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Detoxication and Neutralization of Toxic Industrial Waste Components for Production of Sulfur-Containing Binding Construction Materials

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Abstract

Our studies address issues related reduction of the negative effect of large-tonnage waste on the environment by detoxification and its use as raw materials for construction materials and structures. In our studies we used standard measuring instruments and methods to analyse physicomechanical characteristics of the sulphur-containing binder stone, obtained using modern methods of X-ray diffraction, differential thermal, microscopic analysis and testing equipment. During combined mechanochemical activation and detoxification of industrial waste, in the presence of water, to obtain raw mixtures for production of construction materials, the method of mutual neutralization of chemically harmful substances in industrial waste was used. These methods make it possible to reduce cement consumption by its partial replacement with industrial waste. The properties of sulphur-containing binder samples were studied at 7, 14, and 28 days of age after curing in natural hardening conditions. It was determined that sulphur-containing binders of compositions, hardened in natural conditions, indicate that these binders have a compressive strength of 63.0 MPa by the age of 14 days, and strength of 65.3 MPa is achieved at 28 days of age. The same composition, after curing treatment, after 28 days of age, has a compressive strength of 73.5 MPa, indicating that curing treatment favourably affects the binder's strength gain. The results can be used as an effective binder for production of mortars and concrete in the construction industry.

Keywords: Detoxification, mechanochemical activation, mutual neutralization, thermodynamic calculations, sulphur-containing binders, ferric iron, oxidation and reduction, industrial waste, strength, pyrite cinder, technical sulphur.

INTRODUCTION

In the western regions of Kazakhstan, especially in the Aktobe, Atyrau and Mangistau regions, a great number of raw materials have been accumulated in the form of large-tonnage industrial waste, its disposal as part of construction materials is one of the most important problems to be solved in the national economy. It is known that addition of powdered technical sulphur affects the concrete strength [10-23]. However, the mechanism of the additive effect on the structure and properties of cement composites, rational compositions, methods of preparation and production of sulphur-containing concrete were not determined. It proves the feasibility of studies to obtain highly efficient from the oil and gas industry waste-based construction materials and develop their production technologies.

To solve these problems, we studied the effect of sulphur-containing waste additives of the petrochemical industry on the structure formation and physicochemical properties of composite sulphur-containing binders. The binder detoxification and activation processes, as shown in [10-23], make it possible to improve operational and quality characteristics of the produced construction materials.

During combined mechanochemical activation and detoxification of industrial waste, in the presence of water, to obtain raw mixtures for production of construction materials, the method of mutual neutralization of chemically harmful substances in industrial waste was used. In works [1-25], the possibility of concrete products manufacture with improved physical and technical properties with various methods of additional binder activation was shown. These methods make it possible to reduce cement consumption by its partial replacement with industrial waste.

MATERIALS

The industrial waste of enterprises in the region of Kazakhstan in the form of sludge and solids was the study object.

1. Portland cement, grade 400, produced at Shymkent cement plant and cement chemical composition are presented in Table 1.

Table 1 - Chemical composition of cement produced at Shymkent cement plant

Composition, %									
Basic oxides						Base minerals			
CaO	$Si0_2$	$A1_2O_3$	Fe_20_3	R_2O	SO_3	C_3S	C_2S	C_3A	C_4AF
61.48	23.38	6.38	6.09	0.38	0.60	57.60	17.40	7.90	13.10

2. As an additional additive, pyrite cinders of the former JSC "Phosphorkhim" were used, consisting mainly of a mixture of iron oxides (II, III) Fe3O4 (Fe2O3), calculated on the iron content of 40–63%, and sulphur impurities of 1-2%.The rest is represented by non-ferrous metal oxides.Chemical composition of pyrite cinder, weight % is given in Table 2.

Table 2 - Chemical composition of pyrite cinder, weight %

CaO	SiO_2	Fe_2O_3	AI_2O_3	MgO	SO_3	R_2O	p.p.p
10.5	19.7	66.1	2.3	1.2	-	-	0.2

3. As a modifying additive, technical sulphur was used - a secondary product of high-sulphur oil processing from deposits of the Republic of Kazakhstan.Sulphur is a granular product, meeting the requirements of GOST 127.1-93.The chemical composition of sulphur is presented in Table 3.

Table 3 - Chemical composition of sulphur

Grade	GOST	Sulphur % wt.	Ash % wt.	% wt. of organic substances	Water % wt.
9998	127.1-93	99.060	0.400%	0.053%	0.010%

To prepare the binder, tap drinking water was used in compliance with requirements of GOST 23732 "Water for concrete and mortar."

METHODS

Characteristics of the initial and activated binder were determined in compliance with GOST 30515-97, GOST 31108-2003 and GOST 7473-2010. The tensile strength of sulphur-containing binders for tensile bending was determined using bending test beams with dimensions 40x40x160 mm on IP 2710 instrument. Using X-ray phase analysis, the phase composition of the activated sulphur-containing cement binder was determined. Differential thermal analysis of sulphur-containing cement powders was performed on a photo-recording derivatograph according to the standard procedure. Previously, a thermodynamic assessment of the probability of chemical reactions between indicated components of industrial waste in the sludge was performed using standard thermodynamic values and electrochemical potentials. To produce sulphur-containing binders, the method of mutual neutralization and detoxification of toxic components of industrial waste by their mechanochemical treatment at low temperature was used. During the experiment, the amount of waste based on pyrite cinder and technical sulphur was taken in weight ratio proportional to stoichiometric reaction coefficients, the raw mixture was slightly moistened to the consistency of "damp sand". t the planning stage of studies, the scientific hypothesis was used that for the effect of additional activation of each particle of additives, their joint grinding was used, as a result, there was a mutual detoxification of solid waste having special opposite characteristics in chemical properties. During experimental works on the preliminary determination of the composition and activation of sulphur-containing additives, wet grinding occurred on the designs of a ball mill due to abrasion and impact effects.

RESULTS

The resulting calculations on the binding reactions of sulphur (IV) and iron (III) compounds using emf (E) electrochemical couples are presented in Table 4.

Table 4 - Assessment of reactivity using emf electrochemical couples

Systems and reactions	emf of electrochemical couples
Fe (III) +S° →Fe(II) +S (VI);	E = 0.771 –(- 0.13) = + 0.784 (v)> 0

As it evident from table 4, analysis of the calculated values (emf) of electrochemical systems by normal electrode potentials shows, that reactions are possible, since emf value is > 0 (positive), and pyrite cinder recovery with technical sulphur is more energetically favourable than coal recovery. Ferric iron is able to oxidise sulphur, then it transforms into ferrous iron. It is worth mentioning that iron-containing sludges have pH > 3 (alkaline reaction of aqueous extract) [18], have undergone heat treatment like cement clinker and have binding properties. The values of standard enthalpies ΔH° and entropy ΔS° at temperature of 298° K, taken from literature [19-21], are presented in Table 5.

Calculations of changes in thermodynamic values in chemical reactions were performed according to the well-known formula:

$$\Delta H^{o}298chr. = \Delta H^{o}298(final) - \sum \Delta H^{o}298(transient) \quad (1)$$

Table 5 - Values of standard enthalpies and entropies for substances involved in reactions

Substance	ΔH°298 kcal/mol	ΔS°298 kcal/deg mol
SO_2	-71.0	59.2
Fe_3O_4	-266.5	35.0
FeS	-22.8	16.1
Fe_2O_3	-145.2	21.5
FeS_2	-38.8	12.7
FeO	-64.5	13.4

With mechanical abrasion and mixing of sulphur and iron in the presence of water in the alkaline medium, enthalpies of oxidation-reduction reactions were calculated (calculations by the values of changes in standard thermodynamic potentials were performed at normal temperature T = 298°). The obtained values of ΔH - enthalpies or thermal effects of oxidation-reduction reactions are presented in Table 6 (alphabetical symbols of reactions are given in alphabetical order).

Table 6 - Heat of oxidation-reduction reactions

Alphabetical symbols of reactions	Systems and reactions	Heat of reaction, ΔH^o kcal
A	$3Fe_3O_4 + S \rightarrow FeS + 4Fe_2O_3$	195.9
B	$FeS + S \rightarrow FeS_2$	-16.0
C	$4Fe_2O_3 + S^o \rightarrow SO_2 + 4FeO$	-38.6
D	$2FeO + 3S^o \rightarrow 2FeS + SO_2$	12.4
E	$FeO + S \rightarrow FeOS$	20.8

By comparison of the calculated values with each other and their sign, we can conclude that reactions A, D, E are thermodynamically impossible, the values of enthalpies are greater than 0 C0, i.e. positive (ΔH) > 0, and the rest can occur at normal temperature.The most likely reactions are B and C, because they have the highest values of ΔH. It should be noted that it is recommended to perform the reaction in the presence of a sufficient amount of water, then hydrogen ions in reaction C will bind to neutral water molecules in the alkaline medium, and sulphur dioxide to molecules of CaSO3 salt. For the experiment, the amount of waste based on pyrite cinder and technical sulphur was taken in weight ratio proportional to stoichiometric reaction coefficients, the raw mixture was slightly moistened to the consistency of "damp sand".

The reaction products visually differed in colour from the initial raw material mixture.During the mechanochemical treatment, a pronounced increase in the reaction medium temperature (about 40 °C) was observed.Most likely, the raw material mass [1, 18-21] was heated due to chemical exothermic reactions and transfer of mechanical energy to thermal energy. Apparently, in mechanochemical grinding, the temperature factor plays an instant role in the instantaneous local heating of the reactants at the moment of mechanical shock.Deficiencies of impurity and non-stoichiometric origin in crystal lattices of iron oxide play a noticeable role in solid-phase reactions [18-21].

For example, the sintering rate usually increases with increase of deviation from stoichiometry, and the activation energy of the crystal lattice creep of a non-stoichiometric oxide decreases, compared with normal oxide, by 20–25 kcal/mol.

It should be added that the thermodynamically impossible reaction according to Scheme C in the presence of metallic iron (Fe^o) becomes possible (ΔH <0):

$$3Fe^o + Fe_3O_4 + 2S \rightarrow 2FeS + 4FeO, \Delta H = -37,1 kcal \quad (2)$$

The above results indicate the binding of sulphur to iron oxides during mechanical action at temperatures close to normal.

During experimental works on detoxification and activation of sulphur-containing waste, it was observed that ferric iron is able to oxidise sulphur, with further transformation into ferrous iron, because the processed mixture colour varied from yellowish to grey-green. Joint grinding of sulphur-containing components with cement has a positive effect the mechanical properties of the studied samples. The strength of sulphur-containing samples at 28 days of age increased up to 37.7 MPa. In this case, the pyrite cinder apparently played the role of initiator of the physicochemical process of coagulation of the cementitious mixture. During coagulation process, there is a polarization of the dispersed binder particles and their mutual attraction, enhancing the structure formation process. An interesting option for joint waste management may be the addition of iron filings and iron nanoparticles to improve sulphur binding [23].However, iron compounds have a higher density, leading to an increase in the product weight. Reactions D and E are very important.They show the fundamental possibility and high environmental and economic attractiveness of the rational disposal of toxic sulphur-containing sludge.The environmentally hazardous sulphur oxide in the sludge composition, when treated with a pyrite cinder, transforms into low toxic sulfur oxide, i.e. it can be completely disposed of as part of arbolit concrete.It is rational to dispose such raw mixtures by adding plant waste in the form of cotton stalks or other organic components to obtain light arbolit concrete. The studies also determined the physicomechanical properties of sulphur-containing samples. The study results are shown in Table 7.

Table 7 - Characteristics of sulphur binders with sulphur

Item No.	Binder composition, %				Density in dry state, kg/m³	Tensile strength, MPa	
	Sulphur sulphur, %	Pyrite cinder	Cement	Water Moisture		under compression	under bending
1	8	18	64	9.89	1590	64.7	8.53
2	12	18	70	9.12	1570	65.9	9.14
3	13	20	67	9.27	1590	73.5	10.9

It was determined that introduction of technical sulfur additives in the amount of 8–13% increases the compressive strength of samples, prepared from solutions at water-solid ratio of 0.385 in wet and dry states. A further increase in the technical sulfur additive causes a decrease in the solution strength characteristics, while the laws of change in strength are similar for all samples.

DISCUSSION

It is known [1-25] that an increase in the reactivity of binder components during wet grinding is achieved not only by increase in the liquid phase dispersion, but also by the crystal structure change and particle shape, which is a prerequisite for the intensification of coagulation process of a sulphur-containing mixture. At the same time, chemical and mineralogical composition of the initial binder remain unchanged. The activation mechanism consists in the interaction of newly exposed surfaces of the binder particles during wet grinding, i.e. in giving a mechanical and chemical-energetic impulse to each particle. It can be noted that activation mechanism consists in increasing the forces of interionic mutual attraction and appearance of surface valence forces when the nanoparticles of the colloidal system approach. The study results suggest that by industrial waste activation and detoxification, sulphur-containing binders with high physical and technical characteristics can be obtained.

Conclusion. It was determined that technical sulphur, the petrochemical industry waste, is an effective additive in sulphur-containing compositions, providing increased strength, reduced sorption moisture and water absorption to light arbolitic concrete. It was proved that the most effective way to introduce technical sulphur additives is to grind it together with iron-containing raw materials in the pyrite cinder form. The thermodynamic calculation results prove the possibility of binding sulphur with iron oxides during mechanical action at temperatures close to normal.It was also determined that activation mechanism of sulphur-containing compositions consists in interaction of newly exposed surfaces of binder particles in wet re-grinding. In this case, the coagulation process of the binder mixture is intensified and the crystal lattice structure forms due to crystalline hydrates. In the course of experimental work, it was also determined that additives based on technical sulphur of the petrochemical industry improve physical and mechanical properties of sulphur-containing cement stone. Introduction of sulphur-containing additives in the amount of 8 - 13% provides an increase in strength up to 73.5 MPa with the content of binding components (cement 67% + pyrite cinder 20% + sulphur 13%) in the mixture composition by % wt.

Thus, the proposed binder compositions gradually increase the strength by 1.15-2.5 times compared with the initial strength, which is due to the content of the binder compositions and curing conditions. Developed binding composites can be used for production of wall materials and structures for civil construction.

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