

## THE EFFECT OF HIGH TEMPERATURES ON CEMENT STONE FROM SULFOMINERALS

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### ABSTRACT

Thus, thermograms and radiographs of heated sulfoaluminate samples show that the endoeffect and crystallization transformations in temperature range of 20...200°C are associated with removal of the first stage of crystallization water, in the range of 780...820°C- the second stage.  $C_4A_3\hat{S}$  has high hydraulic activity and heat resistance (up to 1000 °C). Samples from hydrated  $C_5S_2\hat{S}$  when heated to 800 °C have a slight shrinkage and high initial mechanical strength, as well as sufficient heat resistance compared to samples from  $\beta$ - $C_2S$ .

**Keywords:** Anhydrite samples, sulfomineral, sulfosilicate samples, amorphization, crystal lattice, hydrolysis process, endoeffect, deformative changes.

### INTRODUCTION

To identify the physicochemical changes that occur when cement stone from sulfominerals is heated, they studied [3, 69, 190, 195, 200, 201] the effect of high temperatures on them according to the method of KD Nekrasov [202]. According to his data, the strength of  $C_2S$  specimens decreases already starting from 300°C and reaches a minimum at 760°C, which is explained by the modification transformation of  $\beta$ - $C_2S$ . With further heating, the strength of the samples increases and at 1200°C it increases by more than 5 times compared with the initial value.

When heated to 330°C, the strength of  $C_3A$  decreases by almost a factor of 2, and finely dispersed  $C_5A_3$  crystals appear. It is assumed [202] that upon dehydration,  $C_3A \cdot H_6$  is immediately partially decomposed into  $CaO$  and  $C_5A_3$ . This is the reason for the decrease in the strength of samples from  $C_3A$ . When heated to 590°C, the structure loosens and the strength drops sharply. An increase in the heating temperature causes an increase in the strength of  $C_3A$  and at 1200° it is 184% of the initial strength.

The results of the experiments (Table 10) showed that the strength of samples prepared from gypsum dihydrate, fired at 1250°C, decreases by 38-40% at 100°C, and remains constant at 800°C. At 1000°C there is a further decrease in strength to 25%. The insignificant initial strength of anhydrite samples is explained by the low solubility and slow hydration of the calcined gypsum, and its decrease upon heating is due to dehydration and the destruction of crystalline intergrowths. Anhydrite samples stored for 28 days in air-dry conditions have the same mechanical strength as the control samples. This phenomenon is due to the fact that during the initial firing of gypsum at high temperatures, decomposition into lime and sulfur dioxide does not occur. Otherwise, the reverse process of hydration of free lime, which is present in the initially heated samples with atmospheric moisture during subsequent storage for 28 days, would be accompanied by even more significant deformation phenomena.

Table1.Heat resistance of monomineral cements

Minerals and their mixtures	Relative strength (%) after heating to a temperature, °C										
	20	100	200	300	400	500	600	700	800	900	1000
CaSO <sub>4</sub>	100	$\frac{62}{75}$	$\frac{57}{75}$	$\frac{50}{87}$	$\frac{62}{50}$	$\frac{62}{50}$	$\frac{57}{50}$	$\frac{50}{50}$	$\frac{50}{50}$	$\frac{37}{37}$	$\frac{25}{37}$
CA	100	72	$\frac{76}{87}$	$\frac{71}{83}$	$\frac{75}{80}$	$\frac{93}{80}$	$\frac{75}{80}$	$\frac{74}{71}$	$\frac{80}{73}$	$\frac{71}{71}$	$\frac{58}{55}$
C <sub>4</sub> A <sub>3</sub> Ŝ	100	110	$\frac{117}{109}$	$\frac{96}{100}$	$\frac{94}{95}$	$\frac{97}{95}$	$\frac{91}{84}$	$\frac{104}{91}$	$\frac{101}{93}$	$\frac{86}{83}$	$\frac{70}{60}$
77,7%CA+22,3%CŜ	100	$\frac{100}{109}$	$\frac{110}{120}$	$\frac{96}{96}$	$\frac{90}{87}$	$\frac{86}{87}$	$\frac{75}{87}$	$\frac{67}{83}$	$\frac{75}{83}$	$\frac{73}{57}$	$\frac{50}{57}$
C <sub>2</sub> S	100	-	166	195	133	164	58	53	67	-	-
C <sub>7</sub> S <sub>3</sub> Ŝ	100	87	$\frac{94}{89}$	$\frac{110}{85}$	$\frac{100}{87}$	$\frac{107}{90}$	$\frac{112}{90}$	$\frac{96}{95}$	$\frac{75}{70}$	$\frac{61}{60}$	$\frac{56}{60}$
C <sub>5</sub> S <sub>2</sub> Ŝ	100	128	$\frac{118}{100}$	$\frac{110}{110}$	$\frac{110}{111}$	$\frac{100}{105}$	$\frac{92}{105}$	$\frac{95}{105}$	$\frac{73}{72}$	$\frac{69}{65}$	$\frac{51}{60}$
71,7%C <sub>2</sub> S+28,3%CŜ	100	$\frac{94}{141}$	$\frac{100}{125}$	$\frac{115}{122}$	$\frac{80}{122}$	$\frac{80}{122}$	$\frac{80}{103}$	$\frac{82}{80}$	$\frac{56}{60}$	$\frac{31}{60}$	$\frac{50}{60}$
20%C <sub>4</sub> A <sub>3</sub> Ŝ+80%C <sub>7</sub> S <sub>3</sub> Ŝ	100	100	$\frac{65}{64}$	$\frac{41}{53}$	$\frac{48}{43}$	$\frac{44}{40}$	$\frac{54}{40}$	$\frac{47}{37}$	$\frac{41}{31}$	-	$\frac{33}{21}$
20%C <sub>4</sub> A <sub>3</sub> Ŝ+80%C <sub>5</sub> S	100	104	$\frac{43}{43}$	$\frac{37}{54}$	$\frac{37}{44}$	$\frac{40}{44}$	$\frac{40}{42}$	$\frac{40}{40}$	$\frac{38}{25}$	-	$\frac{18}{16}$

Note. In the numerator, the strength after 1-day storage, in the denominator - after 28-day storage of heated samples in air-dry conditions.

It should be noted that the very high strength of samples (1:0) from C<sub>7</sub>S<sub>3</sub>Ŝ and C<sub>5</sub>S<sub>2</sub>Ŝ (7 times greater than that of β-C<sub>2</sub>S) approaches the strength of SA, 3(CA) + CaSO<sub>4</sub> and C<sub>4</sub>A<sub>3</sub>Ŝ. The results of heat treatment showed that these samples are highly resistant up to 700°C. Although their strength decreases by 25% at 800°C, by 30–40% at 900°C, and by 44–50% at 1000°C, it still remains much higher than the strength of β-C<sub>2</sub>S. This is apparently due to the fact that sulfosilicate samples have a better hydration capacity compared to β-C<sub>2</sub>S when stored in an air-humid environment and heated. Here, apparently, the process of hydration proceeds without the release of free lime and a significant amount of gypsum. The product of hydration is obviously 2(C<sub>2</sub>S) mCŜ nH<sub>2</sub>O containing a significant amount of CaSO<sub>4</sub>. After 28 days of storage of heated samples, their mechanical strength does not decrease due to hydration (CaO) and dehydration (CaSO<sub>4</sub> 2H<sub>2</sub>O) processes.

The most thermally stable are C<sub>4</sub>A<sub>3</sub>Ŝ, 3(CA)+CaSO<sub>4</sub> and CA, which is due to the absence of gel hydration products in them. The aluminum hydroxide formed in the gel form already at 100°C passes into the crystalline phase, causing a decrease in the strength of SA samples by 28%. With further heating, this strength is retained up to 900°C and only at 1000°C drops sharply to 42%. It is interesting that C<sub>4</sub>A<sub>3</sub>Ŝ, despite the high water-cement ratio and the content of high-water crystalline hydrates, is the most thermally stable mineral: up to 900°C its strength remains at the level of 86%, and at 1000°C it decreases only to 70%. Comparing the behavior of samples from SA and C<sub>4</sub>A<sub>3</sub>Ŝ, it can be assumed that free CaO and CŜH<sub>2</sub> are not formed in the hydration products of C<sub>4</sub>A<sub>3</sub>Ŝ, AH<sub>3</sub> is not formed in a small amount, and C<sub>4</sub>A<sub>3</sub>Ŝ nH<sub>2</sub>O is the main crystalline hydrate.

In aluminate and sulfoaluminate samples, when heated, small surface cracks appear due to shrinkage (longitudinal and transverse at 200°C). The volume of these samples at 300°C decreases by 0.0215 and 0.0125%, respectively; at 500°C, the volume of samples from SA decreases by 0.0215%; at 800°C from C4A3 $\hat{S}$ , by 0.0512%. The mode and conditions of heating the samples, as well as the very nature of the binder, strongly influence the appearance of cracks. However, such deformation changes do not cause a significant decrease in their mechanical strength. Sulfosilicate samples with small surface cracks do not decrease in size when heated. As is known, samples of Portland cement, heated to 800-900°C, crumble after 28 days of storage in air conditions due to the rehydration of free lime resulting from the hydrolysis of Portland cement in the initial period of hydration.

Under normal conditions (21 days in air-humid and 7 days in air-dry) of SA hydration, along with Al(OH)<sub>3</sub>, hexagonal C3AH8 is formed with endoeffects at 330°C (dehydration) and 520°C (decomposition into CaO and C12A7). The effect at 130-120°C seems to correspond to CA · 10H<sub>2</sub>O, the exoeffect at 900°C corresponds to the crystalline anhydrous mineral CA.

Hydration of 3(CA)+CaSO<sub>4</sub> gives rise to an insignificant amount of CA · 10H<sub>2</sub>O (effect at 130°C), Al(OH)<sub>3</sub>, and hexagonal C3AH8 (effects at 325 and 520°C). The effect at 220°C we attribute to C3A · C $\hat{S}$  · H<sub>12</sub>. On the thermograms of samples from C4A3 $\hat{S}$ , an effect appears at 170-180°C, which differs from the effect of known hydrosulfoaluminates. Therefore, it refers to 3(CA) · C $\hat{S}$  · nH<sub>2</sub>O. If the system contains the C3AH6 phase or its hexagonal form, then the heating curve is accompanied by endoeffects at 330 and 520°C, which is not observed when samples from C4A3 $\hat{S}$  are heated.

Changes in mechanical strength upon heating of C4A3 $\hat{S}$  samples are due to physicochemical processes occurring in them at high temperatures. X-ray diffraction patterns of samples hydrated at 20°C showed that polymineral products are formed in this case. In addition, new lines appear (d=1.38, 1.51, 1.54, 1.62, 1.96, 3.58, 3.73, 7.8 Å) corresponding to 3(CA) · C $\hat{S}$  · nH<sub>2</sub>O. The appearance of ettringite (d=9.5, 5.45, 2.78, 1.66), hydroaluminate C3AH8 and gibbsite (d=2.50 and 2.87) is due to the processes of hydrolysis and recrystallization of 3(CA) · C $\hat{S}$  · nH<sub>2</sub>O. When heated to 100°C, the lines corresponding to the new hydrate (d=1.38, 1.51, 1.54, 1.62, 1.66, 3.58, 5.45, 5.81 Å) disappear, which, apparently associated with the amorphization of the structure. The lines corresponding to C3AH8 become clearer due to the destruction of the crystal structures of other phases, the lines of which previously darkened them. When heated to 200°C, some lines related to C3AH8 (d=2.50, 2.87) become flatter, and some corresponding to the new hydrate (d=2.03, 3.30, 1.89 Å) and ettringite (d=9.5 Å) disappear. The destruction of the crystal lattice of ettringite is accompanied by the appearance of an anhydrite line with d = 3.47 Å. When the samples are heated to 400°C and above, the intensity of the anhydrite lines slightly increases; up to 1000°C, lines appear with d = 3.75, 2.17, 2.67, 2.96, etc., corresponding to the initial anhydrous substance.

The intensity of the line with d = 1.96, 3.73, 7.8 Å, corresponding to the new hydrate, gradually decreases when the samples are heated: the lines with d = 1.96 and 7.8 Å disappear only at 1000°C, and with d = 3.73 Å - at 400-600°C. This phenomenon, apparently, occurs in connection with the stepwise removal of water of crystallization from the new hydrate, which is also confirmed by the occurrence of an endo effect at 800°C and a gradual change in the structure of the crystal lattice.



Thus, thermograms and X-ray patterns of heated sulfoaluminate samples show that the endoeffect and crystallization transformations in the temperature range of 20...200°C are associated with the removal of the first stage of crystallization water, in the range of 780...820°C - of the second stage.

Judging by the X-ray diffraction patterns of samples from a 3(CA)+CaSO<sub>4</sub> mixture obtained at 20°C, a new phase is formed in it (d=1.12, 1.25, 1.44, 1.51, 1.54, 1.96, 3.7), however, ettringite with d=9.6, 5.6, 3.86, 3.24, 3.03, 2.76, 2.20 is present as the main one, partially monosulphate with d=8.8 Å, as well as the phase with d=2.86, 2.47, 1.65 corresponding to C<sub>3</sub>AH<sub>8</sub>. The aluminum hydroxide released as a result of hydrolysis is poorly crystallized, so only a single line with d = 2.36 is found. Meanwhile, under these conditions, complete hydration of SA and CaSO<sub>4</sub> does not occur, which is confirmed by the presence of lines with d = 4.69, 4.00, 2.95, 2.43, 2.18, 1.91, 1.74 Å and with d=3.47 Å. When the samples are heated to 400°C, the phase composition of the hydration products changes dramatically. Thus, ettringite completely decomposes with the formation of C<sub>3</sub>A (d=4.23, 4.08, 2.78, 2.70, 2.50, 2.20, 1.56 Å) and CaSO<sub>4</sub> (d=3.47, 2.85, 2.32, 1.86, 1.64, 1.52, 1.42, 1.39, 1.27 Å), gibbsite crystallizes, additional lines appear with d = 4.85, 4.37, 2.45, 2.38, 2.24 Å.

Heating at 1000°C causes an increase in the number of CA lines and the appearance of lines with d=3.75, 2.66, 2.16, indicating the formation of a small amount of C<sub>4</sub>A<sub>3</sub>Ŝ.

Interesting data were obtained from the study of X-ray diffraction patterns of sulfosilicate samples. X-ray pattern of a mixture consisting of β-C<sub>2</sub>S and ĈŜ (hydrated at 20°C) indicates the presence of mostly non-hydrated minerals in it: C<sub>2</sub>S with d=3.85, 3.51, 3.17, 2.32, 2.27, 2.07, 1.86, 1.74 Å and ĈŜ with d=2.77, 2.74, 2.19, 2.40 Å. In the presence of ĈŜ in the mixture, the amount of formed gel-like products of C<sub>2</sub>S hydration increases. Some neoplasms have NCP=1.570. Sometimes there are tabular grains with the same refractive index, apparently related to tobermorite, which is characterized by lines with d = 3.06, 2.42, 1.97 Å. There are also highly aggregated accumulations of C<sub>2</sub>SH<sub>2</sub> with d=3.01 and 2.66.

Samples from C<sub>5</sub>S<sub>2</sub>Ŝ (at 20°C) significantly differ from samples from mixtures by greater crystallinity. The bulk has NCP=1.546. Grains of scaly, sometimes rhombic shape: scaly belong to gyrolite - C<sub>2</sub>S<sub>3</sub>H<sub>2</sub> with d=9.56, 4.25, 3.84, 3.04, 2.83, 2.61, 2.42, 2.09, 2.02, 1.99 Å, and rhombic - to 2(C<sub>2</sub>S) mĈŜ nH<sub>2</sub>O. ĈŜ lines with d=3.48, 2.28, 1.89, 1.73 Å and C<sub>2</sub>S lines with d=2.77, 2.73, 2.19 Å are observed. This is due to the fact that the process of hydration of C<sub>5</sub>S<sub>2</sub>Ŝ goes with partial decomposition and subsequent hydration. The decomposition products 2(C<sub>2</sub>S) mĈŜ nH<sub>2</sub>O and ĈŜ, which appeared from the crystal lattice of C<sub>5</sub>S<sub>2</sub>Ŝ, determine the defectiveness of the crystals, which is revealed in its higher hydraulic activity compared to β-C<sub>2</sub>S. However, in the initial period of hydration, due to low solubility, the transition of anhydrite to gypsum is greatly slowed down, so the line of gypsum with d = 7.65 and 4.25 is weakly expressed on the X-ray. Under the microscope, gypsum grains have a lamellar shape, their number is small. Anhydrite is difficult to determine microscopically, since the visible crystals have a very fine structure.

The X-ray pattern shows that the crystal lattice of the sulfo-silicate is completely destroyed, but the anhydrite peak is much smaller than in the artificial mixture. It follows from this that not all CaSO<sub>4</sub> contained in C<sub>5</sub>S<sub>2</sub>Ŝ is involved in the hydrolysis process, a part remains in the

composition of  $2(C_2S) mC\hat{S} nH_2O$ . It probably has very close diffraction lines with calcium hydrosilicates. Heating at  $1000^\circ C$  leads again to the formation of  $C_5S_2\hat{S}$ .

Thus,  $C_4A_3\hat{S}$  has high hydraulic activity and heat resistance (up to  $1000^\circ C$ ). Samples from hydrated  $C_5S_2\hat{S}$ , when heated to  $800^\circ C$ , have insignificant shrinkage and high initial mechanical strength, as well as sufficient heat resistance compared to samples from  $\beta$ - $C_2S$ .

To obtain a heat-resistant material, it is necessary to use sulfa-mineral cements, during hardening of which free lime is not formed.

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