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Study of the possibility of using tephritic basalt and lead slag as a substitute for clay and iron-containing components during clinker firing in the production of composite Portland cement

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Abstract Four series of experiments were carried out to study the possibility of replacing clay and an iron-containing component with tephritic basalt and lead slag as part of the initial charge for Portland cement. The experiments were carried out at atmospheric pressure and a temperature of 135[illegible]C. It is shown that the replacement of clay and an iron-containing component with tephritic bazalt and lead slag as part of the initial charge in the cement industry will lead to a decrease in temperature by 100 ° C in the technological scheme of production and a reduction in energy consumption, since the theoretical specific consumption of raw materials is 1.481 t/t of clinker, which is about 70 kg lower than in traditional mixtures. The content of non-traditional components in total is 24.69%. In addition, tephritic basalts improve clinker formation processes, contribute to a decrease in the firing temperature and intensify the clinker firing process. A small amount of lead slag (5.06%) introduced into the mixture changes the structure of the clinker and improves the process of mineral formation, as well as improves roasting. The strength of the experimental composite cements was tested after 7 and 28 days on small samples measuring 2x2x2 cm. The physicomechanical characteristics and structure of composite cements were studied.

Keywords: industrial and technogenic waste; non-ferrous metals; environmental pollution; tefritobasalt; lead slag; clinker; composite materials; genesis; Portland cement.

1. Introduction

The main raw materials in the production of cement are carbonate and clay rocks, as well as some types of industrial and technogenic waste [1-10]. Due to the depletion of stocks of high-quality traditional raw materials, in the future, the maximum use of industrial man-made waste and the search for new types of raw materials that can be used in the production of Portland cement are required [11-19].

Igneous rocks such as basalts, tefritobasalts, etc. are non-traditional materials and industrial wastes that allow reducing energy costs during the firing of cement clinker. It is also possible to completely replace the traditional clay component with coal mining waste from coal mines.

Studies on the use of basalts, tefritobasalts, lead slags and coal mining waste in the production of Portland cement as a raw material were carried out [2, 20-27]. In the technological cycle for the production of Portland cement clinker, the possibility of replacing clay with basalt as the main source of aluminosilicate substance was shown. According to the results of physical and mechanical tests, the strength of cement obtained using basalt raw materials is not lower than conventional cement. The resulting clinker consists mainly of alite, belite, tricalcium aluminate and ferrite. The effectiveness of using basalts to reduce the melting temperature of the mixture and accelerate the process of clinker formation by 60–100°C was also shown [28-34].

In the possibility of using basalts as an additional cementing material in the composition of cement for wells was shown [35-41].

The use of technogenic raw materials leads to significant changes in the content of heavy metals in clinker. This applies mainly to zinc, lead and nickel. In studies focused on the effect of zinc on the sintering process. It has been established that even the first percent of the Zn content causes a decrease in the content of tricalcium aluminate in the clinker. The alloyed cements were at least as reactive as the reference cement [42-45].

The purpose of our research is to study the possibility of using tefritobasalt and lead slag as a substitute for clay and iron-containing components during clinker firing in the production of Portland cement.

2. Materials and research methods

To achieve the set goals, we studied the chemical and mineral composition of raw materials and the clinker obtained from them. Scanning (raster) electron microscopic analysis of raw materials and baked clinkers was performed in the laboratory of local methods for studying substances at the Department of Petrology and Volcanology, Faculty of Geology, M.V. Lomonosov Moscow State University using an energy dispersive spectrometer (EDS) INCA-Energy 350 based on a JEOL JSM-6480LV microscope.

The content of micro components in the initial material and products of the experiment was measured by the ICP-MS method at the Department of Geochemistry, M.V. Lomonosov Moscow State University. Samples for analysis were prepared by sintering with sodium carbonate. 0.1 g sample was mixed with 0.3 g anhydrous sodium carbonate (Merck, Suprapur®) in an agate mortar and transferred to a corundum crucible. Sintering was carried out at 800°C for an hour in a muffle furnace. The resulting sintered pellets were treated with 5 ml of HNO_3:HCl:HF 10:2:1 and after dissolution diluted to 50 ml with deionized water (EasyPure®). For measurement, the solution was diluted with 3% nitric acid. The sintering method was tested and compared with multi-acid microwave decomposition of several standard samples [21].

The measurements were carried out on a high resolution mass spectrometer with ionization in inductively coupled plasma Thermo Element-2. Separation of ions is carried out by an analyzer with double focusing - magnetic and electrostatic modes. The ions were detected by an electron multiplier, which remained linear in the range from 1 to $1 \cdot 10^{10}$ ions

per second. Calibration of the sensitivity of the instrument over the entire mass scale was carried out using reference 68-element solutions (ICP-MS-68A, HPS, solution A and B), which included all analyzed elements in the samples. To control the quality of measurements and take into account the drift of the sensitivity of the instrument, the analyzes of the samples were alternated with the analyzes of the reference sample with a frequency of 1:10. Indium at a concentration of 10 ppb was introduced into the samples as an internal standard. The analysis error ranged from 0.5 to 2 rel. %.

The X-ray diffraction data of the samples were obtained on a STOE-STADIMP powder diffract meter with a curved Ge (111) monochromatic providing strictly monochromatic Co $K_{\alpha 1}$-radiation. Data collection was carried out in the mode of stepwise overlapping of scanning areas from 6° to 90° by 2θ using a position-sensitive linear detector, the capture angle of which was 5° by 2θ with a channel width of 0.02°. The phase composition was determined using the software package WinXPowSoftware // STOE&CIEGmbH, 2000 and the Match! Software // CrystalImpactGbR, 2016 and their associated PDF-2 Powder Database (ICDD-2013).

1. Limestone of the Sastobe deposit

The deposit is located in the Tyulkubas district of the Turkestan region (Kazakhstan). Limestone reserves are about 70 million tons. The productive stratum is composed of limestones of the Tournaisian stage of Carboniferous age.

Table 1. The chemical composition of raw materials, waste and igneous rocks

Name	The chemical composition, mas. %															
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Cl	Cr_2O_3	ZnO	PbO	CuO	Loss of ignition	other	Total
Limestone	3,87	1,04	0,57	52,83	0,88	0,10	-	0,12	0,018	0,02	0,012	-	-	-	40,20	0,37	100,0
Tephrito basalt	45,54	10,70	8,53	10,66	6,95	0,20	4,04	2,50	0,91	0,017	0,007	-	-	-	5,37	4,57	100,0
Coal mining waste	55,50	10,60	2,01	3,21	0,70	0,79	-	2,35	0,38	-	-	-	-	-	24,08	0,38	100,0
Lead slag	25,94	6,44	37,25	14,71	6,15	0,04	1,24	1,36	0,35	0,006	0,063	4,34	0,52	0,94	0,65	-	100,0

The bedlike limestone deposit has a northwest strike and a steep dip to the southwest. Its length is 1200 m, width – 320 m, thickness – 670 m. Physical and mechanical properties of limestones in terms of bulk density - 2.68-2.75 g/cm^3, water absorption,% approximately 0.1-0.54%, loosening coefficient - 1.24, dry compression density is 475-940 kg/cm^2. Limestones of the Sastobe deposit of special molecular strength and frost resistance [22]. The X-ray of limestone is shown in Fig. 1

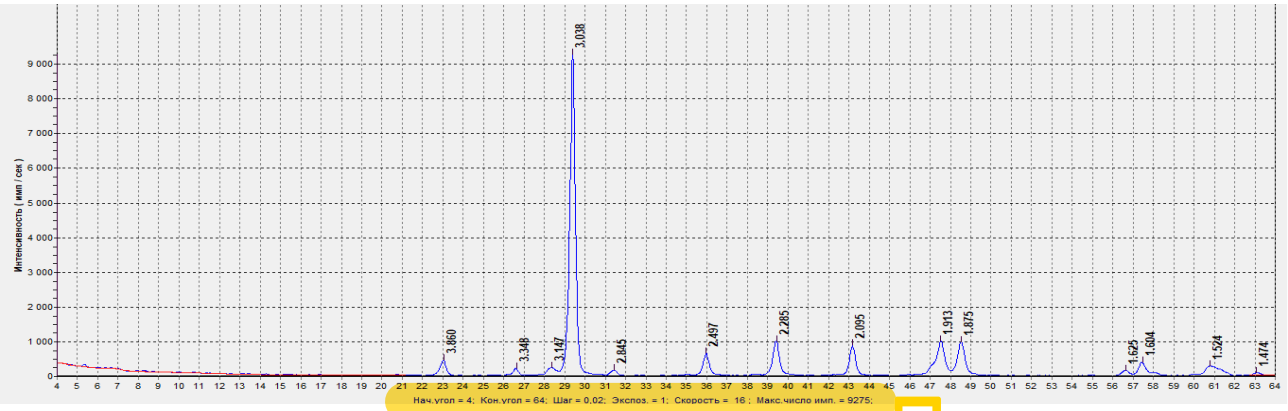


Figure. 1. X-ray of limestone

According to X-ray phase analysis, limestone consists mainly of calcite and quartz, diffraction maxima of calcite were noted on the diffraction pattern d=3.86; 3.03; 2.49; 2.28; 2.09; 1.91; 1.87; 1.60Å, quartz is also present d=3.34; 3.14; 2.84; 1.62; 1.52; 1.47Å. The content of oxides SiO_2, Al_2O_3 is low – 2.67 and 0.26 wt.%, respectively, the content of Fe_2O_3 is very low – 0.57 wt.%. The content of MgO is insignificant – 0.88 wt.%. The limestone is pure, highly basic, the content of CaO is more than 52 wt.%. The content of alkalis is within the normal range (less than 0.54 wt.%).

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2. Coal mining waste.

Coal mines are located in the city of Lenger, Turkestan region (Kazakhstan). More than 6 million tons of waste have been accumulated in the storage facilities. The repository occupies about 25 hectares of land [23, 24]. The X-ray of coal mining waste is shown in Figure 2.

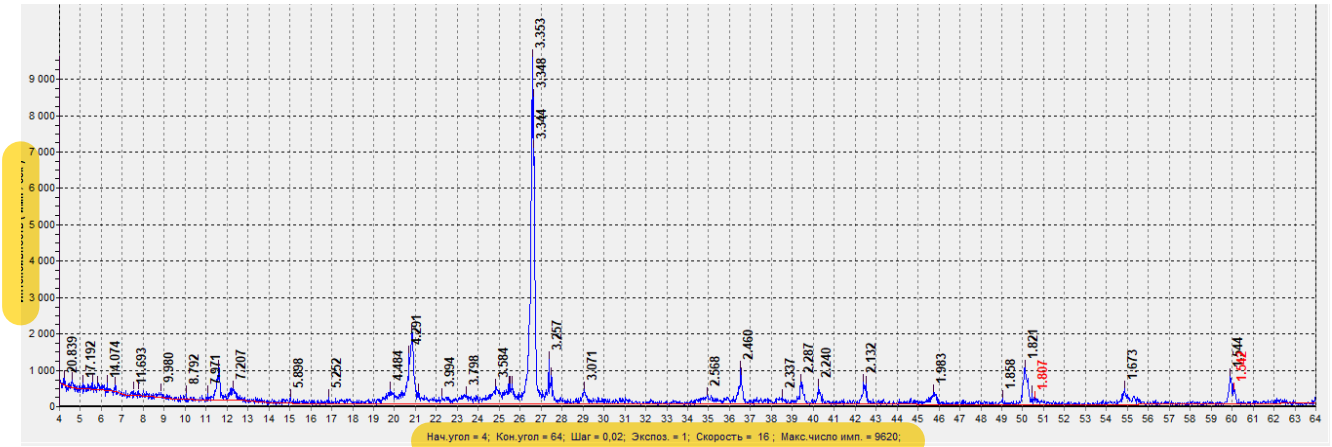


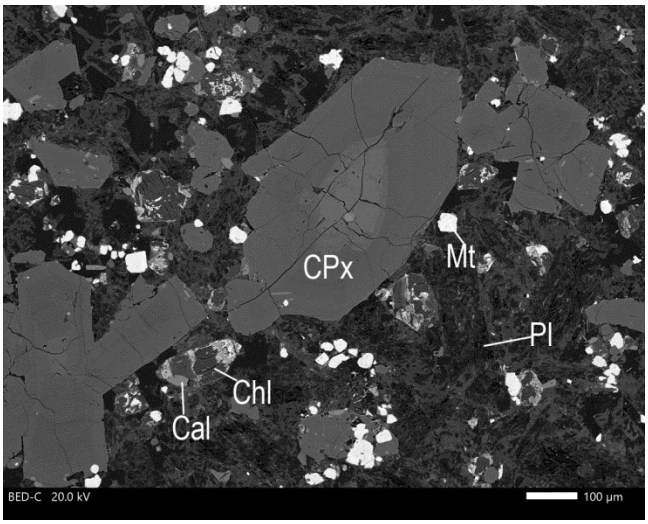
Figure 2. X-ray of coal mining waste

According to the results of X-ray phase analysis, coal mining wastes consist of kaolinite, gypsum, quartz and a small amount of illite. Diffraction maxima were recorded: quartz d=4.29; 3.35; 2.46; 2.28; 1.82; 1.54 Å. There are also minerals of gypsum dihydrate d=3.07; 2.24; 2.13; 1.85 Å, calcite d=2.28; 1.86; 1.60 Å, dolomite d=1.80; 1.54; 1.11 Å, clay minerals kaolinite d=7.207; 3.584; 1.673 Å, illite (hydromica) d=3.798; 3.257; 1.983 Å and carbon d=2.132; 2.568; 4.484 Å. The content of coal in the composition of coal mining waste is 15.23%. The content of silicon oxide is more than 55 wt.%, Al_2O_3 – 10.6 wt.%, the carbon

content in coal mining waste is more than 15 wt.%. They can replace the aluminosilicate component in the raw mix

3. Tefritobasalst.

The Daubaba deposit is located in the Tyulkubas district of the Turkestan region (Kazakhstan). The deposit of Daubaba tefritobasalts has an inclined northeast direction. The length of the deposit is 2200 m, the width is almost 1200 m, the thickness is from 13 to 70 m. The reserves of tefritobasalts are about 20 million tons. Tefritobasalts has a porphyritic structure (Figure 3).



Legend: CPx - clinopyroxene, Chl - chlorite, Cal - calcite, Mt - magnetite, Pl - plagioclase relic

Figure 3. Micrograph of tefritobasalts

Porphyritic phenocrysts are euhedral short-columnar grains of clinopyroxene. The composition of clinopyroxene corresponds to the isomorphic series diopside-hedenbergite. The grain size reaches 0.5 mm in length. They make up about 30% of the total volume of the breed. Phenocrysts also include relics of plagioclase grains replaced by an aggregate of secondary minerals. The predominant secondary mineral is zeolite (analcime). The relics have elongated prismatic outlines. Their size is 0.5-1 mm in length and about 0.1 mm in width. The content in the breed is approximately 15%. Plagioclase is almost completely replaced. The exact composition of the original mineral cannot be determined.

The sample contains isometric grains of magnetite ranging in size from hundredths of a millimeter to ≈0.2 mm. It contains impurities of Al, Mn, V, Si, Cr, Zn. The amount of magnetite in the rock does not exceed 15%. Small, up to 0.1 mm in size, grains of chlorite, calcite, alkali feldspar, and apatite were also found. Their total content does not exceed 15%. The X-ray of tefritobasalt is shown in Figure. 4.

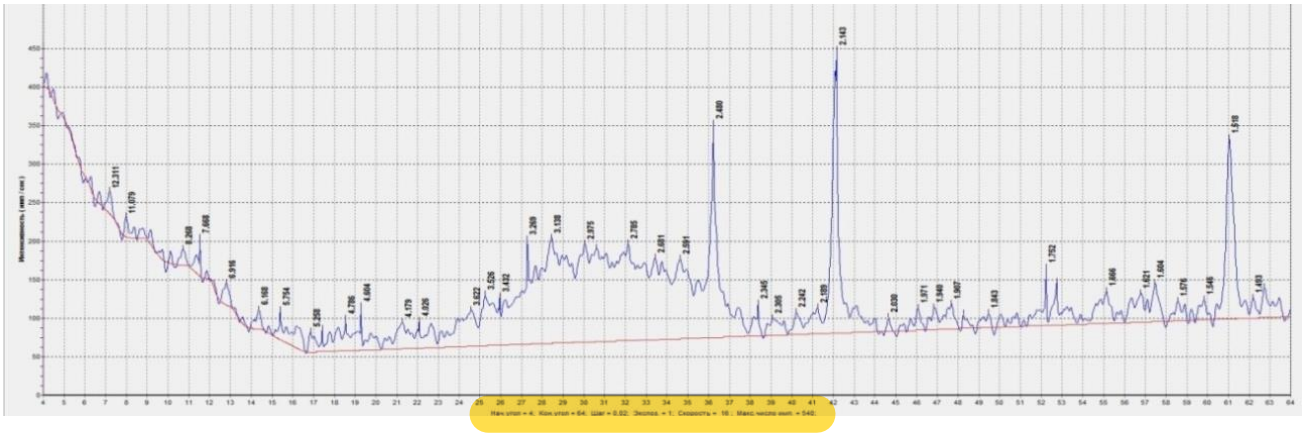


Figure 4. X-ray diffraction pattern of tefritobasalt from the Daubaba deposit

The diffraction peaks of the following minerals were noted on the X-ray pattern of tephritobassalt: pyroxene d=3.62; 3.26; 2.78; 2.30; 2.19; 1.97; 1.94 Å; plagioclase d=4.02; 3.43; 2.68; 2.59; 2.14 Å; biotite d=4.78; 4.60; 3.52; 1.66; 1.60; 1.54 Å; anorthite d=4.17; 3.13; 2.24; 1.90; 1.84; 1.51 Å; olivine d=2.97; 2.48; 2.34; 2.03; 1.75; 1.62; 1.57; 1.49 Å. According to the results of X-ray phase analysis, olivine and clinochlore were also found in the rock in small amounts up to 5%. The groundmass is composed of a submicron aggregate, the mineral composition of which, apparently, is close to that of phenocrysts.

The temperature of the beginning of melting of tefritobasalts, determined by the dilatometric method, was 1280°C. At 1450°C, the rock powder (sifted through a 02 sieve) completely melts, clarifies, and homogenizes within 45 minutes [25]. Physical and mechanical properties tefritobasalts density is 2.0 g/cm^3; compressive strength is 47.6-195.8 MPa. According to chemical analysis, tephritic basalt contains SiO_2 - 45.54 wt.%, Al_2O_3 - more than 10 wt.%, Fe_2O_3 - about 8.5 wt.%. The magnesium content is 6.95 wt.%. Contains a significant amount of alkalis ($K_2O + Na_2O$), which is 6.54 wt.%.

4. Lead slag

Used slag plant JSC "Yuzhpolymetal" located in the city of Shymkent (Kazakhstan). The balance reserves of lead slags are about 2 million tons [26, 27]. Lead slag contains up to 37.25% Fe_2O_3 and can replace the corrective additive. In addition, lead slags contain up to 14% CaO and partially replace the carbonate component. The X-ray of lead slag is shown in Figure. 5.

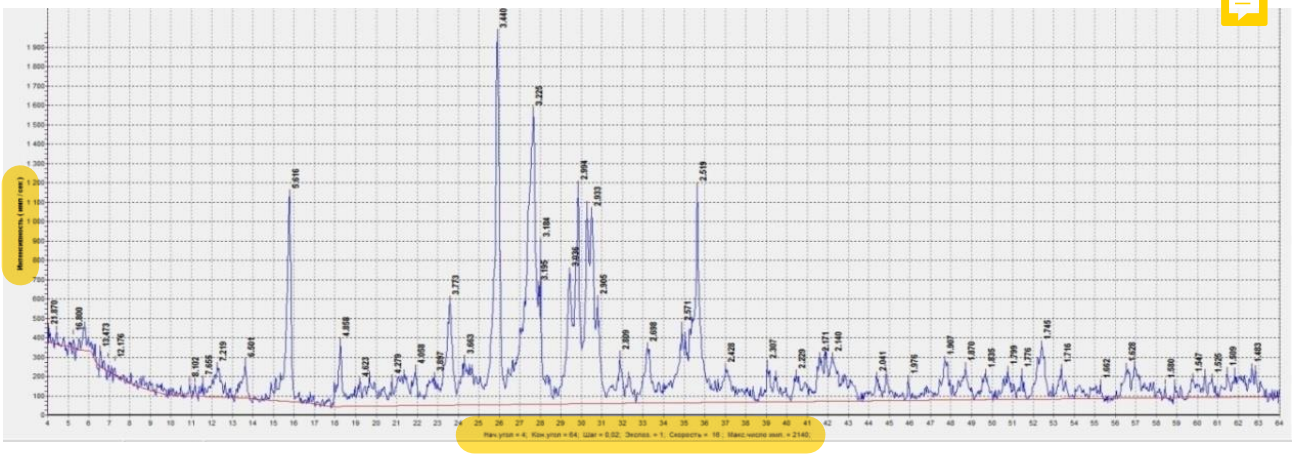


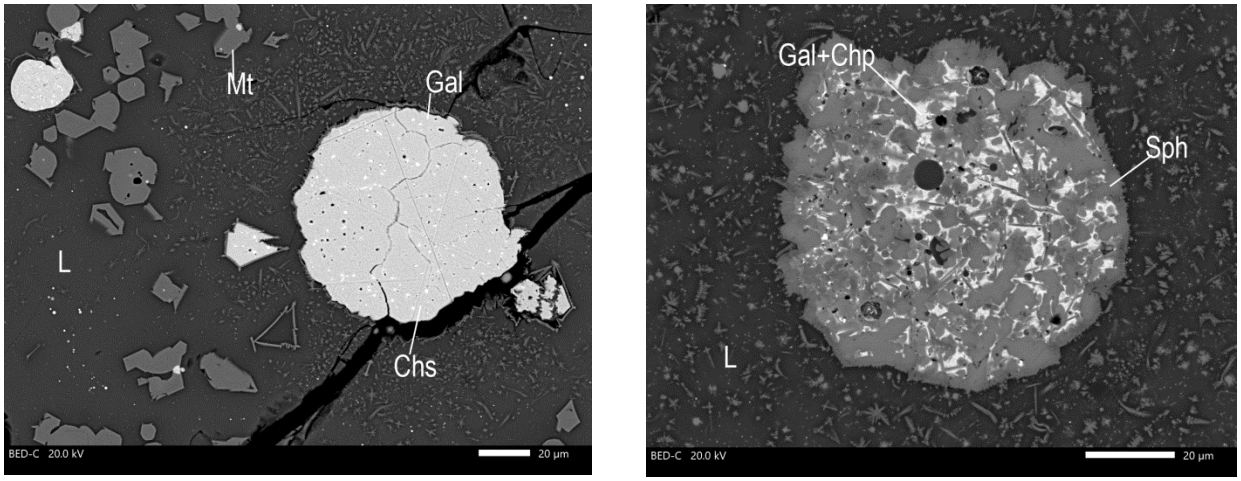
Figure 5. X-ray of the lead slag

According to the results of X-ray phase analysis of lead slag, diffraction maxima were recorded: fayalite d=3.77; 2.81; 2.31; 1.77; 1.58 Å, wustite d=4.27; 2.14; 1.52; 1.50 Å, hematite

d=3.66; 2.69; 2.42; 2.22; 1.83; 1.66; 1.48 Å, melilite d=2.51; 2.04; 1.87; 1.74; 1.71; 1.54 Å, zinc spinel d=1.90; 1.62 Å.

According to the microprobe study, lead production slag has an incompletely crystalline porphyry structure (Figure. 6). The bulk is composed mainly of glass. The amount of glass is approximately 60% of the total volume of the sample. The structure of the ground mass is heterogeneous. It alternates areas with vitrophyric and hyalopilitic structure. In the most crystallized areas, an increase in the content of zinc and sulfur and a decrease in the amount of calcium are noted.

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(a) **(b)**

Figure 6. Micrographs of lead slag with various types of phenocrysts. Symbols: Gal - galena, Chs - chalcocite, Mt - magnetite, Chp - chalcopyrite, Sph - sphalerite.

The phenocrysts are represented by various sulfides that form rounded isometric aggregates. Their size varies from a few microns to ≈0.5 mm. The mineral composition is different. There are aggregates composed of approximately 95% chalcocite (Cu_2S) and 5% galena (PbS) and aggregates composed mainly of sphalerite (ZnS) with a small amount (up to 5%) of chalcopyrite ($CuFeS_2$) and galena. Subhedral grains of hematite (Fe_2O_3) are present as phenocrysts. Their average size is 10 μm. The total amount in the sample is about 20%.

Based on the data on the chemical composition of raw materials in the ROCS program [28], a four-component calculation of the composition of the raw batch was made, consisting of "Limestone, tefritobasalt, coal mining waste and lead slag". For the optimal modular characteristics of the resulting clinkers, the quantitative ratio of the initial components, as well as the calculated chemical and mineral composition of the clinker, were determined.

Raw materials were crushed and sieved through a No.008 sieve. As a result, the surface area of particles per 1 g of material (specific surface area) was 3118–3326 cm^2/g, and the average particle size was 5.67–5.92 μm. In accordance with the obtained calculated composition, a mixture was made from them. This mixture, on a hydraulic press under a pressure of 20 MPa, was molded into tablets with a diameter of 15 mm and a height of 10 mm.

The firing of the tablets was carried out in an electric laboratory furnace SX-2-18TP at the M. Auezov South Kazakhstan University (Kazakhstan). The temperature regime of firing fully corresponded to the temperature regime of a rotary industrial kiln. The rise in temperature to 1350°C occurred within 2-2.5 hours. Exposure at the maximum temperature was carried out for 30 min. A general view of the furnace, unfired pellets and clinkers obtained at a temperature of 1350°C is shown in Fig. 7.

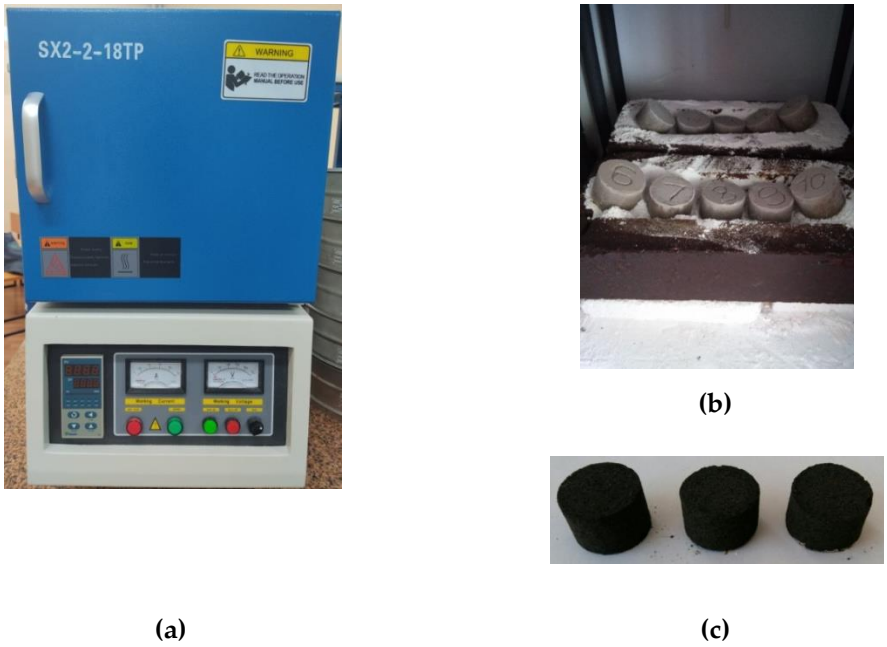


Figure 7. General view of the furnace **(a)**, unfired pellets **(b)** and clinkers **(c)**, obtained at a temperature of 1350°C

The duration of clinker firing was controlled by the degree of absorption of CaO into clinker minerals. Burnt tablets were crushed. The qualitative content of free CaO was determined microscopically. The quantitative content of CaO in clinkers was determined by the ethylene-glycerate method [29].

3. Results and discussion

In accordance with the results of calculating the composition of the raw mixture (Table I), the optimal characteristics of the clinker for these initial conditions are as follows: SC=0.94, silicate module n=2.02; alumina modulus p=0.95. The saturation factor (SC) of clinker is the ratio of CaO remaining after saturation of Al_2O_3 and Fe_2O_3 to $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, to the amount of CaO that is necessary to completely saturate the silica to $3CaO{\cdot}SiO_2$. The SC value of factory clinkers varies within 0.85-0.95 depending on the composition and properties of raw materials, firing conditions, etc. The silicate module is the ratio of the SiO_2 content to the sum of oxides $A1_2O_3$ and Fe_2O_3. The n module value ranges from 1.7 to 4.0. The alumina modulus is the ratio of the Al_2O_3 to the Fe_2O_3 content and characterizes the composition of the aluminoferrite phase in the clinker. The values of the p modulus range from 0.9 to 3.0. The theoretical specific consumption of raw materials is 1.481 t/t of clinker, which is about 70 kg lower than in traditional mixtures. The content of non-traditional components in the mixture is 24.69%.

Table 2. The results of calculating the composition of the raw batch and the resulting clinker

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	L.W.C	Other
Limestone Sastobe	3.87	1.04	0.57	52.83	0.88	0.10	40.71	-
Tefritobasalt Daubaba	45.54	10.70	8.53	10.66	6.95	0.20	7.92	9.50
Coal mining waste from the Lenger mines	55.50	10.60	2.01	3.21	0.70	0.79	24.08	3.11

Lead slag of Yuzhpolimetall JSC plant	25.94	6.44	37.25	14.71	6.15	0.04	0.10	9.37					
By component chemical composition of the raw batch									Component content				
									kg/kg clinker			%	
Limestone	2.91	0.78	0.43	39.78	0.66	0.075	30.65	-	1.1160			75.31%	
Tefritobasalt	9.20	2.16	1.72	2.15	1.41	0.040	1.61	1.92	0.1575			10.63%	
Coal mining waste	0.58	0.11	0.02	0.04	0.01	0.008	0.25	0.033	0.1575			10.63%	
Lead slag	0.88	0.22	1.27	0.51	0.21	0.001	0.003	0.321	0.0508			3.43%	
Raw mix	13.59	3.28	3.45	42.48	2.29	0.13	32.52	2.27	1.4818			100.00%	
By component chemical composition of clinker									Component content				
Limestone	4.32	1.16	0.64	58.95	0.98	0.112	-	-	66.17%				
Tefritobasalt	13.63	3.20	2.55	3.19	2.08	0.060	-	2.845	14.38%				
Coal mining waste	0.86	0.17	0.03	0.05	0.01	0.012	-	0.049	14.39%				
Lead slag	1.31	0.33	1.89	0.75	0.31	0.002	-	0.476	5.06%				
clinker	20.14	4.86	5.11	62.95	3.39	0.19	-	3.37	100.00%				
Chemical composition of raw mix and clinker									KH	n	p	TEC. kcal/kg)	G_{fuel}. kg ref.fuel /t cl)
Raw mix	13.59	3.28	3.45	42.48	2.29	0.13	32.52	2.27	0.94	2.02	2.02	-	-
clinker	20.14	4.86	5.11	62.95	3.39	0.19	-	3.37	0.94	0.95	0.95	364.1	196

Mineralogical composition of clinker						
Minerals	$3CaO·SiO_2$	$2CaO·SiO_2$	$3CaO·Al_2O_3$	$4CaO·Al_2O_3·Fe_2O_3$	$CaSO_4$	MgO
wt.%	57.88	18.82	6.46	11.61	0.32	3.39

Symbols: C_3S – alite ($3CaO·SiO_2$); C_2S – belite ($2CaO·SiO_2$); C_3A - tricalcium aluminate ($3CaO·Al_2O_3$); C_4AF - tetracalcium aluminoferrite ($4CaO·Al_2O_3·Fe_2O_3$); LOI - loss on ignition.

Fig. 8 shows the dependence of the content of alite ($3CaO·SiO_2$) in clinker on the value of SC and the silicate and alumina modules of the raw batch. With an increase in the SC from 0.8 to 0.95 and a n modulus from 1.5 to 3.5. the alite content increases from 40% to 70%. With the silicate modulus n=2.02. the value of the alumina modulus is p=0.95. An increase in the silicate modulus contributes to an increase in the alumina modulus. as well as an increase in the content of tricalcium aluminate. According to the results of calculating the composition of the raw charge. consisting of "Limestone. tefritobasalt. coal mining waste and lead slag" is suitable for producing sulfate-resistant Portland slag cement clinkers of the CEMIII/AC grade according to GOST 22266-2013 [30]. The calculated chemical and mineral composition of the clinker contains no more than 7% of $3CaO·Al_2O_3$. the amount of Al_2O_3 and MgO does not exceed 5%. The total content of $3CaO·Al_2O_3$ + $4CaO·Al_2O_3·Fe_2O_3$ is 18.07% and does not exceed the maximum allowable values ($3CaO·Al_2O_3 + 4CaO·Al_2O_3·Fe_2O_3 < 22\%$). Alite in the composition of clinker is 57.88%. belite ($2CaO·SiO_2$) 18.82%.

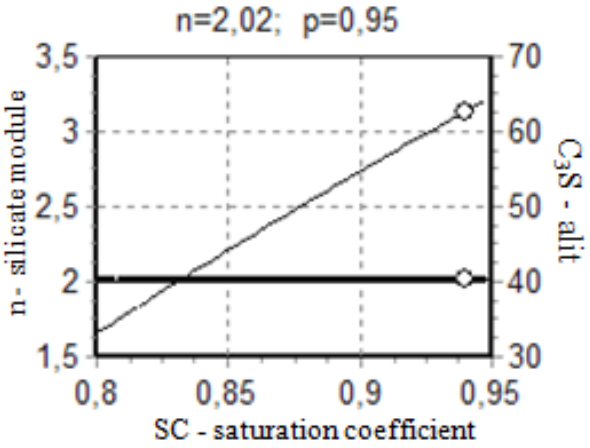


Figure. 8. Dependence of the content of alite (C_3S) in clinkers on the value of modules (n. p) and saturation coefficient in raw mixtures

Clinker firing is characterized by a complex physical and chemical process. The reactions occurring in the process of clinker formation determine the quality of the finished product and its phase composition.

Clinker fired at a temperature of 1350°C reaches almost complete assimilation of calcium oxide within 30 min, the content of free CaO in the resulting clinker was 0.2% (Table 3). The quality of the clinker is high, the chemical and mineralogical composition meets the requirements. It has been established that in the studied raw mixtures the process of clinker formation ends at 1350°C, i.e. 100°C lower than in traditional raw mixes [31-40].

Table 3. Specific consumption of raw materials and the amount of free CaO in the clinker

Mix	The composition of the raw batch, wt.%				Specific consumption of raw materials, t/t of clinker				SC	Modules		The amount of free CaO at 1350 °C, %
	Lime stone	Tefrito basalt	Coal mining waste	Lead slag	Lime stone	Tefrito basalt	Coal mining waste	Lead slag		n	p	
1	66.17	14.38	14.39	5.06	1.1160	0.1575	0.1575	0.0508	0.94	2.02	0.95	0.2

On radiograph of clinker obtained by burning at a temperature of 1350 °C of energy and resource-saving raw mixtures, lines characteristic of free CaO are found (Fig. 9).

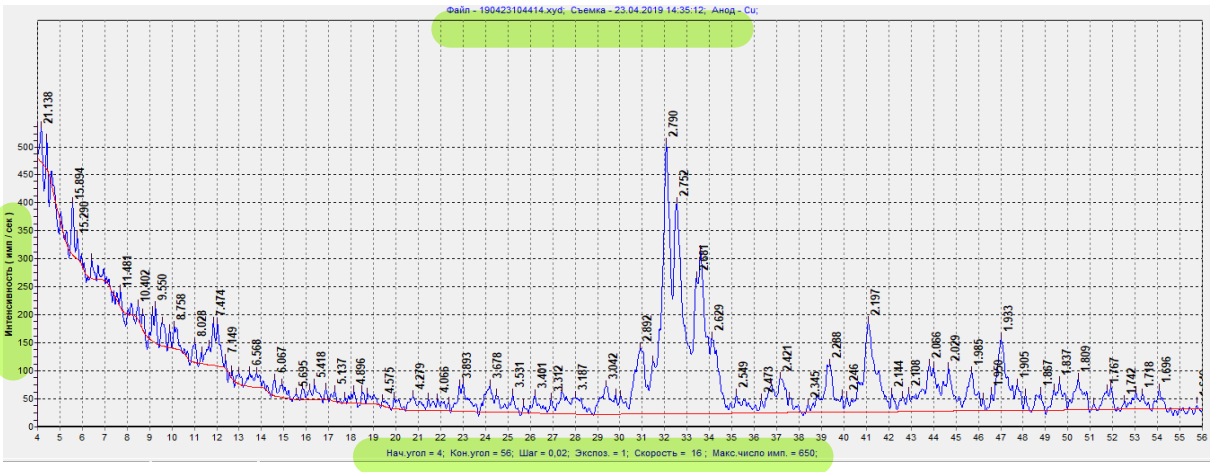
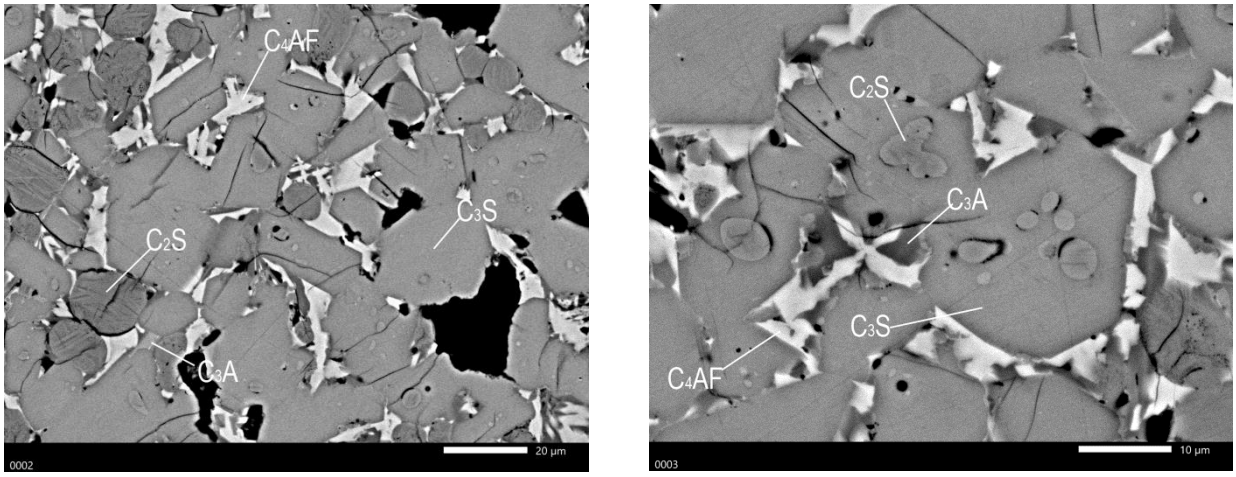


Fig.9. Radiographs of clinkers

When burning at 1350 °C energy resource saving raw material mixture, the following clinker minerals were formed: Alite (C_3S) d = 2,19; 2,62; 2,78; 3,05 Å; Belite (C_2S) d = 1,73; 1,93; 2,74; 2,88 Å; Tricalcium aluminate (C_3A) d=1,87; 1,90; 2,95; 4,04 Å; Four-calcium aluminoferrite (C_4AF) d = 2,03; 2,13; 2,66 Å; The peaks characteristic of CaO free are absent.

Fig. 10 shows micrographs of the polished section of the resulting clinker. The synthesized clinker has a full-crystalline structure, massive texture. The main crystalline phases are evenly distributed over the sample [32-43]. Alite is represented by isometric subhedral crystals 20-50 μm in size. Belite inclusions are observed in large rhombohedral alite crystals. The content of alite in the composition of the clinker is 57.88%. Belite is represented by small grains up to 10 μm in size. The crystals have a round near isometric shape. Belite grains are in direct contact with alite grains, which indicates their formation by reactions in the solid state. The belite content in the clinker composition is 18.82%.



(a) **(b)**

Figure. 10. Micrographs of clinker

Along the grain boundaries of alite and belite, there is an aluminate phase - a dark intermediate substance and an alumino-ferrite phase - a light intermediate substance. The intermediate substance is present in sufficient quantity ($3CaO{\cdot}Al_2O_3 + 4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ = 18.07%). In traditional clinker, the aluminoferrite phase is 14%. The aluminoferrite phase in all parameters (hydraulic activity, hardening rate and strength characteristics) occupies an intermediate position between $3CaO{\cdot}SiO_2$ and $2CaO{\cdot}SiO_2$. Hardening products have increased water and corrosion resistance. In clinker sinters based on tephrite-basalt, well-formed, regular-shaped alite crystals are formed. Tefritebasalt improves and accelerates the processes of clinker formation, helps to reduce the firing temperature (the beginning of melting is 1280°C), and intensifies the process of firing clinker. The traditional raw mix is heated to clinker sintering at 1450-1500°C.

A small amount of lead slag (5.06%) introduced into the mixture changes the structure of the clinker and improves the process of mineral formation. The addition of lead slag to the raw mix improves fireability and calcium silicate formation at a lower temperature. Zinc oxide contained in the composition of the slag contributes as a mineralizer to the dissolution of the residue of free lime at 1350 ° C. Its presence affects the course of solid reactions, and the formation of silicates and calcium aluminates. During the firing process, the material loses a significant amount of these metals. In the finished product, their content is low. According to the ICPMS, the content of lead in the clinker is 41 ppm and zinc 197 ppm.

The microstructure of traditional cement clinker is uniformly granular, finely crystalline. The optimal size of alite crystals is 20-40 microns. The content of tricalcium

aluminate is approximately 8%. The saturation coefficient of the raw mixture is in the range of 0.90–0.92.

In a laboratory ball mill, cement was mixed with 5 % gypsum. The residue on a sieve №02 and №008 was determined every 10 minutes, the total grinding time was 30 minutes. A study of the kinetics of grinding shows that the burning temperature and the amount slag introduced into the raw material mixture have a noticeable effect on the grinding process of cements. After 30 minutes of grinding, the cement residue on sieve №008 is 13 %. The specific surface of the cements was determined on a PSX-K. According to the results of the analysis, the specific surface of cements is 3245 cm^2/g, and the average particle size is 9,97 microns.

Table 4. Physico-mechanical properties of experimental Portland cement

Cement	Sieve residue,%		Specific surface area, cm^2/g	Strength of small samples 2x2x2 cm, (MPa)	
	№02	№008		7 day	28 day
Cement	3,3	13	3245	27,4	41,8

In the laboratory, the physic-mechanical properties of experimental Portland cement were tested in small samples of 2x2x2 cm after 7 and 28 days [41-46]. As can be seen from the data in table III, the tensile strength of the obtained cements increases with increasing hardening time. After 28 days, the compressive strength of cements is 41,8 MPa. These indicators correspond to the cement grade for strength M400 according to GOST 10178-85 or strength class 42,5 according to GOST 31108-2016

4. Conclusions

1. In the studied initial experimental compositions, the replacement of the clay and iron-bearing component with tefritobasalt and lead slag leads to a decrease in the melting point of the mixture by 100°C relative to traditional compositions and is economically feasible.

2. In the samples obtained from the four-component raw batch "Limestone - tefritobasalt - coal mining waste - lead slag", it can be seen that the synthesized clinker has a full-crystalline structure with an alite content of 57.88% and belite 18.82%.

3. According to the calculation results SC=0.94, silicate module n=2.02, alumina modulus p=0.95. The theoretical specific consumption of raw materials is 1.481 t/t of clinker, which is about 70 kg lower than in traditional mixtures. The content of non-traditional components is 24.69% in total.

4. According to the results of chemical analysis, the content of free CaO in the clinker was 0.2%, which complies with the requirements of GOST. The quality of the synthesized clinker is high, the minerals are formed correctly, the size of alite crystals is 20–50 μm.

5. The strength of the obtained Portland cement after 28 days under compression of 41,8 MPa, which corresponds to the cement grade for strength M400 according to GOST 10178-85 or strength class 42,5 according to GOST 31108-2016

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