THE INFLUENCE OF ALUMINUM-CHROME PHOSPHATE ON COMPRESSIVE STRENGTH OF REFRACTORY MATERIALS

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ABSTRACT

Refractory materials bonded to the solution of monoaluminium phosphate or phosphoric acid do not have high initial compressive strength which makes it difficult to transport them to the place of installation, as well as only incorporation into different types of heat devices. The practice shows that better results in this case are achieved using aluminum chromium phosphate as a binding agent.

In this paper, the influence of aluminum chromium phosphate as a binder on the mechanical properties of refractory materials based on quartz sand and chamotte was examined. At the same time, the phosphate bonding of the refractory mixture was performed: chamotte flour + alumina (Al_2O_3) . The reason is the fact that this refractory oxide, by bonding with phosphates, gives monoliths whose initial and final strengths are significantly higher than the strength of the monoliths obtained by bonding the observed refractory materials (quartz sand and chamotte).

The materials used are: alumina, dominated by the alpha form of Al_2O_3 , granulation of 0.0 - 1.0 mm, quartz sand and chamotte flour with the addition of illite - kaolinite clay bonded with a 50 % solution of aluminium-chromium phosphate.

Key words: chemical binder, refractory material, aluminum-chromium phosphate, chamotte, clay, quartz sand, mechanical properties

1. INTRODUCTION

In the refractory industry, various phosphates are used, which are generally added to the aggregate as aqueous solutions.

Monoaluminium phosphate (46-50 % aqueous solution), ammonium phosphate, aluminum chromium phosphate, alkaline metaphosphates and polyphosphates, etc are used.

Hardening of alumosilicate products by phosphate bonding is conditioned by the formation of acid phosphate, their polymerization and polycondensation in the heating process, and also the formation of insoluble phosphates in the reaction of phosphoric acid with oxides from the refractory filler.[9]

Instead of H_3PO_4 , the most commonly used phosphate binder is a 50 % solution of monoaluminium phosphate, Al (H_2PO_4)₃, or abbreviations MAP. It is obtained by neutralizing the first H^+ ions from phosphoric acid with Al(OH)₃. If MAP is further neutralized with Cr₂O₃, all of its binding properties are substantially improved. These binders appear on the market as aqueous solutions, although recently acidic phosphate binders are also offered in powder form.[5]

Refractory materials bonded to the solution of MAP or phosphoric acid do not have high initial strengths, which makes it difficult to transport them to the place of installation, as well as only incorporation into different types of heat devices. The practice shows that better results in this case are achieved using aluminum chromium phosphate as a binding agent.

The stoichiometric composition of Al-Cr phosphate is as follows: $Al_2O_3 \times 0.8 Cr_2O_3 \times 3 P_2O_5$. Studies show that this is not a simple mixture of Al and Cr phosphate, but for a compound of the characteristic structure in which both metals are in the same molecule. In addition, the characteristics of the compounds are determined by the character of the P-O-M bond. In practice, this binding agent is used to prepare various types of refractory materials: thermally unprocessed bricks, special refractory mortars and others. Suitable for both acidic and neutral refractory materials (quartzite, chamotte, corundum, olivine, etc.). Unlike MAP and phosphoric acid, with which only acidic and neutral masses are bonded, Al-Cr phosphate can also be used for bonding basic masses.

In this paper, the studies are focused on the preparation of quartz sand and quartz refractory materials by bonding with synthesized Al-Cr phosphate. At the same time, the phosphate bonding of the refractory mixture was performed: chamotte flour + alumina (Al_2O_3). The reason for this is the fact that this refractory oxide, by bonding with phosphates, gives monolites whose initial and final strengths are significantly higher than the strength of the monoliths obtained by bonding the observed refractory materials, quartz sand and chamotte.

2. PREPARATION OF SAMPLES AND TEST RESULTS

The raw materials used in this study are the following: alumina, dominated by the alpha form of Al_2O_3 , grain size 0,0-1,0 mm (producer TG Birač, Zvornik), quartz sand and chamotte, illite-kaolinite clay as a binding agent, and 50 % solution of Al-Cr phosphate ($\gamma = 1.465 \text{ g} / \text{cm}^3$) synthesized in the Laboratory for Analytical Chemistry on the Faculty of Metallurgy and Technology on the University of Zenica.

The quartz sand used in this test is from the Bukinje deposit, Tuzla. The chemical composition of quartz sand produced by XRF analysis is given in Table 1.

| <i>Table 1. Chemical composition of quartz sand from deposit Bukinje, Tuzla (XRF)</i> | | | | | | | |
|---|-------------------|------------------|-----------|--------------------------------|------|------|--|
| Component | loss by annealing | SiO ₂ | Al_2O_3 | Fe ₂ O ₃ | MgO | CaO | |
| Content (%) | 1,00 | 95 | 1,20 | 0,60 | 0,20 | 0,40 | |

Quartz sand is of high purity and consists of more than 95% alpha quartz. Examples are negligible.

The chamotte used in this study was delivered from the Kakanj cement factory, having the chemical composition shown in Table 2.

| Table 21. Chemical composition of chamotie (XKF) | | | | | | | | |
|--|-------------------|------------------|-----------|--------------------------------|------|------|------------------------------------|-----------------|
| Component | Loss of annealing | SiO ₂ | Al_2O_3 | Fe ₂ O ₃ | MgO | CaO | Na ₂ O+K ₂ O | SO ₃ |
| Content (%) | 3,35 | 63,55 | 28,53 | 1,99 | 0,50 | 1,40 | 0,58 | 0,10 |

Table 21. Chemical composition of chamotte (XRF)

Chamotte flour, which is obtained in principle by the heat treatment of clay (hydrated alumosilicates with quartz, feldspat and muscovite), is expected to have a more complex mineral composition. The dominant mineral phases are unalloyed kaolinite, and aluminum oxide (corundum). In a smaller quantity, silimanite ($Al_2O_3 \cdot SiO_2$), mulite ($3Al_2O_3 \cdot 2SiO_2$) and quartz are present, while hematite is registered in traces.

The clay of the Sočkovac deposit, Gračanica, was added to the refractory concrete in a dry state, particle size below 63 µm. Its chemical composition is given in Table 3.

| Table 5. Chemical composition of clay from deposit Sockovac, Gracanica (ARF) | | | | | | | | |
|--|-------------------|------------------|-----------|--------------------------------|------|------|------------------------------------|------------------|
| Component | Loss of annealing | SiO ₂ | Al_2O_3 | Fe ₂ O ₃ | MgO | CaO | Na ₂ O+K ₂ O | MnO ₂ |
| Content (%) | 4,7 | 71,92 | 14,12 | 0,98 | 1,46 | 3,70 | 1,55 | 1,36 |

Table 3. Chemical composition of clay from deposit Sočkovac, Gračanica (XRF)

Based on semi-quantitative X-ray analysis of clay from the Sočkovac deposit, it has an approximate mineral composition shown in Table 4.

 Table 4. Mineral composition of claj from Sočkovac deposit, Gračanica (XRD)

| Sample | α quartz | kaolinite | illite | feldspar i calcite |
|--------|-----------------|-----------|----------|--------------------|
| Clay | 40 % | 25 % | 15 -20 % | 5 - 10 % |

Three masses were prepared with the following compositions, Table 5.

| | 1 1 |
|--------------------------------|--------------------------------|
| 1. Alumina-chamotte mass | Content (mass parts) |
| Alumina | 40 |
| Chamotte flour | 45 |
| Clay | 15 |
| Binder, | 12 parts by weight / 100 parts |
| 50% soluton of Al-Cr phosphate | by weight of the mass |
| 2. Quartz mass | Content (%) |
| Quartz sand | 80 |
| Clay | 20 |
| Binder, | 12 parts by weight / 100 parts |
| 50% soluton of Al-Cr phosphate | by weight of the mass |
| 3. Chamotte mass | Content (%) |
| Chamotte | 80 |
| Clay | 20 |
| Binder, | 12 parts by weight / 100 parts |
| 50% soluton of Al-Cr phosphate | by weight of the mass |

Table 5. Compose samples

Samples were prepared with dimensions: $\emptyset = 30 \text{ mm}$ and h = 40 mm. The samples were dried at room temperature and then thermally treated at 120, 800 and 1000 °C for 5 hours. After that, their compressive strength was determined.

The obtained results are given in Table 6 and graphically presented in Figure 1.

| T 11 (| α · | , ,1 | C 1 |
|-----------|--------------|----------|------------|
| Tahleh | (ompressive | strength | of samples |
| 1 4010 0. | Compressive | Sucusui | of sumpres |

| Mark of samples | Compressive strength (MPa)/ temperatura of annealing | | | | | | |
|-----------------------------------|--|--------|--------|---------|--|--|--|
| | 20 °C | 120 °C | 800 °C | 1000 °C | | | |
| C ₁ , alumina-chamotte | 18 | 31 | 68 | 102 | | | |
| mass | | | | | | | |
| C ₂ , quartz mass | 6 | 17 | 20 | 23 | | | |
| C ₃ , chamotte mass | 5,5 | 18 | 26 | 24 | | | |



Figure 1. Dependency of the compressive strength and temperature of the samples binding with a 50% solution of Al Cr phosphate

From Figure 1 it can be seen that the samples of the C1 mark (alumina-chamotte mass) at room temperature have a compressive strength of 20 MPa, while the same samples, after 1000 $^{\circ}$ C, have a strength of 102 MPa. Samples with quartz sand and chamotte have lower compressive strength at 20 $^{\circ}$ C, and after annealing at 1000 $^{\circ}$ C their strength are about 24 MPa. Compressive strength values of

samples with quartz sand and chamotte bounded with AlCr phosphate are higher than the compressive strength values of the same samples bounded with MAP or phosphoric acid.

3. CONCLUSION

In this paper, the studies are focused on the use of synthesized Al Cr phosphate as a binder of quartz and chamotte refractory mass. The results obtained show the following:

- 1. Samples with an alumina-chamotte mass have a compressive strength of 20 MPa at room temperature, while the same samples after the annealing at 1000 ° C achieve a strength of 102 MPa. Samples with quartz sand and chamotte have lower compressive strength at 20 ° C, and after annealing at 1000 ° C their strength are about 24 MPa. Compressive strength values of samples with quartz sand and chamotte bounded with AlCr phosphate are higher than the compressive strength values of the same samples bounded with MAP or phosphoric acid which are previously tested.
- 2. Al Cr Phosphate is a much more efficient binder than phosphoric acid and MAP.
- 3. However, the question remains whether to use phosphate-bonded refractory materials to use a more efficient, but also considerably more expensive solution of Al-Cr phosphate, or less effective but cheaper solutions of MAP and phosphoric acid? It is necessary to agree with the conclusions offered by the literature data. Al-Cr phosphate, since it is a more expensive binder relative to MAP or phosphoric acid, is recommended for the preparation of special refractory materials based on valuable high-refractory materials: corundum, mulite, carbon dioxide or graphite, which are installed in particularly sensitive positions of thermal aggregate. Ordinary quartz and chamotte refractory materials can be bonded with phosphoric acid or MAP, as significantly cheaper binders, since they also achieve satisfactory initial and final strengths, ie the prescribed quality of the prepared refractory materials.

4. LITERATURE

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