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SULFATE-CONTAINING CEMENTS BASED ON PHOSPHOGYPSUM AND OTHER MATERIALS

Egamberdiev M. S.
Professor of the Department "Hydrology and Ecology "

Annotation:
The use of phosphogypsum in an amount of 6 to 49 in the composition of raw materials made it possible to obtain clinker of various mineralogical composition, by adjusting which, depending on the need, it is possible to produce non-shrinking, high-strength, expanding and stressing cements of various grades.

Keywords: phosphogypsum, calcium sulfate dihydrate, easily clumping material, Angren kaolinite clay, kaolinite clay, calcium sulfosilicate, calcium sulfoaluminate, sulfosilicate.

Raw materials for the production of sulfate-containing clinkers included Akhangaran limestone used for the manufacture of Portland cement, phosphogypsum, a waste from the extraction phosphoric acid production of the Almalyk Chemical Plant, and Angren kaolinite clay, a by-product of coal mining.
To provide agriculture with highly concentrated phosphate fertilizers, further development of the production of phosphoric acid is required. However, the phosphogypsum formed during the production of phosphoric acid creates a number of problems. Thus, transportation and storage of phosphogypsum are associated with additional capital investments and are reflected in the cost of the final product. In addition, land occupied by phosphogypsum dumps is increasingly expanding, polluting the environment. Therefore, the processing of phosphogypsum into the final product is an important task for the chemical industry.
In Uzbekistan, there are three large operating plants, which, using Karatau phosphorites, annually emit huge amounts of phosphogypsum. Phosphogypsum consists mainly of calcium sulfate dihydrate and contains impurities of undecomposed phosphate, phosphate salts and silicates. The quantitative content of impurities depends on the mineralogical composition of the feedstock and the well-established production. Typically, the fluorine content in phosphogypsum is but more than 0.1 ... 0.4%. Humidity (of phosphogypsum fluctuates depending on the method of its removal. Externally, phosphogypsum of the Almalyk chemical plant is an easily clumping gray material.
It has a specific smell, loose texture, disordered texture, monomineral structure. The slightly moistened material is represented by lumps that form a loose mass with voids between lumps. When dried, it is a fine powder. The predominant fraction of phosphogypsum is particles 1.6 ... 0.4 and 0.16 ... 0.1 mm in size. The content of the fraction less than 50 microns is 2...3%. The specific gravity of phosphogypsum dried under natural conditions is 2.34...2.36 g/cm^3. The specific surface ranges from 3100 to 3500 cm2/g. The chemical composition of the phosphogypsum sample used to produce sulfate-containing cements is characterized by the content of the following oxides, %: SiO2-10.39; Al2O3 - 0.39; Fe2O3 -

ISSN: 2776-1010 Volume 4, Issue 5, May 2023

0.24; CaO - 22.17; SO3 - 45.55; P2O5 - 1.00; TiO2 - 0.07; MgO - 0.11; Na2O3 - 0.10; K2O - 0.12; loss on ignition (p.p.p.) - 9.00.

Angren kaolinite clay is characterized by the predominance of particles smaller than 0.001 mm - 57%. Fraction 0.005 + 0.001 is 21%. It differs in the content of the following oxides, %: SiO2-51.6; Al2O3 - 29.0; Fe2O3 - 4.62; CaO - 0.28; SO3 - 0.2; TiO2 - 0.42; MgO - 0.67; Na2O3 - 0.1; K2O - 1.81; p.p.p. - 12.02. The chemical composition of Akhangaran limestone is characterized by the content, %: SiO2-6.62; Al2O3 - 1.25; Fe2O3 - 0.63; CaO - 50.4; SO3 - 0.05; TiO2 - 0.08; MgO - 0.35; Na2O3 - 0.1; K2O - 0.11; p.p.p. - 40.3.

From the selected raw materials - limestone of the Akhangaran deposit, phosphogypsum of the Almalyk chemical plant, Angren kaolinite clay, raw materials were prepared with the saturation coefficient of silica with lime KH=0.667 and sulfosilicate module ns= 0.1; 0.5; 1.0; 1.5; 2.0; 3.0. At the same time, with an increase in the value of the sulfosilicate module, the content of limestone in raw materials decreased from 72.34 to 45.19%, and phosphogypsum increased from 5.86 to 49.24%; the content of kaolinite clay decreased from 21.80 to 5.57%.

At the same time, with an increase in the value of the sulfosilicate module from 0.1 to 3.0 raw materials, a decrease in the content of oxides of silicon, aluminum and iron was observed due to a significant increase in sulfuric anhydride - from 2.74 to 22.43%.

The raw materials were briquetted and fired in a laboratory silicate furnace at a temperature of 1523 K by the high-speed method for an hour. There is no free lime in the synthesized clinkers, which indicates the completeness of the processes of formation of the necessary minerals. X-ray phase analysis of clinkers also indicates that their mineralogical composition is in accordance with the specified one.

The mineralogical composition of the obtained clinkers differs depending on the value of the sulfosilicate module as follows. At ns= 0.1, the clinker is characterized by the content of 62.9% dicalcium silicate, 6.6% tetracalcium aluminoferrite, 18.4% calcium sulfoaluminate and 9.8% calcium sulfosilicate. The mineralogical composition of clinker with the value of the sulfosilicate module ns = 0.1 differs in the content of 4.9% tetracalcium aluminoferrite, 12.6% calcium sulfoaluminate and 80.2% calcium sulfosilicate.

With the value of the sulfosilicate module ns = 3.0, the mineralogical composition of the clinker is characterized by the content of 2.6% tetracalcium aluminoferrite, 5.0% calcium sulfoaluminate, 57.2% calcium sulfosilicate and 32.4% calcium sulfate.

Depending on the mineralogical composition of the clinkers, the properties of the resulting cements also differ. Table 1 shows that when cements with an increased value of the sulfosilicate module are mixed with water, the normal density decreases, and the setting time is shortened. At ns = 0.1, when mixing, 27% of water is required, the beginning of setting occurs after 55 minutes, and the end after 1 hour 35 minutes. When the value of the sulfosilicate module is up to 3.0, the normal density decreases by 23%, the beginning of setting occurs after 10 minutes, and the end - 25 minutes after mixing.

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Table 1 Properties of sulfate-containing cements

No. of cement	n_s	Normal density, %	Setting time, hour - min		Compressive strength per day, MPa	linear expansion, % in a day				
			start	end		1	3	7	28	90
1	0,1	27	0-55	1-35	46,8	-0,01	0,03	0,09	0,12	0,11
2	0,5	27	0-40	1-15	51,9	-0,03	0,09	0,14	0,17	0,17
3	1,0	26	0-35	1-05	60,7	0,06	0,15	0,19	0,21	0,22
4	1,5	25	0-30	1-00	50,4	0,11	0,19	0,21	0,20	0,30
5	2,0	24	0-25	0-50	47,6	0,18	0,24	0,29	0,34	0,33
6	3,0	23	0-10	0-25	40,5	0,44	0,63	0,84	1,03	1,04

The compressive strength at 28 days of age with an increase in the value of the sulfosilicate module to 1.0 increases and reaches 60.7 MPa. An increase in the value of the sulfosilicate module to 3.0 reduces the hardening strength of the cement. Cements with the value of the sulfosilicate module ns = 0.5; 1.0; 1.5 at 25 days of age have increased strength, the value of which is 50 ... 60 MPa in compression.

The hardening of cements at the value of the sulfosilicate module ns = 0.1 and 0.5 during the day is accompanied by shrinkage, which is further compensated by expansion. The linear expansion increases proportionally with the growth of the sulfoaluminate module of cements. A particularly intensive growth of the stately linear expansion is observed during the hardening of cement, which is characterized by the value of the sulfosilicate module ns = 3.0. The expansion process also depends on the hardening time of cements. By the age of seven days, an expanded structure is mainly formed, by the age of 28 days there is only a slight increase in volume, which is stably maintained for three months or more. Thus, all sulfate-containing cements can be classified as expanding, although their degree of expansion is different and depends on the value of the sulfosilicate module. Undoubtedly, expanding cements must develop self-stressing forces, therefore, to determine the self-stressing forces that occur during the hardening of Portland cement with the addition of 20 and 30% synthesized clinkers at values of the sulfosilicate module nS = 0.1 - 3.0, solutions were prepared with Volsky sand at a ratio of 1: 1 and molded samples of torque rings. The self-stress value was determined after 30 minutes, 1, 2, 3, 4 hours and 1, 3, 7, 28 days, and also after 1 year of hardening in water. Table 2 shows that during the hardening of cement containing 20% sulfonic clinker at a value of sulfosilicate modulus nS = 0.1, self-stress forces occur within four hours and only by the age of one year, self-stress reaches 0.32 MPa. An increase in the content of the same clinker in mixed cement up to 30% leads to the appearance of self-stressing forces already at a daily age, which reaches 0.8 MPa over time.

Self-stress forces arising during hardening of cements, MPa. table 2

No. of cement	ns sulfo-clinker	Amount of PC addition, %	W / C	Hardening time					
				Watch		day			
				1	4	1	7	28	360
1	0,5	20	0,25	0,003	0,03	0,04	0,36	0,50	1,22
2	0,5	30	0,26	0,22	0,12	0,08	0,28	0,42	5,62
3	1,0	20	0,26	0,36	0,16	0,22	0,50	0,68	1,08

ISSN: 2776-1010 Volume 4, Issue 5, May 2023

4	1,0	30	0,26	0,50	0,54	0,58	0,60	0,74	1,14
5	1,5	20	0,26	-	-	0,58	0,84	1,04	1,34
6	1,5	30	0,26	0,01	0,27	0,84	1,56	2,02	5,24
7	3,0	20	0,26	7,14	4,66	5,02	0,78	0,60	0,82
8	3,0	30	0,27	0,19	1,57	2,41	5,82	6,34	6,47

The hardening of cements with the addition of sulfonic clinker at a sulfosilicate module value of up to 0.5 leads to the appearance of self-stress forces in the stone already after 30 minutes, which reaches 1.22 MPa after a year. With an increase in the content of the clinker additive to 30%, the self-stress value increases to 6.62 MPa.

With an increase in the value of the sulfosilicate modulus, the self-lowering of the stone from mixed cement increases. With a 30% content of clinker, the sulfosilicate module of which is ns = 1.5, a self-stress is created at the age of 28 days, sufficient to classify this mixed cement as NTs-20 prestressing grade. A mixed cement containing 30% sulfonic clinker with a value of sulfosilicate module ns = 3.0 can be attributed to the brand NTs-60.

Thus, the regulation of the content of sulfoclinker in mixed cements and the composition of sulfoclinker using the value of the sulfosilicate module makes it possible to obtain stress cements of various grades, and, which is especially valuable, high-quality NTs-40 and NTs-60. As is known, at present stressing cements are produced only at two or three factories in the country, and only low-quality stressing cements of the H-10 and NTs-20 grades are produced.

When using cement in reinforced concrete structures, in addition to the above properties, the alkaline environment created during the hardening of the cement stone is important, since it prevents corrosion of the reinforcement, thereby extending the service life of reinforced concrete structures. Therefore, the value of the pH value of the water in which the samples hardened was determined, which made it possible to observe its alkalinity. The analysis of water in contact with the cement stone was carried out using a pH meter. During water hardening of crushed sulfate-containing clinkers, the sulfosilicate module of which varies from 0.1 to 3.0, the pH of water is in the range of 8.9 ... 11.0. This indicator increases as the amount of sulfonic clinker additive and the value of its sulfosilicate module increase.

The pH value of water after a three-day hardening does not change significantly during the hardening of cement stone, remaining stable during long-term hardening and preventing reinforcement corrosion. The study carried out indicates the possibility of using mixed cements containing sulfonic clinker in the manufacture of reinforced concrete products and structures. Thus, cements obtained from traditional cement raw materials and waste have both the necessary binder and special properties. The grade of sulphocements is 400...600 and it also increases with the growth of the value of the sulfosilicate module up to ns = 1.5. Cements, depending on the composition, are characterized during hardening by various degrees of expansion.

The linear expansion depends on the value of the sulfosilicate modulus of the sulfoclinker and its hardening time. During hardening of mixed cements based on sulfonic clinker with a value of sulfosilicate modulus nS = 0.5, self-stress is created, the value of which increases with increasing nS to 3.0. Thanks to this, tensioning cements of the NTs-20, NTs-60 grades are obtained. Thus, the use of

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