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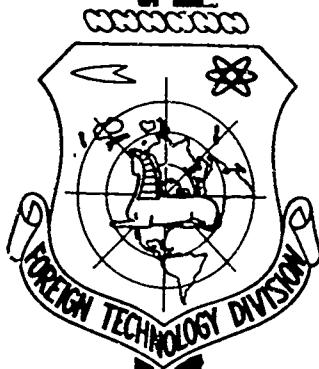
TRANSLATION

CERTAIN PROPERTIES OF CALCIUM-OXIDE REFRACTORIES

By

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CERTAIN PROPERTIES OF CALCIUM-OXIDE REFRACTORIES

Ye. S. Lukin and G. A. Serova

Calcium-oxide, because of its low cost, high refractoriness (the melting point for CaO is 2570°C) and its stability against the action of many melted metals, is currently being used more and more as a basic refractory material [1 - 9]. Its sharply expressed basic properties determine a chemical stability against the action of alkaline metals and their vapors.

The literature contains data concerning the tendency of CaO to cake [7, 8, 12], the effect of various additives [7, 8]; a number of works deal with the questions of the technology [7 - 12] and hydration of CaO products [8, 9 13 - 15]. However there is almost a complete lack of information concerning the mechanical processes of CaO refractories and their properties at high temperatures [16].

The present article deals with the obtainment of CaO refractories, dense (sintered) and granular constructions for use at high temperatures in alkaline-metal vapor. Study was made of the properties of refractories at high temperatures and of their stability under the action of alkaline-metal vapors.

The starting material was CaCO_3 (mark ChDA GOST 453-48) of

chemical composition (in %): ignition losses - 43.37; residue insoluble in HCl - 0.02; Al_2O_3 - 0.04; Fe_2O_3 - trace amount; CaO - 55.20; MgO - 0.09; SO_3 - 0.78.

A study was made of the effect on the tendency for CaO to cake of the following factors: 1) calcination temperature of the original material, 2) quantity of introducable impurity TiO_2 ; 3) temperature and duration of holding during final calcination of the refractories, 4) gas medium of calcination.

The starting material was first calcinated in a flame furnace at 1380, 1500 and 1700°C.

The calcined CaO powder was crushed in a vibrational mill with steel balls for a period of 0.5 hrs with appropriate materials: spheres = 1:8 (according to the data of chemical analysis the yield of iron in this case amounted to 0.01 - 0.03%) and in a porcelain mill with balls of MgO for a period of 10 hrs with the ratio of materials: spheres = 1:2. In this and other cases the materials were pulverized to a predominant dimension of particles below 1 - 2 μ . The specific surface of the obtained balls of CaO amounted to: for a powder calcinated at 1380°C hammered in a vibration mill 3.75 m^2/g , for powder sintered at 1500°C 4.66 m^2/g .

The TiO_2 impurity was introduced in a thinnly dispersed form in a quantity of 0.25, 0.5 and 2% during hammering of the CaO powder.

Samples for testing were prepared on a hydraulic press with a specific pressure of 1000 kG/cm^2 .

Calcination was carried under various conditions: in a Kryptol furnace, in a TVV-4 vacuum furnace in a medium of helium and in a flame furnace (in corundum capsules with covers in a charge of highly calcinated magnesium oxide).

Tables 1 and 2 list characteristics for CaO sintering. The minimum obtained apparent porosity of samples of pure CaO to 9 - 10%.

Introduction into the material of an insignificant amount of TiO_2 (0.25 - 0.5%) makes it possible to obtain a practically sintered material (with zero apparent porosity) at 1650 - 1750°C.

Table 1. Sintering Characteristic for CaO Samples. Calcination in a Kryptol Furnace

Sample number	Temperature of preliminary calcination, °C	Quantity of TiO_2 additive introduced	Volumetric weight of raw material g/cm ³	1600°, Holding for 2 powers					1750°, Holding for 1 hr				
				Water absorption, %	Volumetric weight, g/cm ³	Apparent porosity, %	True porosity, %	Linear shrinkage, %	Water absorption, %	Volumetric weight, g/cm ³	Apparent porosity, %	True porosity, %	Linear shrinkage, %
1	1550	—	1.70	4.0	2.65	11.4	15.0	15.8	3.1	2.90	9.0	13.5	16.5
2		0.25	1.70	3.5	2.90	10.2	13.5	16.4	0.5	2.92	1.4	13.0	16.5
3		0.5	1.71	0.25	2.97	0.7	11.5	16.8	—	—	—	—	—
4		—	1.73	0	3.15	0	16.0	18.2	—	—	—	—	—
5	1600	—	2.07	3.7	2.69	10.7	14.0	10.5	3.7	2.88	10.7	14.0	10.5
6		0.25	2.07	2.9	2.90	8.4	13.5	10.5	0.0	2.94	0	12.5	11.0
7		0.5	2.05	0.2	3.08	9.6	18.0	12.4	—	—	—	—	—
8		—	2.11	0	3.08	0	18.0	12.0	—	—	—	—	—
9	1700	—	2.10	4.8	2.70	12.9	9.5	8.0	4.6	2.74	12.6	18.5	8.4
10		0.25	2.10	3.8	2.89	11.0	11.0	10.0	0.0	2.94	0	12.5	10.6
11		0.5	2.10	0.8	3.02	2.4	10.0	11.5	—	—	—	—	—
12		—	2.11	—	—	—	—	—	—	—	—	—	—

* Specific weight of CaO taken as 3.36

Table 2. Sintering Characteristic of CaO Samples. Calcination in a Vacuum Furnace

Sample number	Temperature of preliminary calcination, °C	Quantity of TiO_2 additive introduced	Volumetric weight of raw material g/cm ³	1700°, Holding for 2 powers					1800°, Holding for 1 hr 45 min					1900°, Holding for 1 hr				
				Water absorption, %	Volumetric weight, g/cm ³	Apparent porosity, %	True porosity, %	Linear shrinkage, %	Water absorption, %	Volumetric weight, g/cm ³	Apparent porosity, %	True porosity, %	Linear shrinkage, %	Water absorption, %	Volumetric weight, g/cm ³	Apparent porosity, %	True porosity, %	Linear shrinkage, %
1	1550	—	1.70	4.0	2.78	11.9	16.5	15	4.2	2.83	11.9	16.5	15.6	3.7	2.83	10.5	15	15.7
2		0.25	1.71	0.45	3.04	1.4	9	17	—	—	—	—	—	—	—	—	—	—
3		0.5	1.73	0.35	3.10	1	7	17.4	—	—	—	—	—	—	—	—	—	—
4	1600	—	2.07	6.8	2.71	18.4	10.2	8.5	4	2.87	11.5	15	16	3.9	2.86	11.2	15	10
5		0.25	2.08	0.6	3	1.8	10.2	11.4	—	—	—	—	—	—	—	—	—	—
6		0.5	2.10	0	3.13	6	6.5	12.4	—	—	—	—	—	—	—	—	—	—
7	1700	—	2.10	7.9	2.62	21	24.2	7.1	6.1	2.75	16.8	19	8.5	4.3	2.83	12.2	15.7	9.4
8		0.25	2.11	4	2.82	11.3	15.5	9.4	—	—	—	—	—	—	—	—	—	—
9		0.5	2.09	0	3.06	0	8.7	11.8	—	—	—	—	—	—	—	—	—	—

* Specific weight of CaO taken as 3.36

It should be noted that samples with TiO_2 additives with zero apparent porosity the minimum obtained true porosity amounts to 6 - 8%.

The presented data concerning calcination of CaO was utilized when selecting a rational technology for preparing refractory parts. The parts were prepared in the form of rings (bushings) of various dimensions both of dense and granular construction (from grains of a sintered CaO briquette). For this purpose chemically pure CaCO_3 was preliminarily calcinated at $1350 - 1400^\circ\text{C}$ and then pulverized for 0.5 hrs in a vibrating mill to a predominant grain dimension of $1 - 2 \mu$. The parts were prepared by pressing on a hydraulic press at a pressure of 1000 kg/cm^2 : from thinly milled CaO - without moistening and the introducing of plasticizing additives, from a powdered mass - with the introduction of 3% paraffin (or wax) dissolved in carbon tetrachloride.

For parts of granular construction fractions of grains of various dimensions were obtained from a briquette prepared by briquetting (pressing) of previously calcinated finely ground CaO .

The briquette was roasted in a flame furnace at 1750°C (in capsules with cemented covers in a charge of MgO). After roasting the briquette had an apparent porosity of 2 - 4% and a volumetric weight of $3 - 3.02 \text{ g/cm}^3$. The calcinated briquette underwent crushing, pulverizing and sifting into fractions.

The TiO_2 additive (0.5%) was introduced during pulverizing of a fine fraction in a vibration mill.

When introducing 0.5% TiO_2 into the material the limit temperature of calcination of the objects was 1650°C , held for 1 hr; objects of pure CaO were calcinated at 1750°C with a residence of 2 hrs at

Table 3. Characteristic of Obtained Parts of CaO

Mass number	Granular composition, %			Calcination in a flame furnace at 1700°, holding for 2 hrs								
	1,5--0,5 M.N.	0,5 0,2 M.N.	< 0,06 M.N.	Volumetric weight, g/cm ³	Water absorption, %	Apparent porosity, %	True porosity, %	Linear shrinkage, %	σ_{com} , ² kg/cm ²	Deformation under loading °C		
										H. P.	4 %	10 %
1	30	40	30	2,51--2,55	8,8	22,3	25	10,9--11,2	385	1740	1880	1930
2	--	70	30	2,48--2,50	8--9,5	20--23,5	26--27	10 --11,5	460	1750	1860	1930
3	--	--	100	2,90--2,93	1,7--1,9	5-5,5	13--14	17,1--17,5	--	---	--	--

Table 4. Certain Properties of CaO Refractories (Fine Grain Masses)

Mass number	Content of TiO ₂ additive, %	Temperature of preliminary calcination, °C	Method of pulverizing metal	Volumetric weight of calcined samples g/cm ³	Apparent porosity, %	Bending strength (KG/cm ²) at t°C				Temperature of onset of deformation under a load of 2 KG/cm ²
						20	1000	1200	1350	
10	--	1380	Grinding in a porcelain mill	2.81	6.2	750	600	350	300	1970
2	0.25			2.87	5.7	1020	760	365	310	1850
14	0.5			3	0	860	190	250	--	--
3	1	1380	Grinding in a vibration mill	3.03	0	850	710	200	--	--
1	2			3.07	0	960	645	395	--	1830
10	--			2.86	7.1	810	710	220	--	--
2	0.25	1500	Grinding in a vibration mill	2.91	0.8	900	510	320	--	--
4	0.5			3	0	870	380	--	--	--
	--			2.92	0.9	800	710	--	460	--

the terminal temperature.

Characteristics for parts obtained from pure calcium-oxide are given in Tables 3 and 4.

The softening point under load and the coefficient of thermal expansion were determined in a vacuum oven with tungsten heater making it possible to obtain a temperature exceeding 2000°C [17].

Bending strength at elevated temperatures is determined in a Silit furnace equipped with the appropriate loading equipment.

The value of maximum bending strength at room temperature for samples with TiO_2 additives was somewhat higher than for samples of pure CaO . At a temperature of 1000°C the strength decreases for samples without additives by approximately 10–20% and with additives by 30–40%. At 1200–1350°C a further decrease in strength is observed (approximately 3 times by comparison with strength at room temperature).

With the introduction of TiO_2 additives to the sample compositions the temperature for the onset of deformation under loading is reduced (thus, with a 2% content of TiO_2 additive the temperature of onset of softening drops to 100°).

Data on dilatometric testing at high temperature of samples of pure calcium-oxide without additives are given in Table 5.

Table 5. Dilatometric Characteristics of Pure Baked Calcium-Oxide

Temperature, °C	1000	1100	1200	1300	1400	1500	1600	1700
Percent expansion	1.24	1.43	1.58	1.74	1.9	2.08	2.20	2.26
$\text{Cal} \cdot 10^{-6}$	12.4	13	13.2	13.5	12.6	13.9	13.8	13.3

Testing the stability of CaO refractories under the action of lithium was carried out on a special installation [18]. Within the apparatus, by means of an arc discharge between a liquid cathode and

a solid molybdenum anode the formation of an ionized vapor of alkaline metal was formed. The alkaline metal lithium in whose vapor it was necessary to test the samples, was used as the cathode. The apparatus was placed in a water-cooled vacuum chamber in which pressure of $8 \cdot 10^{-2}$ to $5 \cdot 10^{-1}$ mm Hg was maintained.

Parts intended for testing in the shape of bushings (rings with an outside diameter of 50 - 70 mm, inside diameter 30 - 50 mm and height 40 - 45 mm) were exposed for 15 - 20 min to the action of ionized lithium vapor formed in the arc discharge. The temperature on the outer surface of the bushings exceeded 2000°C (the exact temperature could not be measured) at a pressure $p = 0.1$ to 1 mm Hg. For a number of samples testing was carried out for a longer period of time. The measured temperature at the inner surface of the bushings amounted in most cases to about 1000°C . During sparked ignition the test samples underwent a sharp temperature shock period under normal operation of the installation the inner surface of the bushing was in contact only with the gaseous phase. But in a number of cases there was a spattering of liquid metal which fell on the inner surface of the bushing.

During testing continuous observation was made of the condition of the refractories, the appearance of cracks and local overheating on the samples being noted. After testing the bushings were subjected to careful visual inspection as well as measurement and weighing.

In order to study the nature of the interaction of lithium with refractory materials the samples were subjected to x-ray and petrographic studies and chemical analysis before and after testing.

During x-ray and petrographic investigations it was established that the material degenerate under the action of lithium to form any

new compounds. X-ray pictures taken of samples before and after testing (see Fig. 1) are similar; characteristic lines of the basic crystalline components of CaO are retained on x-ray pictures of samples which have undergone the action of lithium.

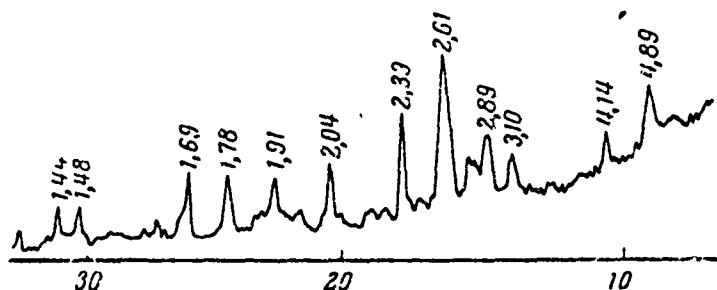


Fig. 1. X-ray pattern of a sample after testing in lithium vapor.

After testing in lithium a white deposit of lithium carbonate (the Li_2CO_3 x-ray patterns) formed on the surface of bushings stored in air due to the oxidation of metallic lithium which settled in small quantities on the sample surfaces when shutting down the installation and during carbonization. The samples also underwent partial hydration of CaO ($\text{Ca}(\text{OH})_2$ on x-ray patterns) during storage.

The results of chemical analysis of samples subjected to the action of lithium which are presented below indicate the absence of an interaction of metallic lithium with refractory materials of calcium-oxide (in %): ignition losses — 21.53; SiO_2 — 2.00; Al_2O_3 — 1.00; Fe_2O_3 — 0.40; CaO — 72.00; MgO — 1.50; Li_2O — 1.35; H_2O — residue.

Thus, samples under the action of lithium vapor (in particular, liquid lithium) exhibited satisfactory chemical stability. The outer surface of bushings adjacent to an aggressive medium remained pure, flat, and without sweating after testing.

It should be noted that certain other materials on the basis of pure oxides, e.g. Al_2O_3 , ZrO_2 , under the action of lithium during

testing under similar conditions are completely destroyed with the formation of new compounds. Refractories of pure magnesium-oxide exhibited the same stability as refractories of calcium-oxide [13].

However, parts made from calcium-oxide exhibited insufficient temperature stability: under sharp temperature shocks during start-up of the equipment and under temperature oscillations during experiments the bushings disintegrated severely (Fig. 2). In order to moderate the temperature shock up to start-up of the installation preliminary gradual heating of the bushings was tried. Disintegration in this case was decreased. Bushings of calcium-oxide of granular structure exhibited a greater thermal stability than dense parts prepared from fine-grained masses.

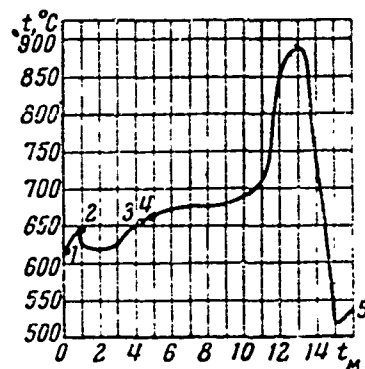


Fig. 2. Variation in temperature of the outer surface of bushings during testing in lithium vapor.

Conclusions

1. A technique for preparing refractory parts of pure CaO has been developed: dense with a volumetric mass of $2.85 - 2.93 \text{ g/cm}^3$ and temperature of deformation onset under loading 1950°C and of parts with a granular structure with a volumetric weight of $2.48 - 2.55 \text{ g/cm}^3$.

2. The introduction of TiO_2 additives (0.5 - 2%) indicates a positive effect on sintering of CaO refractories although it reduces the strength of the parts at high temperatures as well as the temperature of deformation onset under loading.

3. A satisfactory chemical stability of CaO refractories was established in tests under the action of lithium vapors (and liquid lithium) at high temperatures (to 1500°C).

4. Fine-grain parts of CaO exhibited unsatisfactory thermal stability under sharp temperature oscillations during testing.

5. Parts from CaO are recommended for service at high temperatures under conditions of alkaline-metal vapor action and the action of liquid metals in the absence of sharp temperature shocks as well as CO_2 and H_2O .

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