



Research article

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Phase composition of belite cements of increased hydraulic activity

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✉ mirola_1107@mail.ru**Keywords:** cements, clinker, belite, alite, aluminates' phase, binders, hydration, hardening

Abstract. The work is devoted to resource-saving technology development of belite cements. To solve the problem of slow hardening of belite cements, the influence of clinker phases on hydration and structure formation of binders has been studied. Composition and structure of substances were analyzed using X-ray, differential thermal methods and microscopy. Dependence of belite cements' design strength with a saturation rate of $SR = 0.73-0.80$ on the content and properties of C_3S alite was determined. Increase in C_3S activating ability during formation of alite, based on natural silicates structures was revealed. It was found that the combination of C_2S belite and calcium silicoaluminate C_6A_4MS in cement stimulates hydration and hardening processes. Intensive formation of stable hexagonal hydroaluminates and hydrogelenite provides a high rate of structure formation. Advantages of co-hydration of C_2S with C_3S and C_6A_4MS were realized in the mixed cement obtained from belite and aluminate clinkers. Studies of clinkers based on skarn-magnetite ore dressing waste indicate the preference of technogenic raw materials for improving belite cements technology.

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1. Introduction

Cement production status determines the level of industrial potential of the state and the rate of construction. Cement industry is a large consumer of raw materials, fuel and energy. Efficient use of resources is an important condition for effective development of production and cement usage. A fundamental resource saving direction is belite cements technology development, characterized by low content of alite phase C_3S [1, 2]. Belite cements are characterized by low saturation rate (SR), the value of which does not exceed 0.80. When belite cements producing, the consumption of calcium carbonate in the raw material mixture is reduced, the cost of thermal energy for clinker burning is reduced and carbon dioxide emissions are reduced as well [3–7]. Belite cements favourably differ in low liberation of heat during hydration; and ensure concrete durability when used in aggressive environment. However, difficulties in obtaining and using cements with low alite content arise due to low grind ability and slow hardening thanks to C_2S increased belite proportion [1, 6].

To intensify belite cements hardening, it was proposed to stabilize active modifications of C_2S by introducing additives into the raw material mixture [8–10], shifting the process of C_2S formation to a high temperature region [2, 11, 12] and high clinker cooling rate [2, 13]. Attempts to increase clinker activity specifically due to the belite phase require complex technical solutions and therefore have not been implemented yet.

A promising direction of intensification of belite cements curing involves C_2S combination with phases of high hydration activity. This can be achieved by changing a raw material mixture composition to obtain a clinker or by belite cement combining with other cements [14–17]. Most of the developments are devoted to cement containing belite and calcium sulfoaluminate [18, 19]. Information on the effect of other clinker phases on intensification of belite cements hardening is scarce. The relevance of the problem increases with technogenic raw materials involvement in cement production, accompanied by a change in clinker phases' composition [8, 12, 18, 20–26].

The purpose of the work is studying the possibility of intensifying belite cements hardening by adjusting the phase composition.

To achieve the objective, the following areas were identified:

- synthesis and study of belite cements using polymineral technogenic material;
- study of belite cements with different alite contents;
- development of a mixed cement composition based on studies' results of hydration and hardening of belite and aluminate phases.

This work is aimed at creating low-energy-intensive cements characterized by intense hardening, high strength and durability.

2. Methods

2.1. Raw materials

The object of the study was belite cements, obtained by co-grinding of 95 % of belite clinker and 5 % of calcium sulfate dehydrate. Belite clinker was synthesized by raw material mixture burning, consisting of limestone, skarn-magnetite ore dressing waste and silica clay rock (Table 1). Waste contains modifying elements, wt.%: TiO_2 0.50 – 0.53; P_2O_5 0.25 – 0.30; MnO 0.35 – 0.40; V_2O_5 0.04 – 0.06; Cu 0.04 – 0.05. Mineral base of waste is composed of silicates of various genesis, composition and structure, wt.%: pyroxenes 20 – 25; epidote 10 – 13; feldspars 8 – 12; chlorites 7 – 10; scapolite 8 – 11; grenades 7 – 12; amphiboles 7 – 14. The following waste is also present, wt.%: pyrite 4 – 8; calcite 4 – 7; quartz 2 – 4; magnetite 3 – 4.

Table 1. Chemical composition of raw materials.

Material	Containing of the oxide, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	other	loss during sintering
Limestone	0.6	0.1	0.3	50.9	4.9	0.2	0.1	0.1	42.8
Skarn-magnetite ores tails	37.5	9.1	16.8	10.4	5.1	1.2	14.3	1.5	4.1
Silica clay	77.2	5.7	2.5	0.7	1.3	1.2	1.8	0.2	9.4
Lignite-bauxite	13.4	50.2	3.2	0.9	0.4	0.2	5.1	0.1	26.5

To obtain aluminate clinker, raw material mixtures of limestone and lignite-bauxite were prepared (Table 1). Lignite-bauxite includes the remains of carbonized wood. Sulfoaluminate clinker was synthesized from a raw material mixture containing limestone, lignite-bauxite and skarn-magnetite ore dressing waste. FeS_2 pyrite presence in waste determined the possibility of their use as a sulfate-containing component.

2.2. Experimental details

Raw materials were preliminarily crushed to a complete screening through № 008 screen. Composition of raw mixtures for clinkers was calculated by well known methods. Raw mixtures were prepared by thoroughly mixing all the components. Samples of raw mixtures were fired at temperatures of 1300 – 1350 °C until clinkers' formation. Clinker phase composition was determined by the X-ray method.

Cements were obtained by grinding belite clinker with additives (calcium sulfate dehydrate, aluminate clinker). Strength properties of cements were determined on samples of 20×20×20 mm in size, made of cement dough. Cement samples hardened in water. Samples of materials hardened were analyzed using X-ray, differential thermal methods and electron microscopy. Differential thermal analysis method was carried out on a derivatograph of the Q –1500 D of system F. Paulik, J. Paulik, L. Erdey. The phase composition of the cements was determined using general purpose X – ray diffractometer, type DRON – 3M. The diffractometer is equipped with an BSV – 24 type X – ray tube with $CuK \alpha$ – radiation. The diffractograms were processed using difWin program.

3. Results and Discussion

3.1. Features of belite cements based on skarn-magnetite ore dressing waste

The results of chemical and mineral composition analysis of skarn-magnetite ore dressing waste indicate the possibility of using technogenic material in Portland cement technology. Experimental studies have confirmed feasibility of introducing waste into the composition of raw material mixture to obtain clinker cement [7]. Clinker phases of alite C_3S and belite C_2S inherit crystalline structures of natural silicates, characterized by close contact of main elements and impurities. This increases deformation of the crystal lattice and doping of clinker phases. Differences in structures of natural silicates determine the multistage formation of C_2S with the advantage of high-temperature synthesis of belite. It is known [2, 4, 11] that significant amount of C_2S formation in a narrow range of high temperatures increases the degree of thermal effect on the material and activates alite's formation. Convergence of synthesis processes of C_2S and C_3S enhances phase disequilibrium and increases their hydration activity. Modification of β - C_2S belite is stabilized due to increased sulfur concentration in the feed mixture. Belite crystallizes in the form of rounded grains, the size of which increases with increasing firing temperature (Fig. 1).

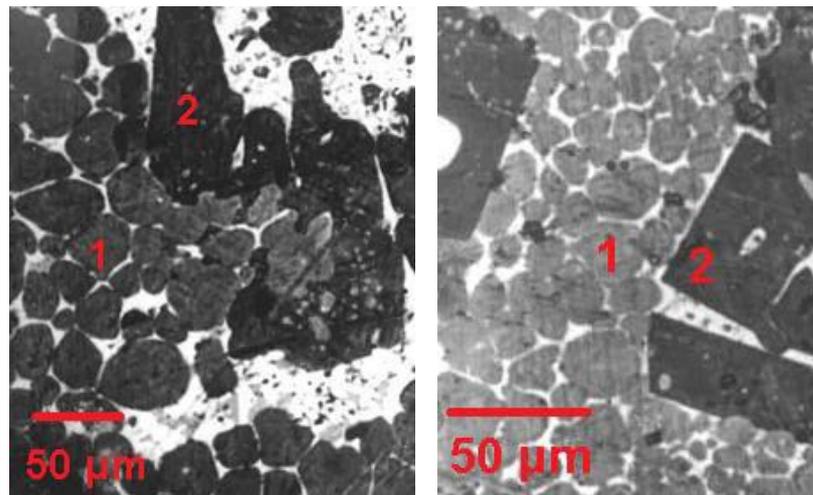


Figure 1. Belite clinkers microstructure (1 – C_2S ; 2 – C_3S).

Clinkers synthesized using skarn-magnetite ore dressing waste are characterized by high grinding ability. This is due to increased defectiveness of macrostructure; deformation of crystal lattices of phases during sulfur, manganese, titanium and phosphorus impurities introduction; coarse-grained microstructure of clinker.

Features of clinker formation with the participation of skarn-magnetite ore dressing waste led to an increase in hydraulic activity of belite clinker at the age of 28 days (Table 2).

Table 2. Characteristics of clinkers based on skarn-magnetite ore-dressing waste.

SR	Burning temperature, °C	Phases composition, %		Compressive strength, MPa, in age, days				
		C_3S	C_2S	3	7	28	60	360
0.80	1350	35	43	54	70	83	102	100
0.75	1330	25	52	32	53	82	98	101
0.73	1310	20	58	28	51	81	98	97
0.70	1300	13	67	11	21	60	77	95
0.67	1250	0	75	n/a	9	18	57	57
0.90	1450	60	20	71	80	95	92	90

Analysis of the results of clinker cement studies with different SR values revealed the dependence of cement strength on C_3S content (Table 2). This determined interest in studying alite effect on belite cements hardening.

3.2. The effect of alite on belite cements hardening

Hydration processes of belite cements, differing in alite content, were studied (Table 2 and 3). For comparison, cement with SR = 0.90 from traditional raw materials was used.

Table 3. Hydration activity of belite clinker phases.

Phase	Duration of hardening, days	Hydration degree of phases,%, in clinkers with SR					
		0.67	0.70	0.73	0.75	0.80	0.90
Alite	1	no	22	24	25	31	18
	3	no	58	58	60	65	45
	7	no	68	71	73	76	61
	28	no	95	92	85	80	70
Belite	1	0	2	3	4	5	7
	3	1	5	6	8	10	12
	7	4	12	17	20	27	18
	28	8	28	31	35	37	25

C₃S modification in clinkers of various compositions (Table 4) was determined by configuration of the maximum in the angle range of $2\theta = 51 - 53^\circ$. The firing temperature and impurity elements modifying the liquid phase have decisive influence on polymorphic state of alite. The monolithic reflex $d = 0.176$ nm characterizes rhombohedral alite form for clinkers with SR = 0.80, fired at a temperature of 1350 °C. In clinkers with small values of saturation rate, synthesized at temperatures of 1300 – 1330 °C, a monoclinic modification was recorded.

Table 4. Diffraction characteristics of alite in clinkers of various compositions.

SR	Intensity of alite's reflection $d = 0.176$ nm in the X-ray diffraction pattern of clinker, rel. units	Configuration of diffraction maxima in the range of angles $2\theta = 51 - 53^\circ$	Alite's modification
0.70	11	Forked peak reflex	Monoclinic
0.75	25	Forked peak reflex	Monoclinic
0.80	56	Monolithic reflex	Rhombohedral

Morphology of alite crystals is diverse. Along with small prismatic grains of a clear cut, there are accumulations of large crystals of irregular shape (Fig. 1).

The degree of clinker phases' hydration is determined by changing the height of analytical diffraction maxima. The amount of belite not participating in hydration was approximately calculated from the difference in intensity of joint reflections of alite and belite $d = 0.278$; 0.219 nm and self reflection of alite $d = 0.176$ nm.

Results' analysis (Table 2) indicates that cements with a low C₃S content are characterized by higher hydration activity of alite. This is due to two factors. First, the gel-like products of belite hydration adsorb calcium ions from a supersaturated solution and thereby contribute to maintaining interaction activity of alite with water [27, 28]. Secondly, these are conditions of C₃S formation in the studied clinker. Hydration ability of alite depends on modification and nature of C₃S crystallization. In the initial period of hydration (1 – 7 days), increased activity of rhombohedral alite (cement with SR = 0.80) is observed. For clinkers with a monoclinic modification of alite, characterized by polygranularity, the dependence of hydration degree on saturation rate in early stages is small, but by 28 days hardening increases.

Hydration of C₃S is accompanied by abundant secretion of Ca(OH)₂ portlandite, which activates belite hardening. With an increase in SR, the rate of hydration of belite in early stages almost doubles (Table 3). Stable hardening of belite cements (Table 2) is facilitated by Ca(OH)₂ involvement in composition of calcium hydrosilicates. The content of portlandite, which is almost the same by 28 days of hydration for various cements, decreases in the stone of belite cement with prolonged hardening (Table 5). This will provide hardened cement with increased corrosion resistance.

Table 5. Portlandite content in hydrated cements (according to differential thermal analysis data).

SR	Weight loss of hydrated cements at a temperature of 550 °C,%	
	28 days	60 days
0.75	10.8	12.5
0.80	11.6	20.8
0.90	12.3	24.2

Active hydration of alite ensures the release of the bulk of $\text{Ca}(\text{OH})_2$ in early stages of hardening. This determines predominant participation of portlandite in primary crystalline framework formation. Such a hydrate formation mechanism is favorable for hardening of the setting mass. Since in a later period, when secondary hydrates are released, smooth crystallization of portlandite is required to achieve high strength. This contributes to even distribution of neoplasm in the structure of the stone.

Studies of composition and structure of long-hardening cement stone revealed that portlandite is the basis of crystalline hydrates. Conservation of readily soluble portlandite during prolonged exposure to water was facilitated by the dense stone structure (Fig. 2).

Calcium hydrosilicates have a cryptocrystalline state. Cement stone is characterized by structural and morphological heterogeneity due to differences in the stages of growth and intergrowth of hydrate particles.

Consequently, characteristics of chemical and mineral composition of skarn-magnetite ore dressing wastes affect the rate of clinker formation, structure and activity of phases, especially alite. As a result, belite cements acquire high hydraulic activity at the age of 28 days, stable hardening and resistance of cement stone with prolonged hardening.

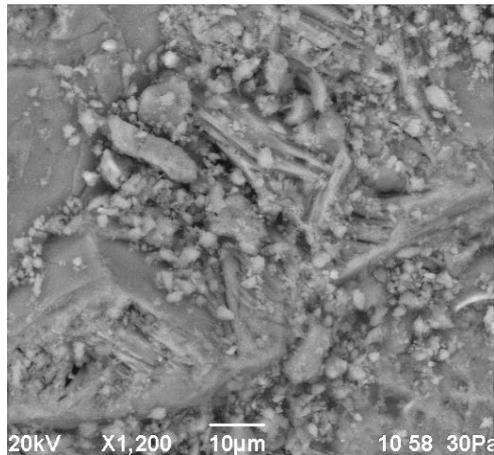


Figure 2. The micrograph of cement stone after 360 days of hardening.

At the same time, the problem of slow hardening of cements during early stages remains unsolved. This is a serious obstacle to the development of low-energy belite cement technology.

3.3. Effect of magnesium calcium silicoaluminate on hydration and hardening of belite cement

Advantages of cements with a high content of belite are realized in synthesis of clinkers containing modified aluminate phases [16, 17, 19]. Firing of modified clinkers is characterized by reduced energy costs. The high hardening rate of aluminate cements allows us to abandon the heat treatment of concrete [29, 30]. Clinkers containing calcium sulfoaluminate were most widely used [18, 19, 31, 32].

The modern raw material base of cement production is expanding due to industrial waste [20–26, 33–35]. To obtain aluminate and sulfoaluminate clinkers, raw materials are used, they contain minerals based on silicon, magnesium, and iron [6, 10, 17, 31, 32, 34, 35]. In clinkers produced from raw calcium mixtures of complex composition, $\text{C}_6\text{A}_4\text{MS}$ magnesium calcium silicoaluminate is formed, which is also called magnesia pleochroite or phase Q [29, 36, 37]. It was established [38] that $\text{C}_6\text{A}_4\text{MS}$ formation is accompanied by minimization or exclusion of inert phases of C_2AS and MgO . The joint presence of $\text{C}_6\text{A}_4\text{MS}$ and $3(\text{CA})\text{CaSO}_4$ clinkers was revealed during the initial and predominant formation of calcium sulfoaluminate. $\text{C}_6\text{A}_4\text{MS}$ formation is promoted by increased concentration of Fe_2O_3 in the raw mixes. High hydraulic activity of cements containing magnesium calcium silicoaluminate indicates advisability of $\text{C}_6\text{A}_4\text{MS}$ phase presence in aluminate clinker. A method for calculating the composition of raw mixes for clinkers containing $\text{C}_6\text{A}_4\text{MS}$ was proposed [39].

Sulfoaluminate clinkers containing various amounts of $\text{C}_6\text{A}_4\text{MS}$ phase were synthesized (Fig. 3). $\text{C}_6\text{A}_4\text{MS}$ phase identified by the following x-ray indices: 0.372; 0.309; 0.289; 0.276; 0.271; 0.244; 0.240; 0.218 nm.

Presence of a little-studied phase in clinkers necessitates a study of the effect of $\text{C}_6\text{A}_4\text{MS}$ on belite hydration. Model binders were prepared by mixing monophasic cements from $\text{C}_6\text{A}_4\text{MS}$ and C_2S , which were previously synthesized from chemical reagents. Results of physical and mechanical tests of model binders are presented in Fig. 6. Composition of binders after hydration was investigated using X-ray.

In C_6A_4MS presence, the early hardening of belite cement is intensified. The increased strength of mixed binders is disproportionate to the content of C_6A_4MS (Fig. 4). An increase in the content of calcium hydroaluminates during hardening of mixed binders indicates accelerated hydration of C_6A_4MS in the presence of C_2S . A strong crystalline framework of cement stone is formed from hexagonal calcium hydroaluminates. A feature of hardening mixture composition is C_2ASH_8 hydrogelite, which provides increase in binder's strength.

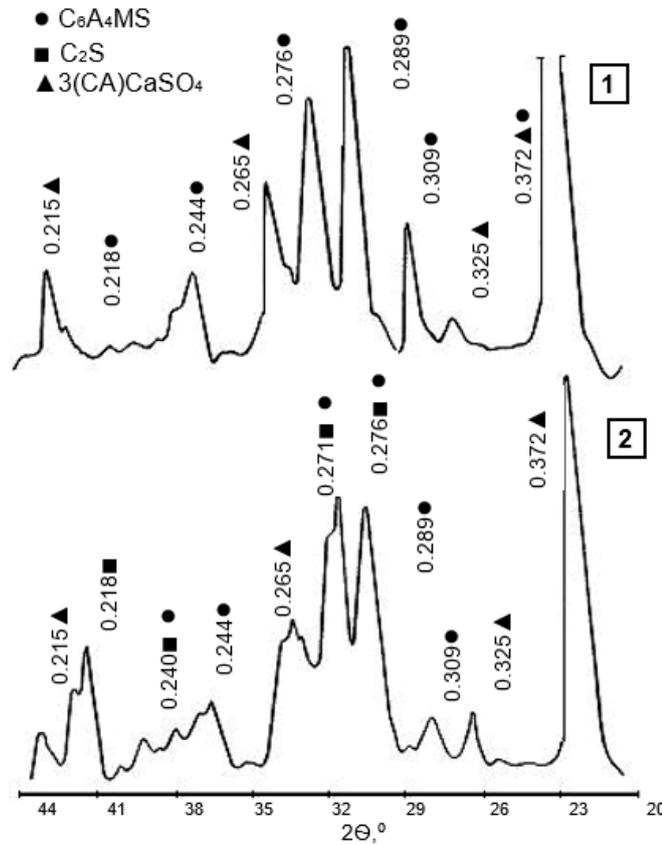


Figure 3. Diffraction patterns of sulfoaluminate clinkers (1 – 60 % C_6A_4MS ; 2 – 20 % C_6A_4MS).

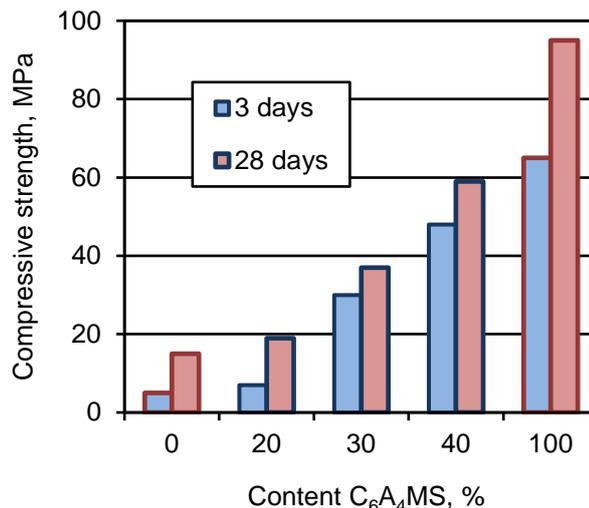


Figure 4. The effect of C_6A_4MS phase on hardening of a model binder.

Hydrogelinite formation is the result of diffusion of calcium hydrosilicates into the matrix structure from metastable calcium hydroaluminates. The nature of hydrate formation in mixed binders (Tables 6 and 7) indicates that C_2ASH_8 hydrogelite is formed with the participation of C_2AH_8 .

Intensity of C_2ASH_8 formation is determined by saturation of the liquid phase with calcium ions and depends on the content of C_2S in the binder. The amount of C_2ASH_8 is limited by C_2AH_8 concentration. This is confirmed by a slight difference in the content of hydrogelite for binders that differ in phase composition.

It is known [40], that calcium hydroaluminates stability decreases with increasing hardening temperature. Influence of heat treatment on hydrate formation in binders with different content of belite is investigated. Cement samples containing 20 % and 60 % of C_2S , after 1 day of hardening at a temperature of 20 °C, were subjected to heat treatment at a temperature of 80 °C (Table 7).

Table 6. The effect of C_6A_4MS phase on hydrates composition of the model binder.

Content C_6A_4MS , %	Intensity of hydrate reflections on the roentgenogram of cement stone, rel. units					
	CAH_{10} (1.41 nm)		C_2AH_8 (1.07 nm)		C_2ASH_8 (1.26 nm)	
	Duration of hardening, days					
	3	28	3	28	3	28
20	9	traces	7	traces	16	17
40	21	12	10	no	13	19
100	18	19	16	17	no	no

With increasing temperature, hydration of C_2S and formation of calcium hydrosilicates are accelerated. This contributes to C_2ASH_8 formation. However, at C_2S content of 20 %, recrystallization of hexagonal calcium hydroaluminates is observed.

Table 7. The effect of temperature on hydrates composition of model binders.

Content C_2S , %	Intensity of hydrate reflections on the roentgenogram of cement stone, rel. units									
	CAH_{10} (1.41 nm)		C_2AH_8 (1.07 nm)		C_2ASH_8 (1.26 nm)		C_3AH_6 (0.51 nm)		AH_3 (0.48 nm)	
	Temperature of hardening, °C									
	25	80	25	80	25	80	25	80	25	80
20	28	no	15	no	no	13	no	18	no	9
60	28	22	no	no	14	16	no	no	no	traces

Therefore, cubic hydrates C_3AH_6 and AH_3 are formed and predominate in the cement stone. With an increase in C_2S content to 60 %, the bulk of C_2ASH_8 is formed at normal hardening temperature. Heat treatment of the binder does not violate hexagonal calcium hydroaluminates stability.

Consequently, the combined hydration of C_6A_4MS and C_2S is favorable for intensive hardening and formation of strong cement stone.

3.4. Mixed cements from belite and aluminate clinkers

The activating effect of C_6A_4MS on C_2S hydration justifies intensification of belite cements hardening by adding aluminate clinker. Obtaining double-clinker cements is an effective technological technique that allows you to adjust composition and properties of binders.

Mixed cements of various compositions were obtained from belite clinkers and aluminate clinker containing 80 % of C_6A_4MS (Table 8, Fig. 5).

Table 8. Characteristics of mixed cements.

Composition of mixed cement, %		SR (belite clinkers)	Content phases, %			Water / Cement, %
aluminate clinker	belite clinker		C_3S	C_2S	C_6A_4MS	
		0.67	0	75		26.0
0	100	0.74	22	56	0	25.8
		0.80	35	43		25.4
		0.84	42	33		25.6
		0.67	0	68		26.1
10	90	0.74	20	50	8	26.0
		0.80	31	39		25.5
		0.84	38	30		25.8
		0.67	0	60		26.7
20	80	0.74	18	45	16	26.2
		0.80	28	34		25.6
		0.84	34	26		26.0

Composition of mixed cement, %		SR (belite clinkers)	Content phases, %			Water / Cement, %
aluminate clinker	belite clinker		C ₃ S	C ₂ S	C ₆ A ₄ MS	
		0.67	0	52		27.1
30	70	0.74	15	39		26.6
		0.80	24	30	24	25.9
		0.84	29	23		26.3
		0.67	0	45		27.4
40	60	0.74	13	34		27.0
		0.80	21	26	32	26.2
		0.84	25	20		26.8
		0.67	0	37		27.7
50	50	0.74	11	28		27.3
		0.80	17	21	40	26.8
		0.84	21	16		27.1

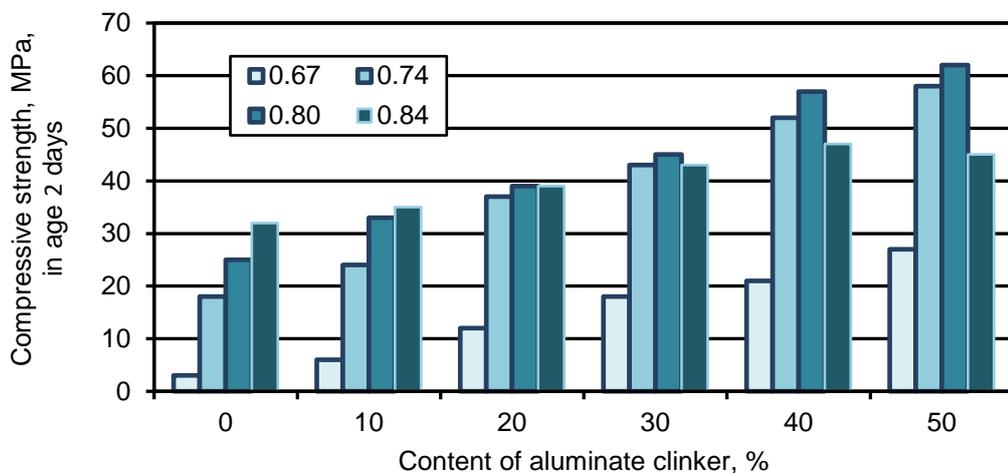
Intensive hardening of mixed cement is provided by mutual activation of the following phases: C₆A₄MS and C₂S. The nature of C₆A₄MS effect on cement hardening depends on clinkers' SR. The greatest increase in strength was achieved for cement made of belite clinkers with reduced SR values. For all the binders studied, the maximum hardening effect in the early stages of hardening is manifested at 30 – 50 % aluminate additives.

The strength of mixed cement at the initial stages of hardening is 1.3 times higher than belite cement's strength. Introduction of aluminate clinker also makes it possible to increase belite cement's strength by 30 % at the age of 28 days.

Presence of aluminate component practically did not affect the activity of cement containing clinker with SR = 0.84. Ambiguous nature of the change in cements strength is due to influence of portlandite released during alite hydration. As the clinker saturation rate in a mixed binder increases, the proportion of highly basic calcium hydroaluminates C₂AH₈ and C₄AH₁₃ increases. In this case, the highest content of hydrogelite is characteristic of hardening cement from clinker with SR = 0.74, and in the cement stone with SR = 0.84, the proportion of C₂ASH₈ is minimal.

Obviously, with an excess of calcium ions, the stability of hydrogelite decreases. A significant increase in CaO : Al₂O₃ ratio in hardening cements contributes to formation of cubic calcium hydroaluminate C₃AH₆. The process is accompanied by cement stone destruction. For this reason, aluminate additive practically does not accelerate the rate of hardening of cement with SR = 0.84.

As a result of the studies, the preferred phase composition of the mixed cement was established, wt. %: 35 – 45 C₂S; 25 – 35 C₆A₄MS; 15 – 20 C₃S.



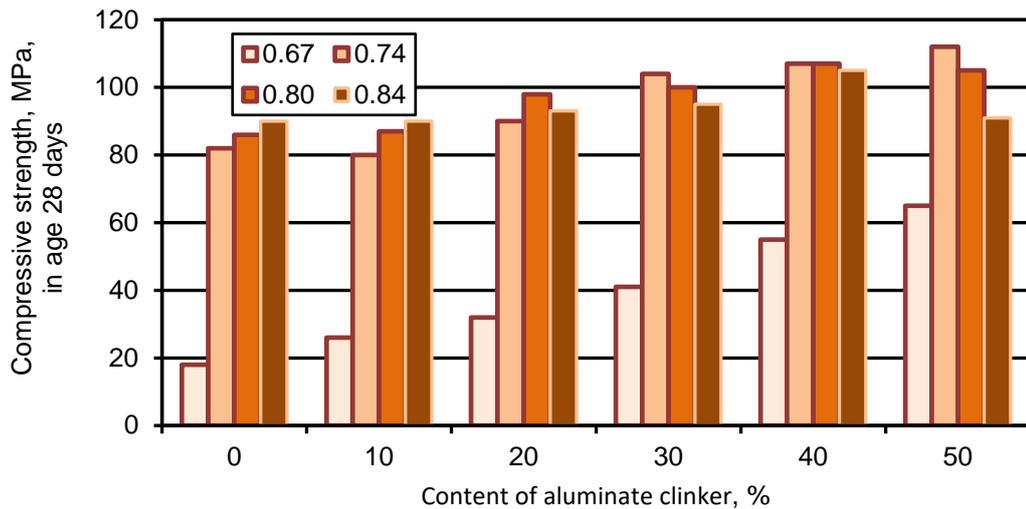


Figure 5. The effect of aluminate clinker additives on mixed cement hardening.

Effectiveness of the combination of clinkers of different phase composition is determined by two factors: intensification of hardening of belite cement with $SR = 0.74 - 0.80$; stabilization of strength properties of aluminate cement stone due to formation of stable hydrates and crystalline structure formation.

4. Conclusions

The results of hydration activity studies of clinkers synthesized with the use of skarn-magnetite ore dressing waste indicate that the rates of hydration and structure formation of belite cements with $SR = 0.74 - 0.80$ significantly depend on accompanying phases composition.

1. It was revealed that the setting rate of belite cements is very sensitive to the content of alite phase. The design strengths of cements with 20 – 35 % C_3S are comparable with characteristics of traditional Portland cement.
2. It has been established that high reactivity of C_3S in belite cement is due to formation of clinker phases based on the structures of natural silicates, influence of modifying impurities contained in technogenic raw materials.
3. The effect of C_6A_4MS phase on hydration and hardening of belite cement has been studied for the first time. It has been proven that C_6A_4MS and C_2S combination promotes intensive hardening and ensures high binder strength. It is substantiated that in the presence of C_2S hydration of C_6A_4MS is accelerated, stability of hexagonal calcium hydroaluminates increases, and hydrogenite is formed. Change in composition of hydrated phases ensures formation of a solid structure of the cement stone.
4. A method for intensifying belite cements' hardening has been proposed, which provides for introduction of an additive with high hydration activity. The developed cement is distinguished by addition of aluminate clinker, which consists mainly of C_6A_4MS , to belite cement.
5. Phase composition of mixed cement, including 35 – 45 % C_2S ; 25 – 35 % C_6A_4MS ; 15 – 20 % C_3S , provides high rates of hardening at all stages of hardening, durability of the cement stone.

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