CHEMICAL ENGINEERING TRANSACTIONS

VOL. 94, 2022

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš, Sandro Nižetić

ISBN 978-88-95608-93-8; **ISSN** 2283-9216

DOI: 10.3303/CET2294109

Ash from Coal-Fired Power Plants as a Raw Material for the Production of Alumina

Leonid Delitsyn[a], Ruslan Kulumbegov[a], Oleg Popel[a], Mikhail G. Sulman[b,*], Yury Kosivtsov[b]

[a]Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya st. 13 Bd.2, Moscow, 125412
[b]Tver State Technical University, A. Nikitin str., 22, Tver, 170026
sulmanmikhail@yandex.ru

The energy sector of the Russian Federation based on coal to generate heat and electricity is a major source of ash and slag. The dumps of this waste occupy large areas and at the same time cause environmental problems. Ash and slag contain alumina and other valuable products such as silica, magnetite etc. The ashes of large thermal coal-fired power plants of the Ural region – Troitskaya, Reftinskaya, Verkhnetagilskaya and others – contain about 28-32 % wt alumina. The waste obtained could become the technogenic raw materials for the production of aluminum. This will allow partially replacing the import of alumina to Russia from foreign countries. The current work presents the results of experimental studies aimed at developing a technology for extracting high-quality alumina from the high-alumina ash of coal-fired power plants. In the study, the sintering method was used to obtain Al_2O_3 from ash for the first time. Because of high silica concentration in ash, the direct sintering cannot be applied. To remove SiO_2, the ash samples collected from three thermal power plants of Ural region were preliminary treated with alkali solution and then thermally treated. The influence of various technological parameters on the process of obtaining the target product has been studied. To obtain an enriched alumina concentrate, the ash was found to be treated with 20 % wt of NaOH solution at 90-100 °C. The further thermal treatment should be performed at a temperature of 1,000-1,200 °C to activate ash. The sintering of the activated ash results in the production of Al_2O_3 with a purity of 97-98 % wt.

1. Introduction

Aluminum is one of the most demanded metals in the world industry. The production of this material reaches the values of 50-55 Mt/y. The annual growth of aluminum consumption by various sources is 3-5 %. The wide possibilities of using aluminum in various industries put it in the position of the leading structural material of the 21st century (Pedneault et al., 2021). Aluminum consumption in the Russian Federation in 2021 amounted to approximately 1.2 Mt. The energy sector accounts for about 13-14 % of aluminum consumption with growth prospects.

Currently, the main source of alumina is bauxite ores, 2/3 of which are imported from foreign countries. Among the various types of traditional alumina raw materials (bauxite, nepheline ores, mudstones, clays, etc.), the ash of thermal power plants (TPP) operating on the coal of the Ekibastuz basin is of particular importance. These include large thermal power plants of the Ural region: Troitskaya, Reftinskaya, Verkhnetagilskaya and a number of others. The ash produced from the indicated power plants is characterized by a high alumina content of 28-32 %. Transport accessibility and developed infrastructure make it possible to consider the ash dumps of coal-fired thermal power plants as promising, large-scale technogenic raw materials for the production of alumina (Khokhlov eta al., 1995). The ash can be additionally considered to produce magnetite concentrate (Kumar et al., 2021), flotation carbon concentrate, a number of silica products (Sadarang and Nayak, 2021), and a number of other useful components (Loginova et al., 2017). The involvement of ash and slag dumps containing similar ash in processing also reduces the environmental burden on the environment (Levchenko, 2014).

Paper Received: 15 April 2022; Revised: 31 May 2022; Accepted: 03 June 2022
Please cite this article as: Delitsyn L., Kulumbegov R., Popel O., Sulman M.G., Kosivtsov Y., 2022, Ash from Coal-Fired Power Plants as a Raw Material for the Production of Alumina, Chemical Engineering Transactions, 94, 655-660 DOI:10.3303/CET2294109

To date, about 350 Mt of ash has been accumulated in the ash dumps of coal-fired power plants in the Ural region. The amount of ash waste is continuously increasing by 7-8 Mt/y. With an average content of 28 % Al_2O_3 in ash, the amount of alumina in ash dumps is about 100 Mt (Rawat and Yadav, 2020). These data indicate the importance of solving the problem of involving thermal power plant ash in the production of alumina. There is no ready-made technology for extracting alumina from ash and alumina processing enterprises in the world (Ghodeswar and Olivier, 2022). Although there are quite a lot of publications that addresses certain issues of ash processing technology (Lavrinenko et al., 2020).

The analysis of recent publications shows the limited number of processes can be effectively used for the recovery of alumina from ash and slag waste (Behera et al., 2021). The flotation (Ramanathan et al., 2020), and alkali treatment (Petrus et al., 2020) are the most widely used techniques. However, to improve the degree of the removal and provide the cost-effective technological scheme, the detailed investigation is required. The main gaps taking place in this field are the lack of data concerning the influence of technological parameters on the removal of alumina from ash.

The purpose of the work is to study the regularities of the technological parameters of obtaining alumina from the ash of thermal power plants. The study was carried out using the ash from the dumps of the biggest coal-fired thermal power plants in Russia. For the first time, the sintering technology was applied to remove alumina from the ash. The results of the study can be applied in the development of a method for the integrated utilization of ash from coal-fired thermal power plants.

2. Experimental

For the experiments, ash from the dumps of three coal-fired thermal power plants (Troitskaya, Reftinskaya, Verkhnetagilskaya) was used. Preliminarily, the ash was flotated to remove carbon and iron-containing fractions. NaOH (state standard - 2263-79), Na_2CO_3 (state standard 83-79), $CaCO_3$ (state standard – 4530-76), CO_2 (technical state standard 8050-85) were applied for the ash treatment.

An amount of 300 g of ash pre-purified from carbon and magnetite to remove part of SiO_2, was dissolved in 750 mL of 20 % NaOH solution with constant stirring in a Stegler MB-6 top-drive agitator (500 rpm) for 180-300 minutes at a temperature of 20-100 °C. The resulting pulp was filtered on a single-stage vacuum pump VE-160. Alumina concentrate was washed with distilled water (T = 50-70 °C) to a neutral pH, dried at T = 105 °C to a constant weight. Dried alumina concentrate was mixed with Na_2CO_3 and $CaCO_3$ and sintered at T = 1200-1250 °C. The resulting sinter was leached with water at T = 75 °C. Alumina from sodium aluminate converted into solution was precipitated by CO_2 bubbling at T = 70-80 °C by reaction (Eq(1)):

$$2NaAlO_2 + 3H_2O + CO_2 \rightarrow Al_2O_3 \cdot 3H_2O + Na_2CO_3 \quad (1)$$

The precipitated aluminum hydroxide was filtered under vacuum and washed with water, dried in an oven SNOL – 3.5/3.5- I5M at T = 105 °C. Heat treatment of the resulting sample was carried out in a muffle furnace "NAKAL" model PL-514 at a temperature of 600-1300 °C for 60 minutes in an air atmosphere in corundum crucibles. The reaction products were analyzed using the Perklin Elmer atomic absorption spectrophotometer, the Jobin Yvon plasma spectrometer, the JMS-5300 X-ray spectral analytical complex and the KFK-2 photometer.

3. Results and discussion

Chemical analysis of the ash samples under study showed approximately the same content of the main chemical components and the silicon module - μSi (Al_2O_3 / SiO_2) (Table 1). As the indicated TPP use the coal from Ekibastuz basin, and the power generation technique is the same for all plants, only a negligible differences are observed.

Among the known methods of producing alumina from low-grade bauxite, the most promising is sintering technology (Liner, 1961). This technique can also be used for ash processing. The high content of SiO_2 does not allow the use of ash for the production of alumina by sintering technology with limestone without its preliminary desilication. In the case of direct sintering of the charge, the consumption of limestone per t of the initial ash becomes very high, and the extraction of alumina from the sinters is low. Since μSi = 0.46-0.48 in the ash (Romanov et al., 1967), it is necessary to remove such an amount of silica from the waste to μSi becomes ≥ 1 (Sazhin, 1979). This stage makes the ash suitable for the production of alumina by sintering method. To prepare ash for the extraction of Al_2O_3, the most technologically advanced method is the chemical enrichment of aluminosilicate raw materials (Zyryanov et al., 2010). This method uses NaOH solutions to separate aluminum and silicon oxides (Abramov et al., 1985). The method is based on the different solubility of silicon and aluminum oxides contained in the ash at a certain temperature and concentration of NaOH (Eremin et al., 1963).

In the first step of this study, the ash of the Troitskaya TPP was used to eliminate the optimal concentration of an aqueous NaOH solution for desalinization (Figure 1). An increase in the SiO_2 solubility was observed while the NaOH concentration increased up to 20 wt. % for both temperatures studied. The further increase of alkali content did not led to the effectiveness of silica removal. During the action of the alkali on the mixture of silica and alumina, the obtained sodium aluminate and silicate tend to form the insoluble sodalite that covers the silica particles preventing its accessibility for NaOH (Xu et al., 2009).

Table 1: Chemical composition of ash from TPP, [% wt.]

Components	Urals TPP		
	Troitskaya	Reftinskaya	Verkhnetagilskaya
SiO_2	57.75	57.4	61.2
Al_2O_3	28.4	27.3	28.9
Fe_2O_3	4.8	5.35	4.2
CaO	0.95	1.4	0.72
MgO	0.48	0.63	0.52
Na_2O	0.37	0.15	0.44
K_2O	0.5	0.55	0.55
TiO_2	1.05	1.1	1.38
P_2O_5	0.59	-	0.27
S	0.11	0.73	0.35
C	5	5.4	1.5
μ_{Si}	0.49	0.48	0.47

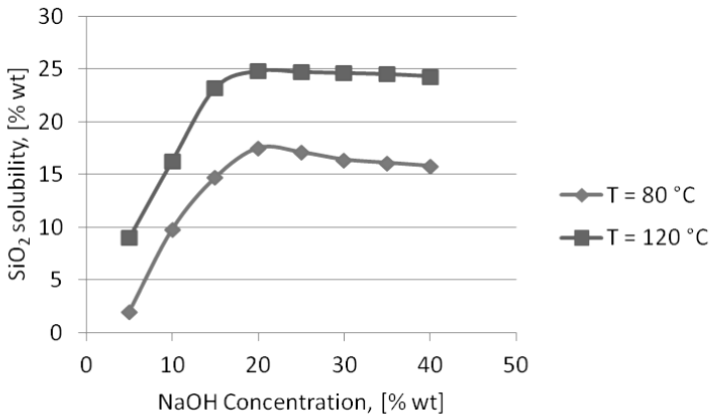

Figure 1: Dependence of the SiO_2 solubility on the concentration of NaOH

Temperature influence on the SiO_2 solubility in alkaline solution is shown in Figure 2. An increase in temperature leads to an increase in the amount of separated silica. At temperatures over 90 °C the silica solubility tends to be constant. Such effect can be connected with the significant increase in the sodalite formation rate.

In the process of ash dissolution, a significant part of SiO_2 passes into the composition of an alkaline solution. Al_2O_3 and Fe_2O_3 are extracted into an alkaline solution in a small amount, approximately 3.6 % and 2.2 %, respectively. Due to the reaction of interaction between the components of the system, part of Na^+ passes into the composition of alumina concentrate forming insoluble aluminosilicates.

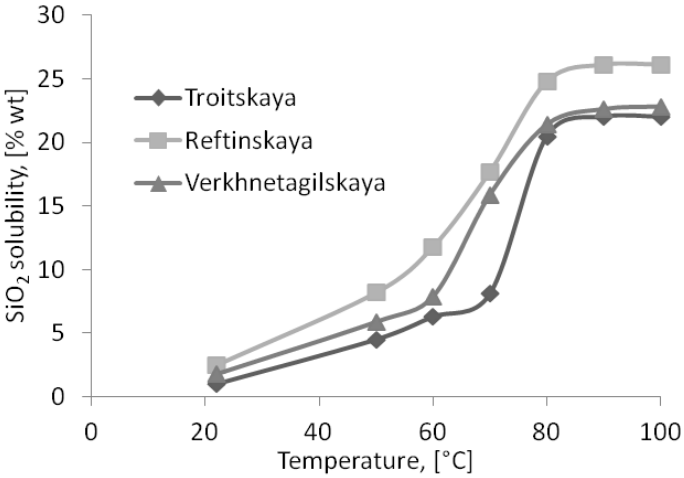

Figure 2: Temperature influence on the solubility of SiO_2

The determining factor in the solubility of coal-fired TPP ash in NaOH is its phase composition. The last one depends on the composition of the coal mineral part, firing of coal fuel in boilers, the conditions of fly ash cooling and many other reasons. In the composition of the ashes, a glass phase (X-ray amorphous substance) was detected as the main substance. A number of crystalline phases represented by mullite, quartz, glaucophane, which are slightly soluble in an alkaline solution, were also observed. Since mullite and glaucophane do not dissolve in alkaline solutions, it is impossible to achieve complete extraction of silica from the ash without its additional activation. One of the ways to increase the activation of ash is the heat treatment. Since the main amount of SiO_2 is concentrated in the glass phase, during heat treatment it begins to recrystallize and turn into various crystalline modifications of quartz (α-quartz, β-quartz, β-cristobalite, β-tridymite, γ-tridymite). According to detailed crystallographic studies (Toropov et al., 1965), the rearrangement of quartz crystal lattice (pure phase opposed to ash) during the phase transition from the low-temperature form of β-quartz to the high-temperature form of α-quartz (β-quartz - α-quartz) occurs in the temperature range from 550 to 580 °C. At the same time, the parameters of the SiO_2 crystal lattice change. The effect of thermal activation of ash on the solubility in an alkaline is not observed at temperatures up to 600 °C. A further increase in the ash activation temperature to 1000-1200 °C leads to an increase in the solubility of SiO_2 (Table 2).

Table 2: Effect of the ash heat treatment temperature on the solubility of SiO_2 and the composition of alumina concentrate (leaching temperature – 98-100 °C)

T, [°C]	Dissolved ash, [% wt]	Content in alumina concentrate, [% wt]		μSi
		SiO_2	Al_2O_3	
20	27.9	39.5	38.0	0.96
600	29.5	38.1	38.9	1.03
700	34	34.0	41.5	1.22
800	33.2	34.7	41. 0	1.18
900	35.0	33.05	42.07	1.27
1,000	36.9	31.0	43.07	1.38
1,100	38.3	29.0	44.6	1.54
1,200	40.4	27.76	45.4	1.65
1,300	39.2	28.4	45.07	1.58

The composition and properties of the insoluble residue are radically different from the original ash. The resulting alumina concentrate becomes a raw material prepared to produce Al_2O_3. Alumina concentrate is a fine powder consisting of finely dispersed beads. The average diameter of the beads in alumina concentrate is by 1.5 - 2 times smaller than the average diameter of glass beads in ash. In the initial ash, the glass beads and their thickening in the glass phase are characterized by a smooth melted inert surface (Figure 3a). After alkaline treatment, the entire surface of the alumina concentrate beads is pitted with etching pits and it becomes chemically active. After the leaching of ash, the alumina concentrate forms the framework insoluble in alkali (Figure 3b).

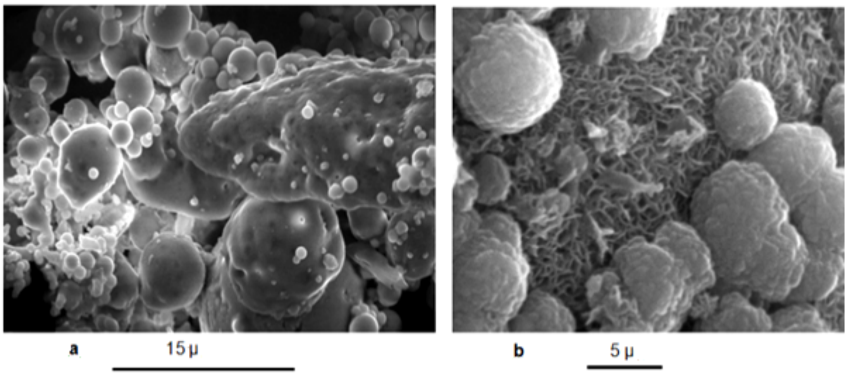

*Figure 3: SEM images: **a** - the ash before treatment with an alkaline solution; **b** – the alumina concentrate*

To obtain alumina from concentrate, sintering was carried out. It has been experimentally established that the optimal sintering temperature is in the range of 1,200-1,250 °C for a charge consisting of alumina concentrate, Na_2CO_3 and $CaCO_3$. During sintering, a water soluble sodium aluminate and a bicalcium silicate practically insoluble in water are formed by the following reactions (Eq(2), Eq(3)):

$Na_2CO_3 + Al_2O_3 \rightarrow Na_2O{\cdot}Al_2O_3 + CO_2$ (2)

$2CaCO_3 + SiO_2 \rightarrow 2CaO{\cdot}SiO_2 + 2CO_2$ (3)

The aluminate solution was decomposed by CO_2 bubbling according to Liner (1961). A residual content of $Na_2O{\cdot}Al_2O_3$ in the solution was found to be less than 5-6 g/L. As a result, aluminum hydroxide crystals fall out of the solution, settling to the bottom of the reactor. The precipitate filtered on a vacuum filter was washed with water, dried and fed to the preparation of the charge to isolate alumina. After calcinations of aluminum hydroxide at 700-800 °C, dehydrated alumina containing Al_2O_3> 98 % by weight was obtained (Table 3).

Table 3: Chemical composition of alumina after calcination, % by weight (t = 700 °C)

Components,[% wt]							
Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
<0.1	0.12	98.5	0.52	< 0.1	0.58	0.008	0.20

Thus, alumina with an Al_2O_3 content > 98% can be obtained from the ashes of coal-fired power plants rich with aluminum oxide. The SiO_2 content in metallurgical alumina, according to state standard, should be < 0.07 % wt. The latter is achieved by the well-known method (Agranovsky et al., 1970) by adding calcium compounds to the aluminate solution.

4. Conclusions

The ash of thermal power plants operating on the coal of the Ekibastuz basin is a major resource for the production of alumina. In order for the ash to become a full-fledged raw material for the production of alumina, it must be processed at the first stage by chemical enrichment. This procedure is aimed at the desilication which makes it possible to obtain an alumina concentrate with a μSi of 1.27-1.65.
In this work, the effect of thermal activation of ash as well as the leaching temperature on the extraction of SiO_2 from the ash is shown. The optimal concentration of NaOH for desilication of ash was found to be 20 % wt. The optimal temperature for the thermal activation of ash is 1,000-1,200 °C. As a result of chemical enrichment of ash, alumina concentrate with Al_2O_3 and SiO_2 content of 45 % and 28 %, respectively can be obtained. Enriched alumina concentrate is a raw material suitable to obtain a product with an Al_2O_3 content > 98 % by sintering. After an additional desilication, the sintering method is prospective for the production of alumina which will correspond to the quality of metallurgical feedstock.

Acknowledgments

This work was funded by the Russian Science Foundation (grant 21-79-30004).

References

Abramov V.Ya., Stelmakova G.D., Nikolaev I.V. (Eds.), 1985, Physic-chemical bases of complex processing of aluminum raw materials (alkaline methods) (In Russian), Metallurgy, Moscow, Russia.

Agranovsky A.A., Berkh V.I., Kavina V.A., 1970, Production of alumina, Chapter In: Baymakov Yu.V., Kontorovich Ya.E. (Eds.), Metallurgist's Guide to non-ferrous metals (In Russian), Metallurgy, Moscow, Russia, 314-318.

Behera S.K., Mishra D.P., Singh P., Mishra K., Mandal S.K., Ghosh C.N., Kumar R., Mandal P.K., 2021, Utilization of mill tailings, fly ash and slag as mine paste backfill material: Review and future perspective, Construction and Building Materials, 309, 125120.

Eremin N.I., Blagoveshchenskaya G.S., Belenina G.A., 1963, Processing of mudstones for alumina (In Russian), Non-ferrous metallurgy, 8, 229, 32-35.

Ghodeswar A., Oilivier M.E., 2022, Trading one waste for another? Unintended consequences of fly ash reuse in the Indian electric power sector, Energy Policy, 165, 112940.

In 2021 RUSAL delivered a record 1.2 million tons of aluminum to the domestic market (In Russian), 2022, Bratsk Television Studio <bst.bratsk.ru/news/48485> accessed 31.03.2022.

Khokhlov B.G., Ni L.P., Romanov V.L., Manankov A.A., 1995, Method of processing the ash of power coals into alumina and gypsum, Patent No. 2027669 C1 Russian Federation, IPC C01F 7/26.: No. 5041606/26 : published on 01.27.1995.

Kumar R., Mandal A.K., Dishwar R,K., Sinh O.P., 2021, Utilization of iron ore slime and bottom ash: An overview, Materials Today Proceedings, 46, 3, 1505-1514.

Lavrinenko A.A., Kunilova I.V., Golberg G.Y., 2020, Features of complex processing of fly ash of thermal power plants, Scientific foundations and practice of processing ores and technogenic raw materials: Materials of the XXV International Scientific and Technical Conference held within the framework of the XVIII Ural Mining Decade 02-11 April 2020, Yekaterinburg, 07-10 April 2020, Yekaterinburg, Russia, 338-341.

Levchenko V.N., 2014, Experience in processing fly ash of Reftinskaya GRES, Ash slags of TPP: removal, transport, processing, warehousing: Materials of the V International Conference, Moscow, Russia, April 24-25, 2014. Moscow, 91-94.

Lainer A.I., Eremin N.I., Lainer Yu.A. (Eds.), 1978, Alumina production (In Russian), Metallurgy, Moscow, Russia.

Loginova I.V., Chaikin L.I., Shoppert A.A., S. Trubetskoy V., 2017, Method of complex processing of ash from coal burning, Patent No. 2605987 C Russian Federation, IPC B09B 3/00, C01B 33/12.: No. 2015129883 : published on 10.01.2017.

Pedneault J., Majeau-Bettez G., Krey V., Margni M., 2021, What future for primary aluminium production in a decarbonizing economy?, Global Environmental Change, 69, 102316.

Petrus H.T.B.M., Olvianas M., Suprapta W., Setiawan F.A., Prasetya A., Sutijan, Anggara F., 2020, Cenospheres characterization from Indonesian coal-fired power plant fly ash and their potential utilization, Journal of Environmental Chemical Engineering, 8, 5, 104116.

Ramanathan S., Gopinath S.C.B., Md Arshad M.K., Poopalan P., 2020, Nanostructured aluminosilicate from fly ash: Potential approach in waste utilization for industrial and medical applications, Journal of Cleaner Production, 253, 119923.

Rawat K., Yadav A.K., 2020, Characterization of coal and fly ash (generated) at coal based thermal power plant, Materials Today Proceedings, 26, 2, 1406-1411.

Romanov L.G., Osipova E.F., Shcherban S.A., Nurmagambetov H.N., Dzhumbaev B.S., 1967, Alkaline enrichment of ash obtained from the burning of Ekibastuz coals, Proceedings of the Institute of Metallurgy and Enrichment, 23, 63-66.

Sadarang J., Nayak R.K., 2021, Utilization of fly ash as an alternative to silica sand for green sand mould casting process, Journal of Manufacturing Processes, 68, A, 1553-1561.

Sazhin V.S., 1988, New hydrochemical methods for complex processing of aluminium silicates and high-silica boxites (In Russian), Metallurgy, Moscow, Russia.

Toropov N.A., Barzakovsky V.P., Lapin V.V., Kurtseva N.N., 1965, Diagrams of the state of hardware systems, Handbook, The first issue, Dual systems, Moscow, Russia, Nauka, 534 p.

Xu B., Wingate C., Smith P., 2009, The effect of surface area on the modelling of quartz dissolution under conditions relevant to the Bayer process, Hydrometallurgy, 98, 108—115.

Zyryanov V.V., Petrov S.A., Matvienko A.A., 2010, Morphology and structure of magnetospheres based on hematite or spinel and glass, Inorganic Materials, 46, 6, 729-737.