

EFFECT OF POTASSIUM SULFATE ON THE PORTLAND CEMENT  
PASTES SETTING BEHAVIOR*Myroslav Sanytsky<sup>1, ✉</sup>, Tetiana Kropyvnytska<sup>1</sup>, Orest Shyiko<sup>1</sup>*<https://doi.org/10.23939/chcht17.01.170>

**Abstract.** The article deals with the effect of potassium sulfates on the setting behavior of cement pastes. It has been established that the main elements (Ca, Si, Al) are distributed in the composition of clinker minerals, while K and S atoms are concentrated locally in the pores with the formation of arcanite. It is shown that the interaction of  $K_2SO_4$  and  $CaSO_4 \cdot 2H_2O$  followed by the formation of syngenite  $K_2Ca(SO_4)_2 \cdot H_2O$  causes destructive phenomena in cement pastes.

**Keywords:** Portland cement clinker, calcium sulfate dihydrate, arcanite, syngenite, setting behavior.

## 1. Introduction

Portland cement for general construction purposes has become the most widely used binders in construction, which is mainly due to its high functionality, satisfactory price/quality indicators, and the available raw material base for its production in the world. At the same time, the production of ordinary Portland cement leads to the large-scale exploitation of natural reserves of limestone, clay and coal. Moreover, the production of one ton of Portland cement results in the emission of 0.8–1.0 tons of  $CO_2$  into the atmosphere. A rational solution to the problem of ensuring low-carbon development of the cement industry is the production of technologically optimized composite cement with favorable combinations of mineral components providing technical, economic and ecological advantages.<sup>1–4</sup>

At the same time, when using Portland cement systems, there are often problems related to their accelerated setting time. In Portland cement clinker, impurity alkalis may appear, which cause rapid shrinkage, decreases the final strength of concrete, and increases seating deformations during the hardening process. Alkalis come from shale, clay, or fuel, which are used in many cement pro-

ductions. Usually, these are sodium or potassium compounds, which are present in sulfate form and appear on the surface of clinker minerals.<sup>5</sup>

One of the main trends in the sustainable development of Portland cement clinker production is the usage of alternative fuels based on combustible waste instead of hard coal for firing in rotary kilns. At the same time, during the clinker firing, some ash of the alternative fuel settles on the clinker in the sintering zone or on the raw material mixture, which moves along the furnace to the sintering zone. Ash also reacts with the oxides of the raw material mixture, and can significantly affect the mineralogical composition of the finished product. When using different types of alternative fuel in the process of burning Portland cement clinker, a certain amount of alkaline oxides and sulfur is added to its composition. As a result, problems associated with abnormal setting often arise during the production of Portland cement. Despite the insignificant content of alkalis in the total mass of clinker (0.1–1.5 wt. % of  $K_2O$ , 0.1–0.8 wt. % of  $Na_2O$ ), their influence is complex.<sup>6,7</sup> The negative effect of alkali sulfates on the hydration and hardening properties of cement is quite significant. Alkali sulfates originating from Portland cement clinker are found in the form of arcanite  $K_2SO_4$ , thenardite  $Na_2SO_4$ , and Ca-langbeinite  $K_2Ca_2[SO_4]_3$ . Typically, Ca-langbeinite in cement slightly reduces compressive strength and increases drying shrinkage, but it can replace gypsum to regulate setting time in Portland cement, while alkali sulfates will promote the growth of C–S–H and portlandite during cement hydration.<sup>8–11</sup>

According to Schneider,<sup>12</sup> for a number of cement plants in the EU countries that operate on hard coal, the  $K_2O$  content can reach 2.0 wt. %, while in clinker the content of  $K_2O$  is 1.32 wt. %, and  $SO_3$  is 1.14 wt.%, in particular, the  $K_2O : Na_2O$  ratio varies from 4 : 1 to 10 : 1. The presence of  $K^+$  and  $SO_4^{2-}$  ions in the liquid phase of the cement paste contributes to the development of destructive phenomena. It is characteristic that such fuel elements as wastes of used tires and peat have a lower content of  $K_2O$ , but an increased content of sulfur. Sulfates are added to the raw material mixture with pyrite cinders and slag. Sulfate components contribute to the neutralization of the negative influence of alkalis on the

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processes of clinker formation. On the other hand, some types of biofuel can contain a high content of potassium oxide, which leads to a decrease in the content of the main clinker mineral – alite – and the creation of low-melting eutectics in the firing zone of the rotary kiln.<sup>13</sup>

In cement with increased content of alkalis, in the early period of structure formation, the phenomenon of "false setting" can be detected, which negatively affects its hydration hardening. During the hydration processes of cement with a high content of potassium ions, the formation of a double salt – syngenite ( $K_2Ca(SO_4)_2 \cdot H_2O$ ) – is possible which often leads to the false or flash setting of cement paste, and an excess of sulfate components causes some declines in the strength of construction products. This can also be manifested in the form of efflorescence, which arises as a result of the sulfates' effect on mortars and various building materials.<sup>14,15</sup>

During long-term storage of cement in wet conditions (cement aging) aggregation processes of Portland cement occur as a result of gypsum or another calcium sulfate reaction with arcanite. This negatively affects the cement properties.<sup>16</sup> The study of the formation conditions for syngenite is important not only for cement technology but also from an industrial point of view because  $K_2O$  content in it is approximately 28 %, which makes it a potential source for obtaining potash fertilizers.

The wide use of alkaline additives as hardening activators in concrete technology also should be noted.<sup>17,18</sup> According to the mechanism of action, alkaline compounds are additives that enter exchange reactions with the products of binders hydration. At the same time, electrolytes must react primarily with calcium hydroxide. As a result, the anionic part of the additive is bound by aluminum-containing phases during the hydration process, and the cations remain in the pore liquid. Thus, the amount of secondary gypsum increases with the formation of lamellar structure crystals up to 5–10  $\mu m$  in length, the early hydration of the cement phases accelerates, and as a result, the early strength increases and the late strength decreases.<sup>19-21</sup> The joint effect of calcium sulfate dihydrate and salts of alkali metals can significantly affect the processes of early structure formation of both pure clinker Portland cement and cementing systems based on it.<sup>22,23</sup> Therefore, to study the nature of this process in cementing systems, it is important to study the influence of the calcium sulfate dihydrate and potassium sulfate ratio on the properties of cementitious materials.

The aim of this article is to identify the effect of potassium sulfate on the setting behavior of cement pastes, which determines the course of their early structure formation, as well as the formation of the technical properties of Portland cement.

## 2. Experimental

### 2.1. Materials

The samples under study were Portland cements CEM I 42.5 R (SSA = 3400  $cm^2/g$ ) and CEM II/A-S 42.5 R (SSA = 3300  $cm^2/g$ ) produced by JSC Ivano-Frankivsk cement (Ukraine). Portland cement clinker was characterized by the following mineral composition (wt. %):  $C_3S$  – 62±3,  $C_2S$  – 14±2,  $C_3A$  – 6.5±1,  $C_4AF$  – 11±1; content of alkaline oxides in the clinker (wt. %) was:  $K_2O$  – 1.0±0.2 and  $Na_2O$  – 0.14±0.03. Cement dust from aspiration mills (SSA = 6500  $cm^2/g$ ) with a high content of alkaline oxides and sulfates was also used for research.

Hard coal, as well as used automobile tires, served as technological fuel. Coal ash contains a high content of  $K_2O$ , and ash from car tires burning has a high content of  $SO_3$  (26.0 wt. %). The ash content of used automobile tires is 5.84 wt. %.

To study the processes of early structure formation, powder of dihydrate calcium sulfate ( $CaSO_4 \cdot 2H_2O$ ), finely ground sand (inert filler) and potassium sulfate ( $K_2SO_4$ ) were used. Arcanite solubility in water is 11.1 g per 100 g at 293 K. The Blaine specific surface areas of  $CaSO_4 \cdot 2H_2O$  and fine ground sand were 3700 and 3500  $cm^2/g$ , respectively.

The growth of single crystals was carried out by the method of chemical reaction with the help of counter diffusion. To obtain single crystals, potassium sulfate  $K_2SO_4$  and calcium chloride  $CaCl_2$  were used. The microstructure of Portland cement clinker, as well as the shape and size of single crystals, were studied using the SEM 106I scanning electron microscope (SEMI, Ukraine). The chemical composition of Portland cement clinker was determined using the X-ray spectrometer ARL 9800 XP. The phase composition of the initial substances and interaction products was studied using X-ray diffractometry.

## 3. Results and Discussion

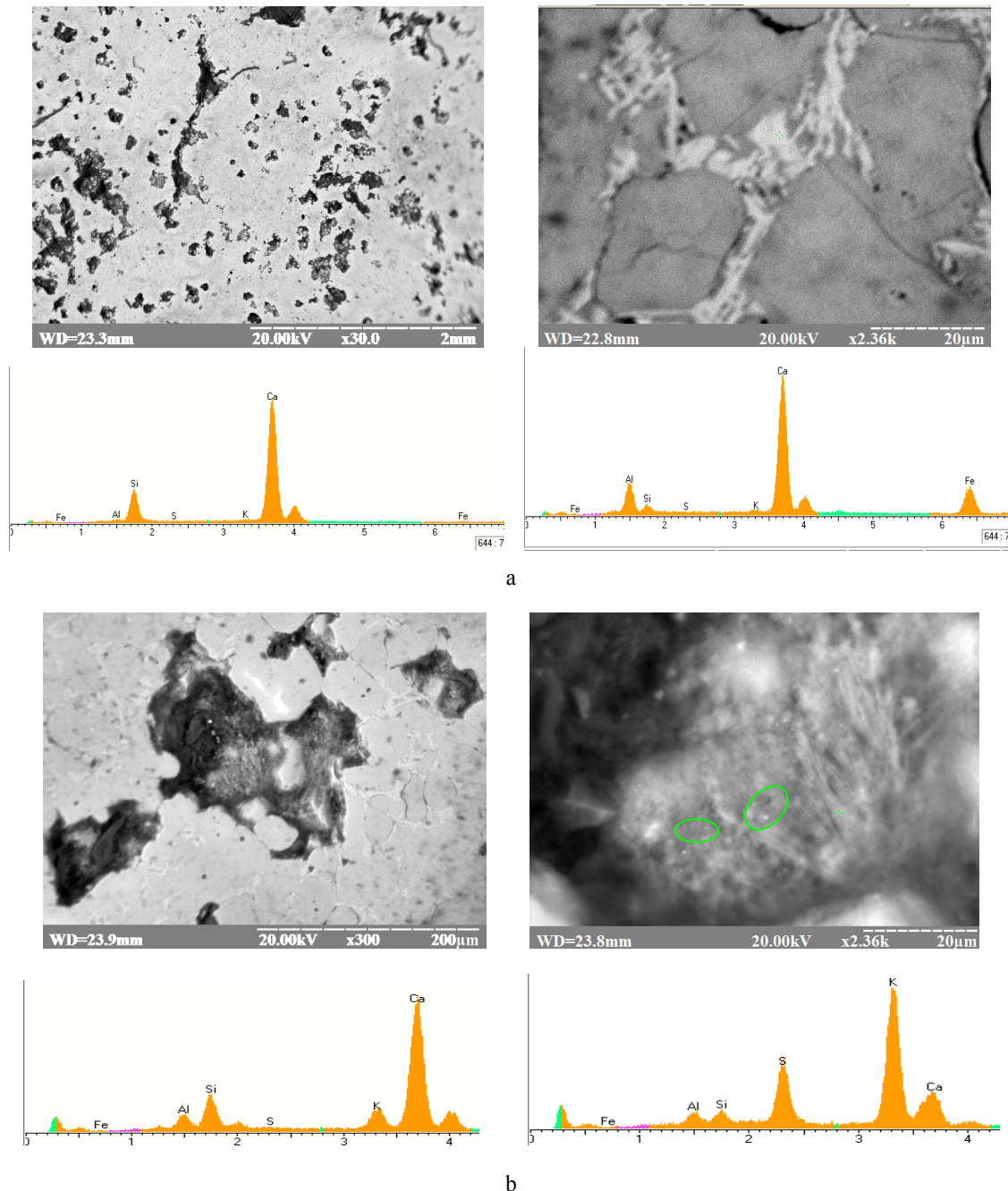
The structural peculiarities of Portland cement depend on many factors: the initial components of raw materials, the influence of secondary admixtures, the clinker burning and production. Apart from the four main oxides, the raw material contains a number of other elements introduced with aluminosilicate and carbonate components, as well as with fuel ash.<sup>24,25</sup>

Using the method of electron microscopic analysis, it was found (Fig. 1a) that the microstructure of clinkers with increased content of alkaline oxides is characterized by the presence of alite phase crystals with a deformed structure. Alkaline compounds such as  $K_2O \cdot 23CaO \cdot 12SiO_2$  and  $Na_2O \cdot 8CaO \cdot 3Al_2O_3$  are also typical, and they are charac-

terized by lower hydraulic activity compared to  $\beta$ - $2\text{CaO}\cdot\text{SiO}_2$  and  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ .

According to the data of X-ray spectral microprobe analysis for clinker of the dry production method (Fig. 1b), the main elements such as calcium, silicon, aluminum and iron are evenly distributed in the structure of cement minerals. At the same time, the content of alkaline oxides is  $1.0\pm 0.2$  wt. % of  $\text{K}_2\text{O}$  and  $0.14\pm 0.03$  wt. % of  $\text{Na}_2\text{O}$ , the content of  $\text{SO}_3$  ranges from 0.5 to 0.8 wt. %. It is characteristic that potassium

and sulfur atoms are locally concentrated in the clinker pores at the phase interface with the formation of the water-soluble mineral arcanite ( $\text{K}_2\text{SO}_4$ ), the amount of which reaches 1.5 wt. %. At the same time, the content of potassium and sulfur atoms in the composition of the intermediate (aluminoferrite) phase is insignificant, *i.e.*, arcanite is practically absent in this phase. It should be noted that arcanite (mp.1349 K) is an independent phase in Portland cement clinker, which does not mix with the clinker melt and crystallizes last in the cooling process.



**Fig. 1.** Electron micrographs and spectra of microprobe analysis of the Portland cement clinker surface (a) and of the pore surface (b)

According to the stoichiometry of the reaction, 1.077 wt. % of  $\text{SO}_3$  is needed for the formation of arcanite at  $\text{K}_2\text{O}$  content of 1.05 wt. %. At the same time, there is only 0.720 wt. % of  $\text{SO}_3$  in the clinker, that is, 0.702 wt. % of  $\text{K}_2\text{O}$  binds to arcanite, and its amount will be 1.422 wt. %. The remaining 0.348 wt. % of  $\text{K}_2\text{O}$  is included in the structure of clinker minerals with the formation of  $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ . The content of free CaO increases up to 1.5 wt. %.

Studies of the fractional composition of Portland cement CEM I 42.5 R with a specific surface area of  $3400 \text{ cm}^2/\text{g}$  have established that the content of the most active small fraction (up to  $20 \mu\text{m}$ ) is 73 wt. %, the content of the fraction up to  $45 \mu\text{m}$  is 88.0 wt. %. Alkaline oxides and sulfates are mainly concentrated in the thin fraction. Thus, in the fine fraction of cement dust aspiration of mills ( $\text{SSA} = 6500 \text{ cm}^2/\text{g}$ ), there is an increased amount of alkalis and sulfates, which is one of the reasons for the high value of the paste standard density, which reaches 45.5 %, while the initial and final setting times are accelerated to 105 and 175 min, respectively. This also leads to an acceleration of the hydration rate at the initial stage and an increase in the intensity of the first exoeffect ( $105.52 \text{ mW/h}$ ) for CEM I 42.5 R compared to CEM II/A-S 42.5 R.

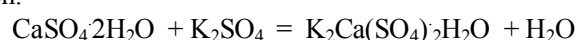
The joint effect of calcium sulfate dihydrate and potassium salts can significantly influence the processes of early structure formation of both ordinary Portland cement and cementing systems based on it.<sup>23</sup> During the hydration processes of Portland cement, water-soluble  $\text{K}_2\text{SO}_4$  from clinker can be the reason for the formation of syngenite  $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ . At the same time, to study the

nature of this process development in cementing systems, it is important to study the effect of the calcium sulfate dihydrate and potassium sulfate ratio on the properties of cementing materials.

In this regard, the effect of potassium sulfate additives on the setting time of systems based on calcium sulfate dihydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was investigated. As can be seen from Table 1, an increase in the amount of potassium sulfate in the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{K}_2\text{SO}_4$  system leads to an acceleration of the model system setting. So, for the binder based on calcium sulfate dihydrate (water/binder ratio  $W/B = 0.44$ ), the initial and final setting times are 11–30 and 14–45 h-min, respectively. For the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{K}_2\text{SO}_4$  (10 : 1) system the setting time is accelerated to 15 and 40 min, and at the ratio of 2:1 – to 4 and 9 min.

To estimate the effect of potassium sulfate and gypsum interaction on the processes of early structure formation of Portland cement, a model system consisting of 95.0 wt. % of fine ground sand ( $S = 3500 \text{ cm}^2/\text{g}$ ) and 5.0 wt. % of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was studied. One can see from Table 2, that the initial setting time of the model system is accelerated from 10 h to 50–40 min with the introduction of 2–4 wt. % of potassium sulfate. This means that even a small amount of arcanite contained in the Portland cement can significantly affect its initial and final setting times.

The given data indicate that during the hydration processes of Portland cement, water-soluble  $\text{K}_2\text{SO}_4$  from clinker can cause the formation of a double salt – the syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) according to the following reaction:



**Table 1.** Effect of potassium sulfate on the setting time of fine ground calcium sulfate dihydrate

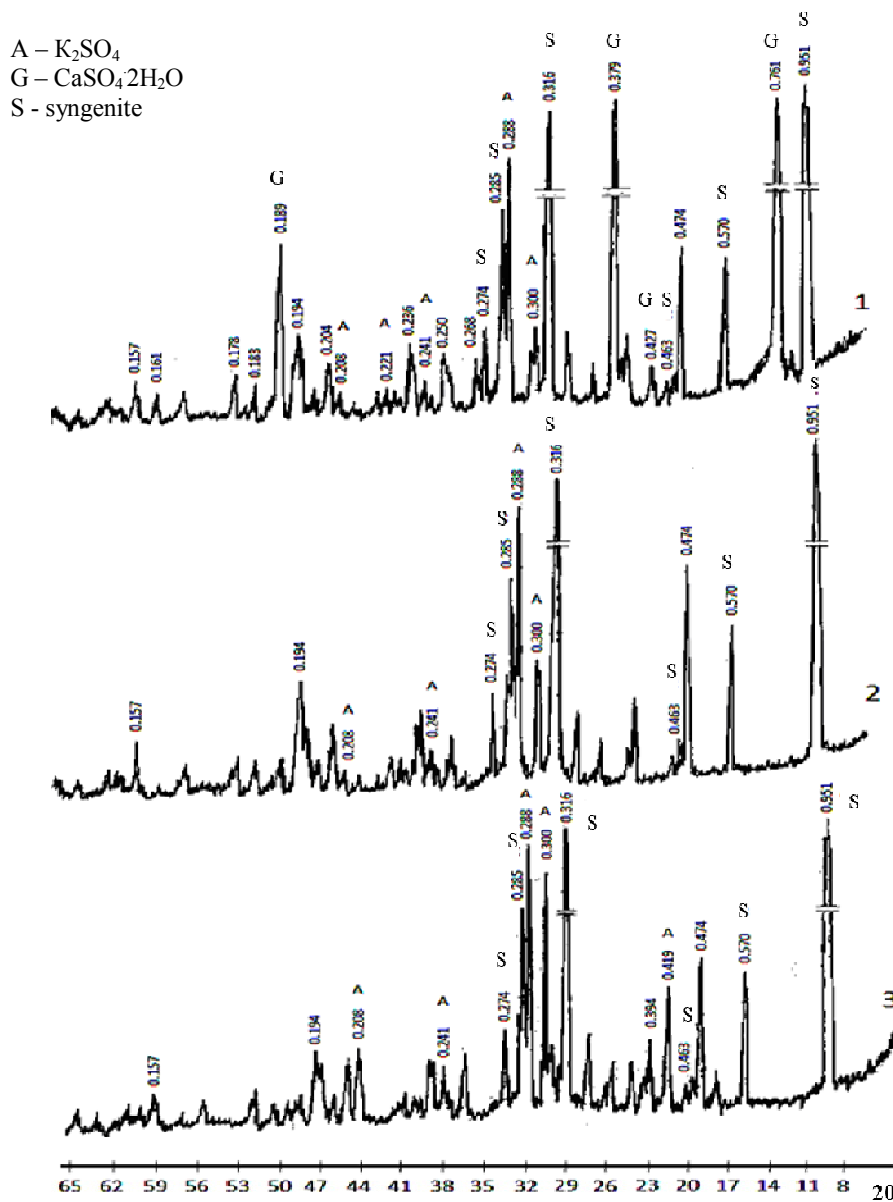
Components ratio	W/B	Setting time, h-min	
		initial	final
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.44	11–30	14–45
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : \text{K}_2\text{SO}_4$			
10:1	0.40	0–15	0–40
4:1	0.37	0–09	0–14
2:1	0.39	0–04	0–09
1:1	0.33	0–06	0–08
1:2	0.30	0–06	0–08

**Table 2.** Effect of potassium sulfate on the setting time of the model system (95.0 wt. % of silica sand and 5.0 wt. % of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

Amount of $\text{K}_2\text{SO}_4$ , wt. %	Water demand	Setting time, h-min	
		initial	final
–	0.24	10–30	27–00
1.0	0.23	8–40	11–00
2.0	0.22	0–50	6–30
4.0	0.23	0–45	4–20

In accordance with the reaction stoichiometry, 1.0 wt. % of  $K_2SO_4$  binds 0.99 wt. % of  $CaSO_4 \cdot 2H_2O$  into syngenite. Usually, the amount of calcium sulfate dihydrate in Portland cement composition is 5.0 wt. %, while the content of arcanite reaches only 1.5 wt. %. The solubility of arcanite in water is quite high (11.1 g per 100 g at 293 K) and significantly exceeds the solubility of  $CaSO_4 \cdot 2H_2O$  (2.05 g/L). Therefore, due to their interaction, a part of the calcium sulfate dihydrate remains unbound and later acts as a setting regulator for the  $C_3A$  mineral. Since at the early stage of structure formation, a certain part of calcium sulfate dihydrate binds to

syngenite, which is only partially soluble in water, the remaining part of gypsum during interaction with  $C_3A$  can form a smaller amount of early ettringite  $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ . At the same time, most of  $C_3A$ , as a result of interaction with water, forms metastable calcium hydroaluminates of the  $C_4AH_{19}$  type, which bind a significant part of water but eventually turn into cubic  $C_3AH_6$ , which can lead to a decrease in strength with the age of hardening. The increased content of  $K_2O$  (over 1.0 wt. %) in Portland cement leads even to instant setting due to  $CaSO_4 \cdot 2H_2O$  binding into a complex compound – syngenite.



**Fig. 2.** Diffractograms of stone based on  $CaSO_4 \cdot 2H_2O - K_2SO_4$  model system in the age of 7 days with different molar ratio: 2 : 1 (1); 1 : 1 (2) and 1 : 2 (3)

For the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{K}_2\text{SO}_4$  system (gypsum : potassium sulfate = 2 : 1) the X-ray diffractograms (Fig. 2) show the lines of calcium sulfate dihydrate ( $d/n=0.761; 0.474; 0.379; 0.189$  nm), arcanite ( $d/n=0.419; 0.373; 0.300; 0.288; 0.241; 0.208$  nm), and the product of their interaction – syngenite ( $d/n=0.951; 0.572; 0.463; 0.315; 0.285$  nm). With an increase in the arcanite amount in the system (ratio 1 : 1; 1 : 2), we observe no lines of calcium sulfate dihydrate, and a greater intensity of syngenite reflexes, which indicates the binding of gypsum into syngenite.

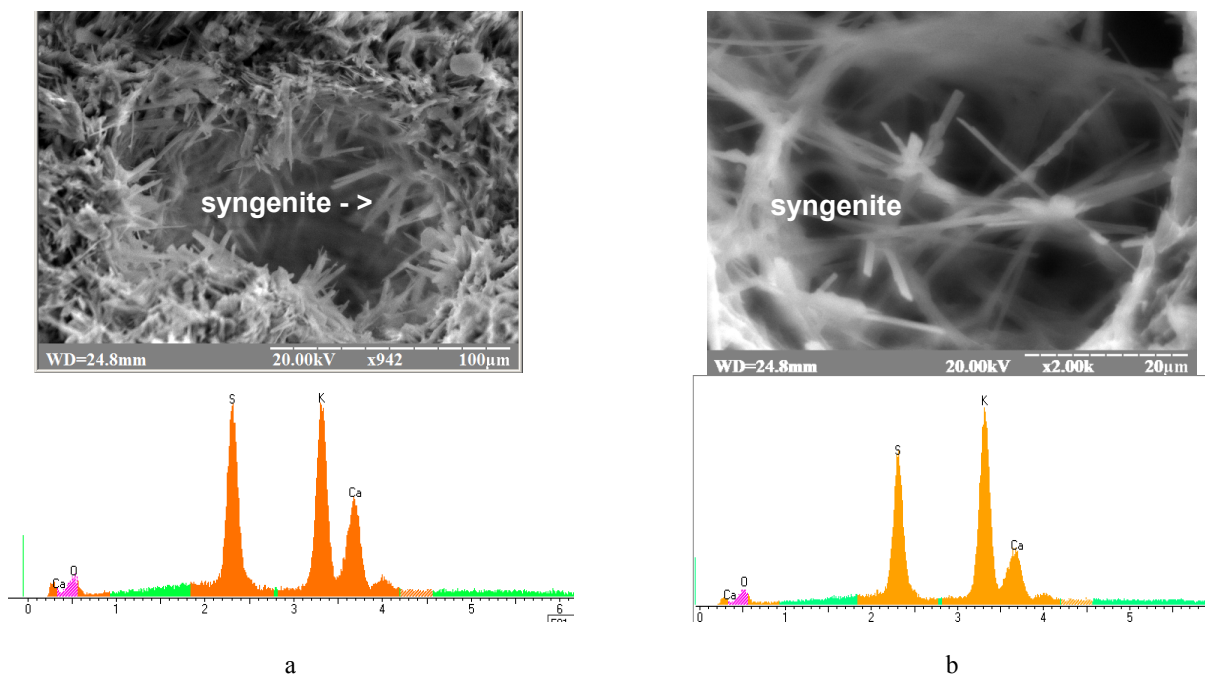
The results of scanning electron microscopy (Fig. 3) show that the paste based on the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{K}_2\text{SO}_4$  model system is characterized by a felt-like structure formed by long, rail-like crystals of syngenite with a length of 10–20  $\mu\text{m}$ . The data of X-ray spectral microprobe analysis confirm that the high relative content of potassium, calcium and sulfur elements in the paste sample based on the above model system corresponds to the syngenite mineral. Peculiarities of the syngenite crystals microstructure formation in cement paste were investigated due to the synthesis of single crystals obtained by the method of counter diffusion. According to this method, the excess concentration of the substance to be crystallized is created due to the chemical reaction of  $\text{K}_2\text{SO}_4$  and  $\text{CaCl}_2$ . Single crystals of syngenite were crystallized after 16 h from the outside of the smaller vessel (Fig. 4a). The maximum growth of crystals was observed after 48 h. The phase composition of the grown

single crystals is mainly represented by syngenite and to a lesser extent by calcium sulfate dihydrate (Fig. 4b).

SEM data (Fig. 5) show single crystals of syngenite, which are characterized by a rail-like shape and have a length of 500-2000  $\mu\text{m}$  with a side of 50-80  $\mu\text{m}$ . The shape of these crystals is similar to the natural single crystals of the Gluckauf Mine deposit (Sonderhausen, Thuringia, Germany). X-ray spectral microprobe analysis established that the potassium, calcium and sulfur ratio in the composition of syngenite single crystals recalculated for  $\text{K}_2\text{O}$ ,  $\text{CaO}$  and  $\text{SO}_3$  is 18.56, 32.93 and 48.51 wt. %, respectively.

During the growth of single crystals, drusen of calcium sulfate dihydrate (Fig. 6) with a spongy structure are formed on the surface of the vessel in some places next to the syngenite. The rail-like crystals of syngenite are longer, denser, and more uniform in comparison with gypsum crystals.

In order to eliminate negative phenomena in the hardening process of Portland cement based on clinkers with a high content of alkaline oxides and  $\text{SO}_3$ , it was proposed<sup>26,27</sup> to optimize the amount of calcium sulfate dihydrate introduced during the cement grinding, as well as to bind alkaline cations into insoluble compounds. Therefore, an increase in the  $\text{K}_2\text{SO}_4$  content in Portland cement clinker should be accompanied by a corresponding increase in the amount of gypsum, as well as the introduction of active mineral additives of hydraulic and pozzolanic action.



**Fig. 3.** Microstructure and microanalysis of the pore surface of the paste based on  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{K}_2\text{SO}_4$  system with the ratio of 2 : 1 (a) and 1 : 1 (b)



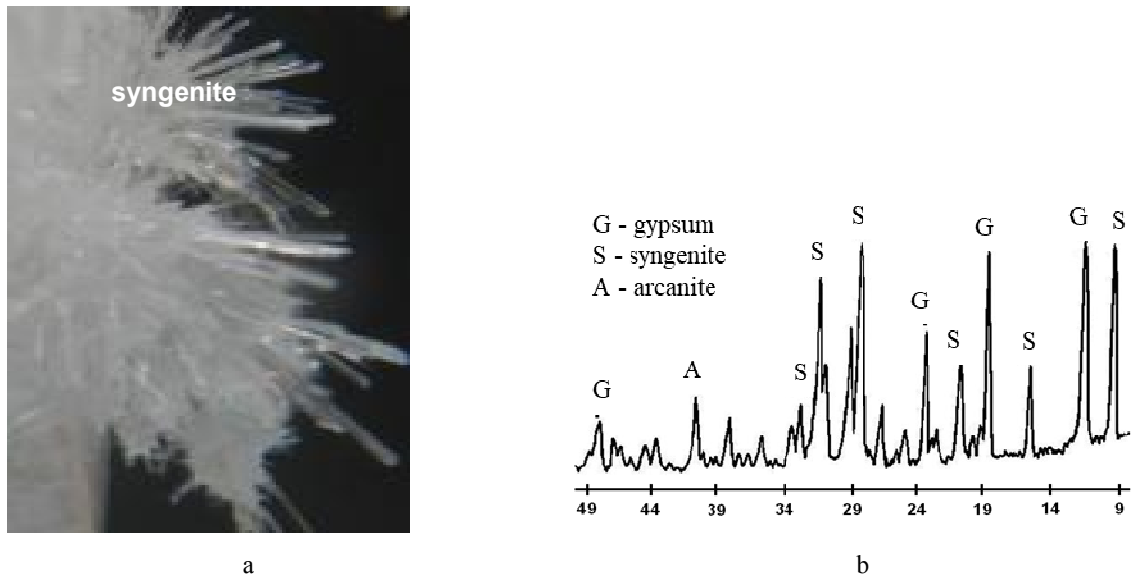


Fig. 4. Photo (a) and diffractogram (b) of single crystals grown by the method of counter diffusion

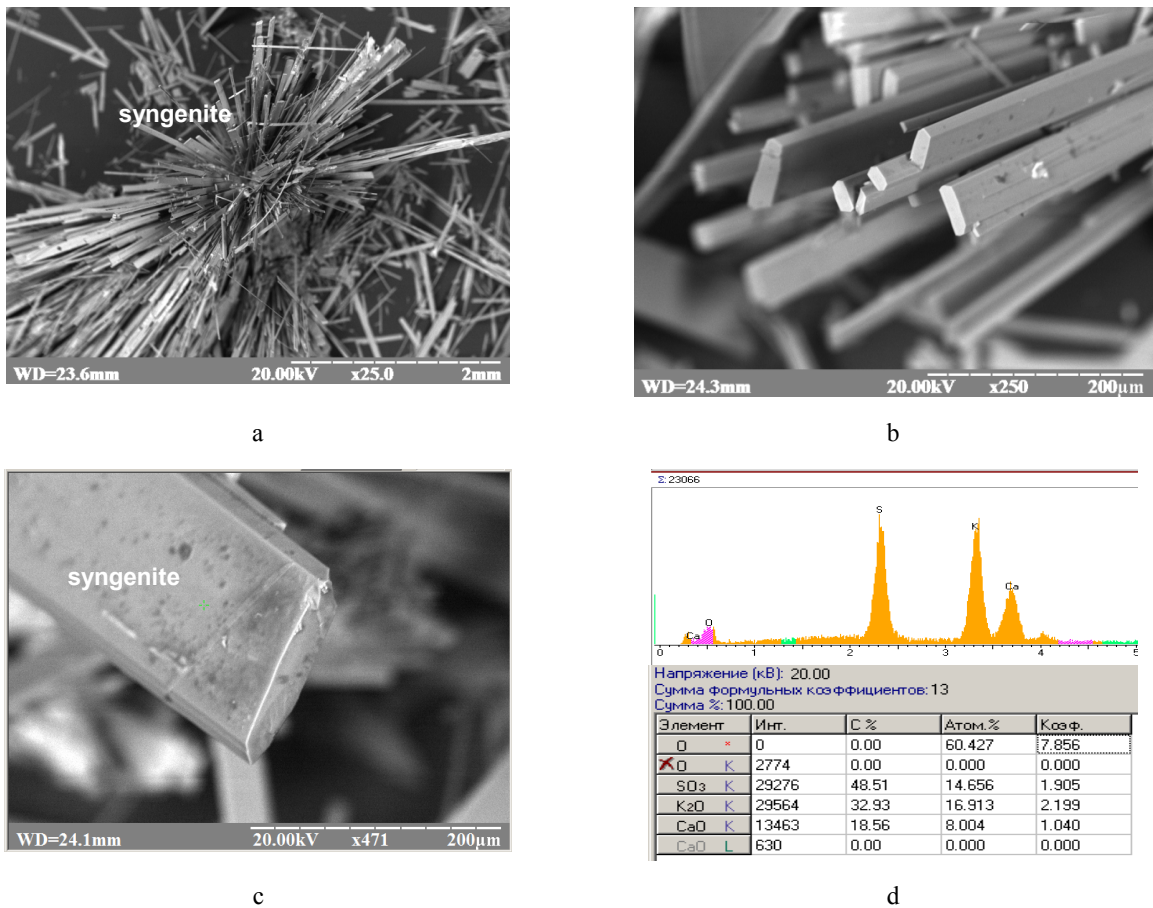
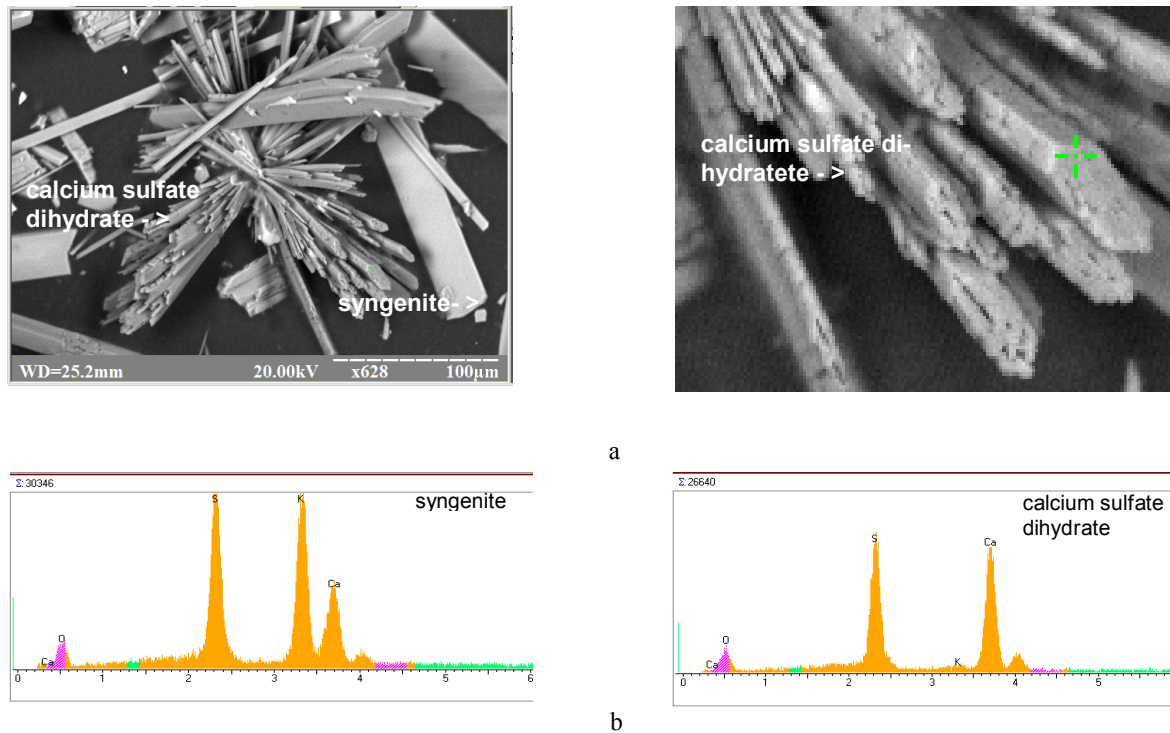


Fig. 5. Microstructure (a-c) and microprobe analysis (d) of syngenite



**Fig. 6.** Microphotographs (a) and microprobe analysis (b) of syngenite and gypsum single crystals

One of the ways of binding alkaline cations in the early period of structure formation of Portland cement in hydrate phases is the introduction into the composition of the cementing system of ground granulated blast furnace slag (GGBFS), which has potential hydraulic binding properties that depend on the ratio of vitreous and crystalline phases. Studies of artificial stone based on GGBFS have established that if 15 % solution of  $K_2SO_4$  is used, the strength after heat treatment increases significantly. When the highly dispersed vitreous phase of GGBFS interacts with potassium sulfate, alkaline components form zeolite-like alkaline and alkaline-earth hydroaluminosilicates. At the same time, in the early period of structure formation, the possibility of syngenite formation decreases, which leads to a decrease in destructive phenomena in the cementing matrix of concrete.

#### 4. Conclusions

By the method of X-ray spectral microprobe analysis, it was established that in Portland cement clinker, potassium and sulfur atoms are concentrated locally in the pores at the phase interface with the formation of the water-soluble mineral – arcanite ( $K_2SO_4$ ), which is an independent phase that does not mix with the clinker melt. In the clinker produced by PJSC "Ivano-Frankivsk cement" the content of  $K_2O$  is  $1.0 \pm 0.2$  wt. %,  $Na_2O$  content is  $0.14 \pm 0.03$  wt. %, and the content of  $SO_3$  ranges from 0.5 to

0.8 wt. %, while the amount of arcanite reaches 1.422 wt. %. Part of  $K_2O$  is included in the structure of clinker minerals with the formation of  $K_2O \cdot 23CaO \cdot 12SiO_2$ ; potassium atoms are practically absent in the composition of the intermediate (aluminum ferrite) phase. For Portland cement CEM I 42.5 R with a specific surface of  $3120 \text{ cm}^2/\text{g}$ , the content of the fraction up to  $45 \mu\text{m}$  is 88.0 wt. %; alkaline oxides and sulfates are more concentrated in the thin fraction. This leads to an acceleration of the hydration rate at the initial stage of CEM I 42.5 R and an increase in the intensity value of the first exoeffect.

When using Portland cement based on clinkers with a high content of  $K_2O$  and  $SO_3$ , elongated rail-like crystals of syngenite  $K_2Ca(SO_4)_2 \cdot H_2O$  are formed in the early period of hydration, as a result of water-soluble arcanite interaction with calcium sulfate dihydrate, which acts as a traditional retarder for the Portland cement setting. As a result, water consumption increases and the initial setting time of the cement paste is significantly accelerated, which causes destructive phenomena in it, an increase in the porosity of the cement paste and a decrease in its early strength.

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## ВПЛИВ СУЛЬФАТІВ КАЛІЮ НА ПРОЦЕСИ ТУЖАВІННЯ ПОРТЛАНДЦЕМЕНТНОГО ТІСТА

**Анотація.** Досліджено ефекти дії сульфатів калію на тужавіння цементного тіста. Встановлено, що основні елементи (Ca, Si, Al) розподіляються в складі клінкерних мінералів, тоді як атоми K та S концентруються локально в порах з утворенням водорозчинного арканіту  $K_2SO_4$ . Показано, що взаємодія  $K_2SO_4$  та  $CaSO_4 \cdot 2H_2O$  з утворенням сингеніту  $K_2Ca(SO_4)_2 \cdot H_2O$  спричиняє деструктивні явища в цементному тісті.

**Ключові слова:** портландцементний клінкер, дво-водний гіпс, арканіт, сингеніт, терміни тужавіння.