UDC 666.762.38

STABILIZED DOLOMITE REFRACTORIES

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A technology of environment-friendly refractories based on briquetted dry-ground dolomite, magnesia-silicate raw materials, and stabilizing additives has been developed. The potential use of the newly designed refractories as an alternative to chromite-periclase refractories is emphasized.

The short supply of raw minerals in Ukraine for manufacture of basic refractories necessitates a search for alternative materials such as substandard dolomite, dolomite dust, magnesia-silicate rocks, etc. that can be used for fabrication refractory products and powders as the replacement of magnesia materials purchased from foreign manufacturers. The situation with the supply of raw materials for production of magnesia refractories in Ukraine has become critical following the disintegration of the former Soviet Union. For manufacture of refractories mostly imported raw materials have been used: periclase powder — from Korea, China, Slovakia, Turkey, Russia; chrome ore — from the Kempirsaiskoe deposit (Kazakhstan), Saranovskoe deposit (Ural, Russian Federation), from the United Arab Emirates, Turkey, and other countries. In this context, expansion of the raw materials base including, in particular, man-made materials, is an issue of major concern for Ukraine.

An alternative to chrome-magnesia refractories are dolomite-containing (lime-magnesia) refractories based on dolomite that have occasionally proved suitable for successful application in high-temperature thermal power units.

At present, dolomite is mainly used in the form of sintered powders, as the fettling material for steelmaking units, or as nonfired, unfriendly to environment resin-bound components for the lining of basic converters.

A route towards improving the situation would be the organization of production of dolomite-containing refractories for other thermal power units, for example, kilns and furnaces in cement, refractory, machine-building and other industries. This might relax the demand on magnesia raw materials, make production less costly, and improve working environment.

Ukraine is sufficiently rich in deposits and reserves of dolomite materials [1]. Dolomites are commercially available from the Novotroitskoe, Yamskoe, Elenovsoe, and Styl'skoe deposits (Donetsk Region). The chemical composition of dolomites, based on data of the USSR Ministry of Geology, is given in Table 1. Disadvantages of dolomite-based refractories are hydration of materials containing free calcium oxide and inconveniences associated with the polymorphism of $2CaO \cdot SiO_2$. The early studies on the production technology of stabilized dolomite components were conducted in the mid-1900s at the UkrNIIO by Prof. Kukolev and co-workers [2 – 5]. By this technology, stabilized dolomite clinker was produced, initially using dry grinding and later wet grinding (slurry) techniques followed by calcination. To prevent the break-up of molded briquettes because of the low-temperature polymorphic $\beta \rightarrow \gamma$ transformation of dicalcium silicate associated with a 12% expansion in volume, the use of stabilizing additives was prescribed.

The proportion of precursor components in the raw mixture is evaluated by the saturation factor K_s to characterize

TABLE 1. Chemical Composition of Dolomites

Deposit	Concentration, %*			
	MgO	CaO	SiO_2	R_2O_3
Kuzinskoe	20.50 – 21.36	29.17 – 30.47	0.48 – 1.71	0.14 – 0.20
Frunzenskoe	18.71 – 19.67	29.70 – 30.52	2.87 – 3.25	1.66 – 1.73
Negrebovskoe	21.1 – 21.5	30.3 – 30.8	0.60 – 3.0	0.15 – 0.17
Zavadovskoe	9.6 – 22.0	21.7 – 32.33	0.9 – 4.0	0.53 – 18.4
Elenovskoe	17.6 – 19.8	30.2 – 34.4	0.3 – 0.77	0.70 – 0.84
Styl'skoe	19.0 – 19.5	31.7 – 33.2	0.2 – 0.37	0.40 – 1.95
Novotroitskoe	18.7 – 20.9	30.6 – 33.4	0.40 – 2.40	0.46 – 2.27
Yamskoe	19.8 – 20.2	29.6 – 30.5	1.58 – 2.58	0.40 – 1.40

* Calcination loss Δm_{calc} for all dolomites ranges from 40.0 to 47.1%

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TABLE 2. Chemical Composition of Precursor Materials

Material	Mass fraction, %							
	Δm_{calc}	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Cr_2O_3	MnO
Dolomite:								
Elenovsoe deposit	38.1	5.42	2.7	3.71	29.7	14.3	(SO_3 5.3)	0.46
Novotroitskoe deposit	45.5	0.63	0.16	0.28	33.5	19.5	–	–
Frunzenskoe deposit 1	45.3	2.36	0.45	0.42	28.2	33.3	–	–
Frunzenskoe deposit 2	44.6	2.86	0.88	0.60	29.2	21.2	–	–
Frunzenskoe deposit 3	46.0	1.40	0.29	0.40	29.9	21.0	–	–
Dolomite dust:								
NDF	18.6	12.4	4.23	2.19	33.1	21.2	–	1.93
SDK	15.2	7.94	4.95	2.27	39.2	19.2	(SO_3 3.44)	–
DFDK	25.9	3.74	1.61	2.03	41.9	21.6	–	–
Talc magnesite (Pravdinskoe deposit)	28.7	20.2	2.5	11.4	3.34	32.5	0.58	–
Talc (Inguletskoe deposit)	7.82	45.4	7.06	10.1	1.0	27.9	–	–
Aglodunite	0.44	38.1	0.15	11.8	2.24	47.4	–	–
Enriched chrome ore waste	19.7	30.1	–	–	4.44	36.8	7.17	–
Chrome ore	4.36	9.00	6.21	12.65	0.70	24.23	43.25	–

the degree of binding of calcium oxide into tricalcium silicate.

The saturation factor is calculated using the formulas [6]

$$K_s = \frac{CaO - (0.35Fe_2O_3 + 1.65Al_2O_3 + 1.18P_2O_5)}{2.8SiO_2} \quad (1)$$

for the ratio $Al_2O_3 : Fe_2O_3 > 0.64$
and

$$K_s = \frac{CaO - (0.7Fe_2O_3 + 1.1Al_2O_3 + 1.18P_2O_5)}{2.8SiO_2} \quad (2)$$

for the ratio $Al_2O_3 : Fe_2O_3 < 0.64$.

For $K_s = 1$, no free CaO is present in dolomite briquettes since silica is bound into $3CaO \cdot SiO_2$; the species $2CaO \cdot SiO_2$ is likewise absent. For $K_s > 1$, free CaO is present in the refractory material, which may lead to dehydration, especially in moisture-laden storage conditions.

With K_s decreasing to 0.65, the amount of $3CaO \cdot SiO_2$ tends to decrease, and that of $2CaO \cdot SiO_2$ — to increase; at $K_s < 0.65$, all silica becomes bound into $2CaO \cdot SiO_2$. With further decrease in K_s (for example, under the action of metallurgical slag), the dolomitic MgO enters into the reaction via formation of low-melting double silicates. For example, these may be merwinite $3CaO \cdot MgO \cdot 2SiO_2$, monticellite $CaO \cdot MgO \cdot SiO_2$, brownmillerite $CaO \cdot MgO \cdot 2SiO_2$, etc.

Thus, the optimum value of K_s for the stabilized dolomite briquette $CaO \cdot MgO \cdot SiO_2$ lies within $0,8 - 0.95$. The briquette material has none of free CaO, contains maximum

$3CaO \cdot SiO_2$, and a minor amount of $2CaO \cdot SiO_2$ which, in turn, becomes stabilized in the β-form in the presence of a P_2O_5 species added or other stabilizers (B_2O_3, Cr_2O_3) capable of forming solid solutions with $2CaO \cdot SiO_2$.

At the A. Berezhnoi UkrNIIO JSC, a technology for the synthesis of dolomite and dolomite-periclase compositions was developed using various (man-made included) raw materials [7 – 9].[2] To simplify the technology and make it more economical, a dry grinding technique of the percursor components (a coarse-grain variant was also tried) was used. The chemical composition of raw materials used in technological laboratory studies is given in Table 2.

Dolomite from Novotroitskoe deposit is low in SiO_2 and sesquioxides; its major impurities are iron oxides and hydroxides, carbon compounds, quartz, and calcite; the dolomite percentage is $75 - 96\%$.

Dolomite dust is high in SiO_2 and sesquioxides and rather low in CaO and MgO; one will note that the calcination loss Δm_{calc} for dust is substantially smaller. Alkali and sulfur are present in the dust in minor amounts. Because of the difference in chemical and mineral composition, the dust and, correspondingly, dust products display a lower temperature of onset of material softening.

In mineral composition, dolomite dusts available from the Nikitovskii Dolomite Factory (NDF) and Severskii Dolomite Kombinat (SDK) are similar and are represented by major components caustic dolomite ($40 - 45\%$), dolomite ($25 - 35\%$), periclase ($5 - 10\%$), and a alkali-silicate glassy

phase (18 – 20%). Dust from the Dokuchaevskii Flux and Dolomite Kombinat (DFDK) displays a somewhat different phase composition: decarbonized dolomite (70 – 75%), periclase (20 – 25%), quartz (3 – 5%), and metal (about 1%). An inspection will reveal quartz crystals, fine-grained quartz aggregates, and nontransparent iron particles.

Talc magnesites from the Pravdinskoe deposit have the following composition: 40 – 45% magnesite, 45 – 50% talc, 5% magnetite, and about 3% spinellide. Reserves of this deposit have been registered by the USSR Mineral Balance Sheet, and the conducted pilot tests have shown talc-magnesites suitable for the production of forsterite refractories and, properly enriched, for the production of periclase. This raw mineral may be classified as a complex one.
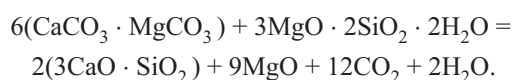
As was mentioned above, in the 1940s at the UkrNIIO, a technology for stabilized dolomite products was developed which recommended the use of a silica component for the formation of tricalcium silicate, produced by fine wet grinding technique for further briquetting. We have conducted tests to prepare briquetting components by dry grinding technology. The precursor materials were raw dolomite and dolomite dust from the Novotroitskoe deposit. The finished dolomite- and dolomite-periclase-based products showed quite satisfactory performance characteristics. The dust-containing products displayed an increased density and somewhat lower temperature (1330 – 1390°C) of onset of material softening. The dolomite-periclase-based products showed somewhat better performance characteristics in comparison to dolomite-based products. Satisfactory results were obtained using stabilizers prepared from chrome ore and crushed chromite-periclase products.

Studies were conducted using mixture components with different SiO_2 concentrations and magnesia-silicate raw materials.

The synthesis using silica was carried out by the reaction [6]

$$3(CaCO_3 \cdot MgCO_3) + SiO_2 = 3CaO \cdot SiO_2 + 3MgO + 6CO_2.$$
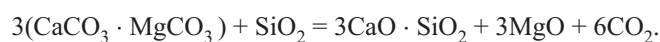
Using magnesium hydrosilicates, the reaction is

$$6(CaCO_3 \cdot MgCO_3) + 3MgO \cdot 2SiO_2 \cdot 2H_2O =$$
$$2(3CaO \cdot SiO_2) + 9MgO + 12CO_2 + 2H_2O.$$

which is a more effective route because of the enhanced MgO content.

The briquetting technology for all kinds of mixture was essentially the same: (i) grinding to the required grain size; (ii) mixing in the component proportion required with lignosulfonate added; (iii) molding under a pressure of 100 MPa; (iv) calcination at 1500 – 1580°C. All the mixtures had stabilizers added, mainly apatite and Cr_2O_3. Mixtures of different grinding fineness (from 0.006 to 3 mm) were used for briquetting. The calcined briquettes were disintegrated using jaw and roll crushers until the required grain size frac-

tions were obtained, finely ground periclase was added, and specimens of dolomite-periclase composition were prepared. The characterization of briquetted specimens prepared from different magnesia-silicate raw materials is given in Table 3; the performance characteristics were higher in products prepared from precursor materials of smaller grain size and with periclase added. Still, the best precursor materials are those containing talc-magnesite (from Ukraine) which enriches the product with periclase, similar to aglodunite and enriched chrome ore waste (from Kazakhstan and Ural).

The beneficial effect of chrome ore used as a stabilizer should be noted. The porosity of the briquette from dolomite with aglodunite added (density 2.25 – 2.62 g/cm^3) is 23.2 – 26.7%; when calcined, it is 9.9 – 10.0% (compressive strength over 80 MPa). The properties of products prepared using dolomite from various deposits differ but slightly; products from dolomite of Elenovskoe deposit show a higher density in comparison to those from dolomite of Novotroitskoe deposit; the former have a somewhat lower (by 80 – 100°C) temperature of onset of material softening, possibly because of the difference in chemical composition. Dolomites drawn from electric filters and from dumping sites can equally be used.

Metallurgic slags (waste products) were also tested for potential applicability. The chemical composition of slags is given in Table 4. Here the main components are calcium and silicon oxides; the blast furnace slag shows an increased concentration of magnesium and iron oxides. In electric furnace slags, appreciable quantities of manganese and magnesium oxides are found (depending on the grade of steel processed).

In mineral composition, the blast-furnace slag contains mainly calcium silicates and aluminates, and a colorless glassy phase. The open-hearth slag is mainly represented by merwinite and a spinellide of complex composition and, in smaller amounts, by monticellite and theophroite. The electric-furnace slag has a complex mineral composition with the following main components: a glassy phase, magnesia-alumina spinel, monticellite, and metal.

The main component for briquetted mixtures was raw dolomite (29.7 – 33.5% CaO and 14.3 – 19.5% MgO, with $\Delta m_{calc} = 38.2 – 45.5\%$). In some mixtures, dolomite dust was used, which was a waste product in the production of calcined metallurgic dolomite; however, under present conditions, most dolomite dust goes to dumping sites.

To prepare dolomite briquettes, the mixture components were ground to a grain size less than 0.5 mm and mixed in the given proportion. The mixture was pressed under a pressure of 100 MPa into briquettes and calcined at 1500°C. The sintered briquettes prepared from open-hearth slag (35 – 40%) had a high porosity (35.2 – 72.3%) and were prone to failure. The sintered briquettes prepared from blast-furnace slag ere mechanically strong and had a porosity of 13.9 – 26.3%.

The electric-furnace slag was used in combination with dolomite dust; the specimens prepared were dense, with a

TABLE 3. Characterization of Dolomite-Periclase Specimens Prepared Using Stabilized Briquetted Products of Different Mineral Composition

Briquetted component (dolomite excepted)	Property			
	open porosity, %	apparent density, g/cm^3	compressive strength, MPa	onset softening temperature, °C
Quartz sand	18.6 – 21.2	2.70 – 2.78	66.8 – 88.0	1500
Aglodunite	9.5 – 13.4	3.06 – 3.12	80.8 – 138.5	1680
Talc (Inguletskoe deposit)	13.3 – 18.9	2.81 – 2.98	61.4 – 99.7	Not determ.
Talc-magnesite (Pravdinskoe deposit)	12.9 – 16.0	2.93 – 3.07	38.6 – 128.2	" "
Enriched chrome ore waste	12.6 – 12.9	3.05 – 3.09	124.3 – 164.8	1480
Dolomite dust:				
NDF	9.8 – 10.9	2.98 – 3.00	63.0 – 67.7	Not determ.
SDK	8.5 – 9.5	3.00 – 3.01	90.3 – 107.5	" "
DFDK	7.0 – 8.4	3.05 – 3.11	178.0	" "
Blast-furnace slag:				
Makeevka Iron-and-Steel Works	20.7 – 21.4	2.68 – 2.71	47.6 – 57.2	1360
Donetsk Metallurgical Works	25.6 – 26.0	2.52 – 2.53	38.2 – 58.6	1410
Open-hearth slag:				
Makeevka Iron-and-Steel Works	19.6 – 19.9	2.77 – 2.78	72.5 – 74.3	1420
Donetsk Metallurgical Works	17.7 – 18.4	2.82 – 2.84	78.9 – 88.4	1380
Dolomite dust + electric furnace slag (Turboatom Research and Production Association)	9.5 – 10.9	3.00 – 3.02	108.4	1360

porosity varying from 12.8 to 14.2% depending on the mixture composition.

The precursor slag dust contained flux impurities in significant amounts; it was used in combination with finely ground periclase to prepare products of dolomite-periclase composition by the conventional technology for magnesia refractories.

Occasionally, the sintered products (primarily, containing open-hearth slag) were prone to failure, which may be due to incomplete stabilization of dicalcium silicate. This implies that the production technology needs further refinement, in particular, concerning the component proportion, grinding fineness, careful mixture homogenization, etc.

Products based on blast-furnace slag displayed a sufficiently high strength (38 – 47 MPa) and a high porosity (20.7 – 34.2%). Better results were obtained using blast-furnace slag and raw dolomite, viz. porosity of 17.7 – 19.9% and compressive strength of 72.4 – 88.4 MPa; these parameters showed improvement with increasing calcination temperature.

Quite good results were obtained using electric-furnace slag: products sintered in a tunnel kiln at 1560°C showed a porosity of 10% and compressive strength of 100 – 150 MPa.

It should be noted that all slag-containing products displayed a decreased temperature of onset of softening (1360 – 1420°C). This behavior will require a more careful choice for their rational application.

Based on the results of tests conducted at the UkrNIIO and NRF, experimental and pilot batches of dolomite and dolomite-periclase products were fabricated.

Products of standard size in a pilot batch prepared from stabilized dolomite briquette with the addition of a finely ground periclase powder had the following characteristics: open porosity, 13.4 – 17.1; compressive strength, 49.1 – 70.5 MPa; 18.5% CaO, and 52.2% MgO. Products of this batch were used as refractory components for the wall and

TABLE 4. Chemical Composition of Metallurgic Slags

Mass fraction, %	Slag		
	blast furnace	open hearth	electric furnace
SiO_2	33.4 – 35.5	20.0 – 24.2	26.7 – 33.7
CaO	45.9 – 46.9	42.2 – 43.0	11.5 – 24.5
MgO	3.97 – 4.31	12.9 – 13.0	19.8 – 32.4
FeO	0.60 – 3.47	5.44 – 10.9	–
Fe_2O_3	0.15 – 0.26	1.26 – 2.0	0.17 – 2.43
Al_2O_3	6.19 – 7.11	6.45 – 7.38	6.97 – 15.6
MnO	0.31 – 1.63	3.09 – 5.77	4.38 – 10.23
K_2O	0.2 – 0.45	0.02 – 0.05	0.25 – 0.74[*]
Na_2O	0.22 – 0.36	0.04	–
SO_3	4.54 – 5.27	1.3 – 1.4	0.06 – 1.39
Cr_2O_3	–	–	1.80 – 8.14

[*] Data for TiO_2.

bottom lining of syphon-pour ladles. The service life of two ladles was 14 and 20 pourings (the average service life of the chromite-periclase brick lining under the actual smelter shop conditions was 17 pourings). The post-service inspection has revealed burnt spots produced by the interaction between refractory material and molten metal. The underlying process was ferrugineous metasomatosis accompanied by the degeneration of basic refractory phases of the dolomite-periclase material.

The likely mineral composition of the affected zone is: periclase + secondary spinellide, 45%; chrome spinellide, 10%; merwinite, 15%; alite, 15%; belite, 15%. The composition of the transition zone is: periclase + secondary spinellide, 40%; chrome spinellide, 10%; merwinite, 15%; monticellite, 35%. At the contact with the working zone, the only silicate is monticellite. The phase composition of the working zone is: periclase (magnesia-wustite solid solution), 20 – 25%; metal, 3 – 5%; monticellite, 70 – 75%.

At the NRF, industrial equipment was used to prepare refractories: the precursor ingredients were synthetic coarse-grained dolomite briquette and finely ground periclase. The mixture was homogenized using an SM-115M high-speed mixer and moistened by adding lignosulfonate; green preforms were molded using a hydraulic press; the density of green preforms was 2.76 – 3.03 g/cm^3. The preforms were stacked in kiln cars which were pushed at intervals in a tunnel kiln for sintering at 1460 – 1470°C. The characteristics of the finished product were: chemical composition, 55.67% MgO, 18.2% CaO, 5.87% SiO$_2$, 5.39% Fe$_2$O$_3$, 2.40% Al$_2$O$_3$, 11.80% Cr$_2$O$_3$; calcination loss Δm_{calc}, 0.38%; open porosity, 20.6 – 24.8%; compressive strength, 32.9 – 74.9 MPa.

These characteristics show that the refractory components prepared can be used for service in high-temperature power units; the thermal stability of the synthetic stabilized dolomite-periclase products is not inferior to that of conventional chromite-periclase products.

CONCLUSIONS

Laboratory tests on the technology of environment-friendly stabilized dolomite and dolomite-periclase refractory components have been conducted. The raw materials used were dolomites from various deposits, dolomite dust, and a magnesia-silicate ingredient composed of dunite, talc-magnesite, chrome ore waste, talc, slags, and stabilizers.

The main parameters — precursor mixtures and their composition, stabilizing additives, and sintering regimes — have been specified. The advantages of dolomite-periclase components and potential use of dolomite dust and metallurgic slag has been discussed. Experimental and pilot batches were prepared and tested, with satisfactory results, for service.

The potential use of dolomite-periclase products as an alternative to chromite-periclase refractories for high-temperature power units has been emphasized.

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