Development of Alumina Production Technology by sintering of TPP Waste

E Yu Fomina and V V Vlasova
Irkutsk National Research Technical University, Russia
E-mail: e_u_fom@bk.ru

Abstract. Russia is experiencing a steady shortage of raw materials for the production of alumina, and therefore, the search for unconventional cheap raw materials for its production is very relevant. In this paper, we consider two types of raw materials for the alumina production - ash and slag waste from CHPP-9 (Angarsk) and New Irkutsk CHPP (Irkutsk) PJSC “Irkutskenergo”, and wet magnetic separation tails obtained after the separation of iron-containing components. Laboratory studies were conducted on the sintering of the charge from ash and slag waste, tailings of wet magnetic separation with limestone and soda. Self-moldering sinter obtained; the recovery of alumina from them during leaching was 87% for New Irkutsk CHPP and 83% for CHPP-9. The optimal conditions of experiments on sintering samples of ash-and-slag materials were determined. Two-stage desiliconization and carbonization of sinter leaching solutions, and calcination of aluminum hydroxide experiments were carried out. Alumina, corresponding in composition to metallurgical alumina (alumina content of 97.77%) was obtained. The technological scheme of alumina production from ash and slag waste of thermal power plants of the Irkutsk region is proposed.

1. Introduction and Background
It is known that Russia over the past 15 years has experienced a steady shortage of raw materials for the production of alumina, in particular in bauxite and nepheline. About 3 million tons of alumina are imported into the country annually for the needs of the aluminum industry, and only 40% of Russia's alumina needs are provided by domestic raw materials [1, 2].

The largest Russian alumina production capacities are concentrated in the Urals (Bogoslovsky and Uralsky aluminum plants) and in Eastern Siberia (Achinsky alumina refinery operating on the nephelines of the Kiya-Shaltyrsky deposit). During the development of the nepheline deposit, a steady decrease in the content of aluminum oxide in natural raw materials and intermediate products of alumina production is observed, and the plant is faced with the task of finding a reserve raw material base [3, 4]. Therefore, the search for new non-traditional low-cost raw materials for obtaining alumina is very relevant.

As non-traditional alumina-containing raw materials of technogenic origin, ash and slag waste from thermal power plants can be used [5, 6]. Over the long-term work of thermal power enterprises in the Irkutsk Region, more than 90 million tons of ash and slag waste have accumulated, and a significant part of them are located in the specially protected Baikal natural zone. The total annual output of ash and slag is 1.6 – 1.8 million tons, of which no more than 20% is effectively used.

Alumina production from bauxite is carried out according to the Bayer method [3, 4]. For unconventional raw materials, the most interesting are the methods for producing alumina, which do
not significantly differ from those used in industry and therefore do not require additional studies of the hardware and technological design of the process, thereby significantly reducing the development time of this type of raw material. Thus, the study of the possibility of processing ASW by the method of sintering soda-limestone charge, which is used at the Achinsk alumina refinery for processing nepheline raw materials, is of undisputed interest.

2. Materials and Research Methods
The purpose of this work was to conduct research and develop a technology for extracting alumina from ash and slag waste of thermal power plants in the Irkutsk region. The composition and properties of fly ash of the New Irkutsk TPP, the ash and slag material of TPP-9, and the tailings after the wet magnetic separation, which were obtained by extracting magnetite concentrate from the feedstock, were studied at the Department of Mineral Processing and Environmental Protection [6].

Technological research in the study of the sintering conditions of both a three-component and a two-component charge were carried out on a laboratory scale. The components of the charge, taken from the calculation of obtaining a given hitch, were weighed to the accuracy 0.001 g and thoroughly mixed manually in a porcelain mortar. The charge in corundum crucibles was placed with a cold laboratory muffle furnace PL-5-14 and heated to a sintering temperature at which the set time was maintained. Sintering mode: heating rate was 8-10 ° per minute; sintering temperatures - 1150 °C, 1200 °C, 1250 °C. After aging, the sinters were cooled together with the furnace to 600 ° in 1-1.5 hours, and then to room temperature in a desiccator.

The quality of the sinters was determined by the value of the chemical extraction of alumina and alkalis into the solution during their leaching. Leaching of the sinters, disintegrated to a particle size of -0.25 mm, was carried out with vigorous stirring in a glass closed vessel, placed in a thermostat. The vessel was equipped with a reflux condenser.

The leaching conditions were adopted in accordance with the standard method of hydrochemical testing of nepheline sinters (from which the ash and slag waste almost do not differ in composition) [7]. According to this technique, leaching was carried out at a temperature of 70 °C for 30 min with an alkaline solution containing 1 mol of Na₂O₉ and 0.25 mol of Na₂O₉ per 1 mol of Al₂O₃ sinter and the ratio L:S = 5:1. Under these conditions, the alkaline leaching solution for sinters contained A g/l Na₂O₉ and B g/l Na₂O₉.

After leaching, the aluminate solution was separated from the sludge by filtration. The sludge was washed on the filter with hot water. Aluminate solutions were analyzed for total alkali and alumina by volumetric methods. The extraction of alumina and alkali from sinters was determined according to chemical analysis of solutions and according to x-ray fluorescence silicate analysis. On solutions of individual experiments, desiliconization was performed to obtain alumina. To study the composition of the waste of the CHPP-9 and New Irkutsk CHPP, the tails of the WMS and sintering products were used: chemical, diffraction x-ray phase and mineralogical analysis methods.

3. Experimental Section
Alkaline methods for sintering aluminosilicates with one limestone or soda and limestone have several advantages. The main advantage of the limestone method is the production of self-decaying sinters and a relatively small consumption of alkali, but there are a number of conditions that complicate the production. These include the following: a higher sintering temperature (100-200 °C higher than for soda-limestone mixtures); the need for a special regime for cooling the sinters in the high-temperature region; a very narrow temperature sintering pad, not exceeding 50 °C, and in some cases 25 °C; increased requirements for starting materials with respect to the content of MgO, which should be minimal. The disadvantages of the method include a 10-20% greater material flow compared with soda-limestone mixture. Three-component charge designed to produce aluminum-aluminum sinters as applied to aluminosilicate raw materials were studied already in the first years of the development of the aluminum industry [7].
Laboratory tests were conducted to sinter ash and slag waste and tailings of wet magnetic separation with soda and limestone. The composition and characteristics of the samples are shown in table 1.

**Table 1.** The chemical composition of ash waste and tailings of wet magnetic separation, %.

| Name of samples | Ash dump CHPP-9 (Angarsk) | Tailings of WMS CHPP-9 | Ash dump Irkutsk CHPP | Tailings of WMS New Irkutsk CHPP |
|----------------|---------------------------|------------------------|-----------------------|----------------------------------|
| SiO₂           | 55.40                     | 57.87                  | 53.66                 | 54.06                            |
| TiO₂           | 0.811                     | 0.833                  | 0.894                 | 0.965                            |
| Al₂O₃          | **28.13**                 | **28.17**              | **24.60**             | **27.93**                        |
| Fe₂O₃          | 5.2                       | 4.36                   | 9.31                  | 4.69                             |
| MnO            | 0.058                     | 0.051                  | 0.105                 | 0.084                            |
| MgO            | 1.378                     | 1.385                  | 2.158                 | 2.134                            |
| CaO            | 4.979                     | 5.035                  | 6.862                 | 6.697                            |
| Na₂O           | < 0.20                    | < 0.20                 | < 0.20                | < 0.20                           |
| K₂O            | 0.658                     | 0.731                  | 1.311                 | 1.381                            |
| P₂O₅           | 0.124                     | 0.123                  | 0.132                 | 0.149                            |
| Ba+Ce          | 0.037                     | 0.039                  | 0.068                 | 0.072                            |
| Sr             | 0.0338                    | 0.0342                 | 0.065                 | 0.072                            |
| Zn             | 0.0343                    | 0.0356                 | 0.0302                | 0.0308                           |
| ignitionloss   | 3.14                      | 1.31                   | 0.67                  | 1.66                             |
| Amount         | 99.99                     | 99.99                  | 99.93                 | 99.95                            |

In order to establish the optimal composition for each sample of ash-and-slag material, several charges were tested that differed from each other in the dosage of soda and calcium carbonate introduced to bind iron and titanium oxides to ferrites and sodium charges were tested that differed from each other in the dosage of soda and calcium carbonate introduced to bind iron and titanium oxides to ferrites and sodium charges were tested that differed from each other in the dosage of soda and calcium carbonate introduced to bind iron and titanium oxides to ferrites and sodium charges were tested that differed from each other in the dosage of soda and calcium carbonate introduced to bind iron and titanium oxides to ferrites and sodium charges were tested that differed from each other in the dosage of soda and calcium carbonate introduced to bind iron and titanium oxides to ferrites and sodium charges were tested that differed from each other in the dosage of soda and calcium carbonate introduced to bind iron and titanium oxides to ferrites and sodium. In this case, the amount of Na₂CO₃ and CaCO₃ in all cases was sufficient for the formation of sodium aluminate and dicalcium silicate.

In order to clarify the optimal composition of the charges, experiments were made on sintering aluminosilicates with different soda contents, as well as with a lack and excess of limestone. The charge was sintered at a temperature of 1150, 1200 and 1250 °C for 0.5-2.0 hours. As a result, the charges of the following composition were tested (table 2).

**Table 2.** The charge composition for sintering.

| Soda                  | Calciumcarbonate | Soda and calciumcarbonate |
|-----------------------|------------------|---------------------------|
| 1. Na₂O:(Fe₂O₃ + TiO₂) =1,0 | 6. CaO:(Fe₂O₃ + TiO₂) =1 | 14. CaO:SiO₂=2; Na₂O:(Al₂O₃+Fe₂O₃)=1 |
| 2. Na₂O:(Fe₂O₃ + TiO₂) =0,5 | 7. CaO:(Fe₂O₃ + TiO₂) =0,5 | 15. CaO:SiO₂=1; Na₂O:(Al₂O₃+Fe₂O₃+TiO₂)=1 |
| 3. Na₂O:(Fe₂O₃ + TiO₂) =0,3 | 8. CaO:(Fe₂O₃ + TiO₂) =0,3 |  |
| 4. Na₂O:(Fe₂O₃ + TiO₂) =0,1 | 9. CaO:(Fe₂O₃ + TiO₂) =2 |  |
| 5. Na₂O:(Fe₂O₃ + TiO₂) =2 | 10. CaO:(Fe₂O₃ + TiO₂) =4 |  |
|                       | 11. CaO:(Fe₂O₃ + TiO₂) =6 |  |
|                       | 12. CaO:(Fe₂O₃ + TiO₂) =10 |  |
|                       | 13. CaO:(Fe₂O₃ + TiO₂) =15 |  |
The experiments made it possible to establish that two-component charges allow alumina to be extracted into the solution from the obtained sinters by no more than 57%. The dependences of the extraction of alumina on the composition of the charge and the sintering temperature are established, which are not of great interest due to the low extraction of aluminum and the frequent formation of an alloy during sintering of two-component charges.

4. Research results and discussion

The results of the experiments show that an increase in the amount of soda or calcium carbonate slightly increases the alumina recovery in two-component charges, however, the highest values were obtained with a three-component charge. So, the maximum recovery of alumina from the ash dump CHPP-9 (Angarsk) was 83.68% on a charge of the composition CaO:SiO₂=2; Na₂O:(Al₂O₃+Fe₂O₃)=1 during sintering for 1 hour at a temperature of 1200 °C; under the same conditions, the maximum recovery of 87.07% was obtained for ash dump New Irkutsk CHPP (Irkutsk).

For the sinters with the maximum extraction of Al₂O₃, desiliconization, carbonization of solutions and calcination studies to obtain the final product – alumina were carried out.

Desiliconization of aluminate solution

During the leaching of alumina-containing sinters, along with aluminum and alkali, silicon passes into the solution. In aluminate solutions, silicon exists in the form of anion SiO₂(OH)₂⁻ and aluminum-silicon complexes.

Therefore, aluminate solutions are subjected to purification from silicon compounds — desiliconization — before decomposition. The essence of the process of desiliconization is the binding of silica from solution to sparingly soluble compounds and their separation from the solution. To clean aluminate solutions from silicon compounds, two methods are practically used:

1) desiliconization with precipitation of sodium hydroaluminosilicates NaₓO·SiO₂·1,7 + 1,75SiO₂·nH₂O;
2) desiliconization with the precipitation of compounds that are significantly less soluble than sodium hydroaluminosilicates with the addition of lime.

In the experiments performed, a two-stage desiliconization method was used with the release of the bulk of SiO₂ in the form of sodium hydroaluminosilicates in the first stage and a small part of it in the form of calcium compounds in the second.

The first stage of desiliconization

The first stage of desiliconization of aluminate solutions was carried out in an autoclave at a temperature of 160 °C with vigorous stirring. Desiliconization is most intense in the first 2 to 3 hours. In the experiment, the duration of the experiment was 2.5 hours, the silicified aluminate solution after filtration was sent to the second stage.

The second stage of desiliconization

In the aluminate solutions, after the first stage of desiliconization, the concentration of silica is close to equilibrium in the Na₂O·Al₂O₃·SiO₂·H₂O system. Such depth of cleaning solutions from SiO₂ is insufficient to obtain high-grade alumina by sintering. A further increase in the degree of desiliconization is possible by binding silica to a compound whose composition is expressed by the formula:

3CaO·Al₂O₃·mSiO₂·(6−2m)H₂O

The pulp after the second stage was subjected to filtration. The filtered solution was sent for carbonation. The main parameters of the process of deep desiliconization: the duration of the process is 2.2 hours; temperature 90 °C; dosage of lime 4.0 g / l. The process was carried out with vigorous stirring.

Carbonization of Aluminate Solution

Carbonization of aluminate solutions is carried out by bubbling a mixture of gases containing CO₂ through a solution to precipitate aluminum hydroxide. The technological prerequisites for the
application of this method are the presence of exhaust gases from sintering furnaces containing 12–14\% CO\textsubscript{2}, and the possibility of using the resulting soda solutions for the preparation of charges [7].

Carbonization is a complex heterophasic process. The essence of the process is to neutralize caustic alkali according to the reaction:

$$2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

As a result of a decrease in the Na\textsubscript{2}O\textsubscript{e} content, the stability of aluminate solutions decreases and they decompose by reaction:

$$\text{NaAlO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_3 + \text{NaOH}.$$  

In addition to aluminum hydroxide, sodium carbonate $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CO}_2 \cdot n\text{H}_2\text{O}$ can be formed during carbonization. Carbonization should be carried out under conditions ensuring the production of coarse-grained aluminum hydroxide with a minimum content of impurities.

In the experiment, carbonization was carried out for 6 hours at 70–80 °C. At lower temperatures, fine crystalline aluminum hydroxide is obtained. Aluminum hydroxide is separated from the mother liquor by filtration. The washed hydroxide is sent for calcination.

**Calcination of Aluminum Hydroxide**

Calcination is the final stage of all alumina production processes. The process consists in firing aluminum hydroxide at 1100 - 1300 °C and obtaining technical aluminum oxide - metallurgical alumina for the electrolytic production of aluminum and non-metallurgical alumina for various industries [7, 9].

Calcination of aluminum hydroxide is accompanied by its dehydration and structural transformations of dehydrated aluminum oxide:

$$\text{Al(OH)}_3 \xrightarrow{200–250^\circ \text{C}} \text{AlOOH} \xrightarrow{450–500^\circ \text{C}} \gamma - \text{Al}_2\text{O}_3 \xrightarrow{930–950^\circ \text{C}} \alpha - \text{Al}_2\text{O}_3$$

*gibbsite*  \hspace{1cm} *boehmite*  \hspace{1cm} *corund*

The quality of alumina is determined by the purity, dispersion and phase composition of aluminum hydroxide. In the experiment, alumina was obtained by calcining aluminum hydroxide at 1150–1200 °C for 30 min.

The content of impurities in alumina depends on the purity of the starting aluminum hydroxide; some discrepancies are usually observed only in the Na\textsubscript{2}O, SiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, Na\textsubscript{2}O remains smaller due to volatilization, while SiO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} remain larger due to abrasion of the lining in the furnace.

The granulometric composition of alumina is very important for electrolysis. Alumina cannot be larger than the original hydroxide, it can only be smaller than it.

As a result of the studies obtained alumina particle size distribution of 80% of the class -100 + 10 microns and chemical composition, in percent: Al\textsubscript{2}O\textsubscript{3} - 97,77; SiO\textsubscript{2} - 0,21; Fe\textsubscript{2}O\textsubscript{3} - 0,014; $\Sigma$ (Na\textsubscript{2}O + K\textsubscript{2}O) - <0,23; P\textsubscript{2}O\textsubscript{5} - 0,002. Thus, the alumina obtained from the ash and slag waste of the Irkutsk thermal power plants, in terms of the content of aluminum, iron, sodium, potassium, zinc oxides, meets the requirements for metallurgical alumina used to produce aluminum by the electrolysis of cryolite-alumina melts [8, 9].

On the basis of our studies, we developed technological schemes for the processing of the TPP-9 and New Irkutsk TPP waste with integrated qualitative and quantitative indicators to produce alumina (Figures 1, 2). Similar technological schemes for sintering nepheline concentrates and nepheline-syenite ore of Siberia were mastered at three Russian enterprises: at the Volkhov aluminum and Pikalevsky alumina plants and the Achinsk alumina refinery [10, 11].

According to the recommended scheme, the initial ASWs are fed to the preparation of the mixture together with crushed limestone, fresh soda, circulating soda solution and circulating products (sludge of desiliconization, lime sludge). The finished mixture is served for sintering in a tube furnace. The sinter after the furnace is sent to a cooler, from where it is discharged for leaching with a circulating
alkaline solution. The sludge after leaching is sent to a dump or for further processing in the production of cement or foam concrete. The aluminate solution is subjected to desiliconization of the first stage in an autoclave plant.

Figure 1. Principle technological scheme for alumina production from ash (New Irkutsk TPP).
Figure 2. Principle technological scheme for alumina production from ash (TPP-9).
Next, the solutions are filtered, the resulting sludge is sent to sintering with the original ash. The aluminate solution is subjected to deep desilicization by treatment with lime. The solution is thickened, filtered and subjected to carbonization, and lime sludge is used in a circulating scheme.

Carbonization is carried out by bubbling through a solution of a mixture of gases containing CO2. The resulting aluminum hydroxide is separated by separation and filtration from the solution and washed. The washed aluminum hydroxide is calcined by calcination in tubular rotary furnace. As a result of calcination, finished products are obtained - alumina.

The estimated consumption of reagents for sintering, taking into account 100% irrevocable consumption, is: for ash waste TPP-9 - 1610.1 kg of limestone; for ash waste New Irkutsk TPP - 2733.15 kg of limestone. The reagent consumption during sintering of three-component blends will be, kg / ton of ash: for the ash waste TPP-9 - 1977.33 kg of limestone and 569.57 kg of soda; for the ash waste New Irkutsk TPP - 1915.23 kg of limestone and 579.66 kg of soda.

5. Summary and Conclusion

Thus, experiments were conducted on the extraction of alumina by sintering the ash and slag waste of thermal power plants with limestone and soda. It has been established that on two-component blends it is possible to obtain sinters suitable for subsequent leaching. However, the extraction of alumina in solution in this case is about 57% for TPP-9 and 37% for New Irkutsk TPP.

Studies were carried out on the sintering of three-component blends. Self-scattering sinters obtained; the recovery of alumina from them during leaching was 87% for New Irkutsk NPP and 83% for TPP-9. Conditions for sintering experiments with ratios CaO:SiO₂=2; Na₂O:(Al₂O₃+Fe₂O₃)=1 for both samples, ASWs are taken as optimal.

Experiments on two-stage desiliconization and carbonization of solutions, as well as calcination of aluminum hydroxide, were performed on leaching solutions of sinters obtained from three-component blends.

As a result of the research, alumina was obtained, corresponding in composition to metallurgical alumina in the content of aluminum oxides (97.77%), zinc, iron, phosphorus, sodium and potassium.

Based on the studies, a technology has been developed for processing ash and slag waste from thermal power plants in the Irkutsk region to produce alumina. Under certain economic conditions, technology may be economically feasible. Simultaneously with the solution of the problem of resource conservation, environmental safety is increased due to the involvement of industrial wastes in the production and reduction of their impact on the environment.

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