THE COMPOSITION OF THE MAGNESIA BATCH AS A FACTOR IN THE STRENGTH OF PHOSPHATE-BONDED GUNITE

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UDC 666.762.3.044.28:620.173.24

It was shown elsewhere [1-3] that magnesia gunites containing added sodium polyphosphate is characterized by adequate strength properties provided the mean degree of polyphosphate polymerization ($\bar{n}$) lies within 21-24. In an investigation of production technologies for unfired refractories, experiments were carried out to determine the relation between the strength of magnesite mixes bonded with sodium polyphosphates and the composition of the starting material [4-5]. According to Di Bello and Pradel [4], the strength of the test specimens in the temperature range 1000-1250°C increases with an increase in the calcium oxide content of the batch from 2.1 to 12 wt. % and a decrease in the magnesia content from 95 to 80 wt. %. Foessel and Treffner [5] relate the variation in the strength to that of the ratio $CaO/(P_2O_5 + SiO_2)$ in the starting material. For maximum bending strength at 1460°C the recommended ratio is 0.98, 1.14, and 1.22 for an MgO content in the batch of 90, 70 and 60 wt. % respectively.

Published data furnish evidence that the strength and therefore the service behavior of phosphate-bonded magnesia gunites depend on the composition of the starting material.

The calcium oxide content of a phosphate-bonded gunite can be increased by adding a suitable calcium-containing component or by producing the gunite from unconditioned dolomitized magnesites. The latter method is very important because it helps to reserve pure high-quality magnesites for the production of special-purpose refractory products.

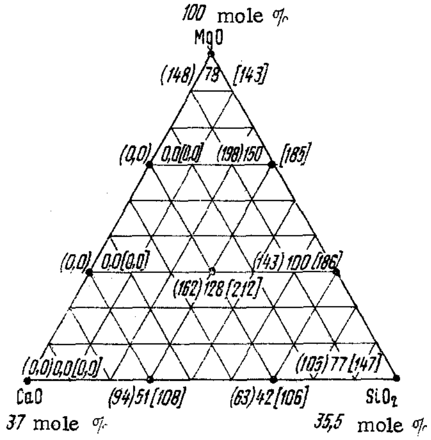
The use of a low-grade unconditioned material for gunite can be justified on the grounds that a layer of gunite applied on the lining of an industrial furnace in the course of the metallurgical process has a limited life of a few melts after which the guniting operation is repeated.

TABLE 1. The Planning Matrix and the Arithmetic Mean Values of the Cold-Crushing Strength of the Batches after Firing at 800°C

Test No.	Comp. of batches in coded form			Comp. of batches in natural form			Cold-crushing strength ($\bar{y}$), kg/cm²
	x_1	x_2	x_3	MgO	CaO	SiO_2	
1	1	0	0	100 (100)	—	—	78 (y_1)
2	0	1	0	55 (63,0)	45 (37,0)	—	0 (y_2)
3	0	0	1	55 (64,5)	—	45 (35,5)	77 (y_3)
4	$^2/_3$	$^1/_3$	0	85 (88,7)	15 (11,3)	—	0 (y_{112})
5	$^1/_3$	$^2/_3$	0	70 (76,5)	30 (23,5)	—	0 (y_{122})
6	$^2/_3$	0	$^1/_3$	85 (89,5)	—	15 (10,5)	150 (y_{113})
7	$^1/_3$	0	$^2/_3$	70 (77,7)	—	30 (22,3)	100 (y_{133})
8	0	$^2/_3$	$^1/_3$	55 (63,6)	30 (24,8)	15 (11,6)	51 (y_{223})
9	0	$^1/_3$	$^2/_3$	55 (64,1)	15 (12,5)	30 (23,4)	42 (y_{223})
10	$^1/_3$	$^1/_3$	$^1/_3$	70 (77,0)	15 (11,9)	15 (11,1)	128 (y_{123})

*Mole % in parentheses.

Ukrainian Scientific-Research Institute for Refractories. Translated from Ogneupory, No. 11, pp. 43-48, November, 1975.



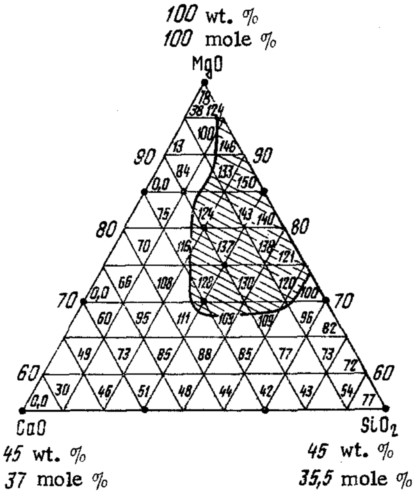


Fig. 1.

Fig. 2.

Fig. 1. Simplex grid for cubic approximation. The points of the simplex show the mean ultimate cold-crushing strength (kg/cm^2) of the experimental batches after firing at 600°C (in parentheses), 800°C (open), and 1200°C (in brackets).

Fig. 2. The theoretical cold-crushing strength after firing at 800°C as a function of the batch composition.

In this article the results are reported of an investigation of the feasibility of producing phosphate-bonded gunite from magnesia compositions containing calcium oxides and silica in amounts exceeding those in the technical specifications for the magnesia starting material for the production of refractories.

The investigation was carried out within the limits of the triangle of the ternary $CaO-MgO-SiO_2$ system starting with a composition containing 100 mole % MgO and finishing with a mix containing 37 mole % CaO and 35.5 mole % SiO_2. The experimental compositions were prepared from chemically pure magnesia and silicic acid, and pure calcium carbonate in accordance with selected points on the phase diagram of the $CaO-MgO-SiO_2$ system. After thorough mixing in a ball mill the compositions were molded into briquets at a pressure of 500 kg/cm^2 which were fired in an open-flame kiln at 1750°C with a holding time of 6 h.

The fired briquets were crushed in jaw crushers and then ground in a vibro-mill to powder finer than 0.09 mm after which 5 wt. % dry sodium polyphosphate of particles finer than 0.088 mm with a degree of polymerization of 22, i.e., $(NaPO_3)_{22}$ was added to the powder. The mixture was wetted to a moisture content of 10% after which cubic specimens with sides of 20 mm were molded from compositions on a laboratory press. The molding effort of the press was 2.4 kg · m. The pre-firing density of the specimens varied 2.0-2.4 g/cm^3 depending on the composition of the batch. The specimens were fired at various temperatures, the rate of increase in the temperature was 6-7 degC/min, and the holding time at the firing temperature 2 h. After the firing operation the cold-crushing strength of the specimens was determined when it was found that the strength was minimum in the case of specimens fired at 800°C — which agrees with earlier data [1, 2].

It was found necessary to establish, within the selected section of the ternary $CaO-MgO-SiO_2$ system, the range of compositions which would give maximum cold-crushing strength after firing at 800°C. To this end use was made of the Simplex method of experiment design [6]. The feasibility of using this method for plotting the relation between the properties and the composition in multiphase systems on relatively smooth sections of the phase diagram was demonstrated elsewhere [7; 8, pp. 68-70]. Klimenko et al. suggest the Simplex method of experiment design for an investigation of the strength of Sitall as a function of the chemical composition [9, p. 40].

In the present case, the arguments in the general function of the cold-crushing strength are, in addition to the chemical composition, the stabilizing parameters like the fineness of the grind, the moisture content of the mix, the molding pressure, and the firing temperature and time. Since in the matrix of the experiment design according to the Simplex method it is only the values in the chemical composition that

TABLE 2. The Standard Deviation of the Reproducibility at the Points of the Simplex

Test No.	Results of parallel meas., kg/cm^2	SD σ_i^2 of reproducibility of parallel meas.
1	76; 78; 80	4
2	0	0
3	80; 76; 75	7
4	0	0
5	0	0
6	147; 153; 150	9
7	97; 102; 101	7
8	50; 50; 53	3
9	41; 41; 44	3
10	126; 130; 128	4

vary, the resulting equation will represent a cross section of the general plane of response for the stabilized values of the parameters not contained in the matrix.

It was decided to use the cubic degree of approximation. The Simplex grid for a cubic degree of approximation is shown in Fig. 1. The matrix and the mean arithmetic values of the cold-crushing strength after firing at 800°C are given in Table 1.*

The strength of the batches containing CaO and no SiO_2 was zero, probably as a result of a high degree of hydration of the calcium oxide. The cold-crushing strength of specimens produced from a batch without phosphate binder was 3-15 kg/cm^2 after firing at 800°C.

Three experiments were set up for each point of the Simplex. The standard deviation of the reproducibility was calculated from the equation

$$\sigma_i^2 = \frac{\sum_{u=1}^{n} (y_{iu} - \bar{y}_i)^2}{n-1}, \tag{1}$$

where σ_i^2 is the standard deviation; $\bar{y}_i$ is the arithmetic mean of parallel measurements, kg/cm^2; y_{iu} is the result of each measurement, kg/cm^2; n is the number of measurements.

The results of the calculation are given in Table 2.

The variance of the standard deviation of the results of the experiment was determined by comparing the theoretical Cochran criterion G_p with the tabulated value G_t with the degrees of freedom $f_1 = n - 1$ and $f_2 = N$ [10, p. 182]. The theoretical Cochran criterion was determined from the equation

$$G_p = \frac{\sigma_{i\,max}^2}{\sum_{1}^{N} \sigma_i^2}, \tag{2}$$

where $\sigma_{i\,max}^2$ is the peak standard deviation of the reproducibility; N is the number of points in the Simplex.

When G_p is less than G_t, the results of the experiments can be combined into a single aggregate described by an equation of regression. For the results of the experiment reported here, $G_p = 0.243 < G_t = 0.445$ for $f_1 = 2$ and $f_2 = 10$.

In its general form the equation of regression for cubic approximation is written as follows:

$$y = \sum_{1\leqslant i\leqslant q} \beta_i x_i + \sum_{1\leqslant i<j\leqslant q} \beta_{ij} x_i x_j + \sum_{1\leqslant i<j\leqslant q} \gamma_{ij} x_i x_j (x_i - x_j) + \sum_{1\leqslant i<j<k\leqslant q} \beta_{ijk} x_i x_j x_k. \tag{3}$$

The coefficients of the equation are calculated from the results of the tests:

$$b_i = y_i, \quad b_j = y_j, \quad b_k = y_k.$$

*Table 1 gives the composition of the batches in natural terms in wt. % and in mole % in parentheses for the relevant section of the ternary $CaO-MgO-SiO_2$ system. The quantities correspond to the coded values in the planning matrix.

TABLE 3. The Experimental and Theoretical Cold-Crushing Strength at the Control Points

Control point	Coded batch comp. at control point			Results of parallel meas., kg/cm²	Arith. mean of parallel meas., kg/cm²	Theor. cold-crushing strength, kg/cm²
	x_1	x_2	x_3			
a	$^6/_9$	$^2/_9$	$^1/_9$	78; 80: 87	81,6	84,37
b	$^5/_9$	$^2/_9$	$^2/_9$	117; 122; 127	122,0	123,88
c	$^4/_9$	$^2/_9$	$^3/_9$	139; 141,3; 132	137,1	137,57

The equations of the effects of the interaction are as follows:

$$\begin{aligned}
\beta_{12} &= {}^9/_4\,(y_{112} + y_{122} - y_1 - y_2),\\
\beta_{13} &= {}^9/_4\,(y_{113} + y_{133} - y_1 - y_3),\\
\beta_{23} &= {}^9/_4\,(y_{223} + y_{233} - y_2 - y_3),\\
\gamma_{12} &= \frac{9}{4}\,(3y_{112} - 3y_{122} - y_1 + y_2),\\
\gamma_{13} &= \frac{9}{4}\,(3y_{113} - 3y_{133} - y_1 + y_3),\\
\gamma_{23} &= \frac{9}{4}\,(3y_{223} - 3y_{233} - y_2 + y_3),\\
\beta_{123} &= 27y_{123} - \frac{27}{4}\,(y_{112} + y_{122} + y_{113} + \\
&\quad + y_{133} + y_{223} + y_{233}) + \\
&\quad + \frac{9}{2}\,(y_1 + y_2 + y_3).
\end{aligned} \tag{4}$$

The results of the calculation of the coefficients were used to determine the model of the cubic degree of approximation:

$$\begin{aligned}
y &= 78x_1 + 77x_3 - 175.5x_1x_2 + 213.75x_1x_3 + 36x_2x_3 - 175.5x_1x_2 \times \\
&\times (x_1 - x_2) + 335.2x_1x_3(x_1 - x_3) + 234x_2x_3(x_2 - x_3) + 1838.25x_1x_2x_3.
\end{aligned} \tag{5}$$

The adequacy of the equation of regression was checked with Student's t-criterion calculated for the results of additional experiments at control points *a*, b, and c which were expressed as compositions in natural terms (content of MgO, CaO, and SiO_2) in mole %:

a — (89.0, 7.5, 3.5); b — (85.2, 7.7, 7.1), c — (81.1, 7.9, 11.0).

The experimental and theoretical values of the cold-crushing strength at the control points are given in Table 3.

Students's t-criterion was calculated from the equation

$$t_{\alpha/t;\, f} = \frac{\Delta y \sqrt{n}}{\sigma_{\{y^0\}} \sqrt{1+\xi}}, \tag{6}$$

where Δy is the difference between the theoretical and experimental mean cold-crushing strength, kg/cm²; and $\sigma_{\{y^0\}}$ is the standard deviation of the test, kg/cm²;

$$\sigma^2_{\{y^0\}} = \frac{\sum_{i=1}^{N} \sigma_i^2}{N}; \tag{7}$$

ξ is a quantity which depends on the position of the point in the triangle of compositions:

$$\xi = \Sigma a_i^2 + \sum_{\substack{k=i\\ k=j}} a_{ijk}^2 + b_{ijk}^2, \tag{8}$$

where

$$a_i = x_i - \frac{9}{2}\,x_i^2\,(1 - x_i),$$

$$a_{ijk} = \frac{9}{2}\,x_i x_j\,(3x_i - 1),$$

$$b_{ijk} = 27x_i x_j x_k.$$

The theoretical values of ξ for points a, b, and c are 0.863, 0.922, and 0.900, and the t-criteria for these points 1.82, 1.21, and 0.31. The tabulated value of the t-criterion for a 5% level of significance (α) referred to the number of control points (l), is $t_{0.016;20} = 2.6$ for 20 degrees of freedom, i.e., considerably greater. It follows that the response plane is described adequately by a third-order polynomial.

The model constructed in this manner was used for calculating the cold-crushing strength of specimens of varied composition (Fig. 2). The diagram shows the range of compositions which give a cold-crushing strength of at least 100 kg/cm^2 after firing at 800°C. It was established that the refractoriness of the compositions in this range is over 2000°C.

The confidence limits of the error for the cold-crushing strength values calculated from the equation of regression (5) was determined as follows:

$$\Delta = t_{\alpha/l;\, f}\hat{\sigma}_{\{y\}}, \tag{9}$$

where $\hat{\sigma}\langle y\rangle$ is the standard deviation of the predicted value of y at a given point in the Simplex. For the same number of experiments at each point of the Simplex

$$\hat{\sigma}_{\{y\}} = \frac{\hat{\sigma}_{\{y^0\}}\ \xi^{1/2}}{\sqrt{n}}; \tag{10}$$

The value of ξ was taken from the relevant section of a graph [9].

In the composition range marked out in Fig. 2 the confidence limits of the error of the theoretical cold-crushing strength were ±1.0 kg/cm^2.

It is therefore quite permissible to produce phosphate-bonded gunite from unconditioned magnesites containing up to 10-12 mole % CaO and SiO_2. Silicified and talc-containing magnesites containing up to 10-12 wt. % CaO and up to 10 wt. % SiO_2 (on the calcined substance) occur extensively in the Vol'chegorsk, Karagai, and Gologorsk deposits of the Satkin group [11]. In the Vol'chegorsk deposits the silicified magnesites are usually dolomitized to an appreciable extent and after calcining may contain up to 15% CaO and up to 3% SiO_2. In the Karagai deposits, on the other hand, some magnesite contains more SiO_2 (up to 10-12%) than CaO (up to 4.0-4.5%) [11]. Siliceous magnesites (up to 14% SiO_2) were discovered in significant quantities in the Savinsk deposits [12, 13]. Their CaO content varies 1.7-4.8% [13, 14]. Large bodies of magnesites containing up to 7% SiO_2 and 12-15% CaO occur also in the overburden of the chromite quarries in the Kempirsai deposits [15].

The results of this investigation thus prompt the conclusion that contaminated natural magnesites can be used as starting material for the production of phosphate-bonded gunite.

CONCLUSIONS

The Simplex method of experiment design was used for establishing the feasibility of using unconditioned magnesian raw material containing up to 10-12 mole % calcium oxide and silica for the production of phosphate-bonded gunite.

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