical processing options are pursued. The simple leaching of fly ash for the recovery of alumina with alkali or acid is very difficult to accomplish as the breaking of the mullite phase is extremely difficult. Under hydrothermal (pressure) conditions also it could not be broken.

In the present study, sulphuric acid leaching method has been adopted in presence of fluoride ions to recover alumina from coal fly ash. The authors in their earlier works presented the effect of fluoride ions by adding sodium fluoride [9] and hydrofluoric acid [10] to solubilize the alumina values under various leaching conditions. In earlier work, leaching studies were carried out taking untreated fly ash whereas in the present study soda leached residue of fly ash was taken for the study (soda ash leaching was performed to leach out a significant portion of silica, which is amorphous in nature) [10]. Additionally, the effects of both NaF and HF were compared. A flow sheet for alumina production from fly ash has also been prepared considering the improved extraction efficiency. The chemistry of the process, tentative cost estimation and various product characterizations have been included.

2. Materials and Method

2.1 Materials

The CFA was collected from the thermal power plant of National Aluminium Company Limited (NALCO), India. The ash had a median particle size of 36.8 μm (d50). All the chemicals used in the present work were of analytical grade (Merck, India). The phase analysis was carried out using the X-Ray diffraction patterns generated from an X-Ray Diffractometer (Philips, PW 1710). The surface morphology was investigated using an optical microscope (Leitz make).

2.2 Method

Hydrothermal sodium hydroxide leaching of ash was carried out in an autoclave of 1 L capacity by varying NaOH concentration and temperature. A detailed study on this has been mentioned elsewhere [9]. At the end of the experiment, the slurry was filtered and then the leach residue was washed and dried for further processing through the acid leaching route to extract alumina. Acid leaching of alkali leached ash residue was carried out in the absence or presence of fluoride ions. Fluoride ions are added in the form of HF or NaF. The leach liquor obtained after filtration was then analysed for aluminium concentration and the leaching efficiencies of alumina were calculated using the standard method. Precipitation of aluminium hydroxide was carried out after separating the iron hydroxide.

2.3 Characterization of Fly Ash

The ash residue after sodium hydroxide leaching was analyzed to determine its chemicalcomposition. The alumina quantity was increased to about 33–34 % from an average CFA composition of 24 % alumina and silica quantity was reduced to about 45–46 % from about 65 %. The compositional analyses of dried ash residue are given in Table 1. The original fly ash containing 24 % alumina before hydrothermal leaching gets upgraded to 33–34 % due to removal of a portion of silica (amorphous variety). The optical micromorphology of original CFA particles was examined and found to contain mullite particles other than quartz and hematite. Figure 1 shows the needle-shaped mullite particles and also irregular shaped or platelet mullite grains.

Table 1. Composition of fly ash residue after alkali leaching.

Constituent	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2
Percentage (wt %)	33–34	45–46	5–6	1–1.5	2–3

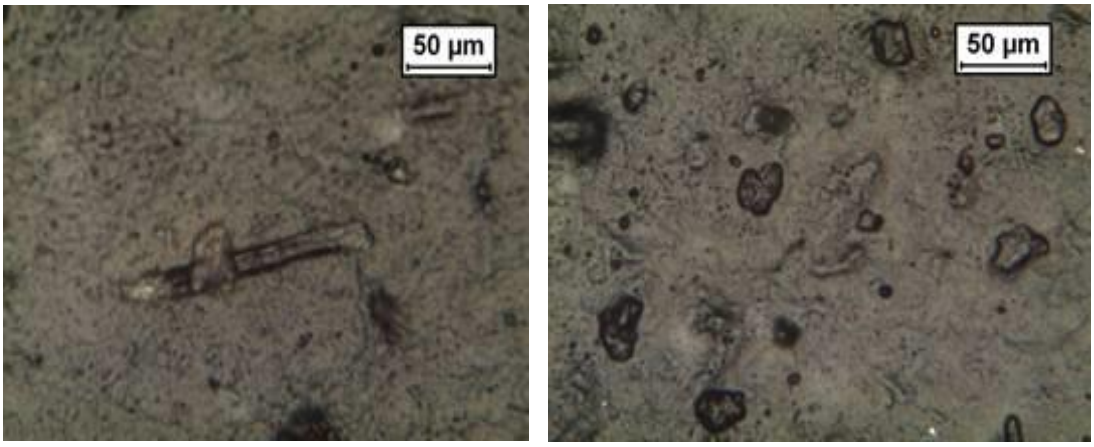

Figure 1. Optical micrograph of fly ash sample showing mullite grains. [left: Needle shaped mullite grain, right: small platelet grains of mullite].

3. Results and Discussion

The fly ash residue after alkali leaching was leached in sulphuric acid solution to dissolve alumina. Mullite, the aluminosilicate phase is present as the main alumina bearing phase in fly ash and it hardly responded to any standard leaching method indicating solubilization of alumina is the major bottleneck in fly ash processing. Highly stringent leaching conditions such as high concentration of acid and high temperature (~200 ℃) are required for its dissolution. Thus, the focus of the present work was to break the mullite matrix to release the alumina for its solubilization during the leaching of fly ash in the H_2SO_4 solution. The presence of fluoride ions added as HF and NaF was found to be very effective.

Authors have investigated in the earlier work [9] that a maximum of 50 % silica of amorphous nature can be removed from the ash under the optimum conditions of 1M NaOH concentration and temperature of 180 ℃. Moreover, it was also observed that under these leaching conditions, the loss of alumina was 0.38 % only. With further increase in alkali concentration more silica could not be removed and the alumina loss was still negligible. Therefore, it may be inferred that through hydrothermal leaching of fly ash the silica of amorphous variety can be removed without any loss of alumina. In the next step, acid leaching studies were carried out using the alkali leached residue and original fly ash for knowing the alumina leachability without any fluoride addition.

Table 2 shows the alumina recoveries under different sulphuric acid concentrations for both samples. It has been observed that the alkali leached residue showed higher recoveries at all the acid concentrations. At 25 % acid concentration, 46 % alumina was recovered as compared to 27 % while processing original fly ash. Therefore, it indicates that after partial removal of silica from the CFA the acid leaching efficiency of alumina was improved.

Table 2. Alumina recovery under H2SO4 leaching conditions.

Leaching condition	Alumina recovery, %	
	Untreated fly ash	Alkali leached fly ash
10% (v/v) H_2SO_4, 90 °C, 2h	12	20
15% (v/v) H_2SO_4, 90 °C, 2h	17	35
25% (v/v) H_2SO_4, 90 °C, 2h	27	46

3.1 Effect of Fluoride Ion as HF and NaF on Alkali Leached Residue

It was observed that in the absence of any fluoride ions, a maximum alumina leaching efficiency of 20 % can be accomplished with 10 % H_2SO_4 concentration whereas that could only be enhanced to 46 % with a higher acid concentration of 25 % at 90 °C. Beyond this acid amount, a marginal enhancement in leaching efficiency was observed under above temperature conditions. Figures 2 and 3 show a comparison between the addition of NaF and HF to sulphuric acid leaching of ash residue. It has been calculated that the addition of 1 g NaF or 1 mL HF in any aqueous system will have a near equivalent concentration of fluoride ions considering the strength of concentrated HF used in this study was 47–48 % (v/v). Figure 2 shows the effect of NaF on the acid leaching of ash residue. It has been observed that with the addition of 1 g of NaF on acid leaching showed 43 %, 52 % and 90 % of alumina recovery efficiencies for 10 %, 15 % and 25 % acid concentrations respectively. With the increase in NaF concentration to 2 g about 92 % alumina recovery was observed for 25% acid and the addition of NaF beyond this concentration recovery was constant. In case of 15% acid, 3 g of NaF addition resulted in 90 % recovery and beyond this, no further improvement in leaching recovery was observed. In case of 10 % acid, 80 % alumina leaching recovery was observed after the addition of 5 g of NaF and it needs a further amount to have a better recovery. Overall, it has been observed that for 25 % acid concentration 1 g NaF is needed and in the case of 15 % acid about 3 g of NaF is needed to achieve 90 % leaching recoveries. In case of 10 % acid, even after the addition of 5 g of NaF leaching recovery for alumina was restricted to only 80 %. Now in comparison to NaF when HF was added better recoveries were obtained with smaller amounts of HF additions in similar concentrations of sulphuric acid quantities.

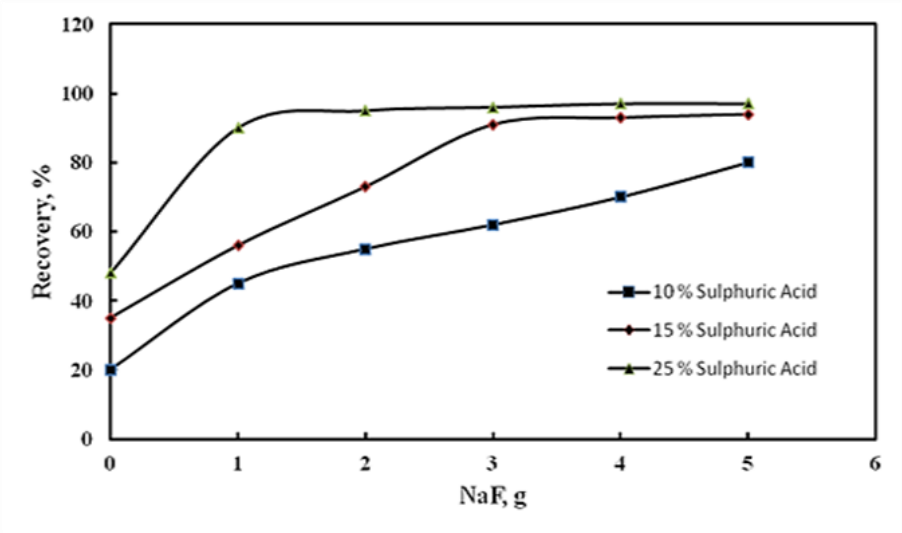

Figure 2. Effect of NaF on recovery of alumina. Residue: 10 g, solution taken: 100 mL, Temperature: 90 °C, Leaching time: 2 h.

Figure 3 shows the effect of HF concentration on acid leaching of fly ash residue. 93 % recovery of alumina was observed when 0.5 mL of HF was added in a 25 % acid leaching experiment. Under similar HF concentrations, about 70 % and 50 % recoveries were obtained for 15 % and 10 % H_2SO_4 acid concentrations respectively. With the addition of 1 mL of HF, the leaching recoveries were improved to greater than 95 %, 90 % and 62 % for 25 %, 15 % and 10 % acid leaching studies respectively. With the addition of 1.5 mL of HF the leaching recoveries of almost 100 % for 25 % acid, about 95% for 15 % acid and 80 % for 10 % acid were obtained. In the case of 10 % acid after 2 mL HF addition of around 90 %, leaching efficiency was obtained. It, therefore, indicates that lower amounts of HF are needed for similar or higher recoveries compared to the amount of NaF. For more than or about 95 % recoveries 1 mL of HF is sufficient in 25 % acid leaching condition. Whereas in the case of 15 % acid, 1.5 mL HF is needed to have 95 % alumina recovery. Therefore, to have higher recoveries with smaller amounts of fluoride ions, HF is the suitable additive compared to NaF and its amount ranges between 0.5 mL to 1.5 mL depending upon the concentration of sulphuric acid.

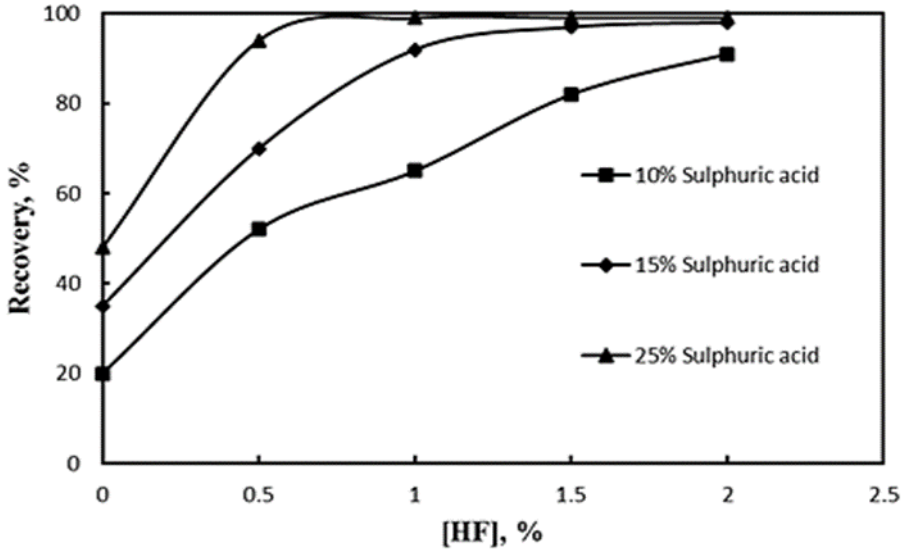

Figure 3. Effect of HF on leaching recovery of alumina. Residue: 10g, solution taken: 100 mL, Temperature: 90 °C, Leaching time: 2 h.

3.2 Reaction Mechanism during Acid Leaching of Alumina-rich Residue

Acid leaching with NaF addition: The role of NaF is as follows,

When NaF is added to the sulphuric acid solution, it reacts with H_2SO_4 and produces HF, this HF, in turn, reacts with the mullite phase and breaks to open the mullite matrix. A small quantity of aluminium fluoride (AlF_3) and SiF_4 is produced. The broken mullite matrix will facilitate the leaching of alumina by reacting with sulphuric acid. The reactions took place as follows

$$2NaF + H_2SO_4 = 2HF + Na_2SO_4 \quad (1)$$

Mullite matrix will break as follows

$$Al_2O_3 + SiO_2 + 10HF = 2AlF_3 + SiF_4 + 5H_2O \quad (2)$$

After breaking of mullite alumina dissolves in sulphuric acid as follows

$$Al_2O_3 + 3H_2SO_4 = Al_2 (SO_4)_3 + 3H_2O \quad (3)$$

$$2AlF_3 + 3H_2SO_4 = Al_2 (SO_4)_3 + 6HF \quad (4)$$

If sufficient HF is present then possibly the following reaction (Equation (5)) may take place else silicon fluoride (volatile) will form and escape from the system. In this case, probably SiF_4 escapes at the reaction temperature as concentrations of fluoride ions are minimal.

With sufficient HF following reaction will take place but it is unlikely in the present case

$$SiF_4 + 2HF = H_2SiF_6 \quad (5)$$

Overall reaction takes place when NaF is added in sulphuric acid leaching condition is as follows

$$Al_2O_3 + SiO_2 + 4NaF + 5H_2SO_4 = Al_2 (SO_4)_3 + SiF_4 \uparrow + 2Na_2SO_4 + 5H_2O \quad (6)$$

And in case when HF was added during acid leaching studies excepting Equation (1) all other reactions will take place and the overall reaction will look like as follows

$$Al_2O3 + SiO_2 + 4HF + 3H_2SO_4 = Al_2 (SO_4)_3 + SiF_4 \uparrow + 5H_2O \quad (7)$$

The two major differences in the case of HF addition are:

i) Equation (1) will be absent and
ii) Generation of sodium sulphate can be avoided in the leaching stage.

3.3 Precipitation of Calcium silicate and Aluminium hydroxide

The alkali leached fly ash solution collected was mainly sodium silicate solution because mostly silica got leached into the solution. This leached solution can be used for the preparation of silica gel, sodium silicate crystals and calcium silicate depending upon the need. A typical calcium silicate X-ray diffraction pattern, which has been obtained from the present study by treating with lime slurry, is shown in Figure 4.

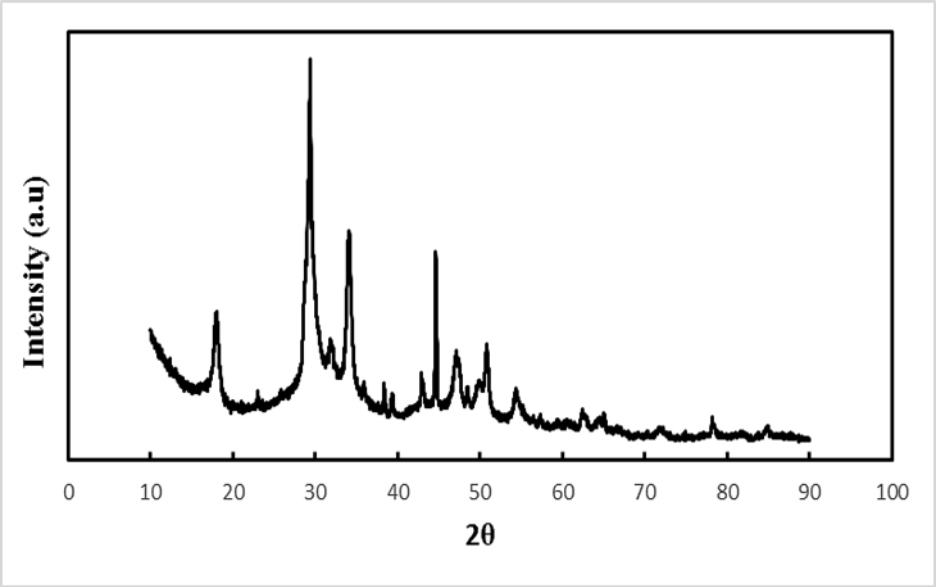

Figure 4. XRD pattern of calcium silicate produced from the sodium silicate leach liquor.

The leach solution obtained after the acid leaching operation was having a pH of about 0.5–1.0. The solution generated was analyzed and found to contain aluminium sulphate along with iron sulphate. While precipitating aluminium hydroxide with alkali, iron also precipitated as iron hydroxide thus contaminating the aluminium hydroxide product and subsequently alumina. In order to avoid such phenomenon, the precipitation of aluminium hydroxide was conducted by adding sodium hydroxide and continued till pH 12–12.5. Initially while adding sodium hydroxide both alumina and iron values were precipitated as respective hydroxides and by adding further the sodium hydroxide solution the alumina present in the precipitate gets dissolved leaving the iron in the residue because iron did not get dissolved in alkali solution. At about pH 12.5, all the alumina value present in the precipitate gets dissolved forming a sodium aluminate solution. This solution was further treated to obtain aluminium hydroxide. The iron hydroxide obtained as residue can be washed thoroughly to obtain pure iron hydroxide product. The sodium aluminate solution generated as mentioned above may be precipitated with the slow addition of sulphuric acid to obtain aluminium hydroxide. Precipitation of aluminium hydroxide could have been carried out through the carbonization decomposition method also. The precipitation with H2SO4 was carried out at about 90 °C and also aged for a sufficient time to obtain low soda hydroxide. The ageing time will differ according to the temperature of the operation. At higher temperatures, less time is needed while at lower temperatures more time to be provided. A typical ageing time requirement is between 3–5 h at 90 °C. The aluminium hydroxide precipitated through this route showed a bayerite structure (Figure 5). The aluminium hydroxide precipitated was then activated at different temperatures (500–1000 °C) to obtain active alumina or around 1200 °C to obtain alpha-alumina (Figure 6) as the requirement might be. The acid leached residue obtained is mainly quartz with contamination of little (about 5 %) unreacted alumina.

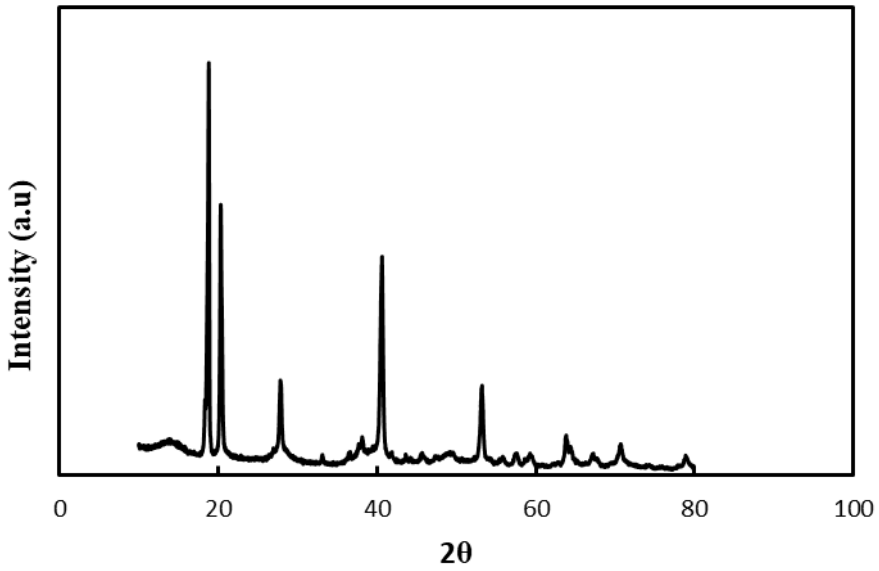

Figure 5. XRD pattern of aluminum hydroxide (Bayerite) precipitated from acid leach liquor.

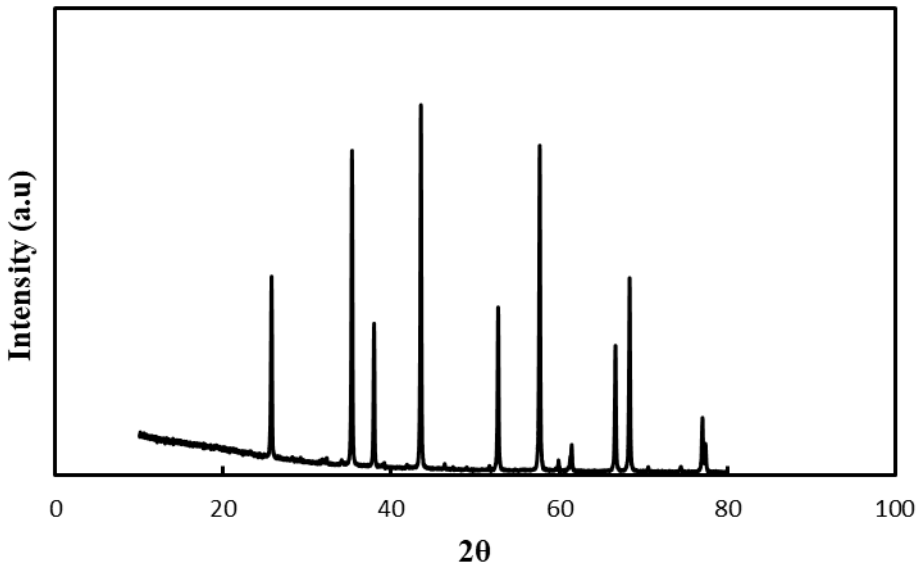

Figure 6. XRD Pattern of α-Alumina obtained after calcining aluminium hydroxide at 1200 °C.

3.4 Process Flow Sheet for the Extraction of Alumina from Fly Ash

A typical process flowsheet (Figure 7) has been proposed for the processing of fly ash, indicating various unit operations and their role in the extraction of alumina and the by-products, such as calcium silicate, calcium sulphate, etc. The acid leached residue also showed pure quartz material with a minimal quantity of alumina. The process involves hydrothermal alkali leaching of fly ash to remove a significant fraction of silica followed by recovery of the solubilised silica as calcium silicate and sulphuric acid leaching of the alkali leach residue in presence of HF or NaF to solubilise alumina followed by recovery of alumina through conventional precipitation route. The final residue generated from this process was quartz with minimal impurities such as alumina, titania and iron oxide.

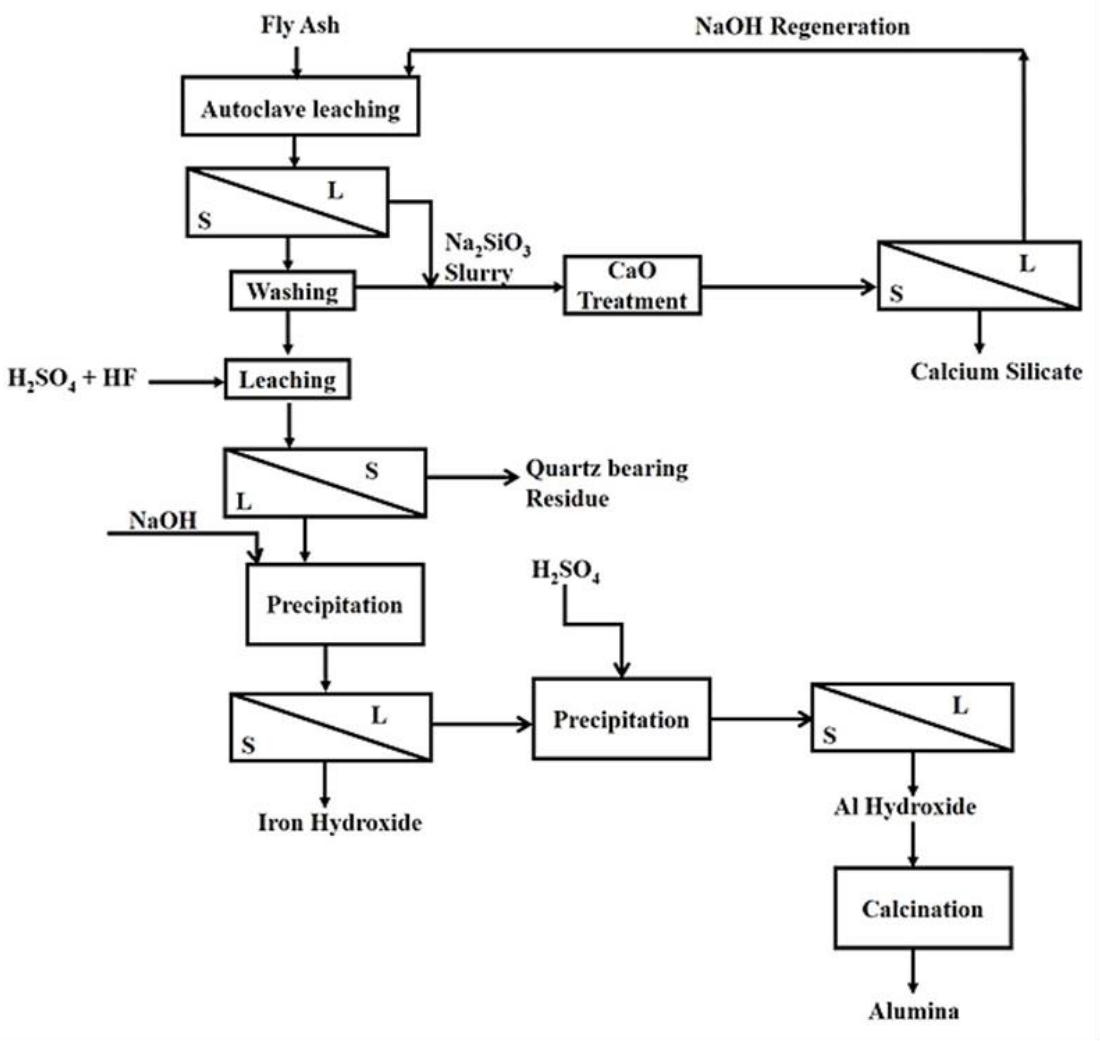

Figure 7. Process flow sheet for the extraction of alumina from coal fly ash.

4. Tentative Cost Analysis

A simple cost calculation has been made based on the laboratory scale study following the flow sheet shown in Figure 7. As the cost calculation is based on laboratory scale study, the outcome only gives an indication of suitability for further testing of the process in higher scale. The actual cost of the processing and capital cost investment on equipment and utility costs can only be obtained after pilot-scale study and commercial-scale capacity. In the present case, the processing cost of 1 tonne of fly ash was shown using chemical consumption cost, energy costs of all unit operations, and utilisation of waste heat. The revenue obtained after the sale of the product was considered for finding a profit margin. The tentative cost calculations based on a laboratory scale study showed a profit margin with a return on investment of about 23 %.

5. Conclusions

The present study showed that the use of fluoride ions during sulphuric acid leaching of fly ash helped in improving the alumina recovery to a value sufficiently higher than 90 %. Mullite present in the ash is highly refractory in nature where alumina is mostly associated. Fluoride ion helps in etching mullite surface initially followed by the attack of sulphuric acid and formation of aluminium sulphate in the leach solution. It has been observed that HF is more reactive in comparison to NaF. It was noticed that 15 % sulphuric acid and 1 % HF are sufficient enough to

extract more than 90 % of alumina whereas to obtain a similar efficiency in the case of NaF an amount of 3 g was needed. Desilication of fly ash has shown beneficial effects in terms of alumina recovery as well as a reduction in chemical consumption. The sodium silicate formed during desilication can be treated with lime to produce calcium silicate as a by-product and sodium hydroxide generated can be recycled back for hydrothermal alkali leaching of fly ash. A process flow sheet has been developed to successfully extract alumina from fly ash. The preliminary cost calculations based on a laboratory scale study showed a profit margin with a return on investment of about 23 %. Subsequently, the process will be tested in pilot scale for recovery of alumina and other by-products. The cost economics of the process will also be carried out based on the pilot scale data.

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