

INTERACTION OF BASIC REFRACTORIES WITH
CONVERTER SLAG

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Using the crucible method, in the All-Union Institute of Refractories we have investigated the slag resistance of basic converter refractories. As the reagent we used the most aggressive, primary converter slag with a basicity of 1.25 of the following chemical composition, %: SiO₂ 24.10, TiO₂ + Al₂O₃ 7.86, Fe₂O₃ 3.27, FeO 17.57, CaO 28.32, MgO 2.22, MnO 15.6, Na₂O + K₂O 0.81, P₂O₅ 0.48, Cr₂O₃ 0.15. The fractoriness of the slag was 1230°C.

To make converter refractories we used roasted dolomite of the Styl' deposit, MI-88 magnesite powder, and NDPK-75 magnesite powder (Table 1). In the preparation of the masses, as binder we used prepared coal tar with a viscosity C₈₀¹⁰ = 43 sec and a coking value of 39%. The amount of coal tar added to the composition of the masses was 5.5%.

For this investigation we pressed crucibles 55 mm in diameter and 60 mm in height; they were subjected to various forms of heat treatment: carbonization in a covering of coke at 800°C, heat treatment in a protective medium of evolved gases at 400°C, and annealing at 1650°C; furthermore, some of the annealed crucibles were impregnated with molten pitch. The crucible characteristics are given in Table 2.

The crucibles, containing cylinders precompacted from finely ground converter slag, were placed in a cold furnace. Tests on the slag resistance were performed in a kryptol furnace at 1600°C for 2 h.

After the furnace had cooled the crucibles were extracted and sawn into half; the area of impregnation or corrosion of the refractory by the slag was measured with a planimeter. As a measure of the slag resistance we took the degree of impregnation or corrosion of the refractory by the slag (K), defined as the ratio

TABLE 1. Characteristics of the Initial Materials

Material	Chemical composition, %					Appar-ent den- sity, g/cm ³	Open porosity, %
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO		
Roasted dolomite*	1,41	0,69	1,0	54,98	39,43	3,23	6,57
MI-88 magnesite powder	2,90	0,73	1,6	2,68	92,09	2,90	16,63
MDPK-75 magnesite powder	0,40	1,20	2,3	5,96	86,07	2,92	15,0

* Calcination loss 1.76%.

TABLE 2. Crucible Characteristics before Test for Slag Resistance

Indices	Values of indices for crucibles*															
	carbonized				heat-treated				annealed				annealed and impregnated			
	TM	TM-75	TDM	TD	TM	TM-75	TDM	TD	TM	TM-75	TDM	TD	TM	TM-75	TDM	TD
Chemical composition, %:																
SiO ₂	2,80	0,39	1,66	1,38	2,78	0,39	1,64	1,38	2,90	0,41	1,72	1,44	2,72	0,37	1,68	1,36
Fe ₂ O ₃	1,55	2,26	1,23	0,89	1,54	2,26	1,22	1,09	1,60	2,34	1,28	1,12	1,50	2,20	1,22	1,05
Al ₂ O ₃	0,70	1,16	0,68	0,68	0,71	1,16	0,70	0,68	0,73	1,20	0,71	0,70	0,68	1,13	0,68	0,67
CaO	2,58	7,05	36,75	53,80	2,57	6,97	36,30	53,60	2,68	7,25	38,09	56,00	2,52	6,72	36,70	53,00
MgO	89,00	87,04	56,20	38,90	88,50	85,50	55,30	39,55	92,09	89,60	57,44	40,05	87,30	83,00	55,60	38,70
C	3,20	2,86	3,42	3,10	4,00	4,10	3,80	3,85	—	—	—	—	5,80	7,40	3,20	5,43
Gas permeability, μm ²	0,034	0,102	0,520	3,455	0,027	0,051	0,234	0,362	0,565	1,275	1,020	6,477	0,255	0,336	0,729	1,831
Apparent density, g/cm ³	2,54	2,55	2,54	2,55	2,65	2,56	2,73	2,65	2,70	2,64	2,90	2,92	2,82	2,79	2,94	2,96
Open porosity, %	24,9	24,9	22,5	24,0	22,4	22,1	17,8	19,3	20,2	21,4	14,9	13,3	16,5	16,9	9,90	10,0

* TM, tar-magnesite based on MI-88 powder; TM-75, tar-magnesite based on MDPK-75 powder; TDM, tar-dolomite—magnesite; TD, tar-dolomite.

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TABLE 3. Results of Determination of Degree of Impregnation of Refractories by Slag

Refractory	Degree of impregnation of crucibles* by slag, %			
	car-bon-ized	heat-treated	an-nealed	annealed and im-pregnated
TM	9,0	4,2	9,1	3,0
TM-75	8,9	5,3	13,3	3,8
TDM	6,0	0	8,1	1,4
TD	2,1	0	3,0	0

* Mean of the results of investigation of two crucibles.

of the area of impregnation or corrosion of the crucible (S_1 or S_2) to the total cross-sectional area of the crucible (S_t):

$$K = S_1/S_t \cdot 100. \quad (1)$$

During the tests we established that corrosion of the crucibles by the slag was absent; therefore, we determined only their degree of impregnation (Table 3).

The data indicate that the presence of carbon in the material reduces its capacity to be impregnated by slag. In all cases the degree of impregnation of the annealed specimens is higher than that of the others (carbonized, heat-treated, or annealed and impregnated with pitch). The open porosity of the refractory exerts a marked influence on the degree of impregnation. Carbonized refractories, with a higher porosity than the other carbon-containing ones (heat-treated and impregnated), are more strongly impregnated by the slag. These refractories are located in the following order with respect to the degree of increase in impregnation: TD—TDM—TM—TM-75.

TABLE 4. Chemical Analysis of Reaction Zone of Crucibles after Tests for Slag Resistance

Oxides	Mass fraction of oxides (%) in reaction zone of crucibles							
	carbonized				heat-treated			
	TM	TM-75	TDM	TD	TM	TM-75	TDM	TD
SiO ₂	2,44	3,30	3,38	3,54	2,88	2,93	2,35	2,06
Fe ₂ O ₃	3,77	4,56	3,72	3,85	4,33	7,90	3,60	4,14
Al ₂ O ₃	0,38	0,72	0,14	0,38	0,46	1,04	0,88	0,22
CaO	5,91	11,85	34,90	48,00	5,76	6,77	30,16	49,30
MgO	84,67	76,87	57,00	42,50	84,95	78,86	59,94	41,30
TiO ₂	—	0,13	—	—	—	0,28	—	—
MnO	2,30	2,50	0,95	1,53	1,75	1,80	3,35	2,73
FeO	—	—	0,44	0,45	—	—	—	—

Oxides	Mass fraction of oxides (%) in reaction zone of crucibles							
	annealed				annealed and impregnated			
	TM	TM-75	TDM	TD	TM	TM-75	TDM	TD
SiO ₂	3,07	3,15	3,31	2,03	2,39	3,80	2,71	2,35
Fe ₂ O ₃	5,84	5,71	2,74	2,00	2,77	3,73	3,18	2,46
Al ₂ O ₃	0,29	0,39	0,75	0,20	1,15	1,08	0,65	0,39
CaO	6,56	5,92	34,90	54,40	2,88	8,39	33,20	53,60
MgO	82,22	81,72	55,85	41,00	89,08	80,98	57,80	40,08
TiO ₂	—	0,10	0,05	—	0,10	0,10	0,12	—
MnO	1,50	1,75	1,39	1,49	1,00	1,25	1,65	1,48
FeO	0,50	0,13	0,27	0,27	0,24	0,24	0,26	0,29

TABLE 5. Chemical Composition of Slag, %

Slag from crucible	Calcium loss	SiO ₂	MnO	Al ₂ O ₃ + TiO ₂	Fe ₂ O ₃ + FeO	CaO	MgO	P ₂ O ₅
TM	0,61	28,30	1,35	0,25	2,75	54,95	9,30	2,28
TM-75	0,52	29,25	1,50	—	2,84	55,84	8,29	2,05
TDM	0,80	28,50	1,25	0,95	2,34	56,65	7,04	2,25
TD	0,44	25,38	1,60	0,76	2,80	53,43	12,96	2,40

The degree of increase in impregnation of the refractory with slag increases with its magnesium oxide content. In magnesite refractories the impregnation with slag decreases with an increase in the purity of the material.

Chemical analysis of the reaction zone of the crucibles after the test for slag resistance (Table 4) indicates an increase in the content of iron and manganese oxides in this zone; this is due to penetration of the slag's low-melting components into the refractory. Confirmation of this assumption is provided by the results of chemical analysis of slag beads left in the carbonized crucibles after the tests (Table 5).

Table 5 shows that the content of oxides in the low-melting phases of the slag (FeO, Fe₂O₃, MnO) was sharply reduced in comparison with that in the initial slag.

A microscopic investigation of specimens of the crucibles* in polished sections and immersion preparations revealed that the reaction zone of the magnesite refractories displays recrystallization of the periclase grains, accompanied by their enlargement and an increase in the porosity of the zone. The increase in the porosity promotes greater saturation of the contact zone with the fused slag. In the deeper layers of the reaction zone, adjoining the carbon-containing zone of the crucibles, iron and manganese oxides are reduced to the metal. In the subzone of the reaction zone of magnesite refractories, in contact with the slag, the periclase grains are saturated with magnesioferrite; calcium ferrite occupies the interstices between them.

In dolomite refractories no significant changes in the large grains of lime are observed; calcium and magnesium ferrites are located between the lime grains. It is characteristic that in all cases calcium silicates are concentrated in the deeper layers of the reaction zone, adjoining the carbon-containing unaltered zone.

Phase chemical analysis of the reaction zone of tar-magnesite and tar-dolomite—magnesite refractories (Table 6) shows that the amount of magnesioferrite in the magnesite refractory is nearly double that in the dolomite—magnesite refractory, their dicalcium ferrite contents being approximately the same. The increase in the calcium silicate content of the magnesite refractory is due to its greater saturation with the fused slag.

Thus, the results of static determination of the slag resistance of converter refractories of various types have shown that magnesite refractories are more strongly impregnated with slag than dolomite refractories. This is due to recrystallization of the periclase grains in the presence of a liquid phase, accompanied by growth of the grains and by their saturation with magnesioferrite; this can induce distention of the reaction zone of the refractory and its spallation at the service temperatures.

* Performed by N. A. Sheveleva.

TABLE 6. Mass Fraction of Compounds Formed in Reaction Zone of the Refractories, %*

Refractory	Dicalcium ferrite	Magnesioferrite	Dicalcium and tricalcium silicates, recalculated to 2CaO · SiO ₂
Tar-dolomite	0,93	6,52	4,59
Tar-dolomite-magnesite	1,07	3,47	3,58

* According to results of phase chemical analysis.

Dolomite refractories are less strongly impregnated with slag. They decompose principally at the binder, which as a result of its reaction with the low-melting components of the slag, gradually becomes similar to it in phase composition; as a consequence erosion of the reaction zone of the refractory during service is possible. The question of the advantage of use of a particular type of artifact can be definitely solved by investigating the disintegration kinetics of tar-dolomite and tar-magnesite refractories.

CONCLUSIONS

Converter slags based on a tar binder are located in the following order with respect to the increase in the degree of impregnation with slag: dolomite → dolomite—magnesite → magnesite. The greater degree of impregnation of magnesite refractories is due to recrystallization of the periclase grains, accompanied by an increase in their size, by saturation with magnesioferrite, and by dilatation of the reaction zone of the refractory.

The degree of impregnation of the refractory with slag increases with the open porosity of the material and its impurity content.

The presence of a coke residue in tar-bound and pitch-impregnated roasted refractories reduces their impregnation by fused slag.

Converter refractories are located in the following order with respect to the degree of influence of preliminary heat treatment on the increase in the penetrability by slag: roasted, pitch-impregnated → heat-treated → carbonized → roasted.

COMPOSITIONS OF MAGNESITE ARTICLES AND THE ANALYSIS OF PHASE EQUILIBRIA IN THE CaO—MgO—SiO₂ SYSTEM

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The reduction of multicomponent systems to a ternary system is well known and is included in textbooks on the physical chemistry of silicates [1, 2]. However, this principle is not sufficiently used. It is only in recent years that a few papers have been published in which it is reported that the compositions of the initial refractory materials and also of local samples after service [3, 4] have been reduced to ternary compositions.

The difficulty lies in the correct calculation of the coefficients which demand a knowledge of the final phases. This is particularly important in the case of silicate systems where it is necessary to reduce several individual oxides, e. g., Al₂O₃, Fe₂O₃, to SiO₂, which is allowed on crystal-chemical considerations

TABLE 1. Norms in Accordance with State Standards (GOST) and Technical Specifications (TU) for the Chemical Composition of Magnesite Refractories

Documentation	Conc., %*		
	MgO, ≥	CaO, ≤	SiO ₂ , ≤
GOST 4689—74	91	3	3
GOST 4689—74	89	4	3
GOST 10360—63	90,5	2,5	3,5
TU of Magnesite combine	88	4	4

* Here and henceforth, mass fractions are given.