Comprehensive solution to the problem of "clean climate", ecology and production of special types of cement in Uzbekistan

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Abstract. The article presents the results of research on the development of a low-energy technology of sulfo-alumina clinkers with a large-scale utilization of industrial waste of inorganic origin, such as screening of limestone, phosphogypsum and recycled slags from copper smelting production. It is noted that when raw mixtures are fired at 1150-1200°C, sulfominerals are formed in clinkers: sulfoaluminate ($C_4A_3\check{S}$), sulfosilicate($C_5S_2\check{S}$), and sulfoferrite ($C_4F_3\check{S}$) calcium, which coexist autonomously, and not in the form of their solid solutions, but cements based on them in terms of strength, they are not inferior to traditional Portland cement.

Keywords: sulfominerals, sulfoaluminate, sulfosilicate, sulfoferrite, hydration interaction, phosphogypsum, limestone screening, processed copper smelting slag, raw material mixture, low-temperature roasting, sulfo-iron clinker, sulfo-iron cement, artificial conglomerate, strength, structure, technological, environmental efficiency.

The production of nanocement makes it possible to revise the development strategy of the world cement industry: to reduce by 2-3 times the specific emissions of CO_2, SO_2 and NOX, and, accordingly, to radically reduce the fuel consumption of the existing cement plants [1]. This is especially true in connection with the need to radically reduce CO_2 emissions under the Paris Climate Agreement. The cement industry, producing about 4.5 billion tons of cement annually, emits about 4 billion tons of CO_2 into the atmosphere, which is about 8% of world emissions [2].

It is known that in terms of energy and material consumption, the building materials industry, in particular the production of cement, takes the second place after metallurgy, therefore, today an important place is occupied by the development of modern technologies that reduce emissions, save energy and resources, firing special types of low-temperature clinkers, production of modified active mineral additives of cements with high performance properties, and for this, whenever possible, use secondary mineral raw materials that have passed a certain stage of pretreatment.

In this regard, all over the world, taking into account the constant increase in prices for fuel and energy resources, and therefore the cost of Portland cement, research is being carried out aimed at the development of low-basic raw materials mixtures for obtaining special types of clinker using low-burning technology and cements based on it. At the same time, it is necessary to conduct research in priority areas focused on solving the following scientific and technological problems: search and study of the suitability for use in clinker production of raw materials containing compounds that help to reduce the firing temperature; study of the ability of pretreated metallurgical, chemical, mining and processing industry waste to reduce carbon dioxide emissions into the atmosphere and reduce the firing temperature of the raw mixture to obtain clinker, the cement on the basis of which will not be inferior in strength to traditional Portland cement; development of scientific and technological foundations for obtaining low-temperature clinkers using highly reactive types of natural and man-made raw materials [3-6].

In our republic, the intensive development of the construction industry and other industries dictates the need to increase the volume of production of building materials and products, including cement and cement concrete, improve their quality and reduce costs. For this, it is of great scientific and practical importance to find effective solutions to a number of existing problems associated with reducing the harmful effects of emissions on the climate.[7]. This is also clearly indicated in the Resolution of the President of the Republic of Uzbekistan, in which special attention is paid to solving problems of "organizing the production of new types of innovative building materials", "introducing scientific achievements into production processes" and "developing and implementing technologies for processing and using secondary raw materials", as well as to reduce energy consumption in the production of clinker with the release of cement with increased resistance to frost, frequent fluctuations in the atmosphere, corrosion and other factors [8].

- Based on this, we put forward an idea aimed at solving 3 major problems - the environmental, technological and economic nature of the metallurgical industries (improving environmental protection through the disposal of industrial waste - limestone screenings and recycled slags from copper smelting), chemical (phosphogypsum) and cement industry (a decrease in carbon dioxide emissions into the atmosphere due to a decrease in the consumption of a carbonate-containing component in the composition of the raw mixture for firing a semi-finished product - clinker by reducing its saturation coefficient due to partial replacement of limestone with phosphogypsum and carrying out the firing process at a temperature not higher than 1150-1250°C). At the same time, a comprehensive study of the processes of mineral formation of new raw mixtures and the stable existence of clinker minerals, the production of special types of cement with high technical and operational properties (resistance against the effects of frost, sharp changes in climatic conditions, aggressive sulfate salts) and low cost are provided.

When performing experimental work, the objects of research were low-temperature sulfo-iron (SAI) raw mixtures, clinkers, and cements based on them. The raw materials were screening of limestone formed as a waste of lime production at the lime plant of JSC "Almalyk MMC", waste of slag processing of the copper smelter of JSC "Almalyk MMC" (WSPCS) and phosphogypsum of JSC Ammophos-Maxam (tab. 1). The synthesis of sulfoclinkers was carried out by firing in an electric furnace with silite heaters.

Table 1

Chemical composition of raw materials

Material	The content of oxides, wt. %								
	SiO_2	$A1_2O_3$	Fe_2O_3	MgO	CaO	R_2O	P_2O_5	SO_3	ppp
Phosphogypsum	14.1	1.11	0.69	2.15	27.3	0.3	1.7	35.3	17.4
WSPCS	36.5	7.68	48.07	0.29	2.76	2.51	-	0.92	0.1
Limestone screening	6.58	2.50	1.15	0.80	48.7	0.36	-	0.33	39.5

The kinetics of mineral formation and the completeness of the process during the firing of sulfo-alumina raw materials were monitored by X-ray phase analysis. The strength of the samples was determined on small sample cubes with a face size of 1.41 cm and a composition of 1:0.

The calculation of the composition of sulfo-iron raw mixtures and the determination of the chemical and mineralogical composition of clinkers were carried out by setting the values of the saturation coefficient (SC) and sulfosilicate modulus (n_S). The physical and mechanical properties of cements are determined in accordance with GOST 310.1-310.4. The phase composition of SAI clinkers and cement stones was studied using X-ray phase and electron microscopic research methods.

The calculation of the composition of the raw mixtures was carried out with the values SC=0.667 and 0.80; n_S=1.0; 1.5; 2.0. At the same time, the content of WSPCS in the raw compositions ranged from 9.6 to 17.6%, phosphogypsum - from 25.63 to 42.16%, limestone dropout - from 48.2 to 57.21% (tab. 2). The reactivity of SAI raw materials was studied in the temperature range 800-1250°C with an exposure every 100°C. It was found that the optimal temperature for the synthesis of SAI clinker with SC=0.667 and 0.80 is 1150°C, and with SC=0.90 and SC=1.0-1200°C. Depending on the SC values and the SAI mineral content of clinkers, it is within the limits given in tab. 3.

Table 2

Ingredient ratio of SAI raw mixtures

SC	n_S	Content of mixture components,%		
		WSPCS	Phosphogypsum	Limestone screening
0.667	1.0	17.16	25.63	57.21
	1.5	14.54	33.16	52.30
	2.0	9.9	51.1	39.0
0.80	1.0	14.81	26.92	58.27
	1.5	10.85	40.82	48.33
	2.0	9.6	42.16	48.24

Table 3

Mineralogical composition of SAI clinkers

Values		The content of the main minerals, wt. %:			
SC	n_S	$C_4A_3\check{S}$	$C_4F_3\check{S}$	$C_5S_2\check{S}+C_2S$	$C\check{S}_{exc}$
0.667	1.0	8.17	20.23	78.40	-
	1.5	7.26	17.39	76.96	3.88
	2.0	5.83	11.67	74.04	19.69
0.80	1.0	4.00	18.00	76.00	-
	1.5	6.28	12.68	71.08	11.9
	2.0	6.32	11.88	72.72	13.07

X-ray phase analysis of clinkers confirms the full compliance of their actual mineralogical composition with the calculated data. Electron-microscopic studies of the surface of the SAI cleavage of clinker with SC=0.80 and n_S=2.0, fired at 1200°C is represented by a melted mass of the smallest rounded grains of $C_4F_3\check{S}$, in which similar grains of sulfoaluminate are dissolved and chaotically located grains $C_5S_2\check{S}$ elongated with melted edges. In some places these grains are arranged in blocks, and in some places - in a circle (fig. 1).

1 2

Figure 1. Relief of the cleaved surface of SAI clinkers with SC=0.667; n_s=1.5, fired at 1150 (1) and 1200°C (2). x 1300

The overall roughness of the relief indicates a high porosity, which is formed, apparently, due to the release of SO_2 during the firing of sulfo-iron-containing raw material mixture as a result of the partial decomposition of $C_4F_3\check{S}$ and $C_5S_2\check{S}$ respectively, into C_2F, C_2S and $C\check{S}$. This indicates the possibility of lowering the firing temperature of the raw material mixture by about 30-50°C to prevent the decomposition of low-heat sulphineral clinker.

By 3 days. hardening in water, standard samples of SAI cement with a composition of 1:3 gain about 75% of the brand strength, which allows them to be classified as fast-hardening cements, and the higher the SC and n_S values, the faster the cement stone gains strength. Strength indicators by 28 days at SC – 0.80; n_S=1.5 and 2.0 are respectively 52.12 and 54.36 MPa. (tab. 7).

Table 4

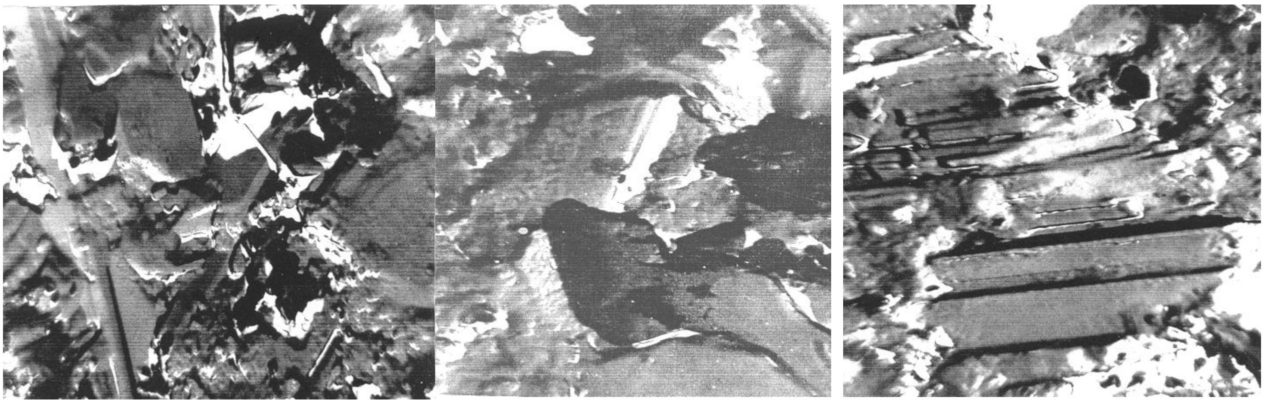
Physical and mechanical characteristics of SAI cements

Values		Setting time, h-min.		Compressive strength (MPa), at the age (days):			
SC	n_S	start	end	3	7	28	90
0.667	1.5	2-32	6-08	31.8	36.6	45.75	56.5
	2.0	2-04	5-42	33.2	36.8	47.22	58.7
0.80	1.5	2-38	5-38	36.4	38.6	52.12	60.6
	2.0	2-19	5-03	39.6	42.8	54.36	61.7
0.92 PC M-400		3-50	4-50		18.6	24.4	44.2

With the age of hardening, the process of hydration of SAI cements slows down, as a result, by 3 months the increase in their strength is at SC=0.667 from 10.75 to 11.48 MPa, respectively, at n_S=1.5 and 2.0, and at SC=0.80 ; n_S=1.5 and 2.0 - 8.48 and 6.54 MPa, respectively. The average strength of cements based on synthesized clinkers, depending on the values of SC and n_S, was 58.0 MPa.

The results of physicochemical studies of the processes of hydration, phase composition and genesis of the microstructure of the stone during hardening of SAI cements substantiate the factor of achieving its high physical and mechanical indicators. It was found that after 10 minutes. after contact with water, lines of weak intensity appear on the SAI diffractogram of the cement at d/n=(0,731; 0,482; 0,301; 0,246; 0,231; 0,217; 0,206; 0,186; 0,182) nm, most likely related to high sulfate calcium hydrosulfoferrite $3CaO \cdot Fe_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$. The $CaSO_4$ line with d/n=0.345 nm has a high activity, the intensity of which changes insignificantly up to 16 h. After 1 day of hardening, reflections of ettringite also appear on the diffractogram at d/n=(0.592; 0.382) nm, the intensity of which significantly increases by 7 days. By day 28, the predominant phase is $3CA \cdot 3C\check{S} \cdot 32H$ and $3CF \cdot 3C\check{S} \cdot 32H$, $Ca(OH)_2$ is absent, and the $CaSO_4 \cdot 2H_2O$ line has a low intensity. The lines of weak intensity at d/n=(0.378; 0.366) nm and rather strong lines with d/n=0.347 nm indicate the presence of anhydrous $C_4F_3\check{S}$ and $CaSO_4$, in the cement-water system, which indicates the ongoing process of hydration. This sequential nature of the hydration process ensures the gradual compaction and hardening of the forming SAI cement stone.

After mixing with water on the smooth surface of the grains of SAI cements, initially welded to each other, the smallest scale-like hydrated neoplasms begin to grow, which by 7 days. hardening completely cover the surface of the cleavage of the hardened cement stone. The surface relief of the SAI cement stone already by 14 days acquires sufficient density due to the formed acicular and prismatic crystals of ettringite and its iron-substituted analog, which by 21 days form blocks with a rough surface and grooved edges that grow together into large aggregates, which by 28 days develop into crystalline intergrowths and form blocks of crystal aggregates, the intercrystalline space of which is filled with new portions of hydration products $C_4A_3\check{S}$, $C_4F_3\check{S}$ and $C_5S_2\check{S}$ (fig.2).



a b c

Figure 2. Relief of the surface of the stone chip SAI cement, hardened: a - 14 days; b - 21 days; at - 28 days

The indicated hydrated compounds, due to the related crystalline structure, are tightly packed and the microstructure of the sulfo-alumina cement stone becomes block-layered, and thus, by strengthening, provide high indicators of its strength and other important operational properties.

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