Magazine of Civil Engineering

ISSN 2712-8172

journal homepage: http://engstroy.spbstu.ru/

DOI: 10.34910/MCE.110.10

Belite-containing clinkers from phosphoric slags for refractory materials

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Keywords: phosphoric slag, carbide lime, belite clinker, refractory material

Abstract. The article studies the possibility of using phosphoric slag (PS) to obtain stabilized belite clinkers. It is shown that granulated PS as a silica-containing component of a cement raw mixture meets the demand of wide and effective use of production wastes. The complexity of using raw materials is increased with the use of carbide residue in the mixture that is a by-product of the synthetic rubber plant. The experimental data were obtained by chemical, optical, X-ray and thermal analysis methods. Chemical and mineralogical composition and materials properties have been studied before and after heat-treating. The optimal composition of belite clinkers has been selected. The physical and technical parameters of clinkers have been determined. A method for producing refractory products from belite-containing materials has been developed. Mathematical models to determine technological parameters for the refractory products manufacturing based on belite-containing clinkers have been composed.

1. Introduction

The research direction of the granulated phosphoric slags (PS) use as a basis for binding composites is considered in [1–2], where it is also emphasized that the entertainment volume of these slags for obtaining construction products does not exceed 30 % of those generated in production. It must be assumed that not all types of granulated PS can be used as active agents to cements, and for such slags any other areas of disposal should be found. The use of granulated PS as a silica-containing component, which completely replaces a clay one in the traditional Portland cement raw mixture, is proposed by different authors (A.N. Toropov, M.A. Bredig and etc.). It meets the requirements of a widespread use of production waste and by-products, complex production of cement with other industrial products. It is known that PS contain phosphoric anhydride and calcium fluoride's impurities. The first is a stabilizer of β-C_2S, and the second is an effective silication mineralizer. High-temperature phase equilibria in the 2CaO, SiO_2 – 3CaO, P_2O_5 system were studied in [3]. Taking into account the above circumstances and the great practical importance of refractory materials, it is of interest to obtain cement of belite composition.

Calcium orthosilicate – $2CaO{\cdot}SiO_2$ and its polymorphic forms have been studied by many scientists (Y.M. Butt, V.V. Timashev, H. Midgley, R. Nares, A.N. Toropov, M.A. Bredig and etc.). Belite synthesized in vitro is based on phosphogypsum [4–11]. Utilization of other wastes to obtain cements of belite composition [12–15] does not include phosphoric slags. The high melting point of C_2S has been known for a long time and, according to the latest data, it is 2130 °C [16]. The possibility of using a belite clinker as a refractory material was proved in [17]. The invention has not found any practical application. It does not contain any data on the optimal technological parameters of production. The results of systematic studies of orthosilicates as refractory materials show a high burning temperature of products and complexity of clinker charge. It seemed to us that these disadvantages could be eliminated, if we use the phosphoric slags as a silica-containing component in the C_2S synthesis. The PS advantages over other silica-containing materials are obvious: slags begin to come into the liquid phase at relatively low temperatures; they contain phosphorus, manganese and fluorine impurities, which stabilize high temperature modifications of C_2S and accelerate silicate formation processes.

Shaikezhan, A., Anuarova, A.D. Belite-containing clinkers from phosphoric slags for refractory materials. Magazine of Civil Engineering. 2022. 110(2). Article No. 11010. DOI: 10.34910/MCE.110.10

This is also confirmed by the studies from [18] in relation to the effects of the P_2O_5 and CaF_2 concentration on clinker with a high alite content.

The aim of the work is to find out the possibility of obtaining a stabilized belite refractory by replacing phosphoric slags known natural silica-containing materials in a cement raw mixture. For this it was necessary:

- to study the characteristics of phosphoric slag as a clay-replacing component of a cement raw mixture;
- to study new raw material mixtures for obtaining stabilized belite clinker;
- to determine the technological parameters for the manufacture of belite refractory.

2. Methods

Mixtures for producing belite-containing clinkers are composed of phosphoric slags and carbonates. In this research, we have used granulated phosphoric slags from the "Kazphosphat" LLP, which operates on the basis of phosphate raw materials from Karatau (the Republic of Kazakhstan). Limestone and carbide air-slaked lime were used as a lime component. The chemical composition of raw materials is shown in the Table 1.

Table 1. Chemical composition of raw materials, mass. %.

Material	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	P_2O_5	CaF_2	MnO	Loss of ignition	Amount
lime	3.51	53.30	1.09	0.62	0.13	–	–	–	–	42.10	100.75
carbide lime	2.74	62.03	1.94	0.40	0.19	0.23	–	–	–	31.59	99.12
phosphoric slag (I)	38.46	42.15	3.50	1.54	3.97	0.31	1.91	5.33	–	2.33	99.74
phosphoric slag (II)	40.20	42.16	2.27	1.91	4.56	0.03	2.02	5.03	0.28	1.02	99.48

The main slag components are calcium and silicon oxides. Its acidity index is 1.00. Under the microscope, the slag particles have a plane-limited fragmental shape with sharp corners and winding edges. The grain configuration is mostly wrong. The slag structure is X-ray amorphous. The IR spectrum is characterized by broad absorption bands in the range of 400–1500 cm^{-1}; two of them are intense with maxima at 500 and 1000 cm^{-1}, three of them are weak in the form of shoulders at 715, 1220, and 1430 cm^{-1} (Fig. 1, a). According to spectroscopic data, slag is a mixture of silicates of various structures, including both ortho (a rather wide frequency interval in the range of 850-1000 and 500 cm^{-1}) and more condensed forms (absorption with maxima at 715 and 1220 cm^{-1}) according N.I. Plyusnina**.** Absorption at 860 and 1430 cm^{-1} in the form of shoulders is due to vibrations of carbonate ion and indicates the presence of calcite impurity in the slag composition. After dissolution of the glass phase with 2 % citric acid in the fixed residue, there identified crystalline phases in the form of wollastonite (d = 4.04; 2.98; 2.70 and 2.54 Å) and quartz (d = 4.23; 3.34; 2.46 Å) (Fig. 2, a) using X-Ray. As for the IR spectrum of this precipitate (Fig. 2, b), in contrast to the slag spectrum, there appear bands in the form of shoulders at 565.600 cm^{-1} and a band of medium intensity at 805 cm^{-1}. The first ones are due to symmetric stretching vibrations γ_S Si – O – Si, the second indicates the presence of precipitated quartz according A.N. Lazarev.

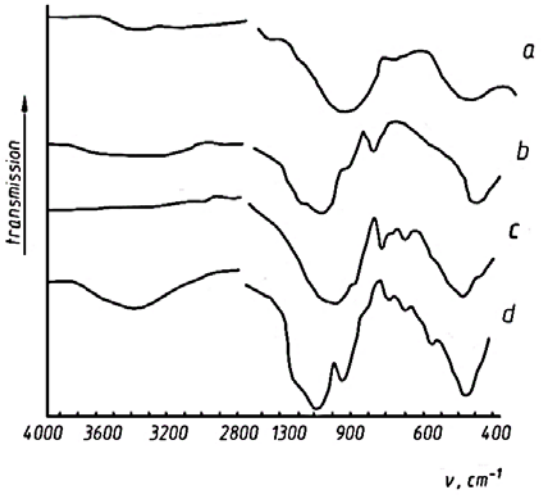


Figure 1. IR spectra of phosphoric slag: a – run-of-mine; b – after washing using citric acid; c – heat-treated at 850 °C – 0.5 h; d – heat-treated and washed with citric acid.

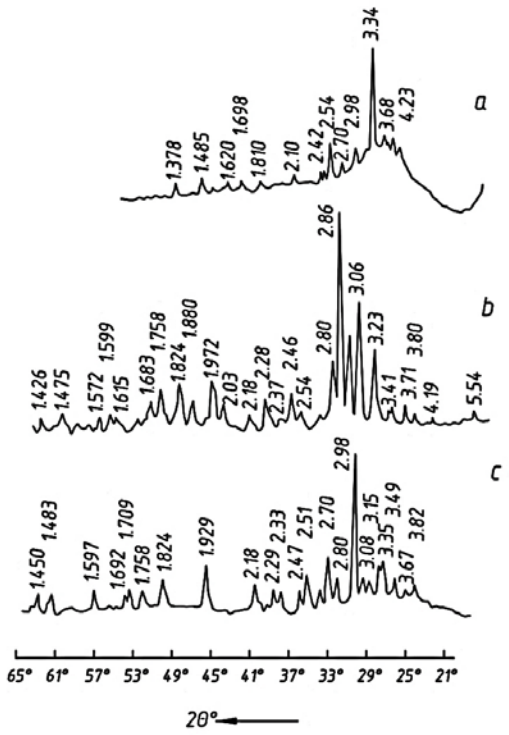


Figure 2. Slag X-ray photographs: a – washed with citric acid; b – heat-treated at 850 °C – 0.5 h; c – heat-treated and washed with citric acid.

Slag DTA curves (Fig. 3) are characterized with endoenergic effect at 680 °C which is due to pre-crystallization softening of the glass phase and the exothermic effect of crystallization of main phases at 850 °C. The crystallizing phases at this temperature are pseudo-wollastonite (d = 3.23; 2.80; 2.46; 1.972 and 1.824 Å), wollastonite (d = 2.96; 2.28 and 1.880 Å) and melilite (d = 3.06; 2.86; and 1.758 Å) (Fig. 2, b). The IR spectrum of the heat-treated slag (Fig. 1, c) is characterized by absorption bands in the range of 450 – 1200 cm^{-1}. In the range of 900 – 1100 cm^{-1}, there are stretching vibrations γ(Si – O) β- wollastonite. Its metasilicate chains [(SiO_3)] are characterized by absorption in the range of 560 – 680 cm^{-1}, caused by stretching vibrations of Si – O – Si (γS Si – O – Si) bridges. These vibrations include the bands at 560.650.680 cm^{-1}.

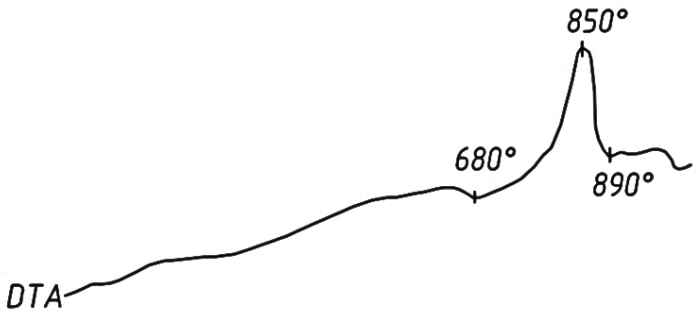


Figure 3. Slag DTA curves.

A characteristic feature of the α-wollastonite spectrum, which contains ring anions $[Si_3O_9]^{6-}$ in its structure, is a band at 725 cm^{-1}, which is due to the symmetric stretching vibration γS Si – O – Si. The absorption bands at 480 and 560 cm^{-1} refer to bending vibrations of the ring anion. The melilite identification using the IR spectrum is rather difficult, since the latter belongs to pyrosilicates containing aluminum as a cation capable to form a covalent links with oxygen. It leads to an increase in the vibration frequencies of Me – O, and makes it difficult to identify the γS Si – O – Si band, which is in the range 640 – 650 cm^{-1}. However, it can be assumed that the spectrum complexity in the region of 500 – 800 cm^{-1} does not exclude melilite presence in the heat-treated slag. But in the spectrum of heat-treated slag washed with citric acid (Fig. 1, d), the bands assigned to α-wollastonite disappear, and the absorption minimum at 1000 cm^{-1} observed in the spectrum of β-wollastonite is clearly revealed. X-ray data of this sediment (Fig. 1, c) also indicate the presence of hematite (d = 2.70; 2.51; and 1.824 Å) and fluorite (d = 3.15 and 1.929 Å). The phosphatic slag taken for these studies consists mainly of glass with a microheterogeneous structure. It contains pseudo-wollastonite, wollastonite, melilite, hematite and fluorine, which crystallizes as fluorite after

being heat-treated. Phosphorus is also a part of glass, since no independent phosphorus-containing phase was found. The slag crystalline phases are represented by wollastonite and quartz. Calcite is present as an impurity.

Limestone particles consist of irregular isometric tabular colorless grains. Well-formed rhombohedrons peculiar to calcite are rarely found. There can be twins too.

Carbide air-slaked lime is a waste product of the Karaganda Synthetic Rubber Plant. A real powder density is 2260 kg.m^3, specific surface is 677.0 m^2.kg. The powder is a mixture of hydroxide N_g = 1.560 ± 0.003; N_p = 1.550 ± 0.003. Calcite crystals have N_g = 1.658 ± 0.003 and N_p = 1.486 ± 0.003; intergrown pieces with a black or dark-brown opaque matter are often observed. The X-Ray shows reflexes at d = 4.85; 2.61; and 1.917 Å is related to portlandite, at d = 3.87; 3.01; and 2.28 Å – to calcite.

The chemical analysis of starting materials was carried out according to was carried out in accordance with the requirements of regulatory documents: Russian State Standard GOST 5382-91 (CIS interstate standard) 'Cements and materials for cement production. Chemical analysis methods'. Raw mixtures and phase composition of clinkers were calculated as described in the common method [19] according to a given value of the saturation coefficient (SC). Raw mixtures burning was carried out in a chamber electric resistance furnace CHO-3.2×6×2.5/15M1 with the U-shaped heaters made of molybdenum silicide with the CM 400/400 type operating in an oxidizing atmosphere. The accuracy of temperature maintenance in the working space is ± 0.5 % of the nominal temperature. Isothermal burning was carried out in a tubular furnace of the /SUOL-0.25.2.5/14k type. The amount of unreacted calcium oxide was determined by the alcohol-glycerate method according to Russian State Standard GOST 5382-91 (CIS interstate standard). The phase composition of clinkers was studied by X-ray, rational-chemical, microscopic, and spectroscopic analyzes.

Presence of wollastonite, cuspidin, fluorite, fluoro- and hydroxylapatites in the cakes was monitored by the X-ray phase analysis of precipitate after citric acid extraction. In this case, the solution passes through alite, belite, phosphates, silicophosphates and intermediate substances. The sintered materials in 2 % citric acid were processed according as per the method described in [20]. To establish the clinkers intermediate phases, we used the method according S.M. Royak and other authors, based on the complete solubility of di- and tricalcium silicates in a 5 % solution of boric acid.

In order to select the optimal compositions for determining physical and technical properties of refractory materials based on belite-containing materials, there were prepared raw materials with SC = 0.60 – 0.85 with an interval of 0.05. To determine refractory some samples were molded from the mixture in the form of cylinders with the following dimensions: ø 5 cm and h = 0.5 cm, for apparent density and porosity – ø 5 cm and h = 5 cm. The burning temperature of materials for determining refractory was 1350 °C with a dwell time of 2 hours, for apparent strength and porosity – 1350 – 1500 °C with an interval of 50 °C without dwell. Cooling was abrupt. Clinkers refractory was determined according to Russian State Standard GOST R 53788-2010 (CIS interstate standard) 'Refractories and refractory raw materials. Methods of refractoriness determination', density and porosity – according to Russian State Standard GOST 2409-2014 (CIS interstate standard) 'Refractories. Method for determination of bulk density, apparent and true porosity, water absorption'. The SC for optimal clinkers was 0.70 and 0.75. A belite clinker is burnt at 1350 – 1400 °C. The rate of temperature rise was 12 – 26 deg.h. Cooling was slow as the oven cools down. The resulting clinkers were crushed using jaw crushers and divided into fractions with the following sizes: coarse 1 – 3 mm, average 0.5 – 1 mm, average 0.5 – 1 mm, fine < 0.5 mm.

When selecting the optimal parameters of the refractories technology from belite-containing materials, the method of mathematical planning of a four-factor experiment at five levels was used. Accordingly, cylinders ø 5 cm and h = 5 cm were molded. The average rate of temperature rise during burning was 8 – 21 deg.h. Sample cooling was abrupt. For certain values of apparent porosity and density using generalized equations, the technological parameters for obtaining refractories were selected.

3. Results and Discussion

There were investigated mixtures of $CaCO_3$ ("h") and granulated PS with the contents (wt. %) 42.53 and 57.47, respectively. Limestone decarbonization at 1000 °C is completed in 15 minutes, and at 1100 and 1200 °C – in 5 minutes. At the last two temperatures, calcium oxide reacts completely in 15 and 10 minutes. The reaction rate is high at the beginning of heating. After 15 minutes it significantly slows down at 1000 °C.

The final product consists almost 90 % of C_2S, which is represented by the β-modification. At 1200 °C, starting from 5 min, the C_2S part is stabilized in the α′ – form. In the X-ray radiograph 4 d = 2.66; 2.22; 1.920 Å belongs to α′ – C_2S; d = 2.93; 1.60; 1.41 Å – C_5A_3. The rest are β – C_2S reflections.

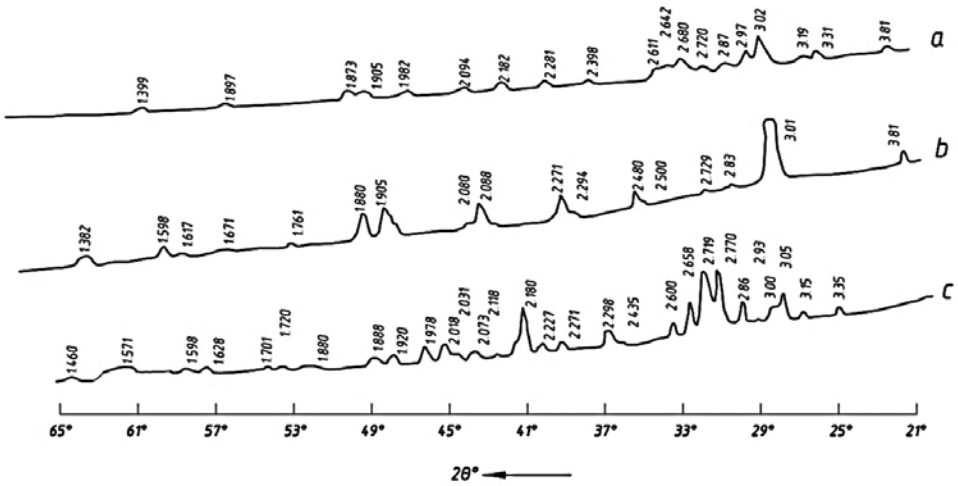


Figure 4. X-ray radiograph of spectra: a – 1000, 5 min; b – 1100, 1 min; c – 25 min.

The mixture was burnt at 1000 – 1200 °C in order to clarify the effect of burning duration on the crystallization of phases. Belite crystals grow from 2 – 4 (1000 °C, 30 min) and 10 min (1200 °C, 30 min) to 5 – 6 and 15 μm after 60 minutes. They form intergrown pieces. After burning at 1200 °C, polysynthetic twins are often found. There were observed rounded isotropic grains from the impurities with a relatively low index of refringence (obviously, $C_{11}A_7 \cdot CaF_2$). When treating the cake with 2 % citric acid, P_2O_5 completely goes into solution in the same way as $C_{11}A_7 \cdot CaF_2$ and C_4AF. Only half of the total amount of fluorite remains in the insoluble part with a trace impurity of periclase. Thus, a mixture of slags with $CaCO_3$ to obtain a belite clinker should be burnt at 1100 °C.

To study the features of high-temperature interaction of phosphoric slags with calcium oxide in carbide air-slaked lime. The mixture is composed of 38.40 % lime and 61.60 % granulated slag. The chemical and phase composition of clinker is shown in the Tables 2 and 3.

Table 2. Chemical composition of clinkers with SC = 0.67, % by weight.

Material	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Mn_2O_3	P_2O_5	CaF_2	SO_3	Amount
clinker	29.49	58.00	2.43	1.62	3.29	0.19	1.42	3.54	0.12	100

Table 3. Phase composition of clinkers.

$2CaO \cdot SiO_2$	$3CaO \cdot 2SiO_2 \cdot CaF_2$	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	$12CaO \cdot 7Al_2O_3$	$3CaO \cdot P_2O_5$	MgO
68.9	16.6:	4.6	2.8	3.1	3.3

In order to select the optimal composition and establish the burning temperature of belite clinkers for obtaining refractory materials, 6 mixtures were made with SC from 0.60 to 0.85. The data on the mixtures composition are shown in the Tables 4 and 5.

The mixtures were burnt under isothermal conditions at 1100, 1200, and 1300 °C with a dwell time of 30 min. The silicate-forming reaction completion was controlled by the degree of absorption of calcium oxide (Table 6).

As shown in the Table 6, in samples with SC = 0.60 – 0.70 (clinker 1 – 3), a complete absorption of lime occurs at 1100 °C with a dwell time of 30 minutes. The completion of silicate-forming reaction was controlled by the degree of recovery of calcium oxide (Table 6).

As shown in the Table 6, in samples with SC = 0.60 – 0.70 (clinker 1 – 3) a complete absorption of lime occurs at 1100 °C. With increasing SC starting from 0.75, the calcium oxide is not completely absorbed as a result of tricalcium silicate formation from excess calcium oxide and dicalcium silicate.

As it can be seen from the data in Table 6, in samples with SE (saturation efficiency) = 0.67 – 0.70 (clinker 1 – 3), complete assimilation of lime occurs at 1100 °C. With an increase in SE, starting from 0.75, calcium oxide is insufficiently absorbed because of the formation of tricalcium silicate from excess calcium oxide and dicalcium silicate.

Table 6. Composition of free calcium oxide in burnt samples, weight %.

Temperature, C	Clinker					
	1	2	3	4	5	6
1100	no	no	0.86	4.35	9.36	12.29
1200			no	2.21	3.86	4.75
1300				2.17	2.41	3.13

On the DTA curve of the belite mixture, the effect (Fig. 5) at 515 °C is caused by the dehydration of $Ca(OH)_2$. Effects observed in the temperature range 805 – 898 °C, due to decarbonization of $CaCO_3$. The first stage of the process characterizes the kinetic stage of decomposition, the rate of which is determined by the energy of formation and crystallization of CaO [21]. The second and third stages (878 and 898 °C) are diffusion stages, the rate of which depends on the thickness of the CaO shell and neoplasms. The exothermic effect at 1042 °C corresponds to the formation of C_2S. With further heating of the mixture, liquid phases appear (endo-effects at 1120 and 1142 °C), which is confirmed by the appearance of exothermic effects at 1135 and 1042 °C during cooling.

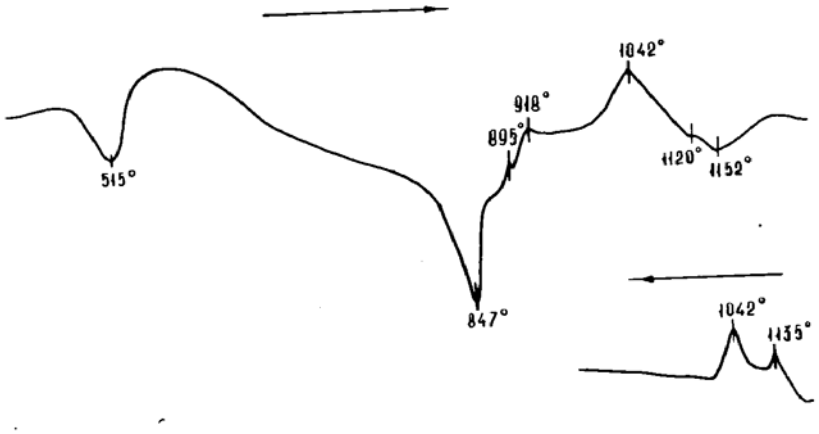


Figure 5. Thermogram of the belite mixture.

Consequently, in the mixture under study, the formation of a liquid phase occurs at a temperature that is much lower than the minimum temperature of the appearance of a clinker melt from a traditional raw mixture, which corresponds to 1280 °C [22–23]. The high reactivity of cement raw mixtures is due to the low softening temperature of phosphoric slags (1050 – 1100 °C) and CaF_2 impurities in them (3 – 6 %). CaF_2 catalyzes belite formation according to the mechanisms previously established by Gatt [24].

The burnt products phase composition was defined by X-ray. The main component of all samples is dicalcium silicate (Fig. 6). Presence of tricalcium silicate in the clinker 3 is confirmed by a reflex at 3.05 Å. With increasing the C_3S content in the samples, another line appears at 1.74 Å (clinker 5).

The X-ray picture analysis of borate extract residues (Fig. 7) shows that impurities are represented by magnesium oxide (d = 2.10; 1.480 Å), fluorite (d = 3.15; 1.937; 1.647 Å) and tetracalcium aluminoferrite (d = 7.23; 2.76; 2.64; 1.910 Å). In clinkers with the SC = 0.60 and 0.65 due to the lack of calcium oxide melilite (d = 2.86; 1.761 Å) and wollastonite (d = 2.97 Å) are found.

The calculated phase compositions of clinkers at 1300 °C are presented in the Table 7. The amount of dicalcium silicate at the maximum absorption of calcium oxide is 49 – 82 %. With increasing the SC, the dicalcium silicate content decreases due to the formation of tricalcium silicate, which number in the 5 clinker reaches 31 %. Silicates amount is about 80 %.

To determine the physical and technical parameters of clinkers 1 – 5, the tablets were molded and burnt at 1350 °C. In the clinkers 1 – 3, calcium oxide is completely absorbed, in the clinkers 4 and 5, the amount of unreacted calcium oxide is 0.40 and 0.82 %.

According to definitions of the “St. Petersburg Institute of Refractories” JSC, the clinkers 1 and 2 have a refractory below 1580 °C, the clinkers 3 – 5 – above 1770 °C. The Table 8 shows that with increasing clinkers’ SC, their burning shrinkage and apparent porosity decrease, but water absorption increases. The apparent porosity of the clinker 4 is 26 – 23 %, the clinker 5 is 40 – 35 %. Water absorption of the clinker 4 and 5, respectively, is 7-10 and 20 – 16 %. The clinkers apparent density at 1300 – 1350 °C is in the range of 200 – 250 $kg.m^3$.

Thus, it has been identified that the clinkers 1 and 2 have low refractory, and the clinker 5 has a relatively high apparent porosity and water absorption. Taking into account these data, clinkers with saturation coefficients 0.70 and 0.75 were selected to determine the possibility of obtaining a refractory material.

Table 4. Component and chemical composition of raw mixtures.

Mixture	Component composition, wt.%		100 % oxides composition									
	lime	slag	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	CaF_2	P_2O_5	MnO	SO_3	LOI
1	38.84	61.16	24.94	46.39	2.57	1.18	2.48	3.27	1.17	0.15	0.19	17.66
2	42.23	56.77	23.39	46.86	2.46	1.14	2.31	3.03	1.09	0.14	0.18	19.40
3	47.12	52.88	22.03	47.27	2.36	1.11	2.17	2.82	1.02	0.13	0.16	20.93
4	50.58	49.42	20.82	47.64	2.28	1.07	2.03	2.64	0.95	0.12	0.15	22.30
5	53.68	46.32	19.73	47.94	2.21	1.05	1.91	2.47	0.89	0.11	0.14	23.52
6	56.47	43.53	18.75	48.27	2.14	1.02	1.81	2.32	0.84	0.10	0.13	24.62

Table 5. Excepted phase composition and clinkers characteristic.

Clinker	C_3S	C_2S	CS	C_4AF	$C_{12}A_7$	CaF_2	MgO	SC	n	p
1	-	73.53	9.13	4.37	4.26	3.97	3.02	0.60	6.65	2.17
2	-	82.89	0.38	4.31	4.16	3.76	2.87	0.65	6.49	2.15
3	15.58	68.13	-	4.25	4.07	3.57	2.74	0.70	6.35	2.14
4	30.21	54.03	-	4.21	3.98	3.40	2.62	0.75	6.20	2.12
5	43.75	40.97	-	4.16	3.90	3.23	2.50	0.80	6.06	2.16
6	56.30	28.86	-	4.11	3.82	3.08	2.40	0.85	5.94	2.10

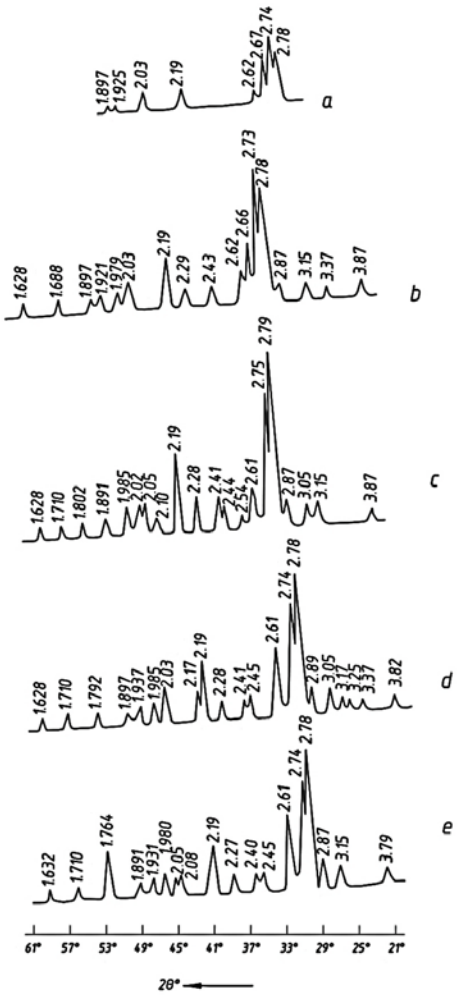


Figure 6. Clinkers X-ray photographs burnt at 1300 °C with a dwell time of 30 min a, b, c, d, e, respectively, clinkers 1, 2, 3, 4 and 5.

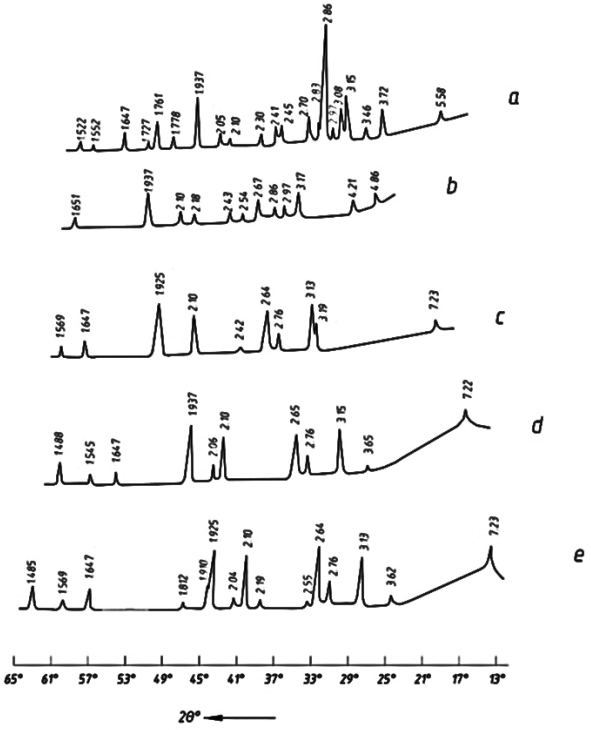


Figure 7. X-ray photographs of clinkers' borate extract residues a, b, c, d, e, respectively, clinkers 1, 2, 3, 4 and 5.

Table 7. Phase composition of clinkers.

Clinker	Phases content, wt.%							
	$CaO_{fr.}$	CS	C_2S	C_3S	C_4AF	$C_{12}A_7$	CaF_2	MgO
1	no	3.98	81.25	no	5.50	2.70	3.30	3.20
2	no	1.37	82.52	no	5.87	2.65	4.15	4.15
3	no	no	65.88	15.66	4.89	2.97	4.34	4.34
4	2.17	no	69.57	10.31	8.21	1.64	2.74	4.67
5	2.41	no	49.18	30.79	5.93	2.33	3.03	4.61

As our research shows, granulated phosphoric slag is an exceptional material that provides synthesis of a belite clinker (C2S ≈ 90 %) at 1100 °C in 15 minutes. Kinetics of the C_2S formation at 1000 and 1100 °C is satisfactorily described (Fig. 8) by the Tamman-Fishbeck equation. The apparent activation energy is 88 kJ.mol.

Table 8. Physical and technical indicators of clinkers.

Clinker	Clinker SC	Burning temperature, °C						
		1350				1400		
		volume burning shrinkage, %	apparent density, kg.m^3	apparent porosity, %	water absorption, %	volume burning shrinkage, %	apparent density, kg.m^3	apparent porosity, %
1	2	3	4	5	6	7	8	9
3	0.70	32.7	1480	2.49	5.93	35.2	1220	2.45
4	0.75	31.5	2370	2.44	9.66	35.1	1810	2.45
5	0.80	25.8	3710	2.04	18.02	20.3	3960	1.97

Continuation Table 8.

Burning temperature, °C								
1400		1450				1500		
water absorption, %	volume burning shrinkage, %	apparent density, kg.m^3	apparent porosity, %	water absorption, %	volume burning shrinkage, %	apparent density, kg.m^3	apparent porosity, %	water absorption, %
10	11	12	13	14	15	16	17	18
4.93	33.4	1940	2.56	7.53	34.9	1480	2.37	6.22
7.79	37.6	2620	2.42	10.71	38.2	2370	2.37	9.95
19.96	26.7	3680	2.16	16.86	30.7	3520	2.11	16.59

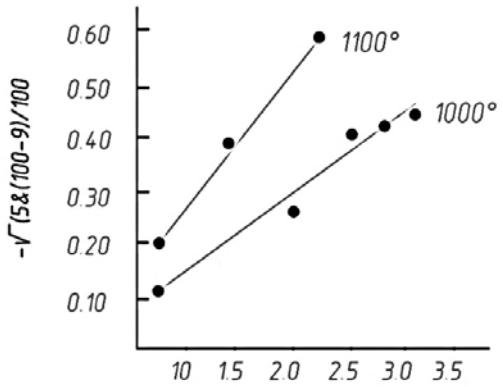


Figure 8. Kinetic data of the C_2S formation reaction.

The high reacting capacity of granulated phosphoric slags is explained by their low softening point (1050 – 1100 °C) and the presence of calcium fluoride which is evenly distributed up to 6 %. The latter has a strong catalytic effect on the C_2S formation.

Carbide lime, mainly consisting of $Ca(OH)_2$ and having a developed specific surface area reduces the burning temperature up to 950 – 1000 °C. In this case, the value of the apparent activation energy decreases up to 44 kJ.mol. A belite clinker is represented by a dicalcium silicate. Secondary phases: C_4AF, $C_{12}A_7$, MgO, and CaF_2. These phases are formed from the CS, melilite and cuspidin at the moment of their initiation or after crystallization according to the reactions:

$$CaO \cdot SiO_2 + CaO = 2CaO \cdot SiO_2 \quad (1)$$

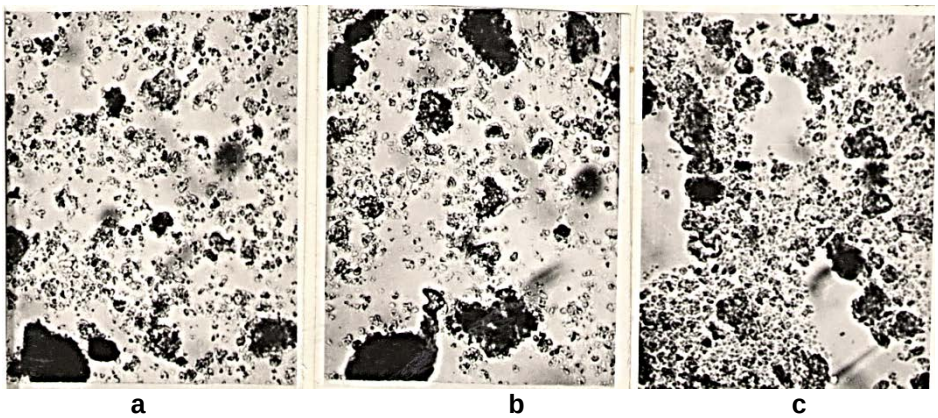
$$3CaO \cdot 2SiO_2 \cdot CaF_2 + CaO = 2(2CaO \cdot SiO_2) + CaF_2 \quad (2)$$

$$7(2CaO \cdot Al_2O_3\ SiO_2 + 12CaO = 7(2CaO \cdot SiO_2) + 12CaO\ 7Al_2O_3 \quad (3)$$

$$2CaO \cdot MgO\ 2SiO_2 + 2CaO = 2(2CaO \cdot SiO_2) + MgO \quad (4)$$

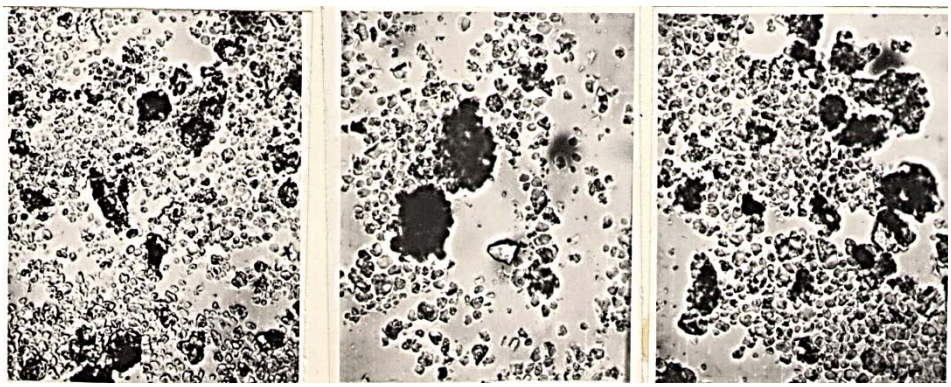
With a lack of CaO or incomplete burning processes, wollastonite, melilite and cuspidin are observed in the reaction mixture along with the reaction products. Fluorine does not evaporate. From a stoichiometric mixture with a single burning, the Nares solid solution characterized by the composition: CaO – 66.5 %, SiO_2.- 26.5 % b P_2O_5 – 7 % according to R.W. Nurse is formed at 1500 °C after 60 minutes. At 1200 °C, the degree of calcium oxide absorption in 30 minutes is 49 % in a mixture of pure reagents and 85 % when SiO_2 is replaced by granulated PS. In the belite clinker, C_2S is in the β-form. After burning at 1200 °C, α′ – C_2S also appears.

Microscopic immersion studies show that belite crystals grow with increasing temperature and firing duration (Fig. 9 and 10). After 1200 and 1000 °C, 30 minutes they have dimensions, accordingly, 10 and 2 – 4 microns, and after 60 minutes – 15 and 5 – 6 microns. Crystals form intergrowths. In cakes fired at 1200℃, polysynthetic twins of belite are often found. C_5A_3 is represented by isotropic grains of a rounded shape and relatively low refractive index.



a **b** **c**

Figure 9. Micrograph of the mixture for dicalcium silicate at 100 °C x 240, N II: a – 30 minutes; b – 60 minutes; c – 120 minutes.



a b c

Figure 10. Micrograph of the mixture for dicalcium silicate at 1200 °C x 240, N II: a – 30 minutes; b – 60 minutes; c – 120 minutes.

For two years, the samples did not show any signs of silicate decomposition. The resistance to silicate degradation does not deteriorate with an increased CaF_2 content, but the reaction rate of the C_2S formation is increased.

When developing a method for refractories producing from belite-containing materials, the effect of grain size composition of clinkers, the samples pressing pressure, the burning temperature and the dwell time were studied. By means of the mathematical planning method of experiment the dependences of apparent porosity and density on these factors were found. The maximum density is achieved with the following ratio of the fraction, wt.%: fine – 70 %, coarse – 25 %, average – 5 %, which is consistent with the literature data. With an increase in the pressing pressure and burning temperature, the refractories density increases proportionally. Sintering occurs due to the formation of a binder from low-melting compounds. The partial dependences of density from dwell time are exponential: when the dwell time increases up to 120 min, the density increases insignificantly, and then practically is not changed.

Compared to density, the porosity dependence on the studied factors is inverse. In the same fraction ratios, the samples have the minimum porosity due to the maximum packing density of grains. As the pressing pressure and burning temperature increase, the porosity decreases. It corresponds to the statement that during heat-treating the grains size and shape increase, and the pores decrease as a result of filling them with a low-melting binder. The samples dwell time in the oven for more than 120 min does not lead to a noticeable change in density and porosity.

Generalized equations of the response function are obtained on the basis of partial functions:

for belite clinker with SC = 0.75, a) density

$$\rho = \frac{\left(-0.000028X_1^2 + 0.003826X_1 + 2.24946\right)\left(2.237 + 0.009\lg X_2\right)}{12.81\left(1.964 + 0.89\lg X_3\right)^{-1}\left(1 - e^{-0.022652X_4{}^{0.010654}}\right)^{-1}},$$

$$R = 0.87,\ t_R = 16.4 > 2.$$

b) apparent porosity

$$P_0 = \frac{\left(0.000563X_1^2 - 0.08306X_1 + 30.1919\left(31.495 - 0.3\lg X_2\right)\right)}{21787.77\left(43.208 - 36.18\lg X_3\right)^{-1}\left(1 - e^{-0.423128X_4{}^{-0.058842}}\right)^{-1}},$$

$$R = 0.87,\ t_R = 16.4 > 2.$$

for belite clinker with SC = 0.70, a) density

$$\rho = \frac{\left(-0.0000354X_1^2 + 0.005096X_1 + 2.21972\right)\left(2.251 + 0.05\lg X_2\right)}{12.747\left(1.794 + 1.28\lg X_3\right)^{-1}\left(1 - e^{-0.02312026X_4{}^{0.005171}}\right)^{-1}},$$

$$R = 0.97,\ t_R = 85.41 > 2.$$

b) apparent porosity

$$P_0 = \frac{\left(0.001288X_1^2 - 0.1633X_1 + 31.6574\left(30.138 - 0.20\lg X_2\right)\right)}{21313.83\left(53.916 - 62.01\lg X_3\right)^{-1}\left(1 - e^{-0.377133X_4{}^{-0.034356}}\right)^{-1}},$$

$$R = 0.81,\ t_R = 10.57 > 2.$$

To obtain refractories with high performance indicators such as mechanical strength, slag resistance, and etc., it is necessary to achieve a low apparent porosity of products with their high apparent density.

In the considered interval, the following levels of factors may be most appropriate:

1. Size composition. The maximum packing density is achieved with 70 % fine, 25 % coarse and 5 % average fractions. But in view of high energy costs required for fine grinding of a large amount of material the following fractions ratio is recommended: fine – 25 %, coarse – 70 % and average – 5 %. With a given grain composition, the porosity value is 2–4 % higher than in the first size composition.

2. Molding pressure. The highest raw material density is provided by the pressure of 80 – 100 MPa.

3. Burning temperature. To ensure the best sintering, it is recommended burning at a maximum temperature of 1450 °C out of the studied ones.

4. Extract. Since the process reaches saturation in 120 minutes, from the point of view of saving energy resources and achieving the maximum density of refractories the burning time can be limited to two hours.

The selected values of technological process were substituted into the response function equations. The results are shown in the Table 9.

Table 9. Rating values of optimization settings.

Belite clinker	Optimization settings	
	ρ, g.cm^3	P_0, %
SC = 0.75	2.49	23.05
SC = 0.70	2.47	22.82

As the table shows, the obtained porosity values are in the range of 7 – 23 %, which meets the regulatory requirements for refractories. The obtained density values are far from the maximum possible. The bulk density by the phase composition is 3.23 g.cm^3.

The melting temperatures range of the main crystalline phases is above the studied region, where only solid-phase reactions and sintering occur due to melting of low-melting phases. Achieving the values of apparent density of refractories close to the maximum is impossible in this area.

Belite clinkers were tested to obtain refractory products, which were characterized by the following indicators: apparent porosity 23–25 %; volume burning shrinkage – up to 10 %; strength in compression – 50 MPa; refractory – above 1770 °C; after shrinkage at 1550 °C – 1.3 ÷ 1.4 %; temperature of the deformation beginning under of load of 2 kp.cm^2 – circa 1400℃; thermal stability – 3–4 water thermal cycling. These data refer to the products obtained by semi-dry molding under a pressure of 80-100 MPa of a size composition burden:

fraction	5-1 mm	80-70 %
	1-0.08 mm	10-15 %
	no greater than 0.08 mm	10-15 %

Mixing moisture content is 10 %. Burning temperature is 1350–1400 °C.

In compliance with the physical and technical indicators of the specified clause 7, belite clinkers were tested to obtain refractory products, which were characterized by the following indicators: apparent porosity 23–25 %; volumetric fire shrinkage – up to 10 %; compressive strength – 50 MPa; fire resistance – above 1770 °C; additional shrinkage at 1550 °C – 1.3 ÷ 1.4 %; the temperature of the onset of deformation under a load of 2 kgf.cm^2 is about 1400 °C; heat resistance – 3–4 water heat cycles.

4. Conclusions

1. The experiments setting up to study the possibility for obtaining a stabilized belite refractory by replacing with phosphoric slags the known natural silica-containing materials in a cement raw mixture has been proved. Both limestone and air-slaked lime were used as the second ingredient of burden.

2. It is shown that granulated phosphoric slag is mainly represented by a pseudo-wollastonite glass. The slag crystalline phases are represented by wollastonite and quartz.

3. Thermal transformations in phosphoric slags and clinker formation processes in the phosphoric slags mixtures with lime-containing components have been studied. The processes of chemical property and kinetics have been described. The parameters for refractory materials obtaining have been determined.

4. Belite clinkers with SC = 0.60–0.85 have been investigated. Clinkers with SC = 0.70 and 0.75 with a burning temperature of 1350–1400 °C are optimal for obtaining refractories.

5. To determine the technological parameters for refractories production based on belite-containing clinkers, a mathematical model has been drawn up. Apparent density and apparent porosity have been selected as optimization parameters, and the factors have been selected as size composition, molding pressure, burning temperature and holding.

6. To obtain refractories with the best physical and technical characteristics, it is necessary to use a raw mixture with 25 % of fine fraction (less than 0.5 mm), 5 % of average – (1–0.5 mm) and 70 % of coarse – (3–1 mm), to apply a molding pressure of 100 MPa, and to burn at a temperature of 1450 °C.

7. Based on experimental data and a mathematical model, a refractory made of belite-containing clinkers with the following calculated physical and technical parameters is proposed: with SC = 0.70 – P_0 = 22.82 %, ρ = 2.47 g.cm^3; with SC = 0.75 – P_0 = 23.05 %, ρ = 2.49 g.cm^3. Belite clinkers were tested to produce refractory products, which confirmed the research results.

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Received 22.10.2020. Approved after reviewing 26.04.2021. Accepted 30.04.2021.