Phase Composition and Structure-Formation of the Low-Clinkered Floured Cements

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Abstract

We have carried out studies on the production of low-clinkered floured cements (LCFC) on the basis of natural and technogenic waste. The research on optimizing the compositions, strength, durability and performance properties of low-clinkered floured cements (LCFC) was carried out. Therefore, we studied the new products in the process of hydration of mechanically activated multi-component cements in the presence of technogenic wastes of the industry (waste of limestone crushing at opencast mines, metallurgical and phosphoric slag) and surface-active reagents (SAR) (superplasticizer S-3); as well as the development of compositions of high-strength and technological sorts of cement concretes.

Thus, the low-clinkered floured cements developed by us based on industrial technogenic waste that meet the modern requirements, i.e. they improve physical-mechanical characteristics of the material and positively influence the ecological situation and allow decreasing the cost of final product.

The physico-chemical research of the processes of hydration of low-clinkered floured cements with additive of superplasticizer S-3 were carried out by modern methods using X-ray diffract-meter D8ADVANCE (Bruker company) with Cu-radiation and synchronous thermo-analyzer STA 409 PC Luxx (Netzsch, Germany) at exposure mode of 10 °/min in the platinum crucibles in the air conditions.

Introduction

The one of acute problems in the cement production of our country is weak providence by raw material as the considerable part of the natural raw material sources located in the nearest closeness is exhausted and hasn't real substitution. In the near future, it can leads to inevitable partial or full substitution of the natural raw material by the technogenic [1-5].

Up to days in the production of the cement, except the slag, we used widely the technogenic correction additives. Due to irreversible exhausting of the sources of natural raw material, the importance of the raw material should increase steadily [6-8].

The ecologic-economic presuppositions for the performance of present work are the annually increasing dumps of slag and bran of limestone quarries. Kazakhstan has 10 million tons of electro-phosphoric slag with annual output of 700-800 thousand tons (Novo-Dzhambul phosphoric plant, Ltd. "Kazphosphat", Taraz City) and 85 million tons metallurgical slag (Karaganda metallurgical plant, Ltd. "Ispat Carmet", Temirtau City) with annual output of 1000 thousand tons.

There is also ash of Thermal Power Stations in the following Cities of Akmolinsk region: Astana, Karaganda, Kokshetau, Petropavlovsk, as well as in the Cities of North-East Kazakhstan.

The richest deposits of carbonate, dolomite and dolomitic species located in the South-Kazakhstan in Tjulkubas district and in the Caratau Mountains of Dzhambul region, with stocks of milliards of tons. It is obvious that year by year the problem of their ecologically efficient recycling becomes more acute, i.e. conversion of those wastes into the complete secondary raw material.

The only one way that can "adsorb" them in production of building materials. The traditional method to recycling of those wastes for reclamation of territories and for the arrangement of the bases of highway is economically ineffective, if consider the hidden potential opportunities of their conversion into the knowledge-intensive hydraulic binding materials. The bases for this are their chemical composition and physical structure.

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We offer the most expedient method to solve this problem by developing the technological bases of the production of low-clinkered floured cement (LCFC), which can contain up to 70% of those wastes and not to concede on properties to civil construction cements of the marks of 400, 500 and 600 (GOST 10178). The basic advantages of LCFC technology are wastelessness, saving the reserves of cement natural raw material, as well as "the pantophagy", specified by the opportunity to use different wastes and non-metallic minerals, as active components of binding materials. Moreover, there is no emission of neither carbon dioxide nor dust as during the production of Portland-cement.

Results and Discussions

Raw materials

As a binding material we applied the Portland-cement of Ltd. "Standard-cement" PC 500 D0 according to GOST 10178 – Portland-cement 500 without additives with normal hardening.

The mineral fillers of carbonate containing rocks (limestones) deposits located in South-Kazakhstan region, Tulkubas district of Ltd. «Umit SD» was used for the research.

The metallurgical and phosphoric slags were used in the research as technogenic fillers.

The metallurgical slag of Karaganda metallurgical industry of JSC "Ispat-Karmet" has the following chemical composition (mass, %): CaO – 40.46; Al_2O_3 – 14.12; MgO – 7.97; SiO_2 – 36.08; TiO_2 – 0.99; BaO – 0.32; MnO – 0.33. The phosphoric slag from the Novo-Dzhambul phosphoric plant of Ltd. "Kazphosphat" has the following chemical composition (mass, %): CaO – 45.1; Al_2O_3 – 2.65; MgO – 2.40; SiO_2 – 42.0; K_2O – 0.15; Fe_2O_3 – 1.25; SO_3 – 0.43; F – 2.20; P_2O_5 – 2.60.

Used chemical additives(superplasticizers) C-3 (TS 6-36-0204229-625-90*) of open joint-stork company "Polyplast" production represents the non-caking powder of brown color, easily soluble in the water.C-3 belongs to anion-active surface-active substances and is a mix of oligomeric and polymeric compounds, which are formed during the condensation of naphthalene with formaldehyde including their further neutralization by the alkali (NaOH) and the technical lingosulphonates, non-reacted β-naphthalene-sulfo-acid and sodium sulfate.

Research Methods

The X-ray phase analysis of a cement stone was carried out by ionizing method of radiation of the intensity of radiation on the X-ray diffractometer D8ADVANCE (Bruker Company) including the use of Cu-radiation.

Thermal, thermo-gravimetric and differential scanning calorimetric were carried out by the synchronous thermo-analyzer STA 409 PC Luxx (Netzsch, Germany) at exposure mode of 10 °/min, in the platinum crucibles in the air conditions.

The Features of Hydration and Hardening Processes of Low-Clinkered Floured Cements

The cement stone sample for X-ray phase analysis (XPA) was prepared by the following manner. The dough with normal thickness is prepared from homogenized binding material and then it is filled into a casting mold. To hardening the dough, the filled casting mold is tapped on a table edge several times. The dough excess is removed by a steel plate; the sample is slightly brought to uniform surface. Then the mold is accurately closed with a cover densely fastened to the mold by screws. The casting mold with the dough is placed into exact environ for hardening the studied binding material, mixture or concrete (steaming, normal or accelerated hardening). At the end of hardening for the fixed term the sample is carefully pressed out of the casting mold and it is immediately subjected to X-ray analysis. The offered method of analysis has an advantage in comparison with the traditional one, which keeps in integrity crystals of binding material hardening and allows obtaining clearer X-ray diffraction with strong intensity of reflexes.

Hydration degree of LCFC prepared with various fillers and in the presence of 2.5% of the additive of superplasticizer S-3 and without it is shown in the Table 1. Thermo-gravimetric data of hardening LCFC and initial Portland cement are given in the Figs. 1-3. The analysis of obtained data shows that hydration degree of initial Portland cement, as a rule, is higher than that for LCFC. The sandy LCFC has the least hydration degree. S-3 injection causes to considerable decrease of hydration degree for both initial cement and LCFC.

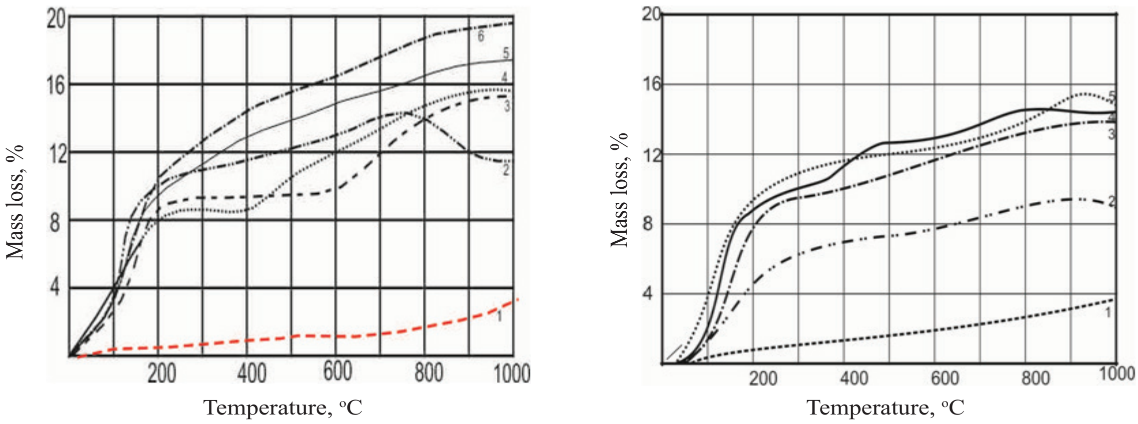
Taking into account of increase of binding material, as a rule, when adding the S-3, one can state that there is not always the direct dependence between the cement and LCFC activity and their hydration degree. Obviously, the provision demands the further research for the proof.

Decrease of binding material hydration degree in the presence of superplasticizer S-3 can be, probably, explained by the reduction of tempering water amount and decrease of clinker content in their composition, and also by the adsorption of superplasticizer on an active surface of binding material grains.

Table 1
Hydration degree of LCFC depending on the hardening conditions

Binding material	S-3 content, %	Hydration degree, %				
		Normal hardening, in days				Steaming
		1	3	7	26	
Initial cement	- 2.5	11.7 7.5	12.3 11.5	12.4 12.2	13.5 12.5	15.2 12.2
LCFC (electro-termo-phosphoric slag)-70	- 2.5	8.5 6.7	12.3 10.5	12.5 12.4	- -	15.0 12.2
LCFC (blast furnace slag)-50	- 2.5	7.5 6.0	11.5 11.0	11.7 11.5	- -	14.5 11.2
LCFC (Portland cement)-50	- 2.5	- -	5.2 4.9	11.0 8.0	11.2 9.0	12.0 7.9

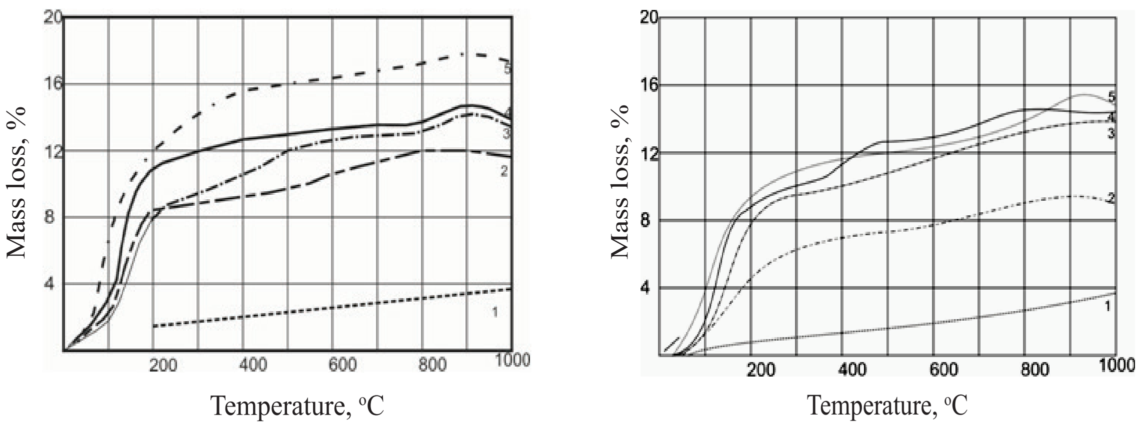
a



b

Fig.1. Thermo-gravimetric curves of a cement stone from Portland cement M500 Д0 without additive (a) and with C-3 additive (b): 1 – initial cement; 2, 3, 4, 6 – after 1, 3, 7 and 28 days of natural hardening respectively; 5 – after thermal-wet-treatment.

a



b

Fig. 2. Thermo-gravimetric curves of a cement stone from LCFC and on the basis of blast-furnace slag LCFC-50 without additive (a) and with S-3 additive (b): 1 – initial LCFC; 2, 3, 5 – after 1,3,7 days of natural hardening respectively; 4 – after thermal-wet-treatment.

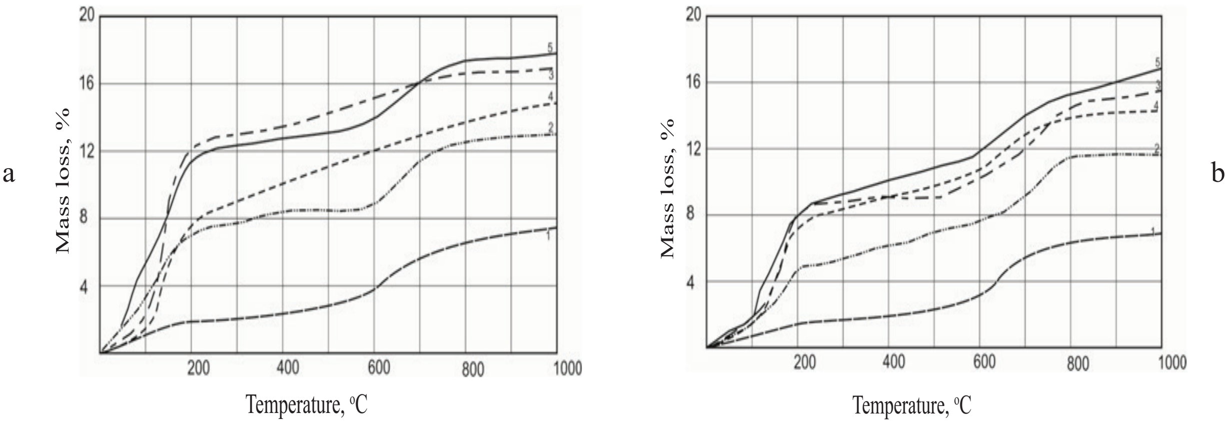


Fig. 3. Thermo-gravimetric curves of a cement stone from LCFC on the basis of sand LCFC-50 without additive (a) and with S-3 additive (b): 1 – initial LCFC; 2, 3, 5 – after 3, 7, 28 days of natural hardening respectively; 4 – after thermal-wet-treatment.

Features of Phase-Formation of Low-Clinkered Floured Cements

Figure 4 shows the thermographic curves of the cement stone from Portland cement with 2.5% of S-3 additive and without it. The first, well developed, contain endothermic effects appear in thermographs in the interval of 120-170 °C and they are caused by adsorbed water loss and dehydration of gypsum, hydro-aluminates and hydro-ferrites of calcium and gel composites. Though configurations of these effects are similar, nevertheless there are some distinctions between them. When adding the S-3 during the hardening the end effects on thermographs decrease and they are displaced towards the increased temperatures. It testifies about adsorbed water reduction and increase of the amount of water chemically bonded with hardening products that should promote the improvement of cement stone properties. The second visible endothermic effects on thermographs are observed in the range of 450-515 °C and they are typical for $Ca(OH)_2$. The analysis of these effects shows that in normal hardening conditions the calcium hydroxide content in the hardening system is increasing up to 7 days, and then considerably decreases. It is predetermined by interaction with a hydraulic additive. The biggest $Ca(OH)_2$ allocation is observed in the cement stone at steaming. In the presence of superplasticizer S-3 the developed $Ca(OH)_2$ effect is observed in thermographs in 3 days of normal hardening. The third developed endothermic effects at the temperature of 730-800 ºC characterize calcium hydro-silicates dissociation and dehydration. The analysis of obtained data shows that when adding the S-3 these effects are displaced towards the increased temperatures. Moreover, in the presence of S-3 the exothermic effects in the range of 433-452 ºC are found in thermographs, which are connected, evidently, with polymer burning-out.

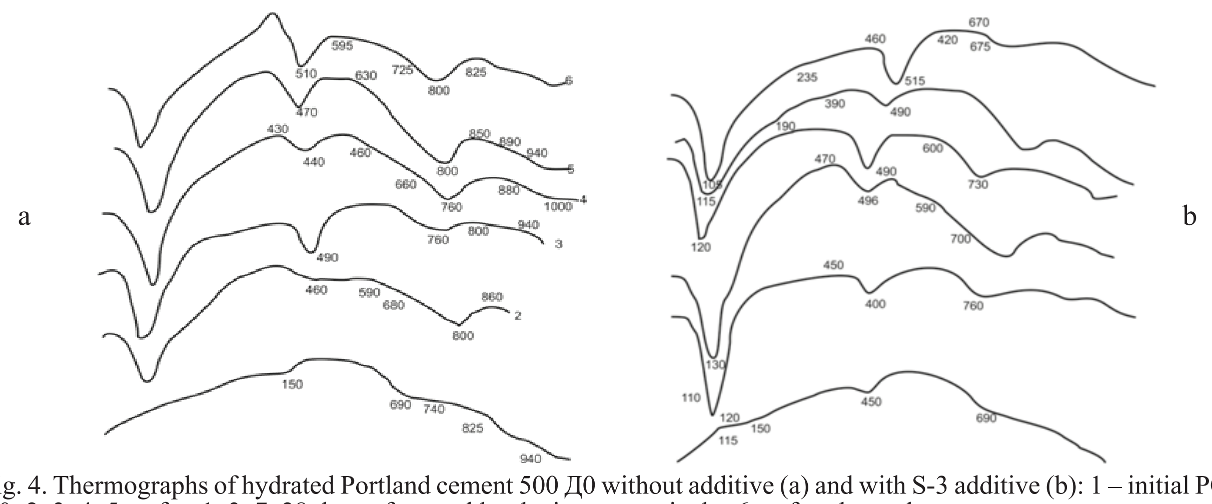


Fig. 4. Thermographs of hydrated Portland cement 500 Д0 without additive (a) and with S-3 additive (b): 1 – initial PC 500 Д0; 2, 3, 4, 5 – after 1, 3, 7, 28 days of natural hardening respectively; 6 – after thermal-wet treatment.

The same hydrate phases are revealed in thermographs of the cement stone from LCFC based on blast-furnace slag and sand (Figs. 5 and 6). In the presence of S-3 there is also no peak typical for $Ca(OH)_2$ in thermographs of hydrated LCFC based on blast-furnace slag and sand.

XPA confirms the presence of hydrated phases in hydrated binding materials, which are found by means of differential thermal analysis (DTA). XPA shows in the presence of free lime in hardened binding materials with the superplasticizer additive; however, its quantity is much less than that in the cement stone without S-3 additive.

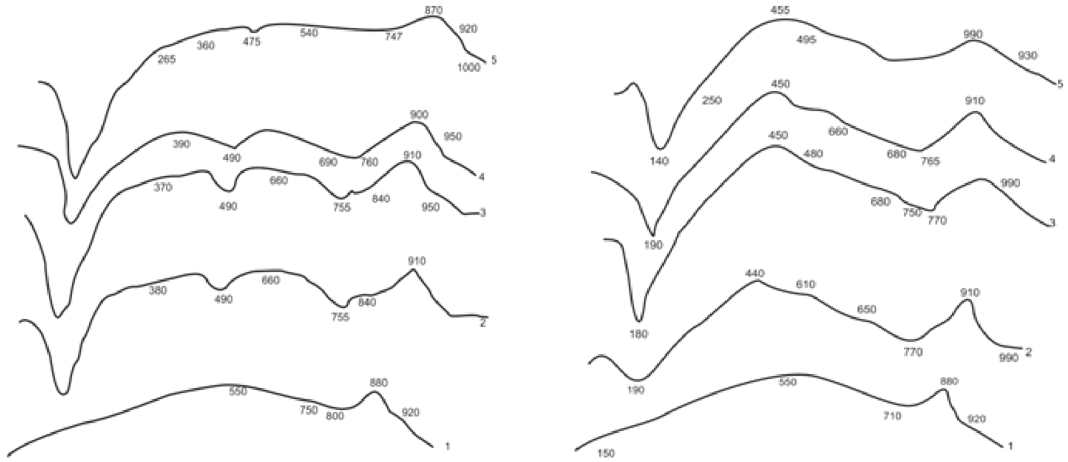


Fig. 5. Thermographs of hydrated LCFC based on blast-furnace slag LCFC-50 without additive (a) and with S-3 additive (b): 1 – initial LCFC; 2, 3, 4 – in accordance in 1, 3, 7 days of natural hardening respectively; 4 – after thermal-wet-treatment.

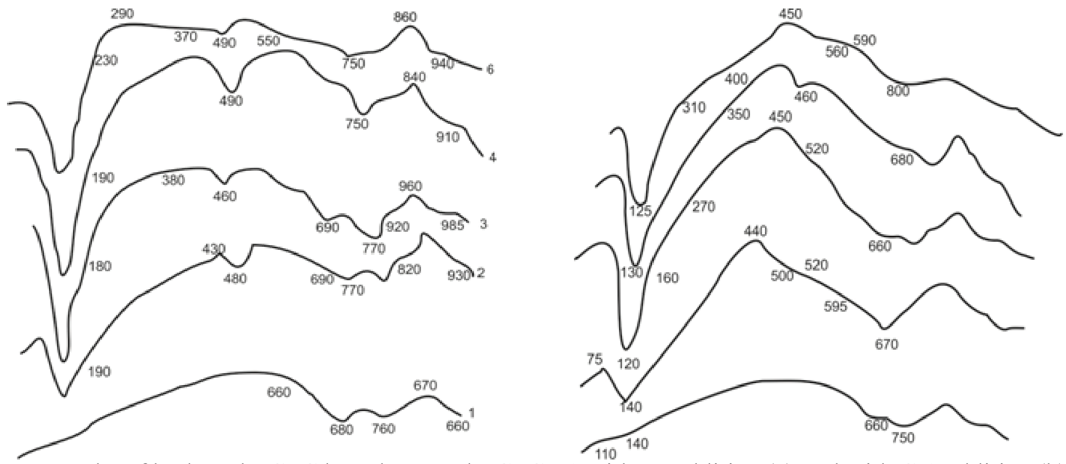


Fig. 6. Thermographs of hydrated LCFC based on sand LCFC-50 without additive (a) and with C-3 additive (b): 1 – initial LCFC; 2, 3, 4 – after 3,7, 28 days of natural hardening; 5 – thermal-wet-treatment.

Conclusions

1. It is established, that LCFC hydration degree is less than hydration degree of Portland-cement. In the presence of superplasticizer the hydration of both cement and low-clinker floured cement on its basis considerably decreases;

2. It is established that the addition of super plasticizer S-3 into the composition of Portland-cement leads to loss of adsorbed water, to the dehydration of gypsum, hydro-aluminates and hydro-ferrites of calcium, as well as gel composites;

3. It is revealed, that the decrease of quantity of adsorbed and increase of quantity of chemically bonded with the products of hardening of water brings to the improvement of strength and performance properties of the cement stone;

4. Free lime content in the cement stone based on LCFC also decreases, in the presence of S-3 it decreases even more (up to complete disappearance). It is predetermined by interaction with a hydraulic additive.

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