Influence of type and quantity of magnesium additive on the hardening process of alumina cement-based cement stone

N Chumachenko and V Tyurnikov
Samara State Technical University, Molodogvardeyskaya st., 244, Samara, Russia, 443100
E-mail address: uvarovang@mail.ru

Abstract. The greatest effect on increasing the residual strength of cement stone based on alumina cements in the temperature range of 800-1200 °C is achieved when replacing part of the cement with thermally activated metakaolin which is associated with the formation of secondary mullite. To intensify the strengthening process of mullite formation, the influence of various magnesium additives-mineralizers has been studied. The effect of chemically pure magnesium oxide, caustic magnesite and magnesium oxide hydration product calcined at 390 - 450 °C were investigated experimentally. The content of additives in compositions based on high-purity high-alumina cement was accepted in the amount of 0.5, 1 and 1.5 %. Experiments have confirmed the positive effect of magnesium additives on the process of hardening of cement stone, both during hardening and after heat treatment. It was found that the type of magnesium additive affects the hardening process. The highest strength after hardening and drying is obtained by using caustic magnesite as a mineralizer additive in an amount of 0.5 %. Exposed to high temperature, the best results are recorded when using a chemically pure magnesium additive.

1. Introduction
Alumina and especially high-alumina cements have high heat-resistant properties. Alumina cement in comparison with Portland cement and aluminium phosphate binders has a higher fire and heat resistance. These properties determine the widespread use of this binder in the composition of heat-resistant concrete [1-3]. However, there are no ideal materials and these binders have one significant drawback - the cement stone based on them during the operation in the temperature range of 800-1200 °C significantly reduces its strength which is associated with the processes of destruction. Thus, according to [4], the residual compressive strength of samples made of high alumina cement after heating: up to 800 °C is 67.6 %; up to 1000 °C – 60.6 %; up to 1200 °C – 48.9 % of the strength of samples before heat treatment. According to [5], the residual strength after heating to 1200 °C is even lower – 14 MPa, which is 22% of the original. This process can be stabilized by introducing additives that allow the destruction products to be bound into a mullite that acts as a reinforcing frame. Cement stone mullitization which strengthens it is observed when an additive of refractory kaolinite clay is introduced into high-alumina cement [5]. In this case, mullite is formed from the clay itself, the so-called primary mullite and due to the interaction of the products of destruction of cement stone from high alumina cement and clay, the so-called secondary mullite.

The strength of cement stone at high temperatures depends on the type of mullite formed (primary or secondary) and its quantity. The process of formation of primary mullite from refractory kaolinite
clay occurs in the temperature range of 600-1100 °C [6]. Percentage of residual strength of cement stone from a combined binder high alumina cement + clay at temperatures above 1050 °C will, be directly proportional to the amount of clay in the binder up to a certain limit.

The greatest effect of hardening is achieved due to the formation of secondary mullite but its quantity is limited since secondary mullitization does not occur completely, as evidenced by the presence of free silica in the form of cristobalite [5].

The type of additive capable of interacting with degradation products with a hardening effect was theoretically justified and then experimentally confirmed. The best results were obtained when replacing part of the alumina cement with metakaolin which has a chemical activity. The effect of the greatest increase in strength was achieved by pre-thermal activation of metakaoline at 520-540 °C. This additive is recommended for all types of alumina cement although its effect is not the same [7, 8].

Further intensification of the strengthening process of mullite formation is the introduction of additives-mineralizers into the heat-resistant composition, along with metakaolin.

It was found that the process of mullite formation in kaolinite clays under the influence of mineralizing oxides decreases in the following series: MgO > ZnO > Fe₂O₃ > CaO > K₂O > TiO₂ [9]. It can be assumed that MgO is the optimal additive for mullite formation. However, the type of magnesium additive can be different and, accordingly, its activity will be different.

2. Methods and materials
In order to study the effect of the type and quantity of magnesium additive on the mullite formation process, experiments were carried out with the following components: chemically pure (c.p.) magnesium oxide, caustic magnesite and hydration product of magnesium oxide, calcined at 390-450 °C.

Lying high-purity high alumina cement (Highly pure high alumina cement) was used as alumina cement. Initially, its activity was 74 MPa, while at the time of the experiment it was 39 MPa. The composition includes metakaolin in the optimal ratio: 85 % Highly pure alumina cement + 15 % metakaolin [8].

The following series of samples of the corresponding compositions were formed:
- 1 series - compositions 1, 2, 3 with the addition of chemically pure magnesium oxide in the amount of 0.5; 1; 1.5 %, respectively;
- 2 series - compositions 4, 5, 6 with the addition of caustic magnesite in the amount of 0,5; 1; 1.5 %, respectively;
- 3 series - compositions 7, 8, 9 with the addition of magnesium oxide hydration product, calcined at 390 - 450 °C in the amount of 0.5; 1; 1.5 %, respectively;
- 4 series - compositions 10, 11, 12 with the addition of chemically pure magnesium oxide in an amount of 0.5; 1; 1.5 %, respectively (compositions of 4 series differ in that their heat treatment has a certain feature: when reaching 390 - 450 °C samples were kept at this temperature for 1 hour to dehydrate Mg(OH)₂, assuming that the most active phase of MgO is formed immediately after dehydration [10], and then burned according to a given scheme).

The amount of water was selected experimentally under the condition of obtaining mixtures with normal density. The obtained mixture was used for making by vibrating samples, which after hardening, drying and appropriate heat treatment at 1000 and 1200 °C were tested for strength. The samples density was also determined.

3. Results and discussions
Figure 1 and figure 2 show the kinetics of changes in strength and density of samples depending on the heat treatment temperature.

The strength data of the investigated compositions with different content of additives after drying at 110 °C shows that introduction of 0.5 - 1.5 % of caustic magnesite additive leads to strength increase 1.5 - 2 times in comparison with pure high alumina cement. In the temperature range of 110 - 1000 °C
a different degree of intensity decrease in strength is observed. At 1000-1200 °C an increase in strength is observed, especially at compositions with chemically pure magnesium additive.

Experiments have confirmed the positive effect of magnesium additive on cement stone hardening process both during hardening and after heat treatment; they have allowed choosing the most optimal type and quantity of additive for different conditions of cement stone application.

The highest strength after hardening and drying was obtained using caustic magnesite as an additive-mineralizer in the amount of 0.5%.

When exposed to high temperature, the best results are recorded when using a chemically pure magnesium additive.

![Figure 1](image_url)

**Figure 1** Dependence of the compressive strength of a composite heat-resistant binder (highly pure alumina cement + metakaolin) with magnesium additives-mineralizers on the temperature of heat treatment:

1, 2, 3 - addition of chemically pure magnesium oxide in the amount of 0.5; 1; 1.5 %;

4, 5, 6 - addition of caustic magnesite in the amount of 0.5; 1; 1.5 %;

7, 8, 9 - addition of the product of hydration of magnesium oxide at a temperature of 390-450 °C in the amount of 0.5; 1; 1.5 %;

10, 11, 12 - addition of chemically pure magnesium oxide, with exposure during heat treatment at a temperature of 390-450 °C for 1 hour, in an amount of 0.5; 1; 1.5 %.
**Figure 2** Dependence of the density of a composite heat-resistant binder (highly pure alumina cement + metakaolin) with magnesium additives - mineralizers on the temperature of heat treatment

1, 2, 3 - addition of chemically pure magnesium oxide in the amount of 0.5; 1; 1.5 %;
4, 5, 6 - addition of caustic magnesite in the amount of 0.5; 1; 1.5 %;
7, 8, 9 - addition of the product of hydration of magnesium oxide at a temperature of 390-450 °C in the amount of 0.5; 1; 1.5 %;
10, 11, 12 - an additive of chemically pure magnesium oxide, with exposure during heat treatment at a temperature of 390-450 °C for 1 hour, in an amount of 0.5; 1; 1.5 %.
4. Conclusions
Conducted experiments:
- confirmed the positive effect of magnesium additives on the process of hardening of cement stone, both during hardening and after heat treatment;
- confirmed the influence of the type of magnesium additive on the studied process;
- allowed to choose the most optimal type for different conditions of application of cement stone;
- allowed to determine the optimal amount of additives;
- the effect of almost complete return of the original activity when using “stale” cement was obtained.
The introduction of the developed compositions will significantly increase the strength of structures during operation. In conditions where such strength is not required it will lead to significant savings in expensive and scarce alumina cements.

References
[1] Standard GOST 969-2019 Alumina and high alumina cements. Technical specifications
[2] Kuznetsova T V and Talaber I 1988 Alumina Cement (Moscow: Stroyizdat) p 272
[3] Kuznetsova T V 1986 Aluminate and sulfoaluminate cements (Moscow: Stroyizdat) pp 38-40
[4] Pushkaryova E K, Glukhovsky V D, Krivenko P V and Chirkova VV 1983 Fireproof binder Patent № 998410 № 7 p 149
[5] Blizgareva T I 1992 Heat-resistant fine-grained concrete on high-alumina cement with addition of refractory clay (Dissertation Thesis Moscow)
[6] Strelov K K 1985 Theoretical bases of refractory materials technology (Moscow: Metallurgy) p 480
[7] Chumachenko N G and Tyurnikov V V 2019 Dynamics of destructive processes of cement stone on the basis of alumina cements at heat treatment Refractories and technical ceramics 1-2 pp 18-22
[8] Chumachenko N G and Tyurnikov V V Fireproof binder Patent (RF) № 2138456, MKI C 04 B 7/32 № 98100467/03
[9] Budnikov P P and Ginstling A M 1965 Reactions in mixtures of solid substances (Moscow: Stroyizdat) p 474
[10] Balkevich V L 1984 Technical ceramics (Moscow: Stroyizdat) p 138