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Efficient Eco-friendly Composite Fluorine Anhydrite-Based Materials

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Abstract. The paper presents possible ways of utilizing technogenic waste – fluorine anhydrite – by its use in production of dry mortars and piece goods from lightweight concrete with expanded polystyrene, as a organic filler, for low-rise construction. The developed dry mortars are based on fluorine anhydrite binder and complex modifier comprising curing activator (sulfate or alkaline) and finely dispersed additive. The fluorine anhydrite-based compositions have improved physical and performance characteristics, including the improved strength and average density and reduced water absorption compared to the control composition. The developed lightweight anhydrite polystyrene concrete has the density grade of 700 kg/m^3 and good vapor and gas permeability. The concrete is stabile while using and fire safe, because each granule of expanded polystyrene is coated with anhydrite matrix, and has the strength sufficient for structural and heat insulating slabs and blocks. All mentioned compositions are eco-friendly and are in great demand for low-rise construction. Therefore the manufacturing of these compositions will consume a large amount of technogenic waste and will reduce the environmental load on the region where the waste is located.

Keywords: technogenic anhydrite, resource and power saving, environmental safety, utilizing, modifiers, physical and mechanical characteristics.

Conference topic: Environmental protection.

Introduction

Currently, there is an acute problem of disposing industrial wastes. Its storing is quite expensive and requires safety excluded areas. Therefore, great importance is attached to the developments based on partial or complete replacement of components for producing traditional materials for large-tonnage waste products. For example, storing fluorine anhydrite, a waste product of hydrofluoric acid production located in the Perm region (Russia), takes large areas for dumping the material, low-cost recycling of which helps to reduce the environmental load on the region, as well as to produce efficient fluorine anhydrite-based materials.

The studied material of fluorine anhydrite has a high potential for use both as a binder in the production of piece goods for low-rise construction and as a component of various composite materials with a wide range of applications from the production of composite binders to the production of low-fired ceramic.

This paper presents the current research and formulations of composite materials for various purposes produced from fluorine anhydrite, the use of which can expand the range of products produced on the basis of industrial production waste.

Utilization and secondary use of construction waste are the areas the construction materials science is focusing on. Recycling secondary raw materials not only significantly reduces the harm caused to the environment, but also decreases costs of producing new composite building materials and products based on them. Therefore, those developments are relevant and in demand which are based on partial or complete replacement of components for the production of traditional materials with large-tonnage waste products. For example, storing fluorine anhydrite, a waste product of hydrofluoric acid production located in the Perm region (Russia), takes large areas for dumping the material, low-cost recycling of which helps to reduce the environmental load on the region, as well as to produce efficient fluorine anhydrite-based materials.

Calcium sulfate-based materials have a number of advantages, including environmental friendliness, cost effectiveness and low energy consumption during production, durability, a set of strength properties, good thermal and sound insulation characteristics (Belov *et al.* 2012; *Volzhenskiy et al. 1979*). At the same time, using gypsum-containing waste will help to solve the issues of resource saving and improving the environmental state (Bessonov, Yalunina 2014).

It is known (Fedorchuk 2003) that a significant amount of technogenic anhydrite (fluorine anhydrite) is a waste product of hydrofluoric acid production. Today, its utilization is a relevant problem. Fluorine anhydrite is a waste product of the reaction of fluorite with 98-% sulfuric acid:

$$CaF_2+H_2SO_4 \rightarrow CaSO_4 + 2HF.$$

This gypsum-containing waste material can be used as a binder in dry mortars (Buryanov, Kolkataeva 2008), and as a modifying additive.

Currently, many studies of binders based on natural and technogenic anhydrite focus on creating dry mortars (Haliullin *et al.* 2003a; Gainutdinov 2007; Richert *et al.* 2008). Using such composite materials for finishing work reduces energy consumption compared with using cement grout (Nowak *et al*. 2006). Moreover, calcium sulfate-based materials are characterized with slight shrinkage during solidification in comparison with Portland cement-based solutions (Haliullin *et al.* 2003b; Vlad *et al.* 2006), which contributes to their effective use as self-leveling screeds (Grandans *et al*. 1989; Buryanov, Kolkataeva 2008).

There is a possibility of using fluorine anhydrite binder for the production of high-strength tongue-and-groove partition walls meeting the requirements of the existing standard. Low cost non-shrink mortars based on fluorine anhydrite binder have been developed with cost-effectiveness and high physical and mechanical properties (compressive strength grade from M50 to M150) (Bondarenko 2008).

When using anhydrite as a binder for construction purposes, a strong, compact and waterproof material must be produced. One of the mechanisms for increasing strength is to increase the system packaging density, reduce total porosity, and change the structure of crystal hydrate new formations and the nature of pores in the structure of the material. This effect can be achieved by means of adding modifiers of different nature and dispersity (Belov *et al.* 2012; *Volzhenskiy et al.* 1979; Korolev 2014).

Anhydrite-based composite materials are known to have a potential for increasing the mechanical strength due to the structuring of interfacial layers at the filler – mineral matrix interface in co-activation of anhydrite curing (curing activator in combination with finely dispersed additive) (Yakovlev *et al.* 2010; Maeva *et al.* 2009; Yakovlev *et al.* 2008). At the same time the physical and mechanical properties of anhydrite matrix can be enhanced due to the synergistic effect, which forms clusters throughout the composite. The clusters comprise anhydrite binder hydrated along the surface of the modifying agent (Krutikov *et al.* 2009).

Thus, the development of fluorine anhydrite-based composite materials with the improved physical and mechanical characteristics is an important area in construction materials science and contributes to the solution of energy and resource saving issues while providing a better environment.

General requirements (main text)

Materials and methods

In the studies, the binder used was fluorine anhydrite, a powdery waste produced by Halogen, PA, which, according to, has more than 92% of anhydrous calcium sulfate $CaSO_4$, up to 5% of calcium fluoride CaF_2 and calcium carbonate $CaCO_3$. The specific surface of fluorine anhydrite of dry neutralization is 60-80 m^2/kg, density 2250–2920 kg/m^3.

The curing activator used was sodium hydrosulfite meeting GOST 246-76 and sodium liquid glass of density 1.39 kg/l and the silicate module of n = 2,7. The inhibitor used was a 15% aqueous solution of trisodium phosphate Na_3PO_4 meeting GOST 210-76.

The ultrafine additive used was blast-furnace dust from steel production of Izhstal, JSC, Izhevsk. The chemical analysis of blast-furnace dust was conducted with Axios mAX X-ray fluorescence wavelength-dispersive spectrometer (produced by PANalytical). The chemical composition of dust: iron (III oxide (Fe_2O_3) – 54%, magnesium oxide (MgO) – 14%, calcium oxide (CaO) – 12%, silicon oxide (SiO_2) – 6%. The impurities (1–2%) were chromium (III), aluminum, manganese and zinc oxides. The average particle size of the additive was 20–30 μm, 50% of the particles being less than 18 μm.

To produce anhydrite heat-insulating composite material the lightweight filler used was expanded polystyrene spherical granules ranging from 2 to 5 mm and the density of 15 kg/m^3. The modifying and reinforcing ultrafine additive used in the developed composite was BSTVst ultra-thin basalt fiber. The original basalt fiber produced by Ural Insulation Plant, LLC in Sarapul (Udmurt Republic), has the fiber length of 70÷120 mm. The uniform distribution of fibers in anhydrite binder was due to preliminary reduction of basalt fiber to the length of 10÷12 mm. The average fiber diameter was 4,5 μm.

The physical and mechanical tests of composite materials were conducted with the beam samples of 40×40×160 mm, and the study of lightweight concrete used cube samples of 100x100 mm. The samples were stored for 28 days at the temperature of 20 ºC and normal humidity.

The strength tests were conducted with PGM-100 hydraulic press with the permissible stress of 100 kN and the loading speed of 0,5 MPa/s, in accordance with the standard. The final test results were considered the average values calculated from three successful measurements.

The microstructure of the samples was examined with JSM 7500 F (produced by JEOL, Japan) and Stereoscan S4-10 (produced by Cambridge Scientific Instruments Ltd, England) scanning electron microscopes.

Results and discussion

The study offers several ways of utilizing technogenic anhydrite:

– Dry mortars with complex modifiers including the activator of binder curing with mineral additive;
– Lightweight concrete with polystyrene filler and basalt fiber for producing structural insulating blocks.

Fluorine anhydrite composition with complex additive based on ultrafine blast-furnace dust and sodium hydrosulfite

The hydration of anhydrous calcium sulfate is known to be slow, and the resulting composite has low physical and mechanical characteristics. To speed up the hydration and create favorable conditions for the formation of calcium sulfate dehydrate, curing activators are added (Belov *et al.* 2012; Ottemann 1951; Altmann *et al.* 1993). Depending on the chemical composition of the curing accelerator, the following ways of activating the hydration process are distinguished: sulfate, alkaline, mostly alkaline and combined activation.

It was found (Grimme 1962) that the sulfate activation provides the increased strength characteristics of the matrix, the alkaline one – volume stability of the cured material. Thus, the researches examine the dependence of physical and mechanical properties of fluorine anhydrite on different activators in combination with finely dispersed modifiers.

Basing on the previous studies (Yakovlev *et al.* 2014) the research has shown that adding blast-furnace dust combined with carbon nanotubes increases the physical and performance properties of gypsum binder.

The physical and mechanical tests of the fluorine anhydrite-based composition (Fig. 1) determined the effect of blast-furnace dust on its strength characteristics and water resistance under the condition of sulfate activation (sodium hydrosulfite – 0,8%) of the tested binder.

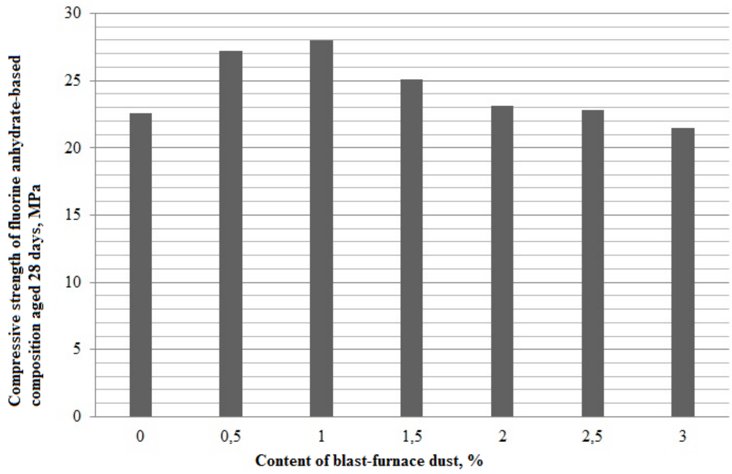


Fig. 1. Dependence of strength of fluorine anhydrite-based composition aged 28 days on the content of blast-furnace dust

The analysis of the given dependence leads to the conclusion that the compressive strength of fluorine anhydrite-based composition, blast-furnace dust being added, increases by 24% (27,9 MPa), the optimum content of the additive being 1%. The further increase of concentration of the dispersed mineral additive is impractical because it leads to the decreased strength characteristics of the material.

The conducted studies determined physical and performance specifications of the fluorine anhydrite-based material (Table 1).

Table 1. Physical and performance characteristics of studied compositions

№	Content of blast-furnace dust, %	Water requirement, %	Average density, kg/m^3	Porosity, %	Water absorption, % after 4 hours	Softening coefficient
1	0	22	2031	24.8	4.86	0.78
2	0.5	22	2055	23.9	5.67	0.85
3	1	22	2000	25.9	5.84	0.87
4	1.5	22	2047	24.2	5.49	0.86
5	2	22	1996	26.0	5.12	0.84

The presented data shows that the water absorption of the studied compositions varies from 4,86 to 5,84%. The softening coefficient of the fluorine anhydrite-based composition increases from 0,78 to 0,89, 1% of blast-furnace dust being added. The enhancement of physical and performance properties of the fluorine anhydrite-based compositions with the combined binder activation with sodium hydrosulfite and blast-furnace dust is likely due to the influence of additives on the structure of the material, which leads to its compaction. This is indicated with the increased average density and reduced porosity.

The images of the microstructure of fluorine anhydrite-based binder with sodium hydrosulfite added (Fig. 2) show a heterogeneous structure consisting of crystals of different dimensions. The matrix of the material contains a large number of pores and capillaries that cause density decrease. These factors lead to the weakening of contacts between new formations, which in its turn reduces the strength properties of fluorine anhydrite-based composition, sulfate curing activator being added.

(a) (b)

Fig. 2. Microstructure (× 5000): (a) – control composition of fluorine anhydrite binder,
(b) – fluorine anhydrite composition, sodium hydrosulfite (0,8%) and blast-furnace dust (0,5%) being added jointly

The dispersed additive based on blast-furnace dust being added, a denser structure (Fig. 2b) forms. It consists of smaller crystals with a dense packing of new crystalline hydrate formations. The number of pores reduces which provides an increase of the contact area between new formations and enhances the strength of anhydrite matrix.

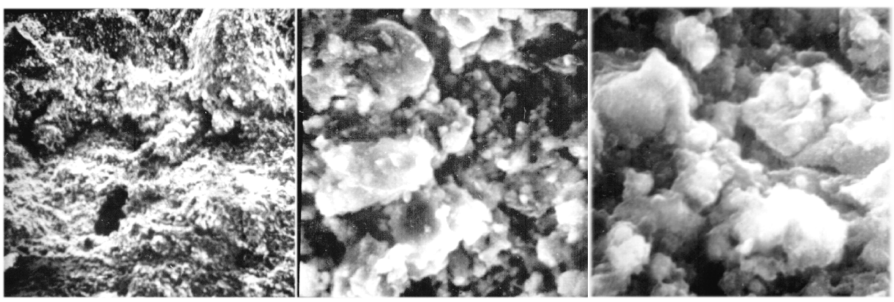
Thus, the formation of a dense and more homogeneous structure of anhydrite matrix, mineral modifier and sulfate activator being added jointly, increases the mechanical properties by 24% with the optimal additive concentration of 1%, in comparison with the control composition, the water resistance of the modified compositions being provided.

Rapid hardening fluorine anhydrite-based composition

Using anhydrite compositions for molding the articles requiring rapid setting and hardening is limited with long periods of strength development. This problem was solved by means of adding sodium water glass up to 18% from the mass of fluorine anhydrite for alkaline activation. It contains silicate ions that accelerate calcium sulfate hydration. The sodium silicate solution contacting with fluorine anhydrite coagulates to form cluster and ultrafine new formations with a negative potential on the particle surface (Jakowlew, Keriene 2000). To slow down the instantaneous coagulation, 15% aqueous solution of trisodium phosphate Na_3PO_4 was used.

The physical and mechanical properties of the optimized technogenic anhydrite-based composition, sodium silicate and trisodium phosphate being added, are the following: the beginning of setting 4–7 minutes, the end of setting 6–9 minutes, the compressive and flexural strength at the age of 28 days 21 and 9,6 MPa correspondingly.

The study of anhydrite matrix microstructure shows that the composite structure (Fig. 3) has fluorine anhydrite particles coated with gel-like formations connecting the system into a monolithic conglomerate.



(a) (b) (c)

Fig. 3. Microstructure of rapid hardening fluorine anhydrite-based composition at the magnification of:
(a) – ×60; (b) – ×1200; (c) – ×3000

The research of the set composition structure shows that the increase in the material strength is due to additional compaction of the structure with new formations appearing during the anhydrite hydration in the long process of hardening. The anhydrite activation in the sulfate-containing waste is stimulated with alkaline medium in the presence of sodium silicate.

The studied fluorine anhydrite-based composition can be widely used in the molding production of architectural and decorative articles.

The conducted research leads to the conclusion that the complex activation of fluorine anhydrite hardening provides favorable conditions for hydration and hardening of dihydrate calcium sulfate. Adding modifiers provides the formation of a dense and strong matrix structure with the less pore volume, which eventually leads to the increased mechanical properties, the average density, and lower water absorption.

Lightweight fluorine anhydrite-based expanded polystyrene concrete

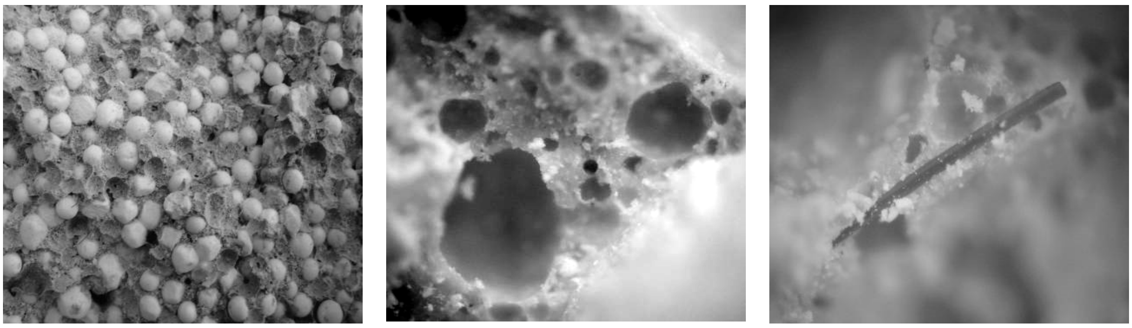
The building construction should use environmentally friendly, low-power building materials produced with low-cost technology mostly based on the use of technogenic waste processed products and local natural raw materials [Khodzhaev *et al.* 2015; Plechanova *et al.* 2007]. Using fluorine anhydrite as raw material for lightweight concretes can simplify the production technology and reduce the manufacturing cost 3–4 times due to excluding expensive Portland cement.

Optimizing the content of lightweight fluorine anhydrite-based concrete was studied. Along with the binder matrix, it contains expanded polysterene as an organic filler, sodium hydrosulfite (0,1%) as a curing activator, ultra-thin basalt fiber as a reinforcing and modifying agent that enhances the density of new formations in matrix, and 0.3% of saponified resin. Adding surfactant not only improves the workability and increases anhydrite matrix porosity, but also increases the wettability between dissimilar concrete particles by means of forming thin liquid phase films of (Deryagin *et al.* 1973; Zhurba *et al.* 2005).

Mechanical tests of 100x100x100 mm samples show the average density of 690 kg/m^3 at the compressive strength of up to 1,86 MPa. The water absorption of polystyrene concrete does not exceed 8%, the softening coefficient being 0,68. The pH analysis of the medium in freshly prepared polystyrene shows pH>11. It determines its use for steel reinforcement in polystyrene concrete without any extra protection from corrosion.

Taking into account that each granule of expanded polystyrene is coated with anhydrite matrix, one can expect the absence of chemical destruction of polystyrene in the continuous operation of polystyrene concrete and enhancement of its fire safety due to water evaporated from calcium sulfate dihydrate at the thermal impact (fire) on anhydrite polystyrene concrete.

The study of polystyrene concrete microstructure shows that its microstructure has good adhesion of anhydrite matrix to expanded polystyrene granules and basalt fiber (Fig. 4).



(a) (b) (c)

Fig. 4. Structure of polystyrene concrete chip (a), porous structure of modified anhydrite matrix (b), adhesion of fluorine anhydrite matrix with basalt fiber (c) at 200-times magnification

Thus, the produced lightweight anhydrite polystyrene concrete has a density grade of 700, good vapor and gas permeability, is fireproof, prevents destruction of polystyrene, and has sufficient strength for producing structural and heat-insulating blocks and slabs. Using fluorine anhydrite in polystyrene as a binder matrix can significantly reduce the cost of the resulting material due to excluding expensive Portland cement from the composite. It has been found that the gas emitted in the chemical interaction of curing activator with fluorine anhydrite components provides additional mortar swelling, reduces the average density, and improves adhesion of basalt fiber with anhydrite matrix.

Conclusions

The possible ways of utilizing technogenic waste – fluorine anhydrite – by its use in production of fluorine anhydrite-based compositions such as dry mortars, and piece goods from lightweight concrete are shown in the work. All mentioned compositions have improved physical and performance characteristics, they are eco-friendly. Therefore they are in great demand for low-rise construction. The manufacturing of these compositions will consume a large amount of technogenic waste and will reduce the environmental load on the region where the waste is located.

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