AA23 - Preparation of Metallurgical Grade Alumina from Coal Fly Ash

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Abstract

Alumina recovery from coal fly ash is being pursued at CSIR-Institute of Minerals and Materials Technology (CSIR-IMMT), Bhubaneswar. As alumina is associated mainly in mullite phase, it becomes very difficult to recover alumina from such matrix. Extraction of alumina from fly ash therefore is a challenging task. Further, the silica content of fly ash is higher than that of alumina, and therefore, directly getting aluminate solution through Bayer digestion method is difficult without employing stringent conditions and pre-treatments. One of the processes developed at CSIR-IMMT goes through partial desilication of fly ash followed by direct leaching in acidic solution in the presence of fluoride ions. The process was developed primarily to produce non-metallurgical grade alumina. Large-scale utilisation of fly ash will be possible if metallurgical grade alumina is produced. Therefore, at CSIR- IMMT, the production of metallurgical grade hydroxides is being developed from the direct acid leached solution through precipitation-soda leaching and conventional seeding route to precipitate out the metallurgical grade hydroxide from the purified aluminate liquor. The characterisation of the produced aluminium hydroxide is being compared with the properties of the aluminium hydroxide produced through Bayer's process which showed positive results. Recycling of the spent solution to the mixed precipitate leaching circuit is also being tested. Further testing is continuing to ascertain the results.

Keywords: Coal fly ash, leaching, fluoride ions, aluminium hydroxide (ATH), metallurgical grade alumina.

1. Introduction

Countries with developed aluminium industry like China, United States, European Union and CIS countries heavily depend on imports of bauxite ore from countries like Australia, Indonesia, Guinea, Brazil, and India as feedstock for the production of metallurgical grade alumina [1]. The depletion of bauxite ore across the globe, made the researchers to think about different innovative methods for the recovery of alumina values from the secondary resources; amongst them, coal fly ash is one of the most prominent ones because of its greater availability.

The annual world generation of fly ash is nearly 800 million tons of which India alone produces more than 200 million tons [2]. Storing such a huge quantity of fly ash requires land. In India around 43 % of fly ash is presently utilised in different sectors including cement (major portion) leaving a vast quantity unutilised [3]. In China and USA utilisation rates are 70 % and 50 %

respectively. Fly ash contains different valuable minerals such as mullite, quartz, hematite, magnetite, alpha-alumina, CaO, TiO_2, etc. including rare earth elements in a matrix of aluminosilicate glass. Nearly 50 million tons of alumina, the major value material which is present in fly ash is getting wasted due to unavailability of suitable technologies in India. The disposal of such a huge quantity of fly ash also creates environmental problem. The greatest disadvantage of fly ash processing is its high silica content, due to which various conventional methods cannot be employed. Furthermore, the main alumina bearing mineral is mullite which is refractory in nature and difficult to solubilize.

Many authors have tried to extract alumina from fly ash using different techniques such as lime stone sintering [4], [5] soda lime sintering [6], calsinter process [7], [8] ammonium sulphate sintering process [9] and acid leaching processes [10], [11]. However, this process consists of many disadvantages. Sintering process generates huge quantity of residue which is few times higher than the original fly ash. In ammonium sulphate process, the requirement of ammonium sulphate is huge (10:1, ammonium sulphate: alumina). The sulphuric acid method requires higher temperature of 200-210 °C, with a ratio of acid to fly ashes 5:1 (v/wt.) and extraction efficiency of 85 %. Bhattacharya et al., [12] patented a process to recover alumina by using sulphation roasting and water leaching technique, where the alumina produced is non-metallurgical grade.

Tripathy et al., [13], has studied the use of sodium fluoride to solubilise the alumina values of fly ash in sulphuric acid medium. Interesting results were obtained, where the leaching efficiency was found to be greater than 90 %. The study was extended beyond leaching to produce the metallurgical grade alumina by employing precipitation, dissolution and further precipitation methods. A tentative flow sheet was developed to produce metallurgical grade alumina and is presented in this paper. Further optimization work is under progress.

2. Materials and Methodology

2.1 Materials

Coal fly ash was collected from the thermal power plant of National Aluminium Company Limited (NALCO), Angul, India. 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). Analyses of the solutions were carried out using ICP-OES and AAS.

2.2 Methodology

All the leaching experiments were carried out in batches. An autoclave of volume 1L was taken for conducting the experiments for silica removal. NaOH solution (500mL) of different concentrations and fly ash (50 g) were added in the reactor. Hydrothermal leaching operations were carried out at various temperatures from 150 °C to 180 °C. The experiments were of 3 h duration. After the experiment, the slurry was filtered. The residue was dried and again leached with sulphuric acid in the presence of NaF varying different concentrations to recover alumina. A standard double walled borosilicate glass reactor of volume 250 mL was used for conducting alumina leaching at a regulated temperature, controlled by a circulatory thermostatic water bath through inlet and outlet ports. The reactor was kept on a magnetic stirrer and agitation was made with the help of a magnetic paddle. The temperature during leaching was varied from 40-90 ˚C and the leaching time was varied from 15 min to 5 h. In each experiment, 100 mL solution was taken with 10 % solids concentration. The leach liquor thus obtained was then analysed for aluminium value and the recovery percent of alumina was calculated (Tripathy et al., 2019) [13]. This study was tested in higher scale (100 g fly ash) to carry out further study on the precipitation of aluminium hydroxide. The leach solution obtained by processing 100 g fly ash has been subjected to precipitation of aluminium hydroxide along with iron hydroxide by adding sodium hydroxide up to a pH of about 7. The mixed hydroxide obtained after filtration was then leached in sodium hydroxide to obtain sodium aluminate liquor which is filtered to reject the Fe. The purified sodium alumina liquor was seeded with aluminium hydroxide for the precipitation of sandy ATH. From the 2^{nd} cycle onwards spent aluminate solution was taken for mixed precipitate leaching. Calcination of ATH was carried out in a muffle furnace at 950-1150 °C to produce alumina. Characterisation of alumina is being carried out to ensure its acceptability as smelter grade alumina.

2.3 Characterization of Fly Ash

The XRD study of fly ash was shown in Figure 1 indicating different phases of elements present in coal fly ash. The ash residue after sodium hydroxide leaching was analysed for elemental composition. The alumina percentage was increased to about 31-34 and silica percentage was reduced to about 45-46 %. The compositional analyses of dried ash residue were presented in Table 1.

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

Sample	**Al_2O_3 (%)**	**SiO_2 (%)**	**Fe_2O_3 (%)**	**CaO (%)**
Fly ash	24-26	60-62	3-4	0.5-1
Alkali leached fly ash residue	31-34	45-46	10-12	1.5-2.0

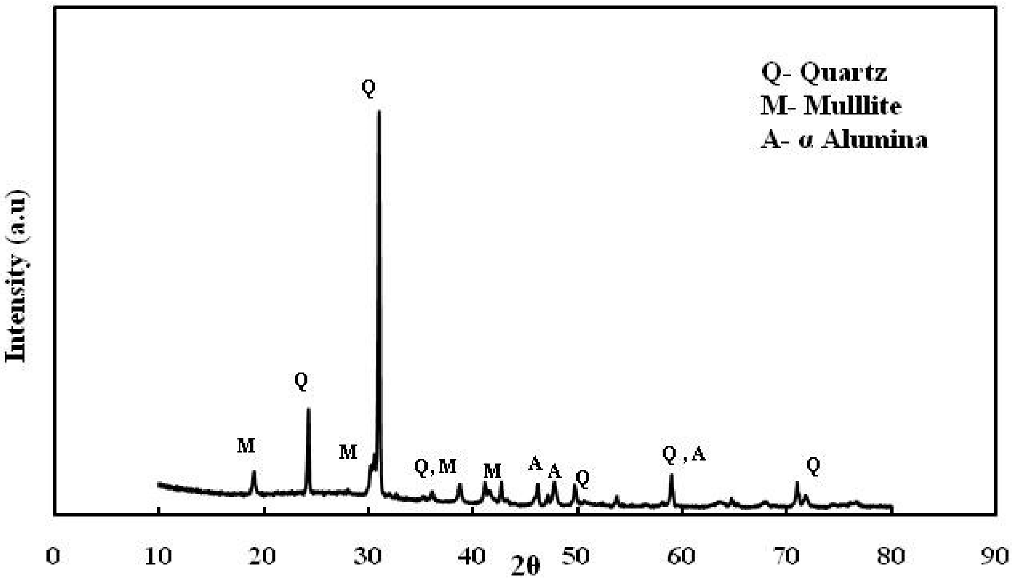

Figure 1. XRD pattern of fly ash.

3. Results and Discussion

The results for obtaining metallurgical grade alumina from the fly ash are presented below.

3.1 Hydrothermal Alkali Leaching of Fly Ash

In the earlier study, alkali leaching of fly ash at about 150 °C temperature and 1M NaOH concentration was able to extract 50 % of silica that is in the amorphous form. The sodium silicate solution thus generated was subjected to calcium silicate precipitation by the addition of lime leading to the production of sodium hydroxide and was recycled back for hydrothermal alkali leaching of fly ash. The detailed study has been presented by Tripathy et al. [13] and in an Indian patent [12].

3.2 Acid Leaching of Alkali Treated Fly Ash

Sulphuric acid leaching of partially desilicated fly ash in the presence of NaF has been investigated. It was reported by Tripathy et al. [13] that the effect of sodium fluoride addition on leaching of alumina was evaluated at varied sulphuric acid concentrations, temperatures and time of leaching. Figure 2 shows the effect of NaF on fly ash leaching with 10, 15 and 25 % H_2SO_4, respectively. It was observed that, the concentration of H_2SO_4 had no significant effect on the leaching behavior of the fly ash. However, when NaF was added to the reaction mixture, the leaching efficiency increased significantly. With 10, 15 and 25 % H_2SO_4 concentration, the leaching efficiencies were 11, 18 and 27 % respectively, whereas when NaF was added to the acid leaching bath recovery of alumina increased with the increase in NaF amount in all the cases. It is interesting to note that higher concentration of acid requires lower amount of NaF for maximum alumina recovery. Thus with 10, 15 and 25 % H_2SO_4 concentration, the amount of NaF required were 5, 3 and 1g to recover 80, 91 and 90 % of alumina, respectively. Thereby, it was concluded that the leaching recovery of alumina can be improved by the addition of NaF. The optimized recovery was achieved with 15% sulphuric acid and 3g NaF for 10 % alkali treated fly ash residue at a temperature of 90 °C for 2 h. The detailed study has been incorporated in Tripathy et al., 2019 [13]. This study has been carried out in a higher scale for further precipitation studies.

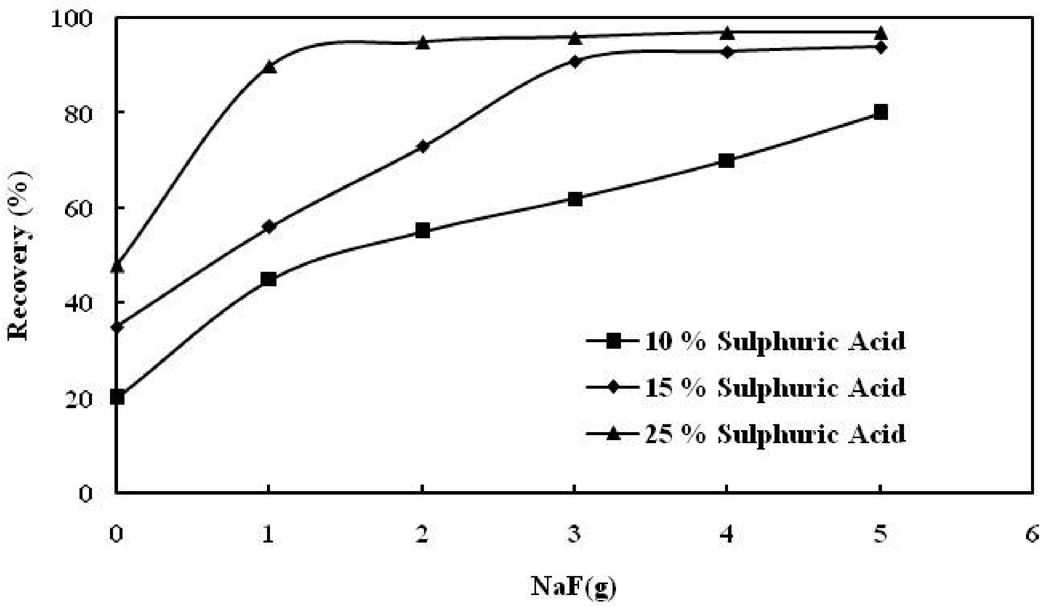

Figure 2. Effect of sodium fluoride on percentage recovery of alumina during leaching with different concentration of H_2SO_4; Tripathy et al., 2019 [13]. Solution quantity: 100mL, Fly ash after NaOH leaching: 10g, Temperature: 90 °C.

3.3 Precipitation of ATH

The leach solution obtained after acid leaching operation was having a pH of about 1.2-1.5. The solution contained mainly aluminium sulphate and iron sulphate. This solution was subjected to sodium hydroxide addition for the precipitation of mixed aluminium hydroxide and iron hydroxide. The final pH of the solution was maintained at around 7 so that all the aluminium and the iron precipitate as respective hydroxide. This mixed precipitate was aged for 3-4 h to reduce the soda as well as sulphate content in the precipitate. All the precipitation studies were carried out at 80-90 °C. The slurry was then filtered to separate mixed precipitate from the solution. The mixed precipitate was dried at 90 °C to obtain dried solid. This solid is taken for further treatment for obtaining smelter grade alumina. The dried mixed hydroxide of aluminium and iron was subjected to hydrothermal dissolution (120-130 °C) in sodium hydroxide solution. During the hydrothermal dissolution, aluminium value gets dissolved in sodium hydroxide solution forming sodium aluminate while iron stays in the solid. The dissolution was carried out in such a way that alumina to sodium oxide ratio equals to 1.0. This ratio has prime importance for obtaining substantial amount of product ATH when seeded. The iron hydroxide obtained as residue was washed thoroughly to obtain pure iron hydroxide product. The purified sodium aluminate solution generated was taken for the precipitation using conventional seeding technique by adding ATH seed. The seeding time and temperature were maintained as 24 h and 60 °C respectively. The product seed was recycled for and tested for 5 cycles. The product was further heat treated at 950-1150 °C to obtain alumina. The overall precipitation efficiency obtained was about 60 %. The slight draw back in this process is the presence of sulphate ion (SO_4^{-2}) in the system i.e., in the sodium aluminate solution. Therefore, there is every chance of contamination of product alumina contaminated with the sulphate ion. To overcome this, a bleeding circuit need to be incorporated to reduce the sulphate ion in the solution to a minimum value so that the product should not incorporate higher than tolerable sulphate concentration. The purity and other properties of the alumina obtained are presented in Table 2. The complete characterization of the alumina for comparing with the smelter grade is underway.

Table 2. Purity and characteristics of produced alumina.

Sample	**Na_2O (%)**	**SiO_2 (%)**	**SO_3 (%)**	**Al_2O_3 (%)**	**Bulk density (g/cc)**	**Angle of repose (deg)**
Produced Alumina	0.38-0.40	0.034-0.035	0.05-0.07	99-99.5	1.12	32.8
Bayer's Alumina	0.5	0.02	-	98.5	0.95-1.05	36 (Max)

3.4 Process Flow Sheet

A typical process flow sheet (Figure 3) has been proposed for the processing of fly ash, indicating various unit operations and products. The process involves hydrothermal alkali leaching of fly ash to remove the amorphous silica followed by recovery of the solubilised silica as calcium silicate and sulphuric acid leaching of the alkali leached residue in presence of NaF to solubilise alumina. The residue generated after leaching was mainly quartz, which can be used for construction materials such as float glass. Then the leach solution was subjected to precipitation of mixed precipitate of aluminium and iron hydroxides by neutralising method with sodium hydroxide. The mixed precipitate was further dissolved in sodium hydroxide to obtain sodium aluminate solution followed by precipitation of ATH through conventional seeding route with the recycling of spent liquor to the dissolution circuit.

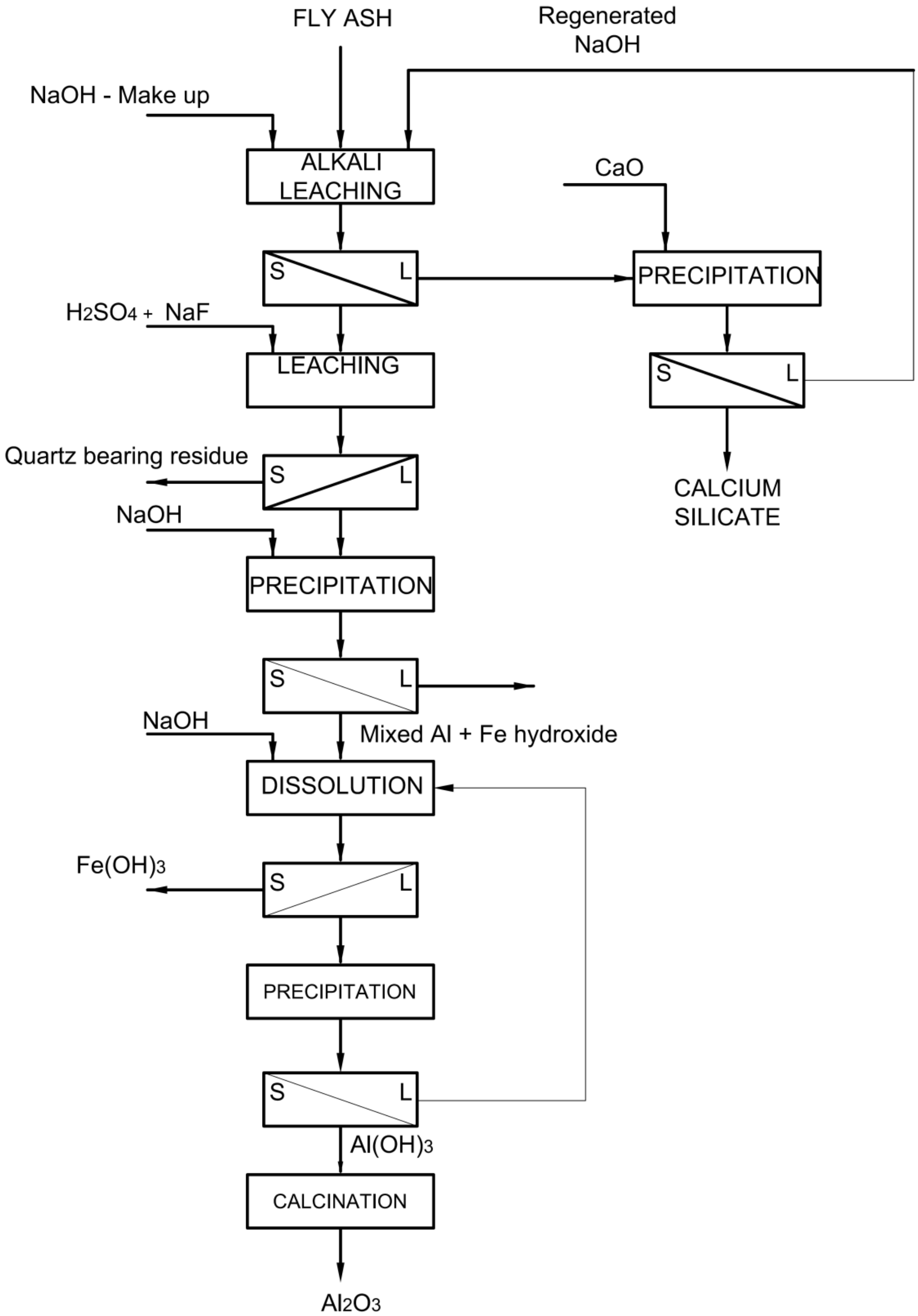

Figure 3. Process flow sheet for the production of metallurgical grade alumina from fly. ash.

4. Conclusions

The present work may open a path for extracting metallurgical grade alumina from the coal fly ash. This study showed an interesting approach of recovering alumina aimed at producing smelter grade alumina. Conventionally, smelter grade alumina is precipitated from sodium aluminate solution generated via alkali treatment of Bauxite. The present approach was to obtain sodium aluminate solution from fly ash and to produce the smelter grade alumina. In this process, by-products have been generated which could minimise environmental problem posed by fly ash while conserving the Bauxite resources. However, the main concern in this process is the contamination of sulphate ions in the product, alumina. After 5 cycles of the present study, very minimum contamination of SO_4^{-2} ion was noticed. Options are being tried at CSIR-IMMT to avoid the contamination of sulphate. One of the options could be to incorporate a bleeding circuit to keep the sulphate ion concentration in the solution to minimum for obtaining proper hydroxide/alumina product. Some of the properties of the produced alumina were compared with the product of the Bayer's process and found satisfactory. Optimization of the flow sheet, complete characterization of alumina and to compare with the smelter grade is underway. If successful, bench studies will be carried out for generating the mass and energy balance.

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6. References

1. V. Sibanda, S. Ndlovu, G. Dombo, Towards the Utilization of Fly Ash as a Feedstock for Smelter Grade Alumina Production: A Review of the Developments, *J. Sustain. Metallurgy,* 2, 2016, 167–184.
2. Yousuf Aadil, Manzoor Shahzada Omer, Youssouf Mudasir, A. Malik Zubair and Khawaja Khawar Sajjad, Fly Ash: Production and Utilization in India - An Overview, *Journal of Materials and Environmental Science*, 6, 2020, 911-921.
3. Arpita Bhatt, Sharon Priyadarshini, Mohnakrishnan AiswaryaAcharath, Arash Abri, Melanie Sattler and Sorakrich Techapaphawit, Physical, chemical, and geotechnical properties of coal fly ash: A global review, *Case Studies in Construction Materials*, Vol. 11, December 2019.
4. R.H. Matjie, J.R. Bunt, H. Van, Extraction of alumina from coal fly ash generated from a selected low rank bituminous South African coal, *Mineral Engineering*, 2005, 18 (3), 299-310.
5. Zhang, B.Y., Zhou, F.L., The limestone sintering process to produce alumina with fly ash. *Light Metals* 2007, (6), 17-18, 27 (in Chinese).
6. G.H. Bai, W. Teng, X.G. Wang, J.G. Qin, P. Xu, P.C. Li, Alkali desilicated coal fly ash as substitute of bauxite in lime-soda sintering process for aluminium production, *Trans. Nonferrous Met. Soc. China*, 2010, 20, 169-175.
7. K.P. Goodboy, Investigation of a sinter process for extraction of Al_2O_3 from coal wastes, *Metall. Mater. Trans. B*, 1976, 7, 175-184.
8. F.G. Seeley, W.J. McDowell, L.K. Felker, A.D Kelmers, B.Z. Egan, 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,* 1981, 6, 277-290.
9. Lai-shi, Li, Xin-qin, Liao, Yu-sheng, Wu, Ying-ying, Liu, Extracting alumina from coal fly ash with ammonium sulphate sintering process, *Light Metals* 2012, Edited by Carlos E. Suarez, TMS, The Minerals , Metals Society.
10. Li Lai-shi, Wu Yu-sheng, Liu Ying-ying, Zhai Yu-chun, Extraction of alumina from coal fly ash with sulphuric acid leaching method, *The Chinese Journal of Process Engineering*, 2011, Vol. 11 (2).

11. Wu Cheng-you, Yu Hong-fa, Zhang Hui-fang, Extraction of aluminium by pressure acid leaching method from coal fly ash, *Transaction of nonferrous metals society of China*, 2012, Vol. 22 (9), 2282-22.
12. I.N. Bhattacharya, B.K. Mishra, C.K. Sarangi, B.C. Tripathy, K. Sanjay, A.R. Sheik, A.K Tripathy, B.K. Satpathy, P.K. Behere, A pyro-hydrometallurgical process for the recovery of alumina and calcium silicate from fly ash, *Indian Patent* No. 344358, filed January 12, 2016, granted August 18, 2020.
13. A.K. Tripathy, B. Behera, V. Aishvarya, A.R. Sheik, B. Dash, C.K. Sarangi, B.C. Tripathy, K. Sanjay, I.N. Bhattacharya, Sodium fluoride assisted acid leaching of coal fly ash for the extraction of alumina. *Minerals Engineering*, 2019, 131, 140-145.