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Cement slurry from electro-phosphoric slag

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Abstract. Possibility to obtain high alite Portland cement of alternative raw materials was established by complete replacement of clay component with electro-phosphoric (EPS) slag. This technology allowed disposal of considerable volume of slag with production of high grade cement and reduction of CO₂ emissions. Fuel saving was about 15 % increase in productivity of kiln was 10–15 %. It was detected after industrial tests that some rheological properties of slag were unknown. We studied properties of limestone-residual slag, aimed at production of clinker with alite content 69.6 and 65.4 %. EPS slag was weak structuring element at the initial stage of coagulative structuring. An increase in the volume concentration of solid phases led to an increase in viscosity, dynamic shear stress, and plastic strength. With an increase in concentration by 3 % from 35 to 38 %, fluidity decreased by 20 mm, and mobility by 1.3 times. Increase of bulk concentration of solid phases led to increase in viscosity, dynamic stress viscosity, and plastic strength. With the increase in concentration by 3 % from 35 to 38 %, fluidity had been decreased by 20 mm, and mobility by 1.3 times. Further growth of concentration led to reduction of these indicators by an order. Coarse limestone-residual slag with moisture content 37 % preserved its mobility during 26 days. Under static conditions, critical structural strength (100 g.cm²) of slag was achieved during 24 days. In case of proper mixing, duration of slags' mobility shall be increased. Therefore 37 % can be recommended for lower limit of slag moisture.

1. Introduction

The industrial program of the Government of the Republic of Kazakhstan defines the task of stimulating the investment flow of the country's economy, which requires improving the quality of construction, in which the development of technology for the production of binders continues to play a leading role. The problem of improving the quality, reducing energy intensity, finding more productive and economical methods for the production of Portland cement remains relevant. An effective way to solve the problem is to increase the alite content in cement, accelerating the rate of reaction of its formation, but not increasing the clinker calcination temperature, for which purpose a new type of raw material, granulated electro-phosphoric slags (EPS) slags, instead of the traditional clay component of the Portland cement raw material mixture, was investigated. The use of granular phosphoric slag in a Portland cement mixture as a complete clay substitute for the production of high alumina Portland cement has shown the promise of this direction. In this role, this material has not been previously investigated. By the beginning of this work, it was known that the addition of EPS slag to the limestone-clay mixture has a mineralizing effect on the clinker formation process. Phosphate-containing composites are distinguished by high construction and operational properties of concrete [1]. Recently, this direction has been intensively developed in China and other countries [2, 3]. In connection with the use of EPS slags as a raw material component in the production of cement by the wet method, it becomes necessary to study the stability of sludge prepared from such raw mixes. The wet method of cement production, widespread in Russia, Kazakhstan, and other CIS countries, has many edges over the dry one [4].

EPS slag is characterized by relatively low melting and softening temperature (1050–1100°C), and on 90 % consists of lime and silica, and molar ratio is close to monocalcium silicate; contains admixtures of phosphoric anhydride and calcium fluoride. The first is stabilizer of β -C₂S, and the second is effective mineralizer of silication. EPS slag has following variation limits of chemical composition, mass. %: CaO = 44.1 ÷ 50.6 (47.1); SiO₂ = 39.3 ÷ 43.0 (42.0); Al₂O₃ = 1.9 ÷ 3.0 (2.3); Fe₂O₃ = 0.4 ÷ 2.3 (1.0);

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MgO = 2.2 ÷ 4.1 (3.2); P₂O₅ = 0.2 ÷ 4.0 (1.8) and F = 1.7 ÷ 3.4 (2.5) (average contents, derived by statistical processing of the results of chemical analyses, which were carried out during 4 years, are given in brackets).

Using EPS slags as primary component in production of cement, it is necessary to study stability of slags, prepared from such primary mixtures.

Task on production of cement with given features and structure is of great importance, sludge with desired properties and structure. It is known, that kinetic stability of limestone-clay slag depends on dispersion and concentration of solid phases, and energy state of particles surface. Slags on the basis of granular blast furnace slags have increased settleability versus to limestone-clay. This is related to higher density of slags and low content of colloidal size particles. Raw slags on the basis of phosphorus slag also have higher sedimentation. Increase of slag content in raw mixture from 14 to 45 % leads to increase in rate of sedimentation of raw slag by 4–8 %.

Established, that tixotropy is peculiar to structure formation of limestone-clay slag and coagulation structure is easily broken by system stirring. Raw mixes from belite component contain 35–55 % of dicalcium silicate, depending on quality and quantity of initial raw materials, which means that slags are not only got thicker, but set. Systems, including granular blast-furnace slags or microsilica [5], are characterized by similar feature.

Performing pilot testing of new technology, we knew that slags demonstrate solidification during long-term storage. Works, devoted to cement raw slags, containing slags of phosphorus production, are small-scale and related to partial clay replacement. Alternative works [6–19] do not contain information on behavior of slag. The study [20, 21] is related only to rheology of activated phosphorus slag. Stated circumstances determined necessity to study structural and mechanical properties of slags of limestone and EPS slag (their stability, viscosity structural strength, dynamic and static shear stresses).

The aim of the article is to evaluate and find out possibility and conditions in order to obtain stable slimes of contained limestone and phosphoric industrial slag. At the same time stability means possibility of slime to preserve solid-state phases in suspension.

2. Methods

2.1. Raw materials

Raw materials were limestone from the Astahov deposit of the Karaganda Cement Plant (Central Kazakhstan) and granular slag from the Taraz phosphate plant (South Kazakhstan). Chemical composition of raw materials is given in Table 1.

Table 1. Chemical composition of limestone and granular electro-phosphoric slags, mass.

Raw material	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	MnO	R ₂ O	F	P ₂ O ₅	TiO ₂	S	loss of ignition*
Limestone	53.62	1.98	1.16	0.52	0.53	0.46	no	0.23	0.03	traces	0.05	42.00
Slag	45.70	41.50	2.32	0.61	4.00	0.58	0.38	1.95	1.97	traces	0.35	0.47
Clay	7.92	55.20	12.11	6.15	2.77	–	2.91	–	–	–	0.10	11.99

*ignition losses.

The density of slag was 2.92 and that of limestone 2.71. The density of clay was about 2.60–2.65. Limestone excels in purity and has the titer 95.75 %. Comparison of data from the table with the abovementioned bulk composition demonstrated that slag sample is chemically representative. Potable water is used for preparation of raw slug.

2.2. Research methods

Limestone – slag slime was studied by the Nurse method [22] for high alit clinker. Saturation coefficient (SC) was taken 0.93 and 0.97 which correspond to 69.6 % and 65.4 % alit content.

The density was determined by pycnometer (bottle) method at 20⁰ C in toluene. Particle-size distribution was determined by sedimentation analysis of pipette method. Grain shape was evaluated by using of microscope NU-2. The features of interaction between the studied objects aggregates with water were estimated on the electronic microscope UEMV-100K.

The specific surface was determined by a standard surface meter T-3 based on the principle of air permeability of powder materials. Suspension was prepared by means of the LE-305 type mixer.

According to fluidity slime moisture content was determined by its flow and optimal diameter was about 70 mm. Fluidity was defined using fluidity meter TN-2 (of the RHTU n.a. D. Mendeleev system). Slime thickening (decreasing of fluidity) during a time was tested in static conditions.

Assessment of sedimentation was accompanied by establishment of sedimentation volume, its moisture capacity and changes over time. Observation continued till achievement of constancy of sedimentation volume. Rotary viscosimeter "Rheotest – 2" (Germany), Waler-Rehbinder device and Rehbinder cone-and-plate rheometer (modified device of VNIINGP, Russia) were used during study of structural-mechanical properties of primary cement slurries. Calculating formulas were adjusted depending on development of system structure.

2.3. Samples preparation

Raw materials were grinded by laboratory tumbling mill with using of standard grinding balls loading. There were prepared two samples. The first sample had the remainder on the 008 sieve 8 %, the second sample 14 %.

Limestone slime, slag slime, two component mixed slime and to compare slime from horizontal stank of Karaganda cement plant (KCP) were studied. The control slime was stored in a hermetically sealed vessel and was subjected to numerous and careful hashing. All this could improve its sedimentation stability and other indicators.

Experimental slimes were tested in a freshly prepared form, i.e. in more adverse conditions in comparison with the control slime. It gives more reliable relative results of supervision.

Two tests were carried out at different dispersion. The first test was carried out at 8 % remainder on 008 sieve. The second test was carried out at 14 % remainder on 008 sieve. Such sifting was the same with low and high limits of grinded material in plants. Controlling plant slime has residual on 008 sieve 14.4 %. Limestone-slag slime was tested at 37 % of moisture content that was typical for industrial slime. KCP slime that was used in tests had 39.5 % and 37 % moisture content.

3. Results and Discussion

3.1. Sludge of a mixture of limestone and granulated phosphoric slag

Materials dispersion. The data of the dispersion are shown in Table 2.

Table 2. Specific surface and results of sedimentation analysis of the powders.

Sample	Specific surface, m ² .kg	Remainder, mass. %.			Content, mass. %			
		on the sieve			Fractions, mm			
		0.2	0.08	> 0.06	0.06 – 0.01	0.01 – 0.005	0.005 – 0.001	0.001
Granulated phosphoric slag								
S – 1	2325	0.6	14.0	33.34	55.06	5.95	4.55	1.10
S – 2	2908	0.4	8.0	14.75	72.50	6.30	4.30	2.15
Limestone								
L – 1	4563	0.6	14.0	14.83	80.77	1.20	2.72	0.48
L – 2	5278	0.7	8.0	13.20	82.10	0.70	2.15	1.85

The data presented in Table 2 show that the granulated slag of phosphoric production in comparison with limestone is more coarse-dispersed when crushed. In case of slag the bulk (about 90 %) of particles has the size more than 10 mc. The raised grinding subtleties by means of decreasing the remainder from 14 to 8 % increase the 0.06–0.01 mm fraction yield at the expense of fraction that is larger than 0.06 mm. At this the number of fractions less than 10 mc remains almost without change.

In limestone there are more fractions that are smaller than 60 mc and their yield grows with increasing the general fineness of grinding i.e. with reducing the quantity of particles that are larger than 80 mc from 14 to 8 %.

According to the content of fraction that is smaller than 60 mcm the specific surface of materials changes. With the remainder of 8 % the specific surface of limestone exceeds that of slag 1.8 times and with the remainder of 14 % – almost twice.

Form of grains. Viewing the powders under the microscope showed that particles of slag have a flat-limited detrital form with acute corners and twisting sides. Configuration of grains in most cases is irregular. There are met grains of the extended form.

Limestone units are more isometric in comparison with slag grains, but they also have an irregular shape with twisting outlines.

Sedimentation of slimes. Sedimentation was studied with the use of slimes which component compositions are presented in Table 3.

The solid phase of the KCP slimes contains to 80 % of limestone and 3–5 % of scale. The other part is presented by clay slate.

Table 3. Component composition and technological indicators of slimes.

Slime	Composition of the mix, mass. %				Slime humidity, %	Slime fluidity, mm	Volume concentration of dispersed phases, %
	S – 1	S – 2	L – 1	L – 2			
1	100	–	–	–	29.0	70.0	45.60
2	–	100	–	–	30.0	70.0	44.41
3	–	–	100	–	30.0	63.0	46.27
4	–	–	–	100	30.0	61.0	46.27
5	41.4	–	58.6	–	30.0	69.0	45.54
6	41.4	–	58.6	–	37.0	97.0	37.90
7	–	41.4	–	58.6	30.0	70.0	45.54
8	–	41.4	–	58.6	37.0	92.0	37.90
KCP slime					39.5	68.0	35.94

Note: S – slime, L – limestone

In limestone-slag slimes the content of limestone is reduced to 60 % but in spite of this it is the prevailing component. In addition, it is necessary to consider the developed specific surface of limestone.

The total surface of limestone and limestone-slag slimes exceeds the slag surface about three times. In this regard it would be possible to expect the decisive effect of limestone on the properties of slimes. In reality there is not observed such a picture.

For example, fluidity of limestone-slag slimes (Table 3, slimes 5 and 7) coincides with fluidity slag (1 and 2) but not with calcareous (3 and 4) suspensions. Similarly, the KCP slime fluidity is strongly affected by humidity of the clay component.

Limestone-slag slimes in a freshly prepared state in comparison with the KCP slime of identical fluidity show water requirement nearly 10 % less. It is entirely connected with the feature of interaction of phosphoric slag with water. As there were tested only freshly prepared slimes, it must be kept in mind the initial stage of water interaction here.

Comparing concrete figures, it is possible to note that slag suspensions are characterized by the smallest values of the lower limit of humidity (29–30 %). These suspensions with identical humidity surpass in fluidity the calcareous ones. The reason is probably in the coarse dispersion of slag suspensions and their smaller a little volume concentration.

Calcareous suspensions with humidity of 30 % show rather high fluidity, too.

In sedimentation duration experimental slimes, as well as the KCP slime don't practically differ from each other. The bulk of the disperse phase in them sediments already in 20 min. despite all distinctions in humidity, fluidity, specific surface and volume concentration spoken above.

Initial moisture capacity of the sediment. Sedimentation volume after 20 min. in Limestone-slag slimes (Table 4, slimes 5 and 8) does not depend on the fineness of grinding the furnace charge at all and is mainly defined by their humidity. Slimes 6 and 8 of high humidity (37 %) forms sediments with moisture capacity of 61.32 % whereas the same slimes (5 and 7) at 30 % humidity allocate sediments with moisture capacity only about 54 %.

Sediments of Limestone-slag slimes and the KCP slimes with identical humidity has almost equal moisture capacities.

However, Limestone-slag slimes of equal fluidity sediment with allocation of a denser deposit in comparison with the KCP slime.

The smallest moisture capacity belongs to the deposit of slag suspension prepared from the powder of the remainder on the 0.08–14 % sieve. However, the low moisture capacity of sediments is not characteristic of slag suspensions. The moisture capacity of their sediments raises with increasing the fineness of grinding. So, for example, moisture capacity of slime sediment twice surpasses moisture capacity of calcareous suspensions sediments, though the specific surface of slag flour is less than the of calcareous 1.6–1.8 times.

Table 4. Moisture capacity of slime sediments.

Slime	Initial moisture capacity after 20 min., %	Final moisture capacity, %	Initial and final moisture capacities ratio, %	Sedimentation volume to slime volume ratio, %
1	48.97	48.97	100.00	89.37
2	54.77	52.16	95.23	98.21
3	53.46	51.52	96.97	99.40
4	53.54	52.27	97.63	99.59
5	53.80	52.01	96.67	98.57
6	61.32	54.67	89.16	98.00
7	53.89	51.85	96.21	98.80
8	61.32	55.93	91.21	98.00
KCP	63.66	58.80	92.37	98.93

Final moisture capacity of the sediment, i.e. the stabilized sedimentation volume of the KCP slime is 57.7 % less than in calcareous and slag slimes. But the deposit of plant slime is condensed very slowly: within 11 days and in experimental ones this consolidation comes to the end in one day.

The final moisture capacity of Limestone-slag slimes sediments still depends on their humidity, though to a lesser extent than in case of the initial moisture capacity.

In values of the final moisture capacity Limestone-slag slimes sediments do not significantly differ from the KCP slime after a daily storage if their humidity coincides.

Suspensions 2, 3 and 4 are almost identical by the final moisture capacity.

Changing sedimentation volume of slime in time (Table 5). The largest duration belongs to changing sedimentation volume of the KCP slime, i.e. 11 days.

Table 5. Sedimentation characteristics of slimes.

Slime	Time of count from the experiment beginning, min.						
	20	40	60	80	100	120	140
Sedimentation volume changing, %							
1	100.00	100.00	100.00	100.00	100.00	100.00	100.00
2	100.00	97.16	95.14	94.53	94.53	94.53	94.53
3	100.00	99.00	99.00	99.00	98.60	98.20	96.00
4	100.00	99.38	98.97	98.77	98.56	98.36	97.33
5	100.00	98.96	98.34	97.52	97.10	96.69	96.28
6	100.00	98.70	97.30	95.90	94.50	93.20	85.30
7	100.00	98.98	98.58	97.97	97.37	96.56	95.75
8	100.00	98.70	97.70	96.50	95.50	95.50	87.70
KCP	100.00	99.35	98.88	98.35	97.83	97.66	91.63

The time of sedimentation volume stabilization of limestone-slag slimes makes 24 hours. The same is observed for calcareous suspensions.

Coarse-dispersion slag suspension (Table 5, slime 1) gives a compact deposit right after sedimentation and its volume does not decrease later on. The duration of changing sedimentation volume in the second slag suspension is equal to 80 min.

Viscoplastic properties of slimes. In these experiments initial materials and furnace charges were the same as were described above. Humidity of slimes covered the lower and top limits of admissibility for each type and include one intermediate point.

Slag and calcareous suspensions are tested at limit temperatures, Limestone-slag slimes at 40 and 60 °C; such temperatures are most probable industrially.

The curve of slime currents is given in Fig. 1–4. As it should be expected, they did not pass through the beginning of coordinates.

For limestone (Fig. 1) at humidity 40 and 43 % the relation between the shearing effort and the gradient of speed remains almost linear. At 28 % humidity a straight line is bent when approaching the axes of shear stresses.

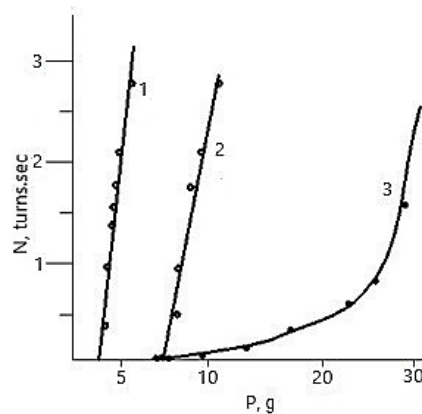


Figure 1. Curves of limestone suspensions currents depending on the speed of rotation (N , turns.sec.) of the mobile internal cylinder of the viscometer, on loading (P , g) rotating the cylinder: 1 – the remainder on the sieve 0.08 – 8 %, humidity – 40 %, temperature 10 °C; 2 – the remainder on the sieve 0.08 – 14 %, humidity – 43 %, temperature 60 °C; 3 – the remainder on the sieve 0.08 – 14 %, humidity – 28 %, temperature 60 °C.

Rectilinear nature of the considered dependence remains also for slag at humidity 37 and 43 %. In case of 28 % humidity the relation is complicated-stepped (Fig. 2) and the initial character of the relation between the shearing effort and the gradient of speed reminds a system having a fragile failure.

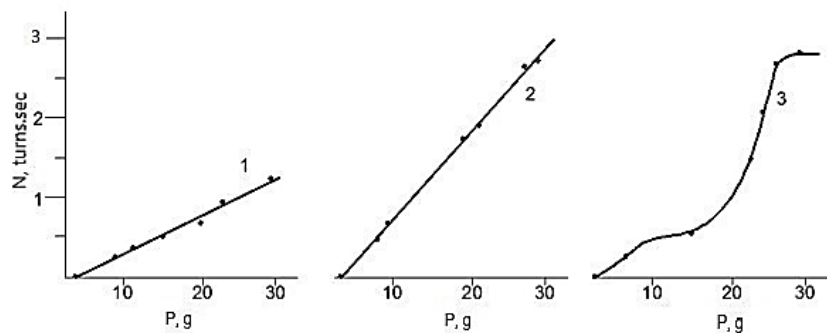


Figure 2. Curve of slag suspensions currents depending on the speed of rotation of the mobile internal cylinder (N , turns.sec.) of the viscometer, on loading (P , g) rotating the cylinder: 1 – the remainder on the sieve 0.08 – 14 %, humidity – 37 %, temperature 10 °C; 2 – the remainder on the sieve 0.08 – 8 %, humidity – 43 %, temperature 80 °C; 3 – the remainder on the sieve 0.08 – 8 %, humidity – 28 %, temperature 80 °C.

The bends of curves of the Limestone-slag slimes currents are sharp at 40 and 46 % humidity (Fig. 3). The LCPZ slime has a similar dependence at all tested temperatures (Fig. 4).

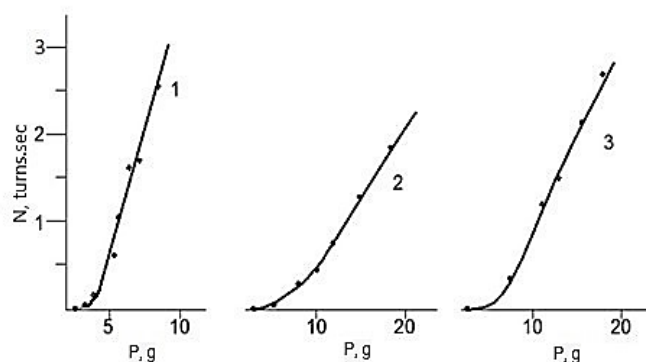


Figure 3. Curve of limestone-slag slimes depending on the speed (N , turns.sec.) of rotation of the mobile internal cylinder of the viscometer, on loading (P , g) rotating the cylinder: 1 – the remainder on the sieve 0.08 – 14 %, humidity – 40 %, temperature 40 °C; 2 – the remainder on the sieve 0.08–8 %, humidity – 31 %, temperature 60 °C; 3 – the remainder on the sieve 0.08 – 8 %, humidity – 46 %, temperature 60 °C.

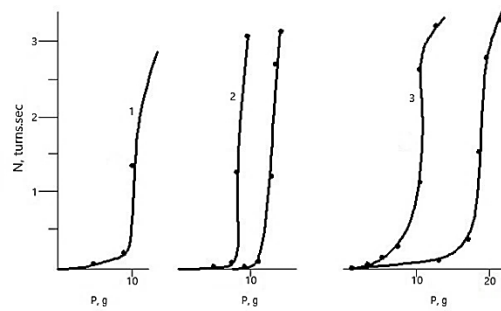


Figure 4. Curve of the KCP slime currents depending on the speed of rotation of the mobile internal cylinder (N, turns.sec.) of the viscometer, on loading (P, g). rotating the cylinder: 1 – 10 °C; 2 – 20 °C; 3 – 40 °C; 4 – 60 °C; 5 – 80 °C (the remainder on the sieve 0.08 – 14 %, humidity – 37 %)

The curve of the calcareous and slag slime current at 31 % humidity has a flatter initial bend.

Viscoplastic properties of slimes are presented in Table 6.

Table 6. Viscoplastic properties of slimes.

Slime	Humidity, %	Volume concentration of dispersed phases, %	Temperature, °C	Largest plastic viscosity, (η_o), poise	Smallest plastic viscosity, (η_m), poise	Static shear stress (θ_s), dn.cm ²	Dynamic shear stress (θ_d), dn.cm ²
1	37	36.8	10	23.9	9.5	51	51
2	28	46.8	80	not defined	7.6	107	107
	43	31.2		30.0	3.6	28	28
3	28	48.7	60	67.3	0.9	28	305
	43	32.8		35.4	0.7	32	32
4	40	35.6	10	53.6	0.4	42	42
5	40	35.0	40	82.8	1.1	34	43
7	31	44.3	60	122.6	3.4	31	88
	46	29.6		20.6	2.8	35	45
KCP	37	38.4	10	117.4	0.4	46	195
			20	95.7	0.8	28	175
			40	74.2	0.5	31	131
			60	34.4	0.7	28	173
			80	27.5	0.6	33	157

The difference $\theta_d - \theta_s$ is not large in limestone-slag slimes (Table 6, slimes 5 and 7).

In the KCP slime $\theta_d > \theta_s$ is 4–6 times as large.

In slag and limestone suspensions $\theta_d = \theta_s$, excluding coarse-dispersion limestone suspension with 28 % humidity and 60 °C temperature that has $\theta_s = 28$, and $\theta_d = 305$ dn.cm².

Static shear stress. Slimes differ from each other but little in this indicator. Slag suspensions do not enter here.

In general, in slag suspensions θ_s significantly depends on their humidity: the lower is humidity, the larger is θ_s . For example, at 28 % humidity slag suspension has $\theta_s = 107$ dn.cm².

Dynamic shear stress. It is high when humidity of slimes is low. Those are suspensions: a slag one with 28 % humidity ($\theta_d = 107$ dn.cm²); a calcareous one with 28 % humidity ($\theta_d = 305$ dn.cm²); and a calcareous, and slag slime with 31 % humidity ($\theta_d = 88$ dn.cm²).

Limestone-slag slimes in comparison with the plant slimes can have θ_d 2-4 times less.

Structural (effective) viscosity of slimes is not given here. It is changeable in the limits between η_o and η_m depending on the applied loading. Therefore below there are considered the values η_o and η_m that are constants under existing conditions.

The largest plastic viscosity of limestone-slag slimes at 40–60 °C depends on their humidity. It is high at low humidity 31 % ($\eta_o = 122.6$ poise). Then there are coarse-dispersion slimes.

In the KCO slime η_o falls with temperature increase. There is an impression that this slime in η_o has no essential advantage before limestone-slag slimes.

At 10 °C a slag suspension in comparison with the plant slime shows by 5 times smaller viscosity η_o , but at 80 °C it is slightly larger in a slag suspension.

Calcareous suspensions 0 °C have a smaller η_o than in the KCP slime. But at 60 °C and 28 % humidity this suspension in this indicator is worse than the plant slime.

The smallest plastic viscosity of the completely destroyed structure in limestone-slag slimes in comparison with the production slime will be higher in connection with the presence of slag in them which suspension has always an increased value. Calcareous suspensions and KCP slime have almost identical viscosity η_m independent of the temperature (Table 6).

The difference $\eta_o - \eta_m$ in the KCP slime is much larger than in calcareous and slag slime. In the small difference $\eta_o - \eta_m$ of the latter there appeared the influence of the slag component.

Slime thickening. For the purpose of studying slimes thickening there were prepared slimes which component composition and technological indicators are presented in Table 7. Changing slimes fluidity in dependence of their storage duration is shown in Table 8.

Table 7. Component composition and technological indicators of slimes.

Slime	Mix composition, mass. %				Remainder on the sieve, %	Specific surface, m ² .kg	Humidity, %	Volume concentration of dispersed phases, %	Fluidity, mm
	S-1	S-2	L-1	L-2					
A	100	–	–	–	14	196.1	31	43.25	100.5
B	–	100	–	–	8	226.5	34	39.93	107.0
C	–	–	100	–	14	456.3	31	45.09	65.0
D	–	–	–	100	8	527.8	34	41.75	70.5
E	41.4	–	58.6	–	14	342.1	31	44.73	69.0
F	41.4	–	58.6	–	14	342.1	37	37.89	97.0
G	–	41.4	–	58.6	8	364.2	34	41.03	98.0
H	–	41.4	–	58.6	8	364.2	37	37.90	100.5

Note: S – slime, L – limestone

The property to get thick is inherent in all slimes their specificity is shown only in the process duration which, except the nature of materials, significantly depends on humidity of slimes.

Among coarse-dispersion (remainder on the sieve 0.08–14 %) suspensions with 31 % humidity and prepared from separate components, the suspension of the granulated slag (5 days) is quickly getting thick and limestone – within 8 days.

The increase in humidity to 34 % did not affect the behavior of calcareous suspension but led to increasing the duration of jelling to 11 days for the granulated slag characterized by the remainder on the sieve 0.08–8 %.

The most coarse-dispersion calcareous and slag slime (it is designated by Z) containing granulated slag but having humidity 37 % kept the mobility within 26 days. This fact shows that in the phenomenon of jelling of Limestone-slag slimes their humidity is of great importance.

The structural durability was determined at the temperature of 25 ± 1 °C and humidity of slimes 37 %. When assessing the time of preservation of grouting cements mobility its structural durability is accepted as the limit of their pumpability equal to 100 g.cm². From this point of view calcareous suspensions (Fig. 5) are mobile within a very long period of time. Calcareous suspensions gain durability slowly. After 36 days their structural durability makes only 14 and 16 g.cm².

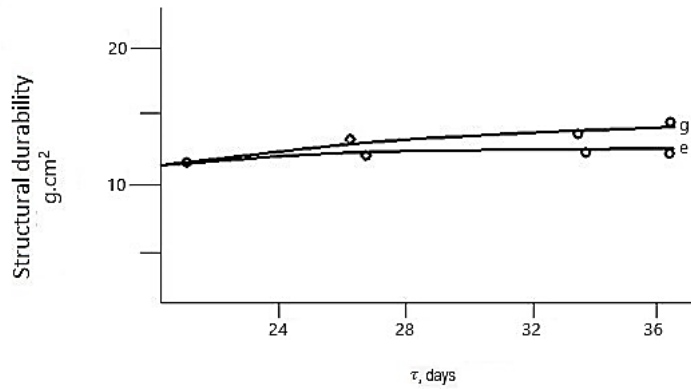


Figure 5. Changing structural durability of limestone suspensions (humidity – 37 %): a – the remainder on the sieve 0.08 – 14 %, b – 8 %.

Table 8. Changing slimes fluidity depending on the storage duration.

Designation	Fluidity, mm									
	Period of slime storage, days									
	0	1	2	3	4	5	6	7	8	9
a	100.5	100.5	103.0	93.0	62.0				thickened	
b	107.0	112.5	113.0	114.0	111.5	104.5	104.5	98.0	90.5	75.5
c	65.0	65.0	63.0	61.0	56.5	48.0	42.0	40.0	thickened	
d	70.5	70.5	70.5	65.0	63.5	57.0	54.0	42.5	thickened	
e	69.0	74.0	70.5	66.5	63.0	53.0	46.5	40.0	thickened	
f	97.0	102.0	105.5	106.0	94.5	101.0	95.0	99.5	99.5	-
g	98.0	96.5	90.0	84.0	81.0	77.5	71.0	62.0	50.0	43.0
h	100.5	108.0	104.0	102.0	-	100.0	96.0	92.0	85.5	80.0

The limit of pumpability of a more coarse-dispersion suspension of the granulated slag is reached in 15 and 23 days respectively for powders, 14 and 8 % of which are characterized by the remainder on the sieve 008 (Fig. 6). In suspensions of the granulated slags structural durability after two-day storage reaches 13 and 17 g.cm². Then it grows rather slowly depending on dispersion of powders till 22 and 14 days. On expiration of the specified terms the growth rates of durability sharply increase, especially for a powder from the remainder on the sieve 008–8 % which suspension after 27 days of storage has durability about 1400 g.cm². The curve of structural durability coarse-dispersion suspension growth has a step character, the rate of increasing durability is slow till 14 days, in the range from 14 to 22 days it is accelerated, then becomes again smooth; after 22 days there comes the second stage of sharp hardening.

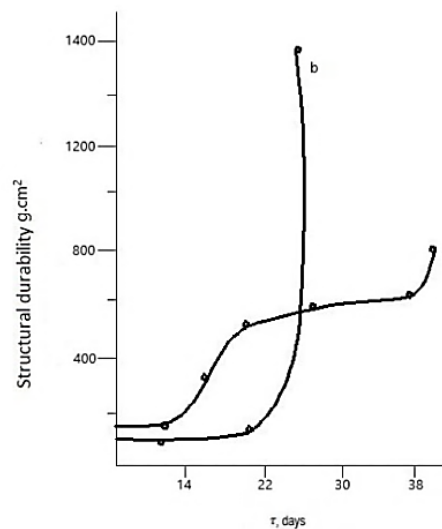


Figure 6. Changing structural durability of slag suspensions (humidity – 37 %): a – granulated slag, the remainder on the sieve 0.08 – 14 %, b – the same, 8 %.

Thus, a suspension of granulated slag considerably loses its pumpability. However, mobility of calcareous and slag slime is larger when using granulated slag that is seen in Fig. 7. Critical structural durability of slimes with granulated slag was reached in 24 days.

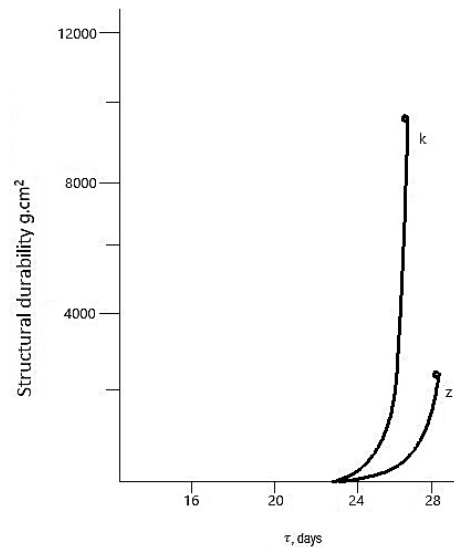


Figure 7. Changing structural durability of limestone – slag slimes (humidity – 37 %): a – slime with granulated slag, the remainder on the sieve 0.08 – 14 %, b – the same, 8 %.

Limestone-slag slimes before achieving the critical structural durability are strengthened gradually, then the growth rates of durability increase sharply.

Summarizing, we can say that thickening is due to the dispergation of slag particles, and setting is due to the formation of calcium hydrosilicates. This is confirmed by the bands established by the IR method at 3450 and 1650–1640 cm^{-1} , according to Nakamoto, K and Lazarev, A.N. [23] which relate to crystallization water, part of calcium hydrosilicates.

General observations permitted to establish the following facts:

1. Phosphoric industrial slags have a higher density than clay.
2. Limestone-slag slime has a low water requirement ability. This slime flow in 70 mm was reached at 30 % of moisture content when KCP slime at 39–40 %.
3. Limestone-slag slime as KCP slime is kinetically unstable. Time of sedimentation is not higher than 20 minutes.
4. Initial water-absorbing capacity of sedimentation volume in two slimes was equal at the same moisture content. But at the same fluidity limestone-slag slime made denser settlement.
5. Limestone – slag slime compacted (reducing of sedimentation volume) in 24 hours. KCP slime in 11 days. Final water – absorbing capacity of limestone – slag and KCP slimes after 24 hours were not very different.
6. Values of static shear stress of slimes were almost equal.
7. Limestone – slag slime's dynamic shear stress was almost in 4 times at the same moisture content and in 2 times at the same fluidity higher than KCP slag's.
8. The difference between dynamic and static shear stresses of limestone – slag slime was not so big. At the same time KCP slime's dynamic shear stress value was in 4-6 times higher than static.
9. Limestone – slag slime had high plastic viscosity of unbroken structure at the same fluidity with KCP slime. But at the same moisture contents these viscosities were almost similar.
10. Completely broken structure's viscosity of limestone – slag slime was in 2–3 times higher than KCP slime's. Also it increased in higher temperature whereas KCP slime's viscosity was not.
11. In KCP slime the difference between viscosities of unbroken and broken structures was higher than this difference in limestone – slag slime.
12. Moisture content strongly affects the thickening of limestone – slag slime. At 37 % moisture content low dispersion slime (008 sieve residual was 14 %) contained granular slag thickened in 26 days. The using of molten slime instead of granular did not improve fluidity of limestone – slag slime.

13. Limestone – slag slime included molten slime set more quickly. Such slime lost its fluidity in 20 days while slime contained granular slag in 24 days.

All described states are useful for recent prepared slimes at testing in static conditions. In case of thorough stirring duration of fluidity keeping must increase.

Described high density of blast-furnace granular slag is considered by researchers as decreasing factor of kinetic stability of cement raw slimes contained that slag. This statement also applies to phosphate slag.

Coefficient of equal falling (e) of phosphate slag and clay can be calculated by:

$$e = \frac{d_c}{d_s} = \frac{\sqrt{\delta_s - 1}}{\sqrt{\delta_c - 1}}, \quad (1)$$

Where δ_s and δ_c is slag and clay density, d_c and d_s is diameter of their particles.

The density of granular slag was 2.92. $d_s = 2.60$ were used. So after calculations equal falling coefficient of slag and clay particles was equal to 1.1. In other words, to obtain slag suspension with the same kinetic stability with clay's it is necessary to increase. At other same conditions dispersion degree of slag almost to 10 % in compare with clay.

Clay is grinded easy. Furthermore, clay can provide considerable product with colloidal size of fraction.

Granular phosphoric industrial slag at typical grinding provides small amount of colloidal size fraction. Increasing of grinding fineness by decreasing of residual on 008 sieve from 14 % to 8 % results in growth of 60–10 mkm fraction.

Therefore, the variant to increase of grinding fineness of granular phosphate slag to 10 % in compare with clay for kinetic stability is not possible.

This statement is based on results of slag tests on laboratory grinding mill. The grinding of limestone was not done there. At the same residuals on 008 sieve limestone powder had considerably higher fineness. Therefore, low dispersion of grinding represents in granular phosphate slag. But it does not mean that such material cannot be grinded more finely. For increasing grinding fineness loading components of grinding mill must be changed.

Cement raw slime is kinetically unstable at all. For example, KCP slime settled in 20 minutes. Almost the same situation was observed in limestone – slag slime. Therefore, there is no necessarily to achieve kinetic stability of limestone – slag slime by increasing of grinding fineness. Consequently, grinding fineness that is used in plants (8–14 % remainder on the 008 sieve) recommended. Slime stability can be carried as usual by mechanical stirring.

Moisture content of cement raw slime is important operation property. Low limit of moisture content commonly is determined by its fluidity on fluidity – meter device.

At the determination of low limit moisture content of limestone – slag slime contained phosphate industrial slag other properties should be taken into account. Properties are such as initial water – absorbing capacity of sedimentation volume, dynamic shear stress and thickening.

There is an opinion that kinetic stability also depends on moisture content. But this dependence is not used in research work because cement raw slime is kinetically unstable.

According to fluidity and shear stress value for limestone – slag slime 30 % of moisture content would be enough. But this moisture content was too low taking into account water – ability capacity of sedimentation volume and thickening of slime.

Water – ability capacity of sedimentation volume of dispersion system is defined by shape of particles and distribution of dispersion composition. Structure formation in system increases its sedimentation volume.

Structure formation at the same time is defined by chemical compositions of solid phases entered into dispersion system and their interaction with dispersion system. Mechanism of structure formation in limestone – slag slime is serious and big issue that is not considered in this research work.

Grinded granular phosphate slime generally contains narrow fraction and its grains are anisodiametrical. It has good effect on increasing of limestone – slag slime water – absorbing capacity of sedimentation volume. But initial water – absorbing capacity of settlement is considerably higher at 37 % moisture content than at 30 %.

Thickening of slime also depends on its moisture content. At 30 % moisture content slime thickens rather quickly. And at 37 % moisture content slime mobility maintains for 26 days.

In accordance with these cases low limit of moisture content for limestone – slag slime can be recommended as 37 %.

Results of that research work show that structure formation of limestone – slag slime occurs from commencement. It reveals because slime viscosity does not obey Einstein's law fluidity curve does not intersect coordinate origin, slime has resilient – plastic properties, etc.

The difference $\eta_o - \eta_d$ in KCP slime is higher than in limestone – slag slime. So its structuring is higher. At the same time resilient is clearer in limestone – slag slime because θ_s and θ_d are close.

At higher moisture content sedimentation volume increasing in limestone – slag slime can be explained by decreasing influence of volume concentration of dispersed phases on structure formation.

Apparently at limestone – slag slime kept in quiescence structure formation should be divided into three stages: initial stage, thickening and gelling accompanied with sharp hardening. And only because of last structure formation stage some doubts appears about the possibility of limestone – slag slime using at cement production. But the fact that slime sets only in quiescence conditions during a long time is omitted. At industrial conditions slag slime does not set and can be used at cement production with moist preparation of raw materials.

Experimental – industrial tests at KCP showed that there was no any property abnormality of limestone – slag slime in horizontal stank. Slime can settle also in vertical stank if it is not mixed. But it cannot be permitted.

According to P.I. Bazhenov, in Russian the Pykalev and Achinsk plants used nepheline slime as a raw component that indicates the possibility of phosphoric slag using in cement production with moist preparation. Nepheline slime generally consists of two calcium silicate that has high hydraulic activity.

3.2. Physical and mechanical properties of lime-slag sludge cement

Based on the carbonate-slag mixtures sludge the strength properties of cement were studied.

There were studied 5 mixtures (Table 9) of CaCO_3 and granulated phosphoric slag I (mixtures 1 and 2) and II (the rest). Mixtures 1 and 3 were composed on the basis of production of a belite clinker, 2 and 4 – an alite, and the mixture 5 – a clinker with the 60 % content of alite (SC = 0.67; 1.00 and 0.87). In the last two, the amount of limestone is 20–25% less than in clay mixtures.

Table 9. Mixtures composition, % by weight.

Component	Mixture				
	1	2	3	4	5
Phosphoric slag	57.47	39.22	61.42	41.40	46.88
CaCO_3	42.53	60.78	38.76	58.60	53.12

The studies show for obtaining an alite clinker the lime-slag mixture with SC = 1.00 can be burned at 1400 °C, in which lime is absorbed with reasonably practicable completeness ($\text{CaO}_{\text{free}} = 0.70$ %) for 10 minutes (slag contains $\text{CaF}_2 - 5.13$ %).

The product consists of the C_3S phase with small inclusions of the C_2S phases and fluorite. When calculating the amount of alite, it was assumed that at temperatures starting from 1300 °C and above, MgO (2.07 %), Al_2O_3 (1.70 %) are dissolved in the C_3S in the form of tricalcium aluminate, $\text{Fe}_2\text{O}_3 - 0.15\%$ and $\text{P}_2\text{O}_5 - 0.26$ %; the C_2S phase dissolves the C_3P . Dicalcium silicate is being formed at 1100 °C after 3 minutes; at 1200 °C and above – from the first minute of heating. The beginning of the C_3S formation coincides with the end of calcite decarbonization process and slag transformation into the C_2S . According to X-ray photographs *a*, *b*, *c* (according to the Fig. 8) and *d* (according to the Fig. 9) in the citric acid draw sediments, there fluorite and wollastonite are present.

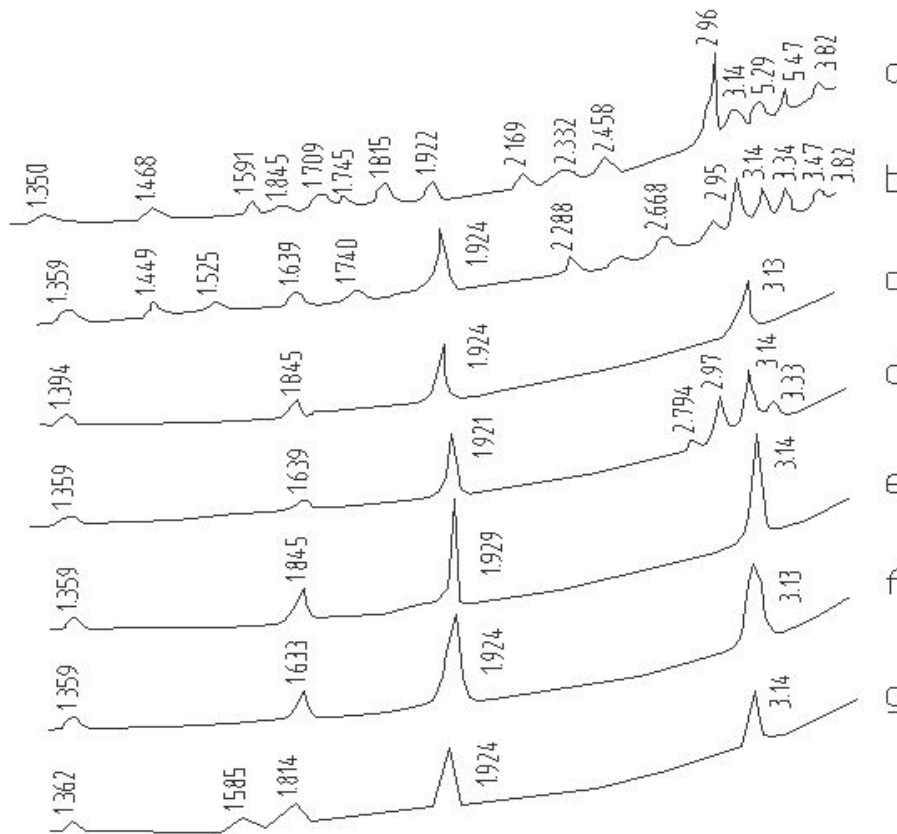


Figure 8. The citric acid draw sediments X-ray photographs
a – 1100 °C, 5 min; b – 1100 °C, 10 min; c – 1100 °C, 25 min; d – 1200 °C, 5 min;
e – 1200 °C, 10 min; f – 1200 °C, 20 min; g – 1200 °C, 25 min.

The amount of free fluorite above 1200°C decreases with increasing the temperature and duration of burning. According to the Fig. 9, g at 1500°C after 20 minutes there remains a tiny amount of the substance. Therefore, the bulk of fluorine was dissolved in calcium silicates.

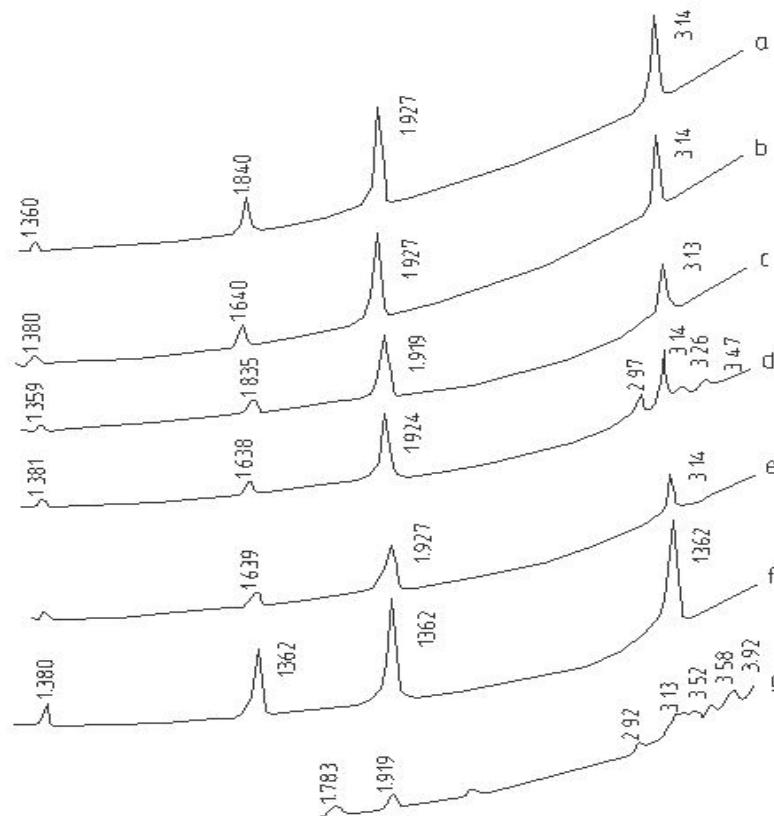


Figure 9. The citric acid draw sediments X-ray photographs
a, b, c – 1100 °C, 5, 10, 25 min; d, e, f, g – 1200 °C, 5, 10, 20, 25 min.

In the mixture 2, after adding 2 % of the CaF_2 into it and burning at 1400°C for 30 and 60 min., there are formed large alite crystals with smoothed angles (according to the Fig. 10). The further increase in burning duration at the given temperature or its increase up to 1500°C leads to a decrease in crystal size to $5\ \mu\text{m}$.

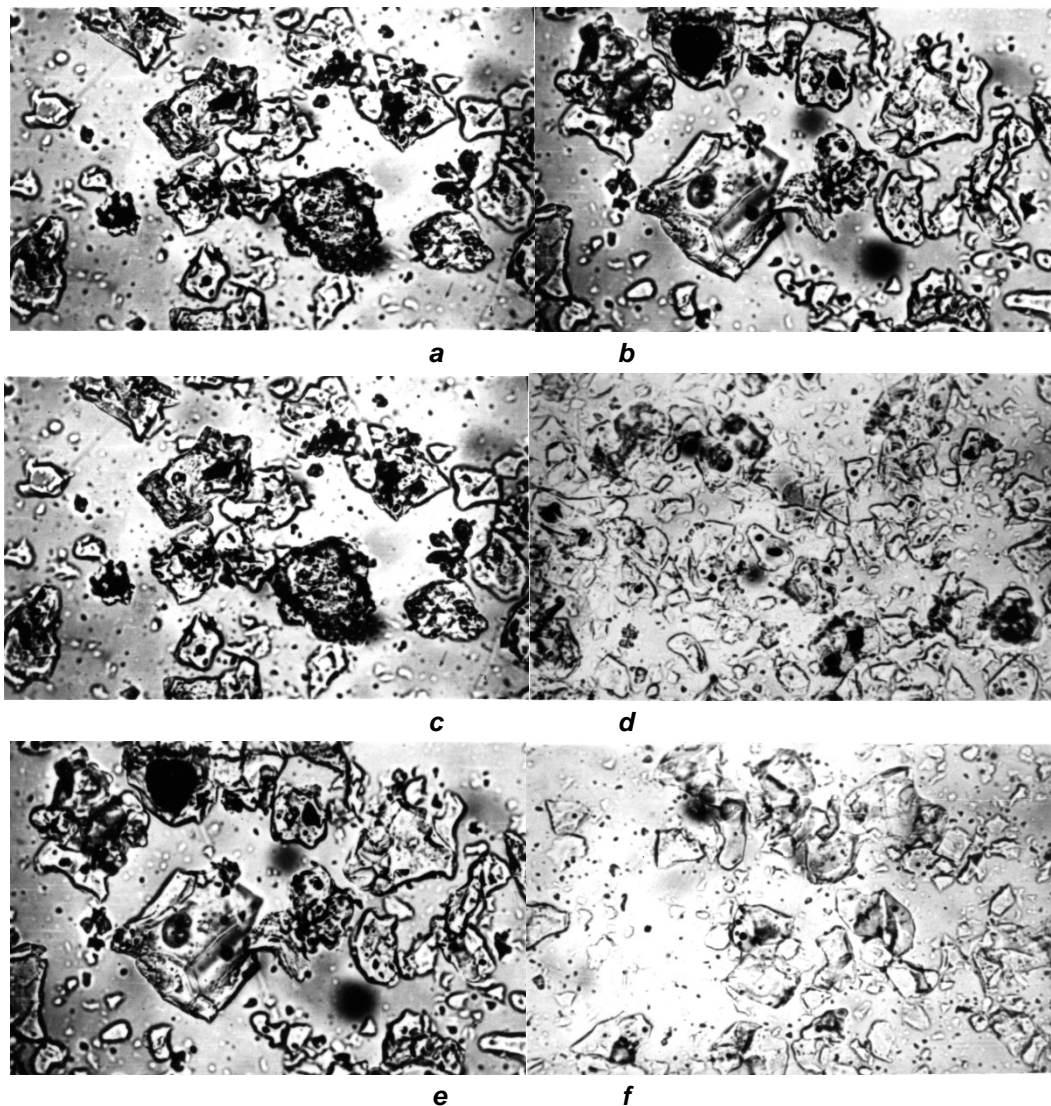


Figure 10. Photomicrographs roasted mixture 2 for C_3Sc 2% CaF_2 , x240.
a – 1400°C , 30 min; b – 1400°C , 60 min; c – 1400°C , 120 min; d – 1500°C , 30 min;
e – 1500°C , 60 min; f – 1500°C , 120 min

The mixture 5 with $\text{SC} = 0.87$ shall be also roasted at 1400°C within 20 minutes (Table 10), i.e. it has no advantage over the mixture with $\text{SC} = 1.0$. The samples roasted at 1300 , 1400 and 1500°C within 60, 20 and 10 minutes consist of alite and belite (according to the Fig. 11). Dicalcium silicate is formed from the first minute of heating. The C_3S lines (alite) appear on the X-ray radiograph of the cakes roasted for 10, 5, and 3 min at 1200 , 1300 , and 1400°C .

Table 10. Free calcium oxide of the mixture 5, % by weight.

Temperature $^\circ\text{C}$	Burning duration, min									
	1	3	5	10	15	20	25	30	60	120
1200	5.82	14.29	14.38	7.27	4.57	4.38	4.00	3.21	3.14	1.75
1300	9.11	17.37	9.10	4.80	3.10	1.36	1.50	1.91	0.47	0.13
1400	11.66	17.82	7.11	3.28	1.13	0.33	0.29	0.23	0.13	no
1500	15.82	8.50	2.24	0.41	0.09	no	–	–	–	–

With slow burning, the formation of belite and alite clinkers ends with a practical acceptable completeness at 1000 and 1400°C . Under slow burning conditions, as in the case of an abrupt one, reactions in the mixture 4 ($\text{KN} = 1.0$) proceed better than in the mixture 5. At 1100°C , there are formed as much alite as at 1200°C in case of abrupt burning. In the final roasted product of the mixture 4, only the alite lines are preserved. Cuspidine, as an intermediate formation, disappears at 1200°C .

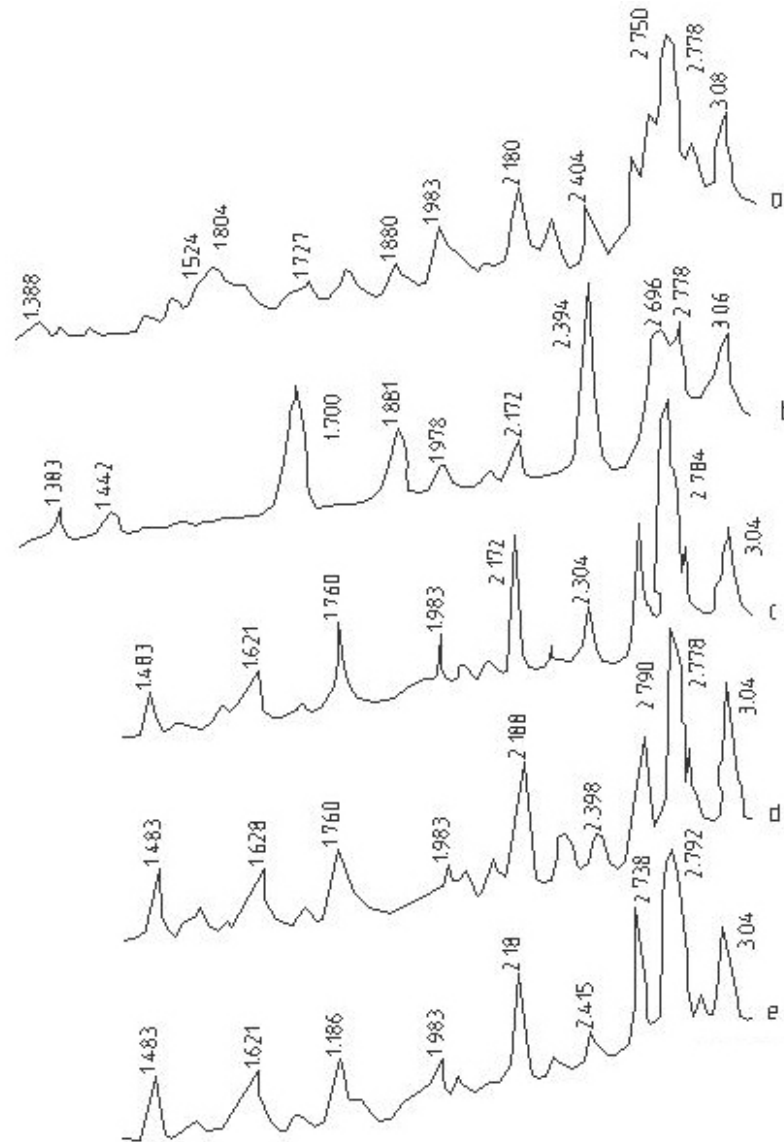


Figure 11. The roasted cakes X-ray photographs
a – C_2S , 1200 °C; b, c, d, e – 60% C_3S , 900, 1300, 1400 and 1500 °C

Mixtures for producing high-alumite clinker were tested at the pilot plant of the Cement Research Institute. A differential characteristic of the obtained clinkers, to be detected microscopically, is their high porosity. It leads to easy grinding.

3.2.1. Physical and mechanical properties of cement based on phosphoric slag and fuel consumption assessment for clinkers

Standard grid cement obtained with adding 3 % gypsum from clinkers 2-7, high-strength (Table 11). The most strength is the cement 6 with SC = 1.00 and containing the maximum alite amount, the least – cement 2 with SC = 0.95. However, the cement strength can be defined not only with the SC value.

Table 11. Cement test results (Water.cement = 0.4).

Cement	Density standard, %	Setting time, h-min		Cone flow diameter, mm	Breaking stress, MP					
		beginning	end		under bending, after			under compression, after		
					3 days	7 days	28 days	3 days	7 days	28 days
2	25.0	2-40	5-00	109	6.5	7.0	7.0	36.7	50.5	50.9
3	23.5	0-50	1-20	109	5.6	6.9	7.9	30.9	47.1	59.3
4	23.5	0-50	2-40	108	4.2	6.7	7.1	38.4	48.5	59.0
5	24.5	0-30	3-10	110	5.3	6.7	7.3	30.9	41.4	57.3
6	24.5	1-20	3-40	108	6.9	6.6	7.6	34.4	48.4	61.8
7	24.0	1-50	4-00	110	5.9	6.7	7.2	34.8	49.7	58.8

There was made an attempt to determine the effect of sulfur content in cinders and the iron amount (Table 12) on cement quality obtained from limestone-slag raw materials with additives.

Table 12. The content of basic oxides in clinkers, % by weight.

Clinker	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	SC	n	p
Used the cinder with the 2.5 % content of SO ₃								
1	66.65	22.00	2.19	3.75	0.92	0.95	3.70	0.58
2	66.53	23.65	2.24	3.95	1.04	0.91	3.82	0.57
3	67.24	21.65	2.24	4.80	1.00	0.99	3.08	0.47
4	65.34	21.40	2.19	4.83	0.90	0.94	3.05	0.45
5	66.53	22.35	2.35	5.05	1.07	0.95	3.02	0.46
6	66.89	21.50	2.49	5.11	0.97	0.99	3.26	0.49
7	67.24	20.70	2.30	5.20	1.15	1.00	2.76	0.44
8	65.83	20.70	2.78	6.62	1.04	0.96	2.20	0.42
Used the cinder with the 12.80 % content of SO ₃								
1	67.81	22.51	1.90	3.80	1.04	0.98	3.95	0.50
2	67.24	22.46	1.97	4.20	1.04	0.97	3.64	0.47
3	66.25	21.85	2.00	4.53	1.02	0.98	3.35	0.44
4	67.24	22.20	2.00	4.73	1.01	0.98	3.30	0.42
5	66.11	21.80	1.92	4.95	1.00	0.97	3.18	0.39
6	67.24	21.75	1.88	5.19	1.00	0.99	3.08	0.36

The data of the table 13 show the following:

Table 13. Cement test results (water.cement = 0.4; gypsum 5 %).

Cement	Density standard, %	Setting time, h-min		Cone flow diameter, mm	Breaking stress, MP					
					under bending, after			under compression, after		
					3 days	7 days	28 days	3 days	7 days	28 days
SO ₃ in cinder with 2.52 %										
1	22.25	0-45	6-32	107.0	5.1	5.4	7.1	37.0	43.8	53.4
2	23.85	0-40	6-45	108.0	4.9	5.4	6.5	35.4	42.0	48.2
3	23.38	2-07	7-27	107.0	4.8	5.2	6.6	35.5	47.5	60.0
4	24.50	0-37	6-47	116.5	4.6	5.5	6.2	30.5	37.7	52.6
5	22.75	1-05	6-35	108.0	4.7	5.4	6.4	30.5	40.0	51.7
6	25.00	2-45	7-05	110	4.8	5.6	6.9	32.5	44.2	49.1
7	22.50	1-20	7-35	110.5	4.1	5.3	6.0	27.1	40.1	48.6
8	23.75	1-12	9-15	110	4.1	4.5	5.9	23.3	31.7	37.3
SO ₃ in cinder with 12.80 %										
1	20.50	0-57	5-55	115.5	4.9	5.9	6.9	24.5	42.6	55.2
2	21.25	1-40	10-20	106.5	3.7	4.8	5.8	19.0	32.7	46.2
3	21.75	1-00	10-53	105.0	3.8	4.9	5.9	20.9	33.4	47.1
4	21.75	0-56	9-20	110.0	4.4	4.7	5.3	20.9	34.6	47.5
5	22.00	0-30	9-45	109.0	4.0	4.8	5.9	22.4	31.0	42.4
6	21.75	0-22	6-17	110.0	3.9	5.1	5.6	23.3	35.5	46.7

– sulfur in cinder and iron oxides in clinker have a significant effect on cements properties. In limestone-slag mixtures the low-sulfur cinders should be used;

– when using low-sulfur cinders the cement of 500 rank can be obtained from the clinker with SC = 0.94 and higher. At the same time, the Fe₂O₃ content in clinker can be brought up to 5 %. Further increase in the Fe₂O₃ amount reduces the cement rank despite its high SC (cements 6–8);

– with polysulphide cinders the cement of 500 rank can be obtained from a clinker with SC of at least 0.97 and the Fe₂O₃ content of not more than 3.80 %.

If the last limit is exceeded, cements do not meet the setting time standard requirements. The reason for this is, obviously, the high content of magnetite in polysulphide cinders. Clinker mixtures were made of limestone and slag with introducing cinders. The content of P_2O_5 was varied by adding tricalcium phosphate in the 3–6 mixture. The SO_3 content in the mixture ranged from 0.67–1.25 %.

Mixtures in the form of bars of 110×110×20 mm were roasted at 1400 °C for 4 hours in a laboratory furnace. The temperature was raised to 1400°C for 10 hours. As a result of prolonged burning the sulfur in cinders burned out, the SO_3 content in clinkers was leveled out. With an increase in phosphorus content the residual sulfur slightly increases in clinkers; it is comparatively larger in the case of using a polysulphide cinder.

Clinker 1. SC = 0.96; n = 3.75; p = 0.77. Alite – 75; C_4AF – 10 and $C_{12}A_7$ – 1%. Alite grains have irregular, angular, often with a rounded shape; there are also tabular or prismatic grains in splices with each other; grains size in cross-section is 0.05–0.2 mm; color is dark gray.

The intermediate phase fills small cavities between alite grains; irregular excreting shape, the borders are wavy, clear; color is light gray to grayish white; dimensions 0.1 mm in cross-section. Clinker porosity is 25–30 %.

Clinker 3. SC = 1.00; n = 3.34; p = 0.73, alite – 80; C_4AF – 11; $C_{12}A_7$ – 1 %. Alite crystals have irregular, isometric, rounded shape, tightly adjacent to each other, form almost continuous drainage aggregate; in some areas, the aggregate is so tight that its grain structure cannot be practically differed, and grain boundaries are difficult to be determined; grains size in cross-section is 0.05–0.25 mm. The intermediate phase fills cavities between the alite grains; with dimensions of 0.01–0.2 mm in cross-section. Clinker porosity is 15–25.

Clinker 5. SC = 0.96; n = 3.81; p = 0.63; Alite – 78; C_4AF – 11 %. Alite grains have irregular, isometric shape, less commonly slightly elongated, and are also tightly against each other; sizes of 0.01–0.3 mm with a predominance of grains of 0.1 mm. The crystals size of the intermediate phase is 0.01–0.1 mm in cross-section. Clinker porosity is 35–40 %.

The clinker crystallization rate using the 8-point Hyprocement system is estimated as average (4 points) with the exception for the 3rd (3.5 points).

The clinkers obtained using a high-sulfur cinder are distinguished by a denser structure and better alite crystallization.

Clinker 2. SC = 0.97; n = 4.24; p = 0.76. Alite – 77; C_4AF – 9; $C_{12}A_7$ – 1 %. Alite grains have irregular, isometric or slightly elongated shape with different sizes; there are also well-formed tabular or short-prismatic grains with slightly rounded peaks; with dimensions of 0.05–0.4 mm in cross-section. The intermediate phase is located in the alite grains interstitial tissue, repeating outlines of the latter; with dimensions of 0.01–0.15 mm in cross-section. Clinker porosity is 10–15 %.

Clinker 4. SC = 1.00; n = 4.12; p = 0.63. Alite – 82; C_4AF – 10 %. Alite grains, except in very rare exceptions, fill cavities without gaps; with dimensions of 0.01–0.2 mm. Clinker porosity is 10–15 %.

Clinker 6. SC = 0.96; n = 3.68; p = 0.58. Alite – 72; C_4AF – 10; C_2F – 1 %. Alite grains have irregular, isometric or elongated shape, are also tightly against each other. A nonequigranular grain structure is characteristic: along with the widely-spread grains of 0.01–0.3 mm, there are areas that sharply stand out against the general background with grains size up to 0.5–1.0 mm in cross-section. In such areas, the intermediate phase content is sharply reduced.

In general, clinkers have a glomeroblastic structure with a crystallization degree of 2 and 6 clinkers equal to four points, and the clinker 4 – three points. Cements from these clinkers were milled at the same duration (1 h 50 min). The fineness of cement grinding is almost the same, about 300 m².kg. The data in the table 6 show the following:

Table 14. Mechanical and physical testing results of clinker cements.

Cement	SO ₃ content, %	008 sieve residue, %	Density standard, %	Setting time, h-min		Water. cement	Cone flow diameter, m	Breaking stress, MP					
								under bending, after			under compression, after		
				beginning	end			3 days	7 days	8 days	3 days	7 days	28 days
1	2.08	5.5	23.25	1-10	5-20	0.39	111	5.6	7.2	8.5	36	54	71
2	1.60	5.8	23.25	1-10	6-55	0.38	109	5.2	5.7	7.4	23	39	63
3	2.00	6.3	23.25	2-35	7-20	0.35	107	6.5	6.9	9.1	32	59	82
4	1.76	5.2	23.50	1-45	6-45	0.37	106	6.0	7.8	9.0	37	57	77
5	2.16	5.6	23.75	3-50	7-50	0.37	107	6.2	7.8	8.2	44	58	72
6	2.08	6.8	23.50	3-25	8-10	0.38	110	5.1	6.6	7.8	31	46	66

– cements are with high strength; among them the cement 2 of furnace blend with a high-sulfur cinder has the minimum strength (63 MPa), and the maximum – with a low-sulfur one (cement 3, SC = 1.00; 82 MPa). In general, when using a high-sulfur cinder instead of a low-sulfur, the cements rank with a high SC decreases by 5–8 MPa. There is no pronounced dependence of cements strength against its phosphorus pentoxide content in the range of 1.00–2.23 %. In terms of three-day strength, cements are referred to the quick-hardening category;

– cements water demand is relatively low. This feature of high alite cement from phosphoric slag we mention above;

– in terms of setting time, cements meet the Russian State Standard GOST 10178-85 requirements. The data in the table 15 show the following:

a) cements grindability is slightly improved with SC increase;

b) cements are characterized by relatively low water demand (water.cement = 0.36–0.37);

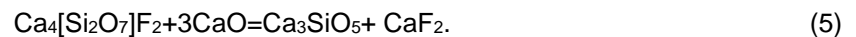
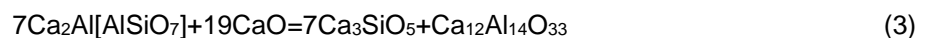
c) cements show a slow initial setting (from 3 h 25 min to 4 h 20 min);

g) cements activity increases from 44.6 to 59.3 MPa, depending on the value of SC = 0.92–0.98.

Table 15. Physical and mechanical parameters.

Cement	SO ₃ content, %	008 sieve residue, %	Density standard, %	Setting time, h-min		Water. cement	Cone flow diameter, mm	Breaking stress, MP					
								under bending, after			under compression, after		
				beginning	end			3 days	7 days	8 days	3 days	7 days	28 days
1	0.4	9.6	22.75	4-20	9-09	0.36	108	4.7	5.2	5.9	22.3	33.3	44.6
2	0.4	9.2	22.50	3-25	7-59	0.37	106	5.1	5.1	6.1	24.5	36.1	50.7
3	0.4	8.0	22.50	3-25	8-09	0.37	108	5.8	5.6	6.4	33.5	43.5	59.3

Theoretical fuel consumption for alite clinker is determined by the total reactions.



Due to reduction in release of the reaction gaseous products, the total consumption of raw materials decreases by at least 1.13 times. The theoretical fuel consumption calculated using the data of the Karaganda Cement Plant for clinker formation in an alite mixture is 2.246.588 kJ.t versus 3.059.315 kJ.t based on carbonate, i.e. it decreases by 1.3 times.

4. Conclusions

1. Study of impact of concentration of dispersion phase on rheological and elastic-plastic-viscous properties of slug of charge materials, consisting of limestone and phosphorus slag, firstly applied for production of high alite Portland cement, demonstrated ability of slag to preserve solid phases of charge materials in suspension.

2. Slags of phosphoric plants can be applied for cement production by wet method of raw materials preparation. Granular slag is preferable to molten as cement raw component.

3. It is recommended to control fineness of grinding of residual slag by quantity of rest on sieves 02 and 008. Rest on a sieve 008 shall be within 8–14 %. Rest on a sieve 02 shall not be more than existing norms.

4. It is recommended that lower limit of slag moisture was 37 %.

5. Stability of residual slag is achieved by the existing methods of slags blending.

6. Blending mode in vertical mixing basins shall be developed taking into account specific features of residual slag.

7. The more strength activity of cements from limestone-slag mixture is, the more the SC is. With the same SC value with a relatively high strength of cement one can achieve controlling the content of C₄AF in it. Of great importance for the strength of cements is also the crystallization degree of clinkers. High alite clinkers with an intermediate content of not more than 20 % have a crystallization degree of not more than 4 points according to the Giprocement system. At this crystallization degree, a clinker with

SC = 1.00 obtained using a low-sulfur cinder provides cement with an activity of 82 MPa with a standard grinding fineness; when using a polysulphide magnetite cinder, the strength of the cement is reduced to 77 MPa.

8. Equivalent fuel consumption, for burning 1 ton of Portland cement clinker from the phosphoric slag mixtures compared to the limestone-clay mixture of the Karaganda Cement Plant with a wet production method is reduced by at least 15 %, which is confirmed by a pilot-plant test performed at the plant.

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