Conference Paper

# Obtaining of Granulated Gypsum Anhydrite on the Basis of Technogenic Wastes of Chemical and Metallurgical Complex for Use in Portland Cement Production

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## Abstract

The composition and properties of fluorine–anhydrite and steel–refining slag which are wastes of production of hydrogen fluoride and steel were determined. It is established that fluorine–anhydrite of the current output does not meet the requirements to materials for the production of Portland cement. Therefore to improve the technical and consumer properties of fluorine-anhydrite (for increasing the amount of $CaSO_4 \cdot 2H_2O$ and neutralization of $H_2SO_4$) the studies of its' conditioning processes with steel–refining slag were carried out. It was found that the mass transfer coefficient of sulfuric acid through the capillary and the degree of its neutralization by slag depend on the dispersion of fluorine–anhydrite, its porosity and initial acidity. The most effective binding of sulfuric acid occurs with the introduction of slag in stoichiometric amounts, the size of fluorine–anhydrite granules up to 20 mm and a processing time of 60 minutes. After storage in air-humid conditions for 12 hours of fluorine–anhydrite treated with slag the strength of its granules, the amount of dihydrate gypsum and toxicological properties meet the requirements.

**Keywords:** techno–gypsum, refining slag, neutralization, conditioning, gypsum stone, Portland cement.

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## 1. Introduction

In cement plants natural gypsum stone or gypsum–anhydrite stone are used to control the setting time of cement, but their stocks and quality inevitably decrease over time.

In addition in some regions there are no any deposits of gypsum stone, and its quarrying, preparation and transportation to cement plants require significant costs.

The studies results [1–9] show that so–called techno–gypsums (phosphogypsum, etc.) which are byproducts of the chemical industry can be used to regulate the setting process of Portland cement. At the enterprises for the production of hydrogen fluoride and steel hundreds of thousands tons of fluorine–anhydrite (FA) and metallurgical slags are formed every year; they are stored in waste fields or in sludge storage polluting the environment.

It is known that one of the possible ways to solve the problem of processing technogenic wastes into useful products and the creation of low–waste technologies is the combination and cooperation of various productions [10]. Therefore the aim of the work was to study the possibility of using steel–refining slag to improve the technological properties of FA (conditioning) that meet the requirements for gypsum–containing materials for the production of Portland cement.

## 2. Results and Discussions

Three FA samples of weigh at least 100 kg each taken from a rotating furnace at 200–250 °C were investigated. Their chemical and material compositions are presented in Tables 1–2. The samples of FA no. 1 and no. 3 consist of the fraction of 1–20 mm and sample no. 2 have 48 % of the fraction 20–60 mm. According to the study of the FA grains microstructure it was established that they mainly have channel and isometric pores which randomly arranged. The length of channel pores is from 188 to 1000 microns and their diameter is from 63 to 178 microns. The number of isometric pores are as following, %: 40–57 – less than 60 μm, 35–45 – from 60 to 125 μm, 5–10 – from 60 to 310 μm, 3–5 μm – more 310. According to the electron microscopy data fluorine–anhydrite has a fairly uniform loose-grained structure which is stacked with prismatic anhydrite crystals with a size of 1–4 μm. When mixed with water FA slowly hardens in the early stages but by 28 day its compressive strength is equal to 3–5 MPa.

Table 1: Chemical composition of FA samples (authors' work).

| Sample number | Quantity [mass %] | | | | |
|---|---|---|---|---|---|
| | $SiO_2$ | CaO | $Fe_2O_3$ | $SO_3$ | $F^-$ |
| 1 | 0.30 | 38.08 | 2.00 | 57.24 | 0.54 |
| 2 | 0.08 | 37.13 | 2.90 | 56.56 | 1.00 |
| 3 | 0.03 | 38.20 | 1.78 | 58.08 | 0.50 |

Table 2: Material composition of FA (authors' work).

| Sample number according Table 1 | Quantity [mass %] | | |
|---|---|---|---|
| | $CaSO_4$ | $H_2SO_4$ | $CaF_2$ |
| 1 | 91.14 | 4.46 | 1.22 |
| 2 | 90.00 | 6.08 | 2.30 |
| 3 | 92.54 | 3.83 | 1.18 |

Thus FA is characterized by a relatively constant chemical composition; it contains mainly anhydrite and 3.8–6.0 % of sulfuric acid. FA does not meet the requirements of Russian Standard no. 4013 by the criteria of content of $CaSO_4 \cdot 2H_2O$ (at least 30 %) as it contains more than 90 % of anhydrous $CaSO_4$ and therefore can not be used in the production of Portland cement. For FA conditioning (i.e. increasing of the $CaSO_4{\cdot}2H_2O$ quantity and $H_2SO_4$ neutralization) steel–refining slag with a specific surface of 270 $m^2/kg$ and containing 43.2 % $12CaO{\cdot}7Al_2O_3$, 31.5 % of $2CaO{\cdot}SiO_2$, 5,9 % MgO and 18.0 % of glassy phase is used. When mixing with water a slag stone has the greatest strength when hardening in air, the lowest – in wet conditions. The granules of acid FA from the furnace were gradually moistened in a mixer and treated with slag powder in an amount of up to 13 % on a disc granulator for 60 min. When humidifying hot FA from the furnace the forming process is very rapid with the release of steam; so the water consumption was 23–25 % due to partial evaporation. The content of $H_2SO_4$, $CaF_2$ and $CaSO_4{\cdot}2H_2O$ in the FA granules as well as the mechanical compressive strength of the granules were determined at regular intervals after slag treatment.

This studies are based on the hypothesis that when moistening and processing granulated FA from the furnace with fine slag (as a result of its interaction with sulfuric acid on the surface of the FA granule) a thin layer of reaction products is formed, which has high adhesion, provided increased strength and water resistance of granules for transportation and storage of FA after conditioning in open areas of enterprises producing of hydrogen fluoride and cement plants. The results of FA conditioning are presented in Table 3 and Figures 1–4. It is stated that the mass transfer coefficient of sulfuric acid in the granules of the first and third samples of FA calculated by the method [11, 12] changes from $3{,}28{\cdot}10^{-4}$ to $1{,}31{\cdot}10^{-5}$ and from $3{,}59{\cdot}10^{-4}$ to $1{,}42{\cdot}10^{-5}$ $m^2/s$ respectively. For granules of the second FA sample the mass transfer coefficient of sulfuric acid ranged from $7{,}81{\cdot}10^{-4}$ to $3{,}2{\cdot}10^{-9}$ $m^2/s$ (see Table 3).

Table 3: The calculated mass transfer coefficients and the degree of neutralization of sulfuric acid in the FA granules when dusting by steel–refining slag (authors' work).

| Sample number according Table 1 | Mass transfer coefficient of sulfuric acid [$m^2/s$] in FA granules of size [mm] | | | | Degree of $H_2SO_4$ neutralization [%] |
|---|---|---|---|---|---|
| | 1–5 | 5–20 | 20–40 | 40–60 | |
| 1 | $3.28{\cdot}10^{-4}$ | $1.31{\cdot}10^{-5}$ | – | – | 64.3 |
| 2 | $7.81{\cdot}10^{-4}$ | $3.93{\cdot}10^{-5}$ | $2.4{\cdot}10^{-9}$ | $3.2{\cdot}10^{-9}$ | 51.6 |
| 3 | $3.59{\cdot}10^{-4}$ | $1.42{\cdot}10^{-5}$ | – | – | 55.2 |

Consequently in FA granules of size from 1 to 20 mm sulfuric acid is actively neutralized as a result of interaction with slag minerals that reduces its content by more than a half. In big FA granules of size 20–40 and 40–60 mm (second sample) acid mass transfer flows slowly. After holding the FA granules treated with slag in air–humid conditions for 12 hours the total acid content in the first and third samples decreased from 4.5 to 0.2 % and from 3.83 to 0.5 % respectively and in the second sample – from 6.0 to 2.1 %. At the same time the total amount of two–water gypsum, mechanical strength and softening coefficient of FA granules for the first and third samples were 36.5 and 31.3 %; 77 and 65 N/granule; 0.82 and 0.78 respectively. As for the second sample of FA the total amount of two–water gypsum was 40.6 % (excluding granules of 20–60 mm), a strength of granules (of size 14–15 mm) is equal to 80 N/ granule, softening coefficient is 0.81. It is noted that the degree of neutralization and mass transfer coefficient of sulfuric acid depend on the amount of acid in the granules and their open porosity which varied from 10.8 to 27.8 %. Thus the greater the concentration of sulfuric acid and the number of open pores in the FA, the more intensively the acid is transferred to the surface of the granule and neutralized by the steel–refining slag on it providing an increase in the amount of two–water gypsum and the strength of the granules (see Figures 1–2). At lower acid concentration in the granules of FA and the increase of closed porosity the mass transfer coefficient decreases, slowing down the neutralization of sulfuric acid with slag and the formation of dihydrate gypsum and the granules strength is not increased. Thus to accelerate the sulfuric acid neutralization a critical grain size of FA should not exceed 20 mm. With the increase of the grain size of FA from 20 to 60 mm closed porosity is increased and the coefficient of mass transfer of sulfuric acid is reduces.

Crushing of coarse fractions of FA reduces the length of the diffusion path of the acid through the capillary providing an increase in the degree of its neutralization and the amount of two–water gypsum in FA to 95 and 45 % respectively. In addition it was discovered that the amount of $CaF_2$ in samples of granulated FA in the first 10 min of slag processing increases from 1.22 to 2.14 %, from 2.3 to 3.1 % and from 1.18 to 1.5 % respectively which indicates the presence of fluorides traces in the original FA and its neutralization by the calcium–containing minerals of the slag.

According to the results of electron microscopy it was found that the pores of FA granules after treatment with slag and subsequent 12 hours of exposure are filled with a white loose substance supposedly a two–water gypsum (see Figure 3–4). Hydrated slag shell includes large areas of amorphous hydrosilicate phase surrounded by a small embryonic crystalline hydrates (see Figure 3, “dark area”).

In the image of the microstructure of the contact area of hydrated slag with the FA granule (see Figure 4) can be seen densely packed tabular crystals of dehydrate gypsum, epitaxies associated with needle crystals of ettringite and rhombohedral crystals of anhydrite. This structure provides high adhesion of the slag shell to the surface of the FA granule and gives it increased strength and water resistance protecting against external factors. Thus the studies confirm the hypothesis mentioned above that the

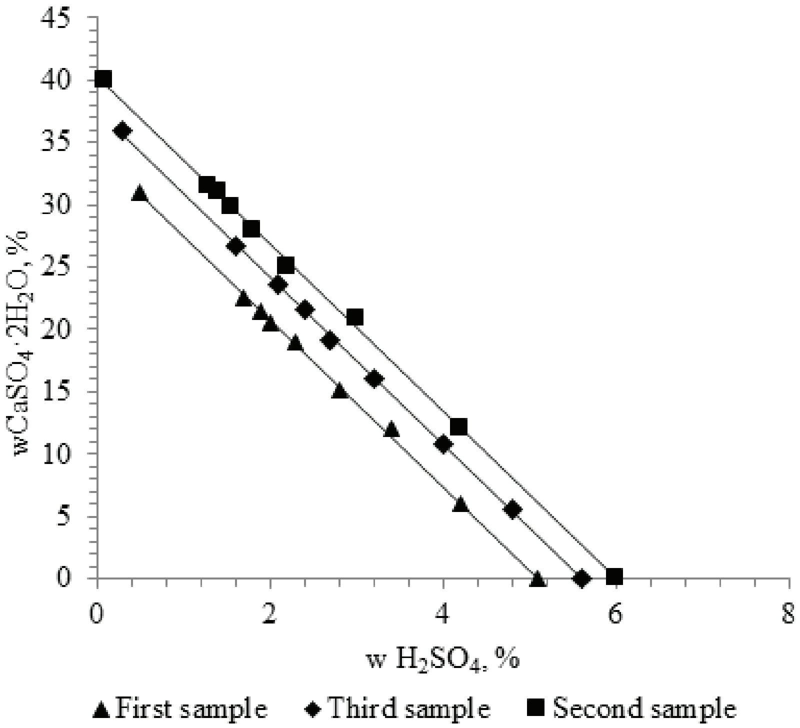


**Figure** 1: Influence of the sulfuric acid amount on the content of dihydrous gypsum in FA granules (authors' work).

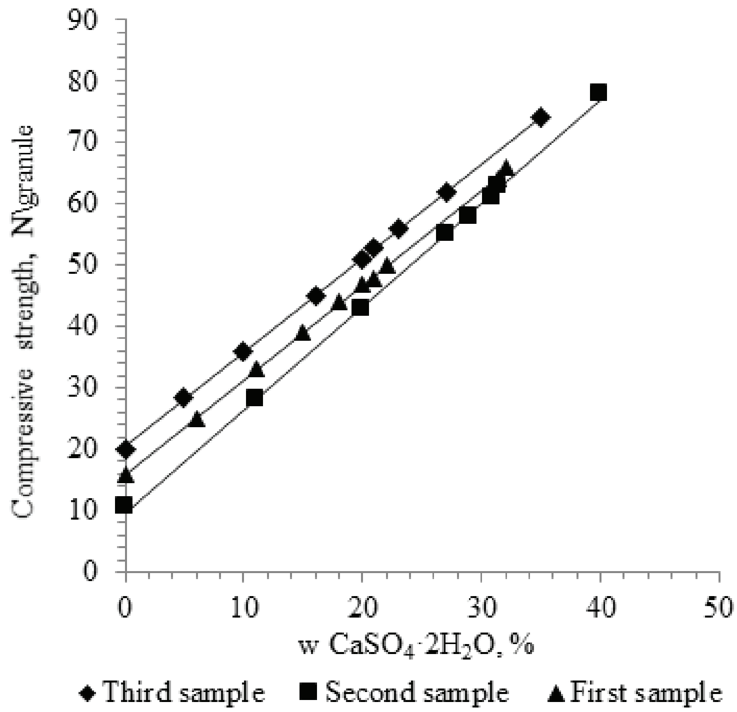


**Figure** 2: Influence of the amount of dihydrate gypsum on compressive strength of FA granules (authors' work).


**Figure** 3: Structure of hydrated slag shell (“dark area”) and FA granule (authors’ work).

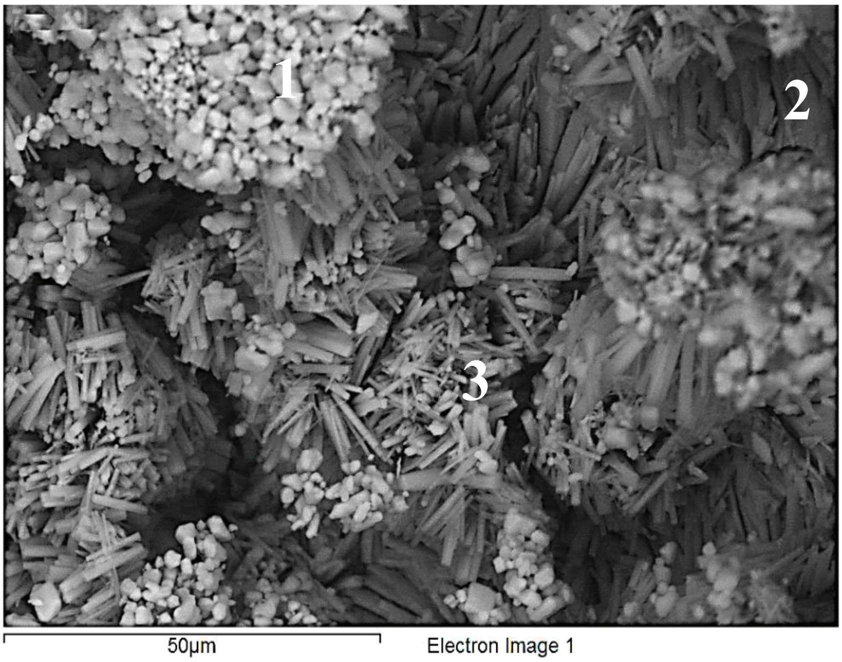


**Figure** 4: Structure of the contact area of hydrated slag with the surface of the FA granule (authors’ work). 1 – $CaSO_4$; 2 – $CaSO_4 \cdot 2H_2O$; 3 – $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ (ettringite)

interaction of slag with sulfuric acid on the FA surface improves the consumer and technological properties of FA.

Granular gypsum anhydrite from FA and steel–refining slag belongs to grade I by the content of gypsum according to Russian Standard no. 4013 and does not contain toxic impurities harmful to the environment and the production of Portland cement.

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