Technogenic anhydrite binder for high-strength concrete

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Abstract. Currently the global trend is to expand the range of construction materials produced using resource-saving technologies that do not generate CO_2 emissions. An important role in this is given to gypsum-anhydrite binders and concretes which can be obtained using a non-burning technology with the involvement of technogenic wastes which excludes the emission of carbon dioxide into the environment in comparison with Portland cement technology. The article is devoted to the results of studies on obtaining anhydrite binder from the by-product of sulfuric acid decomposition of fluorite concentrate – fluorine-anhydrite using other by-products of industry (metallurgical, mining and heat power) acting as active mineral additives. The influence patterns of such additives composition and quantity on the kinetics of milling and neutralization of fluorine-anhydrite are established. It is shown that the milling capacity of the anhydrite binder depends on the degree of binding of the acid component as well as the stoichiometry of chemical reactions between sulfuric acid contained in fluorine-anhydrite and additives minerals. The process of the acid component binding proceeds most actively with the addition of steel-refining slag in an amount of 12.3 % which allows to achieve a high milling rate of the binder. The resulting products of neutralization reactions are centers of crystallization which increases the hydraulic activity of fluorine-anhydrite. As a result, anhydrite binder comparable to Portland cement by physical and mechanical properties have been obtained. This binder is suitable for producing high-strength concrete of B30 class in which granules from neutralized fluorine-anhydrite are used as a coarse aggregate. Thus, the study made an important contribution to the material science of technogenic materials expanding their use in construction.

1. Introduction

One of the most important directions in the construction materials science is the production of clinker-free binders as well as concretes based on them excluding the use of Portland cement which is produced by material-intensive and energy-consuming technology. At the same time a significant reduction in the construction cost is achieved due to significant resource and energy savings. Gypsum and gypsum-anhydrite binders are materials which characterized by low energy consumption in production and better environmental performance compared to Portland cement. Special attention among them is given to non-fired anhydrite cement obtained from a by-product of sulfuric acid decomposition of fluorite concentrate – fluorine-anhydrite (FA) formed in enterprises of various industries (chemical, nuclear and non-ferrous metallurgy). The FA use in construction is constrained by the lack of information about its composition and properties depending on the formation conditions as well as the presence of harmful impurities in the form of sulfuric acid and chemically active fluorine compounds. Therefore it is very prospectively to study the influence of the decomposition mode of fluorine-containing raw materials on composition and properties of FA and also to transform impurities contained in the FA which are harmful to the quality of the binder and enterprises staff and in a useful and environmentally safe one. Similar studies were carried out to get a binder from phosphogypsum using the technologies of Nissan Chemical (Japan) and Central Prayon (France) which allow to decompose phosphate raw materials in such a way that the precipitate of calcium sulfate is recycled into construction materials with cost-effective and technically effective technologies similar to natural gypsum raw materials [1–3].

Gashkova V.I., Tolkacheva L.E. also propose to consider the process of FA obtaining not as the formation of wastes but the formation of a semi-product with properties that meet the requirements of the appropriate standards for raw materials of construction use. However they found that obtaining two high-quality products namely HF and FA simultaneously in one technological cycle is impossible [4]. In this regard the FA utilization can be carried out only separately from the main process of decomposition of fluorine-containing raw materials. According to many researchers for this purpose various mineral and chemical additives can be used; they can neutralize the acidic component of FA, activate its hardening as well as reinforce the structure and increase the water resistance of technogenic anhydrite binder for its use in concrete [5–22]. But in these works there is no single approach justifying the choice of certain additives and the method of their introduction to obtain a binder from FA suitable for high-strength concrete. According to this paper such approach should be based on the understanding and choice of external energy effects on the FA in accordance with the combined laws of thermodynamics providing five types of energy effects aimed at reducing the free energy of the system: mechanical, additional milling leading to the formation of a new surface, chemical, electro-physical and thermal. As it is known the lower the value of free energy the more work is performed by the cement system during hardening and the stronger the formed concrete structure [23]. Technogenic materials containing metastable phases in which a large amount of energy is accumulated fully correspond to this criterion.

Based on the thermodynamic approach the activation of FA during its mechanical-chemical treatment with the use of technogenic mineral additives of different composition neutralizing the acidic component and being the centers of crystallization of new formations during hardening of the binder, providing high strength of concrete on its basis was investigated.

The aim of present work is to investigate the possibility of obtaining of anhydrite binder using mineral additives which are technological wastes of various industries and high-strength concrete based on it.

To achieve this goal the following tasks were solved:

1. to determine the composition and properties of FA as well as mineral additives to neutralize it;
2. to study the kinetics of milling and neutralization of FA in joint milling with mineral additives;
3. to determine the physical and mechanical properties of the binder based on neutralized FA;
4. to obtain artificial porous aggregate for concrete on the basis of fluorine-anhydrite and mineral additive;
5. to determine the properties of the resulting aggregate;
6. to prepare the concrete mix, to mold the samples and to determine the concrete properties.

2. Methods

Anhydrite binder was obtained by joint milling of acidic fluorine-anhydrite (FA) with mineral additives in a laboratory ball mill. During the milling process samples were taken at regular intervals and were exposed for determination of the content of free sulfuric acid, calcium fluoride and dispersion. Milling was carried out in a mill of 5.5 liters volume. Dispersion was controlled by the residue on the sieve No. 008 (not more than 10 %). The kinetics of milling and neutralization of acidic FA with mineral additives was studied using formal kinetics equations:

$$R_\tau = R_o \cdot e^{-k_1 \tau^m}, \tag{1}$$

$$\alpha = 1 - e^{-k_2 \tau^n}, \tag{2}$$

where R_τ is the content of the coarse fraction in the material through time τ, %;

R_o is the content of coarse fraction in the initial material, %;

k_1 is the milling rate constant, min[is1];

m is the relative milling rate;

τ is milling time, min;

α is degree of neutralization;

k_2 is the reaction rate constant, min[is1];

n is kinetic parameter.

Steel-refining slag, ferrochrome slag, fly ash and limestone crushing screening formed at the crushing and grinding complex of microcalcite production were used as mineral additives.

The chemical composition of acidic FA was determined by the methods of Russian State Standards GOST 5382-9, 19181-78, 7619.5-81 and 7619.6-8; the quantity of crystallization water in FA – according to Russian State Standard GOST 4013-82 (after removal of sulfuric acid with alcohol). Determination of sulfuric acid content in FA is based on its neutralization by sodium hydroxide in an alcohol solution in the presence of methyl red indicator. The FA sample dried to a constant mass in an amount of 40–50 g was crushed until it completely passed through a sieve No. 008; 0.5 g of powder was taken from it (up to a quarter of the decimal point) and was placed in a dry glass with a volume of 100 cm^3. 10 cm^3 of ethyl alcohol was poured into it, an indicator was added until the bright red coloring of the solution which was periodically stirred for 10 minutes and then titrated with a NaOH solution until the color transition from red to yellow-green. The arithmetical mean of two parallel tests was taken as the result of the analysis, the permissible difference between them should not exceed 0.15 % with a variation coefficient of 0.95.

The quantity of sulfuric acid (W) was calculated by the formula:

$$W = \left(\frac{V \cdot K \cdot 0.004904 \cdot 100}{m} \right),$$

(3)

where V is the volume of sodium hydroxide solution of 0.1 mol/dm^3 concentration which was used to titration of the tested solution, cm^3;

K is the correction to the titer of a solution of NaOH;

0.004904 is the mass of sulfuric acid corresponding to 1 cm^3 of sodium hydroxide solution with a concentration of exactly 0.1 mol/dm^3, g;

m is mass of the sample to be tested, g.

The quantity of CaSO$_4$ in FA was determined by the CaO quantity obtained from the difference between the content of total CaO (according to chemical analysis) and CaO associated with fluorine. The fluorine ion is determined by potentiometric titration.

The FA macrostructure was studied using a Levenhuk 2ST binocular microscope with a photo-nozzle. Electronic-microscopic studies were carried out on a scanning electron microscope JSM 6490 with specialized SEM and micro X-ray diffraction analysis tools. The image of the FA structure was obtained in the following mode: back-scattered electrons, the pressure in the chamber is 100 Pa, the accelerating voltage on the gun is 20 kV, the beam length is 60 nm.

The chemical composition of mineral additives was determined according to Russian State Standard GOST 5382-2019, as well as using the electronic-raster device "Superprobe 733" by "Joel" company with the box for energy dispersion analysis. Determination of the mineral composition of slag and ash was performed by the method based on the complete solubility of two- and tricalcium silicates and free lime in a 5 % solution of boric acid and on insolubility of the intermediate phase. 10 % aqueous solution of sugar completely decomposes calcium aluminates and lime soluble in sugar during the treatment of residue insoluble in boric acid corresponds to CaO bound in calcium aluminates.

The quantity of mineral additives taken to FA neutralization was calculated taking into account stoichiometry of chemical reactions of interaction of minerals with sulfuric acid. The possibility of reactions was estimated by the Gibbs energy.

The granulometric composition of the raw materials was determined according to Russian State Standard GOST 8269.0-97, the open, total porosity and apparent density – according to Russian State Standard GOST 2409-2014, the true density by pycnometrical method, bulk density – according to Russian State Standard GOST 9758-2012, the specific surface – by Blaine and BET method.

The hardening kinetics of the samples, the composition of the hydration and neutralization products were controlled by x-ray phase analysis (XPA), differential thermal analysis (DTA) and SEM. XPA was carried out at the DRON-3 device by the following mode: cobalt radiation (with an iron filter), 2θ from 10 to 50°, 2 s accumulation time, 35 kV voltage, 20 mA anode current were used. Differential thermal analysis was performed on the Q-1500 device under the following conditions: material mass – 200 mg, crucible material – Pt, reference substance – Al$_2$O$_3$, sensitivity – 200 units, maximum temperature – 1000 °C, heating rate – 10 °C/min.

Physical and mechanical properties of the binder based on neutralized FA were determined using mortar with normal sand (1:3) according to DIN 4208 and the addition of 0.3 % superplasticizer Melment F15G produced by "BASF Construction Solutions" (Trostberg, Germany) together with mixing water. Further the FA neutralized with a mineral additive was used as a binder for the concrete preparation. Natural quartz sand with a size modulus of 2.5 according to Russian State Standard GOST 8736-2014 was used as a fine aggregate. Granules on the basis of the binding mix consisting of FA and neutralizing mineral additive taken in certain

proportions were a coarse aggregate. Granules were obtained on a disc granulator having a bowl diameter of 0.7 m and tilt angle to the horizon of 45°. 10 kg of binding mix were used to obtain granules of 8–10 mm in quantity not less than 90 %, aqueous solution of superplasticizer been added during granulation. The granules mentioned above hardened in air-wet conditions. The properties of granules were determined according to Russian State Standard GOST 9758-2012 and then they were used as an aggregate in the concrete composition. The concrete mix was formed into samples-cubes with an edge of 70 mm. The mobility grade was P2 (5–9 cm) according to Russian State Standard GOST 7473-2010. Physical and mechanical tests of concrete were carried out in accordance with the requirements of Russian State Standard GOST 26633-2015. The coefficient of constructive quality was calculated as relation of the strength and density of concrete.

3. Results and Discussion

The composition and properties of FA selected from a revolving drum furnace with a diameter of 3.2 m, a length of 50 m with internal heating are shown in Table 1. The material temperature at the furnace outlet was 200 °C.

Table 1. The composition and the properties of FA for conditioning.

Fractions quantity, mass %, mm				Material composition of fractions, mass %			Apparent density,	Open porosity,	Total porosity,	Closed porosity,
1-5	5-20	20-40	40-60	$CaSO_4$	H_2SO_4	CaF_2	kg/m^3	%	%	%
30.0	–	–	–	93.20	5.80	1.00	2100	27.8	28.1	0.3
–	22.2	–	–	92.90	5.10	2.00	2285	21.1	21.7	0.6
–	–	18.0	–	86.23	6.77	3.00	2300	14.2	20.6	6.4
–	–	–	30.0	89.92	6.08	4.00	2350	10.8	19.5	8.7

It is established that FA from the furnace is a granular material. It has a grain size of 1–60 mm, with a total porosity of 19.5–28.1 %, a free sulfuric acid content of 5.1–6.7 %, and 1–4 % calcium fluoride. X-ray phase analysis showed that calcium sulfate in FA is represented by a low-activity modification – insoluble anhydrite (β-$CaSO_4$) (d = 3.50; 2.84 Å). Lines belonging to $CaSO_4 \cdot 2H_2O$ and γ-$CaSO_4$ (soluble anhydrite) were not found. It was found that when FA is heated in the temperature range of 100–400 °C, two phase transitions are observed on the derivatogram; these transitions are accompanied by endothermic effects and mass changes of the sample: the first – in the temperature range of 120–169 °C (mass loss is 2.6 and 4.0 %) and the second – in the range of 234-310 °C (mass loss is 6.0 %), Fig. 1(1).
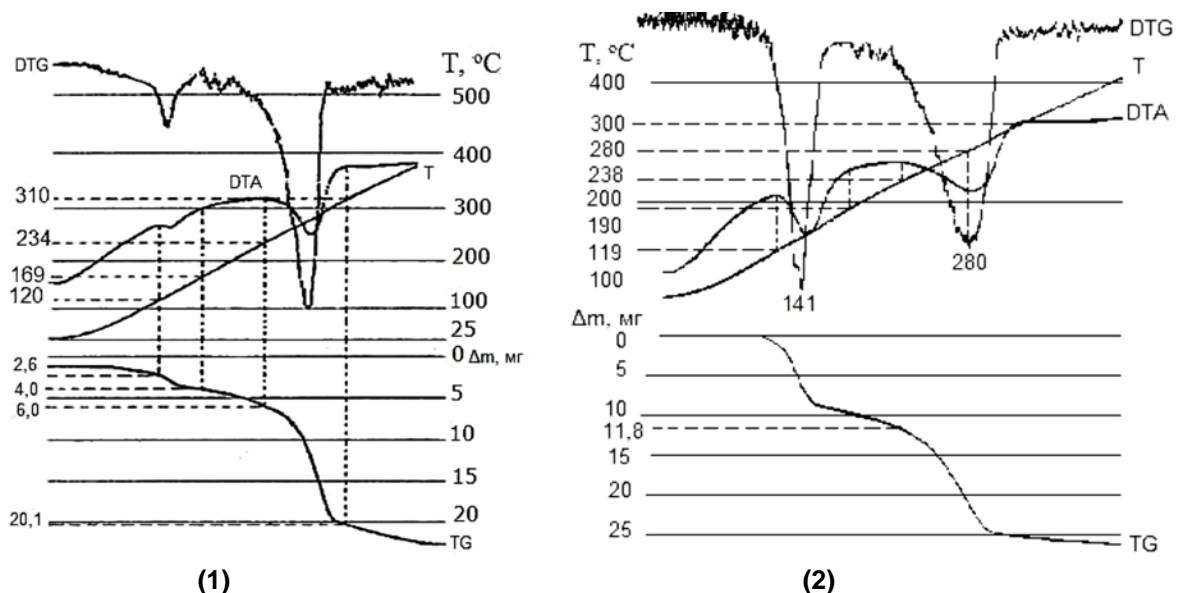
(1) **(2)**
Figure 1. Results of DTA of FA from furnace (1)
and fluorine-anhydrite stone at the age of 28 days of air hardening (2).

The first phase transition is associated with the desorption of moisture from the surface of the FA and the evaporation of fluorosulfonic acid (HSO_3F) and the second – with the evaporation of free sulfuric acid and the decomposition of calcium fluoro-sulfonate ($Ca(SO_3F)_2$). When mixing water with the powder of acidic FA of specific surface area of 200 m^2/kg a paste of 42 % normal density is formed, its initial setting time is after 14 h and the final setting time is after 17 h. Fluorine-anhydrite stone slowly hardens in the early stages but it has a compressive strength of 3-5 MPa by 28 days. According to DTA hardened acidic FA has an endothermic effect at 141 °C associated with the decomposition of dihydrous gypsum to semi-aqueous and an endothermic

effect at 280 °C indicating the removal of the rest of the crystallization water from semi-aqueous gypsum and the formation of anhydrous calcium sulfate. Also at 310 °C free sulfuric acid evaporates, Fig. 1(2).

Fig. 2 shows the macrostructure and microstructure of the original FA. Channel and isometric pores located randomly are mainly dominated. The length of the channel pores is from 188 to 1000 microns and their diameter is from 63 to 178 microns. The number of isometric pores are as follows, %: 40–57 – less than 60 microns, 35–45 – from 60 to 125 microns, 5–10 – from 60 to 310 microns, 3–5 – more than 310 microns. It was found that part of the pores in the FA were filled with a white substance presumably calcium fluoro-sulfonate.

According to the SEM data the FA of the current output has a loose-grained rather homogeneous structure composed of prismatic anhydrite crystals of 1-4 microns size, Fig. 3.

Thus the FA of the current output is represented by granules of inhomogeneous composition, it contains a significant amount of insoluble anhydrite, sulfuric acid as well as impurities of hydraulically inert calcium fluoride and easily volatile calcium fluoro-sulfonate. Acidic FA has weak binder properties so it is necessary to neutralize the acidic component to improve them and increase the environmental safety of the material for its use in construction. For this purpose mineral additives were used; its chemical composition, physical and hydrophysical properties are presented in Tables 2-3.
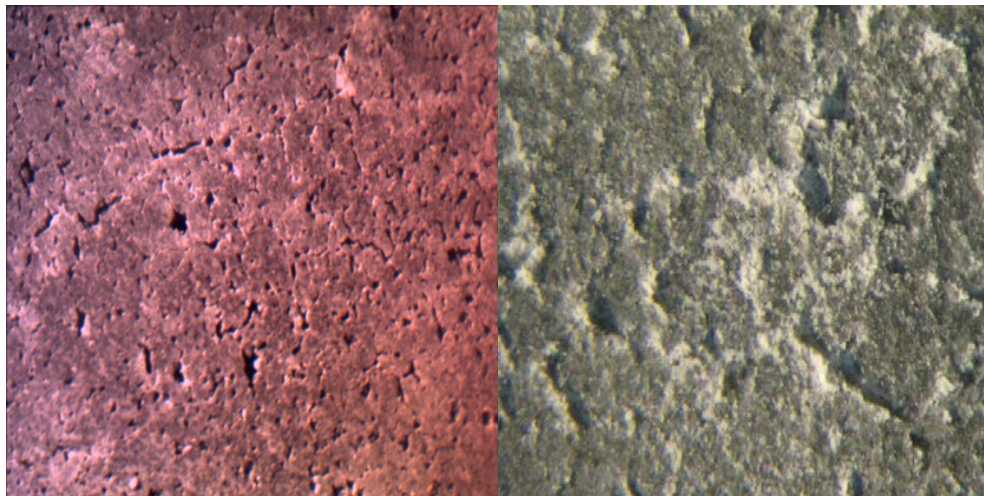
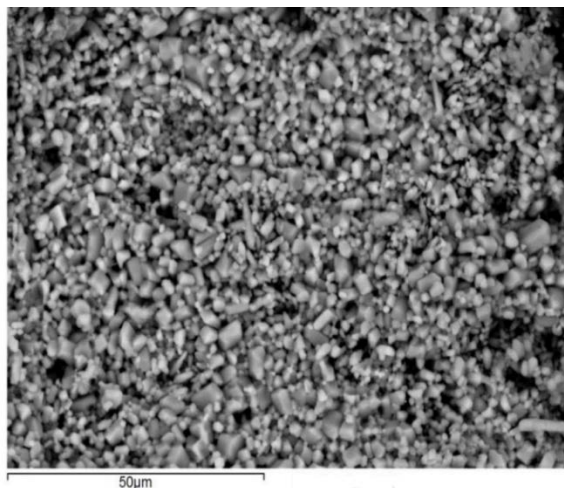

Figure 2. FA macrostructure (×16, ×40).

Figure 3. FA microstructure.

Table 2. Chemical composition of mineral additives

Additive	The content of oxides, mass %								Loss of ignition, mass %
	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	SO$_3$	R$_2$O	Other	
Refining slag	43.27	15.14	27.16	0.86	5.93	4.70	0.07	2.24	+0,63
Ferrochrome slag	50.90	26.10	5.83	0.83	8.79	–	–	5.74	1.81
Fly ash	36.00	31.30	6.16	11.54	6.25	2.36	–	0.92	5.45
Limestone crushing screening	50.40	3.53	0.63	0.33	1.92	0.06	0.42	0.79	41.92

Table 3. Physical and hydrophysical properties of mineral additives.

Additive	Granulometric composition, mass % of fractions, mm			ρ, kg/m3	W/S, %	Setting time, min	
	0.16-0.315	0.08-0.16	<0.08			initial	final
Refining slag	3.3	33.4	63.3	2846	38	8	30
Ferrochrome slag	2.1	32.3	65.6	2790	42	720	1440
Fly ash	–	28.1	71.9	2600	50	30	50
Limestone crushing screening	–	13.9	86.1	2720	–	–	–

Mineral additives are basic by chemical composition. According to XPA the crystalline phase of refining slag contains $12CaO7Al_2O_3$ (d = 4.90; 2.68; 2.19 Å), β- and γ-C_2S (d = 4.06; 3.22; 2.78 Å) and MgO (d = 2.11 Å). The actual phase composition of this slag is 43.2 % $12CaO·7Al_2O_3$; 31.5 % $2CaO·SiO_2$; 5.9 % MgO and 18.0 % vitreous phase. Ferrochrome slag mainly consists of β-C_2S (d = 5.60; 3.01; 2.73 Å), a solid solution of the composition $(Mg, Fe)(Cr, Al, Fe)_2O_4$ (d = 4.77; 2.48 Å), periclase (d = 2.11 Å) and okermanite (d = 2.67; 2.21 Å) which is typical for ferrochrome slag of low-carbon ferrochrome. Fly ash contains bicalcium silicate (b = 3.49; 2.76; 2.68 Å), ferromagnetic spinel (d = 2.97; 2.57 Å), quartz (b = 3.34 Å) and free calcium oxide (b = 2.39; 2.76 Å).

However it was found that the amount of bicalcium silicate in fly ash is less than in metallurgical slags. Limestone crushing screening contains calcite with quartz admixture. Metallurgical slags and fly ash have different water demand and setting time when mixing with water. The amount of mineral additives taken to neutralize sulfuric acid and calculated taking into account the thermodynamics and stoichiometry of chemical reactions according to the equations presented in Table 4 was as follows, %: 12.3 of refining slag; 13.4 of ferrochrome slag; 24.8 of fly ash and 6.1 of limestone crushing screening.

Table 4. Results of thermodynamic calculation of enthalpy and Gibbs energy of formation of possible products of sulfuric acid neutralization from minerals of metallurgical slags, fly ash and limestone crushing screening in the system "FA-mineral additive".

No	The chemical reaction of neutralization	The calculated ΔH^o_{298}, kJ/mol H_2SO_4	The calculated ΔG^o_{298}, kJ/mol H_2SO_4
1	$C_{12}A_{7(sol)}+6H_2SO_{4(liq.)}+71H_2O_{(gas)}\rightarrow 2C_3AC\hat{S}_3H_{31(sol.)}+10AH_{3(sol.)}$	−477	−344
2	$C_{12}A_{7(sol.)}+3H_2SO_{4(liq.)}+45H_2O_{(liq.)}\rightarrow 3C_3AC\hat{S}H_{12(sol.)}+8AH_{3(am.)}$	−655	−430
3	$C_{12}A_{7(sol.)}+12H_2SO_{4(liq.)}+33H_2O_{(liq.)}\rightarrow 12C\hat{S}H_{2(sol.)}+14AH_{3(am.)}$	−312	−264
4	$C_2S_{(sol.)}+H_2SO_{4(liq.)}+2H_2O_{(r.)}\rightarrow C\hat{S}H_{2(sol.)}+CSH_{(sol.)}$	−713	−581
5	$MgO_{(sol.)}+H_2SO_{4(liq.)}\rightarrow MgSO_{4(sol.)}+H_2O_{(gas)}$	−67	−131
6	$MgFe_2O_{4(sol.)}+4H_2SO_{4(liq.)}\rightarrow MgSO_{4(sol.)}+Fe_2(SO_4)_{3(sol.)}+4H_2O_{(gas)}$	−20	−19
7	$CaCO_{3(sol.)}+H_2SO_{4(liq.)}\rightarrow C\hat{S}H_{2(sol.)}+CO_{2(gas)}+H_2O_{(gas)}$	−65	−127
8	$2Al(OH)_{3(sol.)}+3H_2SO_{4(liq.)}\rightarrow Al_2(SO_4)_{3(sol.)}+6H_2O_{(liq.)}$	−82	−91
9	$Mg(OH)_{2(sol.)}+H_2SO_{4(liq.)}\rightarrow MgSO_{4(sol.)}+2H_2O_{(liq.)}$	−41	−30

Table 4 shows that lower Gibbs energy values by 1 mole of H_2SO_4 correspond to reactions (4) and (2) the products of which are dihydrate calcium sulfate and calcium hydrosulfoaluminate in monosulfate form. This paper suggests that these compounds can serve as centers of crystallization of new formations in particular secondary dihydrous gypsum during the hardening of neutralized FA having a positive effect on its binding properties. However to obtain thermodynamically stable centers of new formations crystallization at least two conditions are to be met. In accordance with the statements of the classical theory of the process of new phase nucleation described by equations (4) and (5) the formation of stable crystallization centers is possible; firstly, if the surface of the phase boundaries is large and secondly, the size of the crystal germ should reach the limit value at which the effective crystallization of new formations is provided. The joint milling of acidic FA with mineral additives is satisfied by these two conditions.

$$P = C \cdot \exp\left[-\frac{16\pi \cdot \sigma^3 \cdot M^3 \cdot N_A}{3R^3 \cdot T^3 \cdot \ln^2\left(\dfrac{c}{c_\infty}\right) \cdot p^2}\right], \tag{4}$$

$$\ln \frac{C}{C_\infty} = \frac{2M \cdot \sigma}{R \cdot T \cdot \rho \cdot r_\kappa},$$

(5)

where P is possibility of formation of an equilibrium crystal germ;

C is constant;

M is molar mass;

c is solubility of small crystals;

c_∞ is solubility of large crystals;

σ is the specific interfacial energy;

N_A is Avogadro number;

r_κ is the critical radius of the crystal germ;

ρ is the density of the solid phase;

R is gas constant;

T is temperature.

When studying the kinetics of milling and neutralization of FA with mineral additives it was found that refining and ferrochrome slag and fly ash introduced into FA in stoichiometric quantities provide a high degree of H_2SO_4 neutralization which was equal to 92.0; 73.4 and 71.8 % respectively. Herewith the rate constants of material milling and sulfuric acid neutralization were 0.344; 0.279; 0.119 and 0.848; 0.435; 0.323 min^{-1} respectively. With the introduction of limestone crushing screening in stoichiometric amount the degree of H_2SO_4 neutralization was 41 % and the constant of the milling rate of FA and the neutralization of sulfuric acid in it was 0.075 and 0.137 min^{-1} respectively. It is seen from the experimental data that metallurgical slags especially refined one react most intensively with sulfuric acid because the acid content after FA milling decreased from 6.10 to 0.48 %. The reason is that the refining slag contains a chemically active and easily milling mineral $C_{12}A_7$ for which the Gibbs energy of interaction with sulfuric acid by 1 mol of H_2SO_4 is from -264 to -430 kJ. When using ferrochrome slag less intensive acid neutralization and milling rate are due to that it mainly contains of hard-to-mill C_2S, okermanite and a solid solution of the composition (Mg, Fe)(Cr, Al, Fe)$_2$O$_4$ and does not contain chemically active and easy-to-mill $C_{12}A_7$. Fly ash and limestone crushing screening have a low ability to neutralize sulfuric acid during joint milling with FA because the amount of chemically active mineral C_2S in the ash was about 2-3 times less than in metallurgical slags and the surface of free CaO particles in the ash is covered with a vitreous phase that limits the binding of sulfuric acid. In addition the interaction of sulfuric acid with minerals $MgO \cdot Fe_2O_3$, MgO of ash and $CaCO_3$ of limestone crushing screening according to reactions (5)–(7) is less thermodynamically probable compared to calcium-containing minerals of metallurgical slags.

The quantity of CaF_2 in the ground FA with the addition of refining slag increased from 2.3 to 3.4 % what indicates the neutralization of HF which may be formed by the interaction of heated water vapor released during the binding of sulfuric acid with HSO_3F and $Ca(SO_3F)_2$.

Thus it can be concluded that there is a interrelation between the Gibbs energy of chemical reactions, the rate of neutralization of sulfuric acid (neutralization degree) in FA as well as the composition of mineral additives. The lower the Gibbs energy of the interaction reactions of minerals with sulfuric acid of FA the greater the work performed by the system and the more intensively the acid is neutralized during the FA milling.

The presence of dihydrous gypsum (d = 7.63; 4.29 Å) and calcium hydrosulphaluminate (d = 5.63; 2.61 Å) in FA milling together with refining slag was established by XPA (Fig. 4) what confirms the thermodynamic possibility of chemical reactions (1)-(4), Table 4. There is still an unreacted mineral $C_{12}A_7$ in FA after milling and sulfuric acid neutralization what is confirmed by strong lines at interplane distances of 4.90 and 2.54 Å. This indicates that the formation of a dihydrous gypsum is possible both by reaction (3) and reaction (4) which is more likely by Gibbs energy.
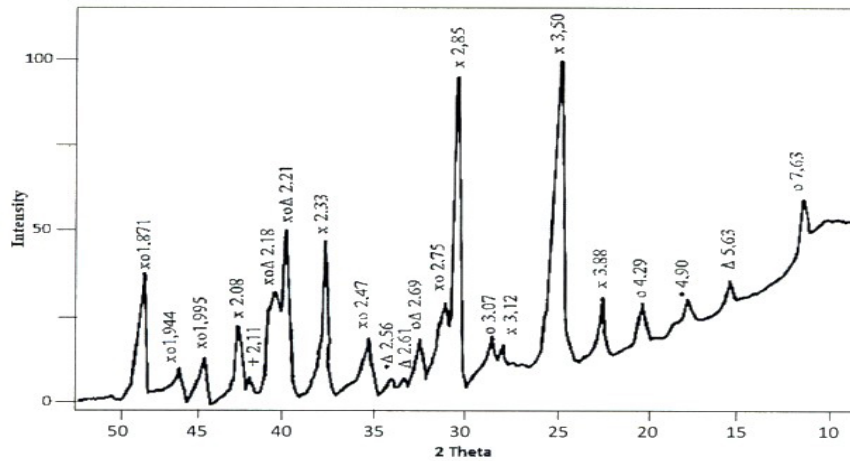
Figure 4. XPA results of FA milled together with refining slag
Δ – 3CaO·Al$_2$O$_3$·3CaSO$_4$·31H$_2$O; o – CaSO$_4$·2H$_2$O; x – CaSO$_4$; • – 12CaO·7Al$_2$O$_3$; + – MgO.

From the kinetic point of view the process of FA neutralization when milling with mineral additives can be divided into two stages. The first stage includes mechanical deformation of solid components, the second – the formation of neutralization products. In the first stage due to a powerful hydrodynamic impact of grinding bodies porous grains of FA are destroyed and sulfuric acid located in the pores is squeezed out and gets to the surface of the particles of the mineral additive.

The neutralization process proceeds at a low rate and is determined by the increase in the specific surface area of the material (the rate of milling) as well as the amount of acidic composition. After that in the second stage a layer of fine neutralization products is removed from the surface of the particles due to mechanical abrasion and the neutralization rate increases. Thus FA neutralization and activation of the binding properties are provided as a result of constant updating of the surface during FA milling with mineral additives. At the same time it was observed that long-term milling of FA (more than 2 hours) does not cause an increase of the neutralization rate of the acidic component because the surface of the particles of the mineral additive is covered with a thin layer of remilled and aggregated FA. In addition the temperature of the medium in the mill has a great influence on the process of FA neutralization during its milling with mineral additives. Thermodynamic calculations showed that the process of acidic component neutralization of FA is accompanied by the release of heat and heating of the material which was observed during the experiments. With the increase of temperature the growth of the material surface area and the degree of neutralization decreased. For these reasons FA after milling contains up to 0.5 % unbound sulfuric acid. The study of physical and mechanical properties of the binder based on FA neutralized by refining slag with the addition of 0.3 % superplasticizer showed that it has a high specific surface area indicating a greater reactivity and is characterized by shorter setting times, high mechanical strength and water resistance of gypsum slag stone (softening coefficient is 0.75) compared to acidic FA from the furnace, Table 5.

Table 5. Physical and mechanical properties of the binder based on neutralized FA.

Specific surface area, m^2/g	W/S ratio, %	Setting time, min		The strength, MPa after			
		initial	final	3 days		28 days	
				bending	compression	bending	compression
10.0	28	45	120	4.5	15.4	6.7	43.0

Fig. 5 shows the microstructure of hardened binder based on FA neutralized by refining slag and with plasticizer Melment F 15 G after 28 days.
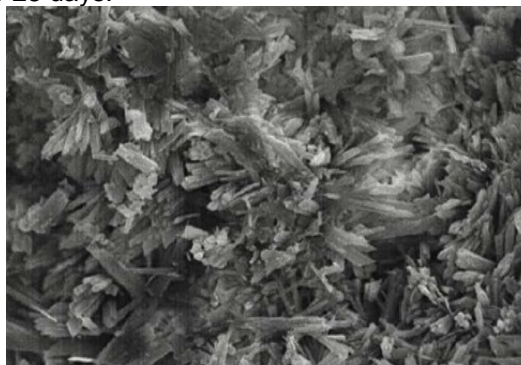

Figure 5. Microstructure of hardened binder based on FA neutralized by refining slag and with plasticizer Melment F 15 G at the age of 28 days (×1000) SEM.

Thus gypsum and calcium hydrosulfoaluminate formed during the FA neutralization by refining slag positively affected the binding properties of the FA.

When granulating of the obtained technogenic anhydrite binder (TAB) with the addition of an aqueous solution of plasticizer in a quantity of 12 % it was found that this amount of the liquid phase is sufficient for the formation of isometric granules of 8–10 mm in size but not enough for the processes of their hydration and hardening. Formed granules reach the strength of about 2.6–2.8 N/granule which is not sufficient for their use as an aggregate in high-strength concrete composition, Fig. 6. When more water was added to the granulation process of the binder an overmoistened sticky mass was formed that could not be granulated.
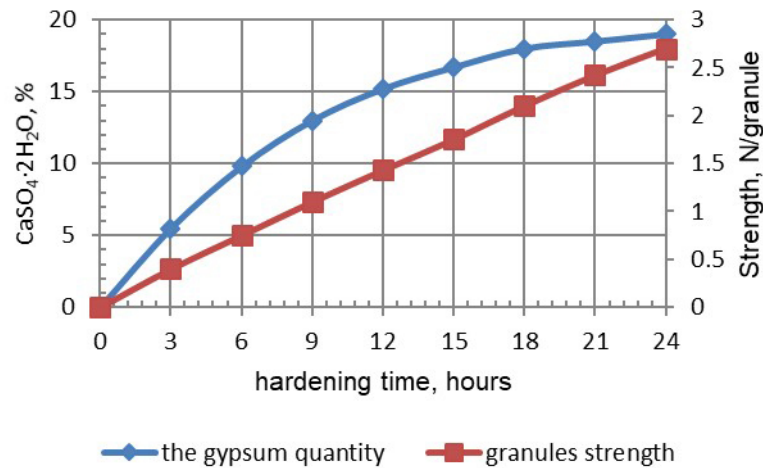
Figure 6. Hardening kinetics of granules on the basis of the neutralized FA.

Therefore during granulation of FA neutralized by refining slag its binding potential is very limited while the binding potential of the refining slag proper containing high-basic calcium aluminate (mayenite) and the vitreous phase is practically not used. In this regard the amount of refining slag in relation to acidic FA should be increased to obtain strong granules. As it is known binders including calcium aluminates and calcium sulfate are characterized by increased strength in the early stages of hardening. One of these binders is gypsum-alumina expanding cement developed by Soviet scientists and consisting of 70 % high-alumina slag and 30 % gypsum or anhydrite [24].

It was found that during granulation of a binder composition pre-milled to a fraction of less than 80 microns and consisting of 70 % of refining slag and 30 % of acidic FA, granules are formed with the following properties according to Russian Standard 9757-90: bulk density – 1100 kg/m^3, average density – 1800 kg/m^3, compressive strength in the cylinder – 17.0 MPa. High physical and mechanical indicators allow to use such granules as an artificial porous aggregate for concrete (non-fired slag-anhydrite gravel – NFSAG) [25]. The composition and properties of concrete with a binder based on FA neutralized by refining slag and aggregate from NFSAG are presented in Table 6.

Table 6. Composition and properties of concrete.

TAB	NFSAG	Quartz sand	Water	Plasticizer Melment F 15 G	Concrete density, kg/m^3	Compressive strength, MPa after		Coefficient of constructive quality
						7 days	28 days	
300	900	600	150	1	1895	24.7	43.4	23

The test results show that obtained concrete has B30 compressive strength class. Such concrete on an anhydrite binder, in contrast to concrete on Portland cement (high-strength concrete on Portland cement is usually referred to as concrete with a strength class from B55-B65 and higher) can be considered high-strength. It can be assumed that the strengthening of concrete is due to the high strength of non-fired slag-anhydrite gravel and slag-anhydrite stone synthesized during the hardening of FA neutralized by refining slag in the superplasticizer presence, which is also indicated in [26, 27]. In addition an important factor is the structure of the contact zone between the aggregate and the cement stone which in this case has the highest possible strength due to the chemical affinity of the binder and the aggregate.

Such concretes may be in demand in the manufacture of wall stones or to obtain large-size structures and the construction of high-rise buildings by monolithic technology due to their high coefficient of structural quality and water resistance of the binder. It should be noted that the concrete hardening proceeds in an accelerated mode and does not need curing. From a material and technical point of view, the transition to the use of anhydrite binders and concretes based on them allows reducing the cement intensity of construction

that is increasing the share of linker-free binders instead of Portland cement. At the same time, labor productivity increases and construction costs decrease due to significant resource and energy savings, while solving environmental problems in the production of binders.

4. Conclusions

1. It was established that acidic FA is a porous granular material which contains insoluble anhydrite with a crystal size of 1–4 microns as well as sulfuric acid, calcium fluoride, fluorosulfonic acid and calcium fluorosulfonate which subjected to hydrolytic decomposition in air.

2. The influence of the composition and quantity of mineral additives on the kinetics of sulfuric acid neutralization and FA properties during milling was studied. The neutralization process of sulfuric acid in FA proceeds most actively with the introduction of stoichiometric amount of additives: 6.1 % of microcalcite, 12.3 % of steel-refining slag, 13.4 % of ferrochrome slag and 24.8 % of fly ash.

3. Anhydrite binder on the basis of fluorine-anhydrite neutralized by refining slag and with superplasticizer was obtained. The binder is normally hardening, sufficiently high strength and water resistant so it can be used for the manufacture of construction materials applied in conditions with high humidity.

4. Cement-free high-strength concrete of B30 strength class which does not require curing was obtained on the basis of anhydrite binder and non-fired gravel.

References

1. Zhang, P. Comprehensive recovery and sustainable development of phosphate resources. Procedia Engineering. 2014. Pp. 37–51.
2. Garg, M., Minocha, A.K., Jain, N. Environment hazard mitigation of waste gypsum and chalk: Use in construction materials. Construction and Building Materials. 2011. Vol. 25. Pp. 944–949.
3. Prasad, M.N.V. Resource Potential of Natural and Synthetic Gypsum Waste. Environmental Materials and Waste: Resource Recovery and Pollution Prevention. 2016. Pp. 307–337.
4. Gashkova V.I., Tolkacheva L.Ye., Pureskina O.A., Katyshev S.F. Issledovaniye vliyaniya rezhima raboty reaktsionnykh pechey na svoystva ftorangidrita iz pechi [Investigation of the influence of the reaction furnace operation mode on the properties of fluorine anhydrite from the furnace]. Khimicheskaya promyshlennost. 2008. No 7. Pp. 331–338. (rus)Singh, M., Garg, M. Activation of fluorogypsum for building materials. Journal of Scientific and Industrial Research. 2009. Vol. 68(2). Pp. 130–134.
5. Pureskina, O.A., Gashkova, V.I., Petrov, N.S., Katy`shev, S.F. Sposob polucheniya angidritovogo vyazhushhego [Method for producing anhydrite binder]. 2010. Patent Russia no. 2382743, 2010. (rus).Zhou, M., Zhang, W., Hou, H., Huang, X., Wang, W. The activation of fluorgypsum with slag activator and the fluorine solidification mechanics. Journal Wuhan University of Technology, Materials Science Edition. 2011. Pp. 1023–1026.
6. Batalin, B.S., Eremin, O.G., Ivenskix, D.V., Popov, V.S. Sul`fatnosilikatnoe vyazhushhee i sposob ego polucheniya [Sulfate-silicate binder and method of its preparation]. Patent Russia no. 2450989. 2012. (rus).Žvironaitė, J., Pundienė, I., Gaidučis, S., Kizinievič, V. Effect of different pozzolana on hardening process and properties of hydraulic binder based on natural anhydrite. Journal of Civil Engineering and Management. 2012. Vol. 18(4). Pp. 530–536.
7. Sychugov, S., Tokarev, Y., Plekhanova, T., Kazantseva, A., Gaynetdinova, D. Binders based on natural anhydrite and modified by finely-dispersed galvanic and petrochemical waste. Procedia Engineering. 2013. Pp. 1022–1028.
8. Garg, M., Pundir, A. Investigation of properties of fluorogypsum-slag composite binders – Hydration, strength and microstructure. Cement and Concrete Composites. 2014. Vol. 45. Pp. 227–233.
9. Khalil, A.A., Tawfik, A., Hegazy, A.A., El-Shahat, M.F. Effect of some waste additives on the physical and mechanical properties of gypsum plaster composites. Construction and Building Materials. 2014. Vol. 68. Pp. 580–586.
10. Magallanes-Rivera, R.X., Escalante-García, J.I. Anhydrite/hemihydrate-blast furnace slag cementitious composites: Strength development and reactivity. Construction and Building Materials. 2014. Vol. 65. Pp. 20–28.
11. Magallanes-Rivera, R.X., Escalante-García, J.I. Hemihydrate or waste anhydrite in composite binders with blast-furnace slag: Hydration products, microstructures and dimensional stability. Construction and Building Materials. 2014. Vol. 71. Pp. 317–326.
12. Huang, X., Jiang, M., Zhao, X., Tang, C. Mechanical properties and hydration mechanisms of high-strength fluorogypsum-blast furnace slag-based hydraulic cementitious binder. Construction and Building Materials. 2016. Vol. 127. Pp. 137–143.
13. Bigdeli, Y., Barbato, M. Use of a low-cost concrete-like fluorogypsum-based blend for applications in underwater and coastal protection structures. OCEANS 2017 – Anchorage 2017. Pp. 1–5.
14. Sychugov, S., Tokarev, Y., Plekhanova, T., Mikhailova, O., Pudov, I., Faizullin, R., Gaifullin, A., Sagdiev, R. Line of Approach to a Problem of Water Resistance of Anhydrite Cements. Procedia Engineering. 2017. Pp. 982–990.
15. Tokarev, Y., Ginchitsky, E., Sychugov, S., Krutikov, V., Yakovlev, G., Buryanov, A., Senkov, S. Modification of Gypsum Binders by Using Carbon Nanotubes and Mineral Additives. Procedia Engineering. 2017. Pp. 1161–1168.
16. Bigdeli, Y., Barbato, M., Gutierrez-Wing, M.T., Lofton, C.D. Use of slurry fluorogypsum (FG) with controlled pH-adjustment in FG-based blends. Construction and Building Materials. 2018. Vol. 163. Pp. 160–168.
17. Bigdeli, Y., Barbato, M., Gutierrez-Wing, M.T., Lofton, C.D., Rusch, K.A., Jung, J., Jang, J. Development of new pH-adjusted fluorogypsum-cement-fly ash blends: Preliminary investigation of strength and durability properties. Construction and Building Materials. 2018. Vol. 182. Pp. 646–656.
18. Pedreño-Rojas, M.A., Flores-Colen, I., De Brito, J., Rodríguez-Liñán, C. Influence of the heating process on the use of gypsum wastes in plasters: Mechanical, thermal and environmental analysis. Journal of Cleaner Production. 2019. Vol. 215. Pp. 444–457.
19. Cordon, H.C.F., Cagnoni, F.C., Ferreira, F.F. Comparison of physical and mechanical properties of civil construction plaster and recycled waste gypsum from São Paulo, Brazil. Journal of Building Engineering. 2019. Vol. 22. Pp. 504–512.

20. Sychova, A.M., Svatovskaya, L.B., Starchukov, D.S., Soloviova, V.Y., Gravit, M.V., The improving of the concrete quality in a monolithic clip. Magazine of Civil Engineering. 2018. 80(4). Pp. 3–14. doi: 10.18720/MCE.80.1

21. O vliyanii sostava modificirovannogo gipsoglinozemistogo rasshiryayushhegosya cementa na prochnost` i temp tverdeniya [On the influence of the composition of modified gypsum-alumina expanding cement on the strength and rate of hardening] [Online]. URL: http://naukovedenie.ru/PDF/01TVN615.pdf (reference date: 01.11.2019).(rus)Behera, M., Minocha, A., Bhattacharyya, S., Deoliya, R. Durability and In Situ Performance Evaluation of Sustainable Recycled Aggregate Concrete Using Fluorogypsum as Cementitious Binder: Select Proceedings of SEC 2016. Lecture Notes in Civil Engineering. 2019. Pp. 985–997.

22. Tolstoy, A.D., Lesovik, V.S., Milkina, A.S. Improving New Generation Concretes (NGCs) by Introducing Technogenic Mate-rials. IOP Conference Series: Materials Science and Engineering. 2018. Vol. 463(2). DOI: 10.1088/1757-899X/463/2/022095

23. Khezhev, T.A., Pukharenko, Y.V., Khezhev, K.A., Klyuev, S.V. Fiber gypsum concrete composites with using volcanic tuffsaw-ing waste. ARPN Journal of Engineering and Applied Sciences. 2018. No. 13(8). Pp. 2935–2946.

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