An H_3O-Alunite Method for Production of Smelter Grade Alumina from an Ammonium Alum Solution after High-Pressure Acid Leaching of Coal Fly Ash

Dmitrii Valeev[1, 2], Andrei Shoppert[3] and Fengting Li[4]
1. Leading research fellow
Laboratory of Sorption Methods, Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences, Moscow, Russia
2, 3. Professors
Dept. of Non-Ferrous Metals Metallurgy – Ural Federal University, Yekaterinburg, Russia
4. Professor
Institute of Environment for Sustainable Development – Tongji University, Shanghai, China
Corresponding author: dmvaleev@yandex.ru
https://doi.org/10.71659/icsoba2025-aa049

Abstract

Precipitation of H_3O-alunite from an ammonium alum solution using boehmite as a seed was studied. The ammonium alum solution was obtained after high-pressure leaching of mullite-type coal fly ash (CFA) with a mixture of 7.5 M H_2SO_4 + 40 % NH_4HSO_4 at 200 °C. Fe(III) was extracted from the ammonium alum solution by ion exchange sorption using the Purolite S957 resin. Effects of temperature (70–90 °C), seed boehmite (100–400 g/L), ammonium alum (60–240 g/L), and precipitation duration (2–8 h) on the Al precipitation degree were evaluated. Calcination of the precipitate at 300–950 °C to obtain alumina powder was studied next. Concentration of impurities, specific surface area, phase composition, morphology, and the average particle size distribution of alumina powders were investigated. The results show that smelter grade aluminium (SGA) can be obtained at optimized parameters of precipitation and calcination

Keywords: Coal fly ash, Ammonium bisulphate method, H_3O-alunite precipitation, Smelter grade alumina, Waste utilization.

1. Introduction

The rapid growth of the aluminium industry requires a search for new cheap sources of aluminium. Such raw materials can be industrial waste: a bauxite residue (“red mud”) [1], coal gangue [2], or salt aluminium dross [3]. Nonetheless, the most promising raw material is coal fly ash (CFA) from coal-fired power plants because its annual generation in the world is more than 1000 Mt [4]. This waste occupies vast territories and leads to pollution of soils and rivers [5]. A search for new recycling methods will reduce the negative impact of this waste and will help to obtain, in addition to alumina, many valuable products such as iron-based alloys [6], lithium (Li) [7], rare-earth elements [8], coagulants [9], silicon-potassium mineral fertilizer [10], $CaSiO_3$ and silica gel [11], unburned carbon [12], Al–Si master alloy [13], Ni and V [14], zeolites [15], cenospheres for construction materials [16].

The Al_2O_3 content of CFA reaches 25 to 40 %, and silicon oxide (SiO_2) concentration is 35 to 65 %. This Al/Si ratio makes it difficult to employ traditional alkaline Bayer and sintering methods in order to produce SGA because some of the sodium hydroxide will be wasted due to the interaction with SiO_2 during the leaching process [17]. Therefore, acidic methods are being developed that involve hydrochloric acid (HCl) [18], sulphuric acid (H_2SO_4) [19], or nitric acid (HNO_3) [20]. The most promising approach is to use a mixture of sulphuric acid and ammonium bisulphate (NH_4HSO_4) [21]. This technique allows the separation of Al from the solution by precipitation of ammonium alum [$(NH_4)Al(SO_4)_2·12H_2O$] after filtration of the leaching solution with a temperature decrease from 90 to 25 °C [22].

There are many ways to obtain aluminium oxide from ammonium alum: direct roasting at 900–1300 °C [23] or precipitation of pseudoboehmite (AlOOH) by neutralization with ammonia under atmospheric [24] or hydrothermal conditions [25] with subsequent calcination at 1100 °C [26]. Additives (sodium dodecylbenzene sulphonate) can be employed to increase the average particle size from 20.1 to 31.3 μm in the pseudoboehmite powder [27]. An increase in the particle size of boehmite was observed when a significant amount of ammonium alum was added and the neutralization process was undertaken for a period of 18 h [28]. The coprecipitation method with the addition of ammonium hydrogen carbonate (NH_4HCO_3) has also been studied [29]. During precipitation, ammonium aluminium carbonate hydroxide [$NH_4Al(OH)_2CO_3$] has been obtained, and after calcination at 900 °C, a powder mixture containing γ-Al_2O_3 and α-Al_2O_3 has been produced [30]. Recent studies have shown the possibility of precipitation of aluminium from ammonium alum solution by neutralization method using gibbsite as a seed [31]. However, the temperature of calcination from gibbsite for smelter grade alumina production is 1200 °C [32]. This is 300 °C higher than the temperature of boehmite calcination [33], so the emphasis in this research was on the use of boehmite as a seed.

In the present paper, for the first time, a method is proposed for the precipitation of the H_3O-alunite salt on the surface of seed boehmite without additional reagents. As a result, it is possible to produce smelter grade alumina from CFA by the ammonium bisulphate method in accordance with Russia, China, and India state standards.

2. Materials and Methods

2.1 Materials and Reagents

CFA was collected from Reftinskaya GRES (Sverdlovsk Oblast, Russia; 57.10°N, 61.70°E): the largest coal-fired power plant in Russia. The raw CFA consisted of 62.43 wt.% of SiO_2, 24.66 wt.% of Al_2O_3, and 3.32 wt.% of Fe_2O_3. Phase composition of CFA was as follows: mullite ($3Al_2O_3·2SiO_2$), quartz (SiO_2), and magnetite (Fe_3O_4) [34]. Seed aluminium hydroxide was obtained from Urals Aluminium Smelter (Sverdlovsk Oblast, Russia; 56.36°N, 61.96°E). Analytical-grade sulphuric acid (H_2SO_4, 93%) and ammonium bisulphate (NH_4HSO_4) were purchased from SigmaTek (Moscow, Russia).

2.2 Experiments

To conduct experiments with boehmite powder, seed aluminium hydroxide [$Al(OH)_3$] was calcined in a PM-1 muffle furnace (Plavka.Pro, Russia) at 350 °C for 3 h. The yield after calcining was 74–76 % of the initial mass of gibbsite. In addition to the change in phase composition, SSA (Specific Surface Area) of the powder enlarged from 0.5 to 213.6 m^2/g.

In precipitation tests, the temperature of the ammonium alum solution (50 mL) was 70, 80, or 90 °C; seed boehmite concentration was 100, 200, or 400 g/L, ammonium alum concentration 60, 120, or 240 g/L; and precipitation time 2, 4, or 8 h. The slurry obtained after the precipitation was filtered, and the powder was washed with hot water and dried at 105 °C for 4 h. Next, the powder was weighed and analysed, and the Al precipitation degree was calculated using the following equations.

$$M_{H_3O\text{-alunite}} = (M_p \times C_s/100) \times 6.16 \quad (1)$$

4. Conclusions

A bisulphate method for CFA recycling for SGA production was investigated in this work. The main conclusions are as follows:

The effects of solution temperature, seed boehmite amount, ammonium alum concentration, and of precipitation duration on Al precipitation were examined by the ANN method. The use of optimized parameters [$T = 90$ °C, seed AlOOH at 400 g/L, $(NH_4)Al(SO_4)_2{\cdot}12H_2O$ at 120 g/L, and $\tau = 8$ h] led to an Al precipitation extent of 88 %.
The phase transformation, the sulphur content, and BET values of boehmite with H_3O-alunite were determined after calcination at 300–950 °C. The resulting SGA powder contained approximately 20 % κ-Al_2O_3 and 80 % γ-Al_2O_3 at 900–950 °C. The sulphur content was 0.34 wt.% and SSA was 51.7 m^2/g at the calcination temperature of 950 °C. A method for sulphur removal from boehmite with H_3O-alunite by NH_4OH treatment is proposed. The sulphur content of SGA was reduced to 0.06 wt.%.

The chemical composition and the particle size distribution of the SGA powder derived from CFA were also analysed. It was demonstrated that in terms of chemical composition and SSA, the SGA powder meets the state standards of Russia, China, and India.

5. Acknowledgements

The present study was carried out funded within the state assignment of the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences (GEOKHI RAS).

6. References

1. W. Li et al. Selective separation of aluminium, silicon, and titanium from red mud using oxalic acid leaching, iron precipitation and pH adjustments with calcium carbonate, *Hydrometallurgy*, Vol. 223 (2024). https://doi.org/10.1016/j.hydromet.2023.106221
2. Y.-J. Zhang et al. Kinetics of alumina extraction from coal gangue by hydrochloric acid leaching, *Transactions of Nonferrous Metals Society of China (English Edition)*, Vol. 33 (2023) 1932–1942. https://doi.org/10.1016/S1003-6326(23)66233-8
3. J. Tang et al. Two-stage process for the safe utilization of secondary aluminium dross in combination with the Bayer process, *Hydrometallurgy*, Vol. 209 (2022). https://doi.org/10.1016/j.hydromet.2022.105836
4. D. Darmansyah et al. Advancements of coal fly ash and its prospective implications for sustainable materials in Southeast Asian countries: A review, *Renewable and Sustainable Energy Reviews*, Vol. 188 (2023). https://doi.org/10.1016/j.rser.2023.113895
5. D. Das et al. A Review of Coal Fly Ash Utilization to Save the Environment, *Water, Air, & Soil Pollution*, Vol. 234 (2023). https://doi.org/10.1007/s11270-023-06143-9
6. H. Chen et al. Fe-Si alloys production and alumina extraction from coal fly ash via the vacuum thermal reduction and alkaline leaching, *Fuel Processing Technology*, Vol. 244 (2023) 107702. https://doi.org/10.1016/j.fuproc.2023.107702
7. M. Xing et al. Selective recovery of lithium from high-aluminium fly ash by using alkali-dissolution-assisted HBTA–TOPO synergistic extraction, *Journal of Cleaner Production*, Vol. 434 (2024). https://doi.org/10.1016/j.jclepro.2023.139998
8. M. Dardona et al. From ash to oxides: Recovery of rare-earth elements as a step towards valorization of coal fly ash waste, *Separation and Purification Technology*, Vol. 314 (2023). https://doi.org/10.1016/j.seppur.2023.123532
9. S. Xiong et al. Extraction of Al and preparation of polyaluminium chloride from coal gasification fine slag by high-pressure HCl leaching method, International *Journal of Coal*

Preparation and Utilization, Vol. 43 (2023) 1897–1911. https://doi.org/10.1080/19392699.2022.2142782

10. X. Chao et al. Sustainable application of coal fly ash: One-step hydrothermal cleaner production of silicon-potassium mineral fertilizer synergistic alumina extraction, *Journal of Cleaner Production*, Vol. 426 (2023). https://doi.org/10.1016/j.jclepro.2023.139110
11. X. Zhao et al. Efficient separation and comprehensive extraction of aluminium, silicon, and iron from coal fly ash by a cascade extraction method, *Journal of Cleaner Production*, Vol. 406 (2023). https://doi.org/10.1016/j.jclepro.2023.137090
12. C.-C. Nie et al. Environmentally-friendly emulsion-like collector prepared from waste oil: Application in floatation recovery of unburned carbon in coal fly ash, *Journal of Cleaner Production*, Vol. 379 (2022). https://doi.org/10.1016/j.jclepro.2022.134561
13. W. Tao et al. A novel process for recovering aluminium and silicon from fly ash in cryolite molten salt *Journal of Cleaner Production*, Vol. 375 (2022). https://doi.org/10.1016/j.jclepro.2022.134170
14. A. Hamidi et al. Valorization of fly ash by nickel ferrite and vanadium oxide recovery through pyro-hydrometallurgical processes: Technical and environmental assessment, *J Environ Manage*, Vol. 344 (2023). https://doi.org/10.1016/j.jenvman.2023.118442
15. Y. Xu et al. Upcycling rice husk ash and coal-fired fly ash as Si/Al sources into hierarchical ZSM-5 for efficient mercury capture from industrial flue gas, *Journal of Cleaner Production*, Vol. 470 (2024). https://doi.org/10.1016/j.jclepro.2024.143260
16. Y. Zhang et al. Reinforcing efficiency of nanomaterials on mechanical and interfacial characteristics of green concrete incorporating fly ash cenosphere, *Journal of Cleaner Production*, Vol. 447 (2024). https://doi.org/10.1016/j.jclepro.2024.141531
17. H. Wang et al. Alkali Methods for Alumina Extraction from the By-products of High Alumina Coal: A Review, *Mining, Metallurgy & Exploration*, Vol. 40 (2023) 1681–1694. https://doi.org/10.1007/s42461-023-00833-y
18. M. Chen et al. Preparation of high-purity crystalline aluminium chloride based on aluminium separation from circulating fluidized bed fly ash, *Powder Technology*, Vol. 433 (2024). https://doi.org/10.1016/j.powtec.2023.119199
19. J. Li et al. Energy-efficient leaching process for preparation of aluminium sulphate and synergistic extraction of Li and Ga from circulating fluidized bed fly ash, *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, Vol. 44 (2022) 4398–4410. https://doi.org/10.1080/15567036.2022.2077476
20. H. Hou et al. Wang, Sustainable process for valuable-metal recovery from circulating fluidized bed fly ash through nitric acid pressure leaching, *Journal of Cleaner Production*, Vol. 360 (2022) 132212. https://doi.org/10.1016/j.jclepro.2022.132212
21. D. Xu et al. A new process of extracting alumina from high-alumina coal fly ash in NH_4HSO_4 + H_2SO_4 mixed solution, *Hydrometallurgy*, Vol. 165 (2016) 336–344. https://doi.org/10.1016/j.hydromet.2015.12.010
22. X. Yang et al. Crystallization mechanism of ammonium aluminium sulphate during cooling process, *Journal of Crystal Growth*, Vol. 560–561 (2021) 126064. https://doi.org/10.1016/j.jcrysgro.2021.126064
23. H. Shen et al. Aluminium–iron separation in high-acid leaching solution and high-purity alumina preparation, *Asia-Pacific Journal of Chemical Engineering*, Vol. 16 (2021) 1–16. https://doi.org/10.1002/apj.2623
24. W. He et al. Crystallization kinetics and crystallization process of pseudoboehmite from ammonium aluminium sulphate solution, *Journal of Crystal Growth*, Vol. 614 (2023). https://doi.org/10.1016/j.jcrysgro.2023.127215
25. J. Wang et al. The Influence of Hydrothermal Temperature on Alumina Hydrate and Ammonioalunite Synthesis by Reaction Crystallization, *Crystals (Basel)*, Vol. 13 (2023). https://doi.org/10.3390/cryst13050763

26. Y. Wu et al. Synthesis of alumina with coarse particle by precipitating aluminium ammonium sulphate solution with ammonia, *Advanced Powder Technology*, Vol. 27 (2016) 124–129. https://doi.org/10.1016/j.apt.2015.11.006
27. X. Ma et al. Wang, Effect of SDBS on Crystallization Behavior of Pseudoboehmite, *The Journal of Physical Chemistry C*, Vol. 125 (2021) 26039–26048. https://doi.org/10.1021/acs.jpcc.1c08074
28. J. Wang et al. Growth process of boehmite with large particles in ammonia system, *Ceram Int*, Vol. 50 (21) (2024) 41436–41447 https://doi.org/10.1016/j.ceramint.2024.07.460
29. J. Su et al. Effect of composite additives on phase transition and dispersibility of α-Al_2O_3, *Ceramics International*, Vol. 47 (2021) 9771–9778. https://doi.org/10.1016/j.ceramint.2020.12.117
30. L. Zhang et al. Synthesis and characterization of mesoporous alumina with high specific area via coprecipitation method, *Vacuum*, Vol. 133 (2016) 1–6. https://doi.org/10.1016/j.vacuum.2016.08.005
31. J. Wang et al. Role of Crystal Seed in Aluminium Hydroxide Crystallization from Ammonia System with Added $NH_4Al(SO_4)_2 \cdot 12H_2O$, *Journal Wuhan University of Technology, Materials Science Edition*, Vol. 39 (2024) 945–953. https://doi.org/10.1007/s11595-024-2957-8
32. F. Gao et al. Fabrication of nano-layer-structure alumina powders from an alumina concentrate through an intensified Bayer process, *Chemical Engineering and Processing - Process Intensification*, Vol. 175 (2022) 108907. https://doi.org/doi.org/10.1016/j.cep.2022.108907
33. H. Wang et al. Alkali Methods for Alumina Extraction from the By-products of High Alumina Coal: A Review, *Mining, Metallurgy & Exploration*, Vol. 40 (2023) 1681–1694. https://doi.org/10.1007/s42461-023-00833-y
34. A. Shoppert et al. Kinetics of Aluminium and Scandium Extraction from Desilicated Coal Fly Ash by High-Pressure HCl Leaching, *Metals (Basel)*, Vol. 13 (2023). https://doi.org/10.3390/met13121994
35. H. Vu et al. Recovery of pigment-quality magnetite from jarosite precipitates, *Hydrometallurgy,* Vol. 101 (2010) 1–6. https://doi.org/10.1016/j.hydromet.2009.10.007
36. E. Salinas et al. Characterization and alkaline decomposition-cyanidation kinetics of industrial ammonium jarosite in NaOH media, *Hydrometallurgy*, Vol. 60 (2001) 237–246. https://doi.org/10.1016/S0304-386X(01)00149-9
37. Y. Ji et al. Synthesis and characterization of pseudoboehmite by neutralization method, *Ceram Int*, Vol. 47 (2021) 15923–15930. https://doi.org/10.1016/j.ceramint.2021.02.166.
38. J.T. Kloprogg et al. Thermal decomposition of bauxite minerals: Infrared emission spectroscopy of gibbsite, boehmite and diaspore, *Journal of Materials Science*, Vol. 37 (2002) 1121–1129. https://doi.org/10.1023/A:1014303119055
39. A.V. Sergeeva et al. Infrared and Raman spectroscopy of tschermigite, $(NH_4)Al(SO_4)_2 \cdot 12H_2O$, *Vibrational Spectroscopy*, Vol. 105 (2019). https://doi.org/10.1016/j.vibspec.2019.102983
40. S. Roy et al. Crystallinity mediated variation in optical and electrical properties of hydrothermally synthesized boehmite (γ-AlOOH) nanoparticles, *Journal of Alloys and Compounds*, Vol. 763 (2018) 749–758. https://doi.org/10.1016/j.jallcom.2018.05.356
41. P. Chen et al. Effects of Ionizing Radiation on the Thermodynamic Stability of Boehmite and Gibbsite, *Journal of Physical Chemistry C*, Vol. 128 (2024) 3578–3587. https://doi.org/10.1021/acs.jpcc.3c08456
42. Yves Noël et al. Ab initio quantum mechanical study of γ-AlOOH boehmite: Structure and vibrational spectrum, *Physics and Chemistry of Minerals*, Vol. 36 (2009) 47–59. https://doi.org/10.1007/s00269-008-0257-z
43. H.D. Ruan et al. Comparison of Raman spectra in characterizing gibbsite, bayerite, diaspore and boehmite, *Journal of Raman Spectroscopy*, Vol. 32 (2001) 745–750. https://doi.org/10.1002/jrs.736

44. W.W. Rudolph et al. Study of aqueous $Al_2(SO_4)_3$ solution under hydrothermal conditions: Sulphate ion pairing, hydrolysis, and formation of hydronium alunite, *Journal of Solution Chemistry*, Vol. 30 (2001) 527–548. https://doi.org/10.1023/A:1010334818580
45. D. Valeev et al. A review of the alumina production from coal fly ash, with a focus in Russia, *Journal of Cleaner Production*, Vol. 363 (2022) 132360. https://doi.org/10.1016/j.jclepro.2022.132360
46. GOST 30558-2017 Smelter grade alumina. Specifications, https://www.aluminas.ru/projects/ГОСТ_30558-2017-Глинозем.pdf (accessed April 11, 2025).
47. P. Wang et al. Production of aluminium oxide from coal fly ash: A new acidic process based on crystallization and pyrolysis of potassium alum, *Zhongguo Youse Jinshu Xuebao/Chinese Journal of Nonferrous Metals*, Vol. 31 (2021). https://doi.org/10.11817/j.ysxb.1004.0609.2021-36613
48. Metallurgical grade calcined alumina (sandy type), (2024). https://nalcoindia.com/export/calcined-alumina/ (accessed April 11, 2025).
49. IS 17441 : Part 2 : 2021 Calcined Alumina - Specification Metallurgical Grade, (2024). https://standardsbis.bsbedge.com/BIS_SearchStandard.aspx?Standard_Number=IS%2017441%20:%20Part%202&id=35106 (accessed April 11, 2025).
50. A. Suss et al. The quality of alumina produced by the hydrochloric acid process and potential for improvement, *Proceedings of 33rd International ICSOBA Conference*, Dubai, UAE, 29 November–1 December 2015, Paper AA16S, *TRAVAUX* 44*,* 287–294
51. YS/T 803-2012 «Smelter grade alumina», (2024).