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EVALUATION OF THE PERFORMANCE OF ADVANCED REFRACTORY MATERIALS INTENDED FOR THE ROOF OF AN ELECTRIC FURNACE FOR HIGH-LEVEL WASTE VITRIFICATION

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This paper presents the results of the studies of refractory materials produced by the company Keralit, the Borovichi Refractories Plant, and Scientific and Technical Center Bakor (STC Bakor) and intended for the roof of an EP-6 electric furnace for high-level waste vitrification. These studies determined the strength properties and acid resistance of these materials when exposed to nitric-acid in vapor and solution forms. The results of the studies show that the optimum materials for constructing the melter roof are MKRTU-50 and MKV-65 produced by the Borovichi Refractories Plant and STC Bakor, respectively.

Keywords: vitrification furnace, high-level waste, acid resistance, refractory material, melter roof, compression ultimate strength, ultimate bending strength, weight loss.

INTRODUCTION

Vitrification is the main technology for solidifying generated liquid high-level waste (HLW) and has gained worldwide recognition. At Mayak Production Association, in the mid-1980s, an HLW vitrification shop was put into operation, marking a new era in waste management technology at the enterprise. Immobilization of liquid HLW into a stable matrix material occurs in nonevacuable EP-500 direct electric heating melters. In the past, at the enterprise, five similar electric furnaces have completed their design period and have been decommissioned. Currently, Mayak PA continues to develop a new EP-6 direct electric heating furnace. Experience from operating previous furnaces showed the need to develop a new roof design that remained stable throughout the service life of the new melter. The main roof design option being considered is a prefabricated structure of several slabs made as rectangular metal welded boxes with a lining made of refractory blocks inside, which are not rigidly connected with the metal structures. This design ensures the integrity of the blocks when the geometric dimensions of the metal and refractory materials change during heating/cooling (due to the difference in the thermal coefficients of linear expansion). The development of the roof of the new EP-6 electric furnace at the initial stage (since March 2020) was performed in close cooperation with DINUR specialists. According to the results of tests performed in 2020 – 2021, the fireproof MKRBS-53 brand material of DINUR was chosen to manufacture EP-6 roof blocks [1].

Since December 2021, because of the difficulty of providing raw materials, the DINUR enterprise has suspended the production of these products for an indefinite period. In this regard, there was a need to search for new refractory materials for the EP-6 roof that not only had high-quality indicators but could also be supplied by the manufacturer, considering the current economic situation. After a preliminary market analysis, CERALIT CAST AL58007 by Keralit, MKRTU-50 by the Borovichi Refractories Plant, and MKV-65 by STC Bakor were selected for further testing (Table 1).

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TABLE 1. Refractory Materials for Testing

Manufacturer	Material brand	Material	Chemical composition, wt.%	Ultimate compressive strength	MPa	Open porosity, %
Keralit	CERALIT CAST AL58007	Low-cement vibrocast concrete with hydraulic bonding	Al_2O_3 no less than 57.0, Fe_2O_3 no more than 0.8	No less than 50	No more than 17	No less than 2.4
Borovichi Refractories Plant	MKRTU-50	Compacted mullite– siliceous products from thixotropic masses	Al_2O_3 no less than 50.0, Fe_2O_3 no more than 1.5	No less than 65	No more than 19	No data
STC Bakor	MKV-65	Cementless mullite– siliceous concrete material	Al_2O_3 no less than 65.0, Fe_2O_3 no more than 2.0	No less than 50	No more than 22	No more than 2.6

TABLE 2. Results of the Strength Tests of Refractory Materials

Material brand	Weight loss, %	Water absorption, %	Sample ultimate compressive strength σ, MPa		Δσ*, %	Ultimate bending strength (MPa)
			Initial	After exposure to acid vapor		
CERALIT CAST AL58007	4.1	5.6	34.0	27.8	18	7.6
MKRTU-50	1.9	7.2	48.5	37.9	22	12.1
MKV-65	0.2	7.3	47.1	42.3	10	10.4

* Δσ — reduction in the strength of the refractory material after contact with acid and its vapors relative to the original material strength.

The reliability of refractory material for manufacturing a furnace roof is determined by its strength characteristics after exposure to a nitric-acid solution and its vapors because during normal technological operation of an EP-500 type electric furnace, the vapors of nitric-acid and the gas phase condense near refrigerators, water-cooled devices, and walls. Consequently, the refractory materials of the furnace roof are exposed to a nitric-acid solution and its vapors, reducing their mechanical strength.

For all tested materials, a set of tests was performed on compressive and bending strength and acid resistance. To compare the test results of the selected materials with those of the previously selected MKRBS-53 material, the tests were performed on the same equipment using similar methods [1, 2].

To test materials for acid resistance in nitric-acid vapors, cubic samples with an edge of 25 mm were used. These samples were continuously kept in vapors of a solution for 100 h to simulate a humid environment (mass fraction in solution, g/l: HNO_3 250, Cl^- 1, PO_4^{3-} 1). The test solution with a volume of 5–10 cm^3 per 1 cm^2 of sample surface was poured into a flask with a reflux condenser. The samples were suspended in flasks at a height of at least 20 mm above the solution surface using fluoroplast threads (one sample per flask). The junction of the reflux condenser and the flask was sealed with a heat- and acid-resistant silicone-based sealant. Flasks with reflux condensers were placed on an electric heater.

After completing exposure, the samples were removed from the flasks, weighed in a wet state, and dried in a drying cabinet at 120°C until constant weight. The total drying time was approximately 8 h. The samples dried after exposure to acid vapor, in parallel with samples not exposed to acid vapor, were tested on a RIEHLE hydraulic press in a range of applied loads of up to 100 kN to determine their ultimate compression strength. Using the same press, the ultimate bending strength was determined on bar samples with dimensions of 120 × 30 × 30 mm. In all tests, five parallel measurements were performed. Table 2 presents the average values of the results obtained.

Thus, it was determined that all three tested refractory materials have sufficiently high acid resistance (the strength of materials after exposure to nitric-acid vapors decreased by no more than 22% relative to the initial material strength). STC Bakor has the best strength characteristics. Its initial compression strength was 47.1 MPa, and after exposure to nitric-acid vapors, it decreased by only 10% (to 42.3 MPa). The initial compression strength of the refractory material tested by Keralit was 34.0 MPa, and after exposure to nitric-acid vapors, it decreased by 18% (to 27.8 MPa). Notably, the ultimate compression strength of the refractory material MKRBS-53, selected based on the results of tests in 2020, decreased by 19% after exposure to nitric-acid vapors (from 59.7 to 48.2 MPa with test specimen sizes of 35 × 35 × 35 mm), and its ultimate bending strength was 9.6 MPa. That is, relative to the previously selected material MKRBS-53, the ultimate bending strength of MKRTU-50 and MKV-65 is higher, and that of CERALIT CAST AL58007 is lower.

Long-term tests of refractory materials in a nitric-acid solution were also performed according to a scheme similar to that used in previous years [1, 2]. The studied cubic refractory samples with an edge length of 35 mm were placed in glasses, which were then filled with a nitric-acid solution in the ratio S:L = 1:5, and the samples held for 1, 2, and 3 months. A nitric-acid solution of the same composition as that used for testing refractories in nitric-acid vapor was used. This solution was replaced with a new one twice a month. Next, the weight loss and moisture absorption of the samples, as well as the ultimate compression strength, were determined by considering the direction of pouring the mixture when forming refractory blocks at the manufacturing plant in accordance with cl. 6.4 and cl. 6.5 of GOST 4071.1–2021. Three parallel measurements were performed. The research results are presented in Table 3 (average values).

The average weight loss of CERALIT CAST AL58007 samples increased from 3.9% to 7.1% with increasing exposure time in a nitric-acid solution. The weight loss of MKRTU-50 samples was insignificant (1.3%), and the weight loss of MKV-65 products in nitric-acid solution was not registered. The moisture absorption of all products was approximately the same (CERALIT CAST AL58007 (7.8 ± 0.7)%, MKRTU-50 (7.3 ± 0.3)%, and MKV-65 (7.2 ± 0.2)%).

During testing, deterioration in the strength characteristics of CERALIT CAST AL58007 was noted after contact with a nitric-acid solution. Its ultimate compressive strength decreased by 42% relative to the strength of the original material after 2 weeks of keeping the samples in a nitric-acid solution. After 2 months of contact with an acidic environment, the decrease reached 58%, and the average value of the ultimate compressive strength was only 17.6 MPa. The average values of the ultimate compressive strength of the MKRTU-50 and MKV-65 samples after 2 months of exposure in a nitric-acid solution were 53.9 MPa and 37.1 MPa, respectively. Note that all tested materials have strength indicators lower than those stated by the manufacturers. These discrepancies were possibly due to the different sizes of the tested samples. The edge length of the samples tested by the manufacturer was 100 mm, while at Mayak PA, cubes with edges of 35 mm and 25 mm were tested. From a formal perspective, the tested cubic samples with dimensions of 25 × 25 × 25 and 35 × 35 × 35 mm meet the requirements of GOST 4071.1–2021.

An analysis of Table 3 data reveals that for MKRTU-50 and MKV-65 samples, no patterns of changes in strength characteristics are observed with increasing exposure time in a nitric-acid solution. This result may be due to defect formation during the manufacture of samples, the heterogeneity of the material (the influence of filler grains), noncompliance in the plane parallelism of the faces, and the occurrence of internal defects when cutting samples.

TABLE 3. Results of the Long-Term Tests of Refractory Materials

Duration of contact with the nitric-acid solution	Weight loss, %	Moisture absorption, %	Ultimate compressive strength σ*, MPa	Δσ, %
CERALIT CAST AL58007				
2 weeks	3.9	6.9	24.3	42
1 month	5.8	7.7	18.6	55
2 months	7.1	8.5	17.6	58
MKRTU-50				
2 weeks	1.3	7.0	50.3	18
1 month	1.3	7.2	40.7	34
2 months	1.3	7.7	53.9	13
MKV-65				
2 weeks	0.03	6.9	50.1	–9
1 month	0.06	7.1	52.9	–15
2 months	0.09	7.4	37.1	19

* The initial ultimate compressive strengths of CERALIT CAST AL58007, MKRTU-50, and MKV-65 samples are 41.6, 61.6, and 45.9 MPa, respectively.

TABLE 4. Comparison of the Ultimate Compressive Strength of Materials of the MKRTU-50 and MKV-65 Grades with the Previously Selected MKRBS-53 Material

Refractory material grade	Sample ultimate compressive strength, MPa		Δσ, %
	Original	After 2 months of exposure to nitric-acid solution	
CERALIT CAST AL58007	41.6	17.6	58
MKRTU-50	61.6	53.9	13
MKV-65	45.9	37.1	19
MKRBS-53	59.5	31.0	48

The comparative characteristics of the tested materials and the material MKRBS-53, selected based on the results of tests in 2020, are presented in Table 4.

In terms of residual strength and resistance to acid, MKRTU-50 and MKV-65 materials are superior to the previously selected MKRBS-53. Therefore, MKRTU-50 and MKV-65 can be used to manufacture the EP-6 electric furnace roof.

CONCLUSION

The refractory materials CERALIT CAST AL58007 made by Keralit, MKRTU-50 by the Borovichi Refractories Plant, and MKV-65 by STC Bakor were studied for the development and manufacture of the roof of a new

EP-6 melter. The strength characteristics (ultimate compressive and bending strength) and acid resistance in vapors of a nitric-acid solution and during prolonged contact with a nitric-acid solution were determined. The tested materials were compared with each other and with the previously selected material MKRBS-53 by DINUR.

All three new tested refractory materials have sufficiently high resistance to the effects of nitric-acid vapors (the strength of materials after exposure to nitric-acid vapors decreased by no more than 22% relative to the original material). MKV-65 has the best strength characteristics (the initial ultimate compressive strength is 47.1 MPa, and after testing, it decreases by 10% to 42.3 MPa). The initial ultimate compressive strength of CERALIT CAST AL58007 is 34.0 MPa, and after exposure to nitric-acid vapor, it decreases by 18% to 27.8 MPa.

According to the results of prolonged contact with a nitric-acid solution, the CERALIT CAST AL58007 grade material has the lowest strength characteristics. After 2 months of aging in a nitric-acid solution, its ultimate compressive strength decreased by 58% relative to the original material strength. The MKRTU-50 and MKV-65 grades have satisfactory strength characteristics. With prolonged exposure to a nitric-acid solution (2 months), MKRTU-50 weight loss was 1.3%, whereas MKV-65 had no weight loss. The ultimate compressive strength of MKRTU-50 after 2 months of contact with an acidic environment decreased from 61.6 MPa to 53.9 MPa (i.e., by 13%), and that of MKV-65 decreased from 45.9 MPa to 37.1 MPa (by 19%). Both new materials have superior strength characteristics to the previously selected MKRBS-53 material.

Considering the results obtained, it was established that the optimal materials from all those presented are MKRTU-50 of the Borovichi Refractories Plant and MKV-65 of the Scientific and Technical Center Bakor (STC Bakor). These materials can be used to manufacture the roof of the EP-6 electric furnace.

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REFERENCES

1. P. V. Kozlov, M. B. Remizov, E. V. Polyakov, et al., "Promising refractory materials of "DINUR" for the roofs of electric furnaces of HLW vitrification," *Nov. Ogneup.*, No. 7, 20 – 25 (2022).
2. I. D. Kashcheev, K. G. Zemlyanoy, P. V. Kozlov, et al., "Physico-mechanical characteristics of refractories for the vitrification furnace of liquid high-level waste," *Nov. Ogneup.*, No. 3, 64 – 69 (2023).