The use of technogenic raw materials to produce a high-alumina chamotte

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Abstract. When fused corundum is crushed, a finely dispersed powder is formed with an \( \text{Al}_2\text{O}_3 \) content of 93–95\%, in the form of substandard material. It is advantageous to utilize this powder to obtain high-alumina chamotte with \( \text{Al}_2\text{O}_3 \) content of more than 62\%. High-alumina aggregate (chamotte) was obtained by semi-dry technology with intermediate briquette molding from a mixture of corundum dispersed powder and enriched kaolin. Based on a final \( \text{Al}_2\text{O}_3 \) content of 65 wt. % the batch composition of the mass to produce a high alumina aggregate (chamotte) was calculated. From a mixture of dispersed corundum powder and kaolin moistened with a 5–7\% technical lignosulfonate solution with a density of 1050 kg m\(^{-3}\), a briquette was formed at a specific pressing pressure of 15–20 MPa. The briquette was fired at a temperature of 1700°C. The fired briquette had a strength of 164 to 193 MPa. The water absorption of briquettes was 11–12\%. The phase composition of the briquette is represented mainly by corundum and mullite. The enriched kaolin did not show sintering effect on fine corundum.

1. Introduction

To produce mullite refractories with an \( \text{Al}_2\text{O}_3 \) content of 62–72\%, the minerals of the sillimanite group are used: kyanite (distin), andalusite, sillimanite, etc [1–3]. These minerals have the same composition corresponding to the formula \( \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \) (62.9\% \( \text{Al}_2\text{O}_3 \) and 37.1\% \( \text{SiO}_2 \)). After firing at appropriate temperatures, they all go over to mullite by the reaction: \( 3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SiO}_2 \). The theoretical yield of mullite is 86\%, the remaining quantity of 14\% is silicic acid, which passes into cristobalite during firing. Minerals of the sillimanite group are mainly found in quartz rocks, in which other impurities (muscovite and sericite) containing alkali are simultaneously present. Therefore, to produce high-alumina refractories, it is necessary to enrich it preliminary. The \( \text{Al}_2\text{O}_3 \) content in the enriched concentrate should be about 60\%. The total fluxes (\( \text{CaO, MgO, Na}_2\text{O, K}_2\text{O, Fe}_2\text{O}_3 \)) should not exceed 3\%, which is very difficult to achieve. This is the main reason for the weak development of the production of high-alumina refractories from them, despite the significant reserves of this raw material. Deposits of kyanite that do not require enrichment are rare.

Another type of raw material to produce high alumina refractories is alumina hydrates: hydrargillite, boehmite, diasporas. These minerals are less likely than diasporas in the rock bauxite. Bauxites are sedimentary rocks, in addition to alumina hydrates, contain iron oxides (up to 20\%). To produce high-alumina chamotte, low-iron bauxites (up to 5\% \( \text{Fe}_2\text{O}_3 \)) are suitable, the deposits of which are very rare. Due to the high content of iron oxides and other impurities, bauxite must also be pre-enriched.
The most common raw materials to produce mullite refractories are mainly technical alumina, pure refractory clays, kaolins and quartz. Mullite refractories are obtained in two stages: first, the synthesis of mullite, and then products from it. Technical alumina is produced in large quantities mainly for the production of aluminum by calcining artificial alumina hydrates. The content of Al₂O₃ in it reaches 99–99.8%. The mineral composition is represented by γ-alumina, which is represented by porous spherulites with a diameter of 20–70 μm, which makes it difficult to sinter and obtain dense products from it. Therefore, industrial alumina is usually ground to particles less than 3 microns in size. In addition, technogenic raw materials are used, for example high-alumina coal ash [4–5].

From technical alumina, electrocorundum is produced by melting at 2000–2400°C with a content of 97–99% Al₂O₃. Corundum is used in the production of corundum and mullite-corundum refractories. When fused corundum is crushed, a finely dispersed powder is formed with an Al₂O₃ content of 93–95%, in the form of substandard material. The low Al₂O₃ content is explained by the fact that the least stable phase in fused corundum is the glass phase, which is formed during the melting of alumina due to the content of impurities. This low-strength glass phase in comparison with crystals of corundum is transformed into a dust-like state during crushing first. Thus, it is of interest to utilize the resulting fine powder. Due to the low Al₂O₃ content, finely dispersed powder can be claimed in the production of high-alumina refractories with a lower Al₂O₃ content. It is advisable to utilize this powder, for example, to obtain high-alumina chamotte with an Al₂O₃ content of more than 62%. It is proposed to use kaolin of wet enrichment after filter pressing as a binding component. It is proposed to mix the obtained fine powder. Due to the low Al₂O₃ content, it is difficult to sinter and obtain dense products from it. Therefore, industrial alumina is usually ground to particles less than 3 microns in size. In addition, technogenic raw materials are used, for example high-alumina coal ash [4–5].

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2. Experimental procedure
Phase composition was determined by an X-ray phase method in a Miniflex 600 (Cu Kα-radiation, λ = 1.541862 Å, recording interval 3–90°, scanning step 0.02 deg), Rigaku, Carl Zeiss, Japan, with MiniFlex Guidance and PDXL Basic data treatment package program control and data collection. Identification of diffraction maxima was carried out using a JSPDS data bank. The chemical composition of quartz sand was determined by emission spectral analysis with inductively coupled plasma in an Optima 4300 DV(Perkin Elmer, USA) optical emission spectrometer.

The water absorption, open and total porosity and apparent density were determined according to [6]. The grain size composition of finely milled powders was determined by sedimentation analysis in a SLAD 2201 (Shimadzu Corp.) particle laser diffraction analyzer according to [7]. Sieve analysis was carried out in accordance with [8].

3. Results and discussion
To produce a high-alumina aggregate (chamotte) using briquette technology, plastic molding was used with kaolin from the Kyshtymskoye deposit. The chemical composition of kaolin and substandard fine powder of corundum are given in Table 1.

Table 1. The chemical composition of materials.

| Material                  | SiO₂ | Al₂O₃ | CaO | Fe₂O₃ | MgO | R₂O | TiO₂ | LOI  |
|---------------------------|------|-------|-----|-------|-----|-----|------|------|
| Kaolin (%)                | 46.0–49.6 | 36.1–38.5 | 0.1–0.6 | 0.5–1.0 | 0.2–0.8 | 0.4–0.6 | 0.8  | 12.2–13.8 |
| Fine substandard corundum | 0.05–0.3 | 93.0–95.0 | 0.2–0.24 | 0.13–0.5 | 0.44–0.62 | 0.3–0.55 | 2.2–5.0 | –    |

The dispersed composition of kaolin is shown in Figure 1. The content of particles less than 2 microns is 8.15%. The maximum particle size is 112 microns. The main fractions are distributed uniformly and are in range of 60 to 2 microns. Particles larger than 60 microns are about 6%.
Figure 1. The dispersed composition of kaolin.

The grain composition of finely dispersed corundum is presented in Table 2. The main dusty fractions are particles smaller than 0.16 mm and more than 90%.

Table 2. The distribution of fine fractions in corundum.

| Particle size (mm) | > 0.5 | 0.5–0.16 | 0.16–0.063 | < 0.63 |
|-------------------|-------|----------|------------|--------|
| Fraction content (%) | 3.07  | 4.52     | 51.45      | 40.96  |

According to the X-ray diffraction results, distribution of crystalline phases of corundum dust is represented by the following minerals (%): corundum 89.5, dialuminumtitaniumoxide 1.2, rutile 0.16, $\alpha$-SiO$_2$ 8.7.

To produce a high-alumina aggregate, the composition of the mixture with an Al$_2$O$_3$ content of 65 wt. % was calculated. To increase the density of the briquette and reduce the water absorption of the aggregate, the technology of pressing the briquette through ‘false grain’ was used [9]. Corundum dust was mixed with kaolin in a plastic way, dried at 105°C. The obtained material was crushed before passing through a mesh with a mesh size of 3 mm.

The strength of the briquette is affected by mass composition, moisture and pressing pressure. Samples with a relative humidity of 5, 7, 9% were formed from the obtained powder at various pressing pressures of 5, 10, 15, 20, 25 MPa. For wetting, the technical lignosulfonate solution with a density of 1.05 g cm$^{-3}$ was used. The samples were dried, and the compressive strength was determined. The results are presented in Figure 2. The briquettes molded at a pressing pressure of 5 MPa and at a moisture content of 5–9% do not have enough strength (4 MPa) [10]. When firing in a furnace, such briquette will crumble, that results in a decrease in the yield of the finished product. When the pressing pressure is increased to 10 MPa, the samples molded at a moisture content of 9% are characterized by enough strength. A further increase in the pressing pressure to 15 MPa results in a strong briquette molded at a moisture content of 7–9%. With increasing pressing pressure above 20 MPa, the briquette molded at a relative humidity of 5–9% is also characterized by ample strength.

Chamotte firing is carried out in rotary or shaft furnaces. To reduce the dust and prevent the destruction of the granules during firing of the briquette, its transport strength should be at least 4 MPa [10]. The samples were fired at a temperature of 1700°C. The characteristics of the obtained chamotte are given in Table 3.
Figure 2. Dependence of compressive strength of unfired briquette on specific pressing pressure and relative humidity.

Table 3. Post-firing properties of the samples.

| Total shrinkage (%) | Water absorption (%) | Open porosity (%) | Apparent density (kg·m⁻³) | Compressive strength (MPa) |
|---------------------|----------------------|-------------------|---------------------------|---------------------------|
| 4–6                 | 11–12                | 27–28             | 2310–2330                 | 16.4–19.3                 |

The distribution of crystalline phases of chamotte is as follows (%): corundum 35–38, mullite 46–50, cristobalite 6–7, quartz 4–6, β-Al₂TiO₅~4.

According to the results of this project at this stage, positive results were not reached on such properties as water absorption and density. The synthesis of mullite did not pass in full.

4. Conclusion

At this stage of project, high-quality high-alumina chamotte with an Al₂O₃ content of 65 wt.% with water absorption of less than 2% was not obtained. The enriched kaolin used with the contents of SiO₂ and Al₂O₃, respectively, 46–50% and 36–39% (the rest of the impurity) did not show sintering effect on finely dispersed corundum. To obtain chamotte with water absorption of less than 2%, it is necessary to turn 6–7% of cristobalite into mullite. In addition, it is necessary to introduce sintering components into the mixture and use the intergrinding of clay or kaolin with finely dispersed corundum powder.

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