CHEMICAL ENGINEERING TRANSACTIONS

VOL. 88, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš

**ISBN** 978-88-95608-86-0; **ISSN** 2283-9216

DOI: 10.3303/CET2188098

# The Use of Fluoro-Anhydrite for Building Materials Production

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The work comprises researches on studying the possibility to use Fluoro-Anhydrite - fluor-hydric acid production waste in building industry. The effect of the dispersion and the amount of the neutralising agent on the completeness of the neutralisation reaction of acid Fluoro-Anhydrite is investigated. A method for obtaining a synthanite from hydrofluoric acid production waste is proposed, including neutralisation of the waste with a lime-containing component, followed by grinding and separation of the binder, characterized in that the production waste is additionally denaturalised by its chemical activation with quicklime to pH 12 and a sulfate additive, followed by grinding to a specific surface area of 9,000 $cm^2/g$. Ensuring that the pH level of the binder mixture reaches 10-12 leads to an improvement in the physical and technical properties of synthanite: an increase in strength by 3.5-4 times, a reduction in the setting time by up to 9-12 times. The possibility has been proved to produce M25 and M50 dry plasters intended for finishing work based on developed air-hardening synthanite. It is recommended to use plasters inside the premises when air humidity is not higher than (60-70) %.

## 1. Introduction

Literature data analysis shows that some wastes of chemical and metallurgical production found application in building industry (Rashad, 2017). At the same time waste of fluoric production refer to hazardous wastes and have complex composition in this connection they are not processed and disposed to dumps. 1.8 tons of by-product (technogenic anhydrite - $CaSO_4$) is produced per 1 ton of HF production. A number of authors show the prospects of using calcium sulfate waste, including in the construction industry. Anikanova et al. (2015) suggest to use acid fluoride for wall blocks production for low-height construction. Fedorchuk (2003) notes that such wastes are individual in their chemical and mineralogical composition, phase structure, physical-mechanical properties and they require individual approach in their studying, processing, and usage. Zhakupova et al. (2019) indicate in their research that acid fluoride properties are unstable and there is a risk of incomplete neutralisation of sulphuric acid. So they suggest a new approach to fluorine-containing materials neutralisation process.
The goal of the research is to develop the method of anhydrite binder production from wastes of fluoric production which provides complete neutralisation of acid fluoride and improvement of physical and technical properties of the binder that are required for dry mix mortars production. The object of the research is the waste from metallurgical enterprise of East Kazakhstan - Fluoro-Anhydrite.

## 2. Materials and methods

Acid Fluoro-Anhydrite and an additive-neutraliser (lime) were used to produce air-hardening synthanite and dry plasters with Fluoro-Anhydrite. Acid Fluoro-Anhydrite used in work was taken directly from the furnace of metallurgical enterprise in Ust-Kamenogorsk – JSC “UMP”. The chemical composition of acid waste is following (mass, %): CaO – 30.9; $SO_3$ – 44.2; $Fe_2O_3$ – 0.45; MgO – 0.04; $TiO_2$ – 0.02; $Na_2O$ – 0.02; $K_2O$ – 0.02; MnO – 0.02; $P_2O_5$ – 0.04. Acid waste pH level was 1.81. Bulk density of the waste was 1.42 $t/m^3$, true specific gravity – 2.66 $g/cm^3$. During mixing with water acid Fluoro-Anhydrite didn’t show any binding properties, that can be explained by some amount of acid. To neutralise excess amount of acid, lime from

Paper Received: 22 May 2021; Revised: 3 September 2021; Accepted: 1 October 2021
Please cite this article as: Galkina D.K., Rudenko O.V., Sadenova M.A., Kulenova N.A., 2021, The Use of Fluoro-Anhydrite for Building Materials Production, Chemical Engineering Transactions, 88, 589-594 DOI:10.3303/CET2188098

Sazhaevsky deposit of East Kazakhstan was used as the cheapest raw material of almost unlimited reserves in this region. As a hardening activator, quicklime CaO was used, as well as sulfate additives of monovalent metals ($K_2SO_4$, $Na_2SO_4$). Cellulose ester (methyl- hydroxyethyl-cellulose) – Tylose MH 60010 P4 produced by Clariant (Germany) was used as water-retaining admix to dry plasters. It is fine powder recommended for usage in gypsum and cement plasters. Natural sand of Zaisan deposit was used as the filler.

Chemical and phase composition of the research object was defined with inductively coupled mass spectrometer ISP-MS Agilent («Agilent Technologies», USA). To define chemical composition on an inductively coupled mass spectrometer, Fluoro-Anhydrite was dried at temperature 100-110 $^oC$ until the constant weight. Water extract pH was defined on pH-meter device Anion 4100. Distilled water at room temperature (100 ml) was added to the material (5 g) and was mixed for 10-15 mins and was hold for 24 h and blended from time to time. The liquid was separated from precipitation by decantation and pH was measured. Specific surface was defined at ПСХ-10а device by Kozeni and Karman gas permeability method in accordance with the instruction to the device. Physical and mechanical testing of original and developed materials was carried out according to the standard documented procedures relevant on the territory of the Republic of Kazakhstan.

Initially the researches were carried out in order to select the optimal neutraliser for the given type of calcium sulphate waste and to define optimal parameters for neutralisation process. Lime from Sazhaevsky deposit of East Kazakhstan was chosen as neutralising agent as it is the cheapest raw material of nearly unlimited reserves in this region. Neutralisation process was carried out by dry method in a laboratory rod mill. Acid Fluoro-Anhydrite charge was weighted on the scales and put into the rod mill. At the same time powder lime was charged there too. Neutralisation process lasted for 10 mins. Mechanical activation was carried out in a laboratory vibrating mill during 10 mins, till specific surface was Ssp.= 600 $m^2$/kg. Fluoro-Anhydrite neutralised up to pH=7.3 was used for activation, after neutralisation in a rod mill its specific surface was 420 $m^2$/kg, ultimate compressive and bending resistance at the age of 7 d was respectively 2.72 and 0.54 MPa, it was characterised by prolonged setting time (h-min) – beginning – 19-50, end - 29-10.

Chemical activation was carried out by Fluoro-Anhydrite neutralised to pH=7.3. Previous experiments proved that sulphate additives of monovalent metals ($Na_2SO_4$, $K_2SO_4$), lime (CaO, $Ca(OH)_2$), liquid glass, hemihydrate plaster ($CaSO_4$•0,5$H_2O$) have positive effect on resistance increase and setting time reduction. Caustic lime (CaO) in the amount 10-20 % was preferred hardening activator as it contributes to improving strength properties and reducing setting time. As lime was added in the amount 5, 10 and 20 %, pH level increased from 7 to 9, 10 and 12 respectively and went along with improvement of strength properties. In case it is required to reduce setting time further (at the customer's request), it can be recommended to add sulphate additives of monovalent metals ($Na_2SO_4$, $K_2SO_4$) in the amount (0.5-1.0) %, or the additive of hemihydrate plaster ($CaSO_4$•0,5$H_2O$) in the amount (5-10) %.

Further there was a range of experiments for defining optimal degree of synthanite grinding. Fluoro-Anhydrite neutralised up to pH=7.3 was used as a component of synthanite in the amount of 90 %, hardening activator-additive was caustic lime with specific surface 300 $m^2$/kg in the amount 10 %. Binder components were mixed to a homogeneous condition. Synthanite specific surface was 350 $m^2$/kg, compressive and bending resistance at the age of 28 d was 4.1 and 4.2 MPa respectively, The beginning of setting time was 3-50 h-min, the end of setting time was 6-05 h-min. Synthanite was finely ground in a laboratory vibrating mill for 5, 10, 20, and 50 mins, and its specific surface was 460, 610, 840, 960 $m^2$/kg. When Fluoro-Anhydrite-based air-hardening synthanite was developed, interstate standard procedures GOST 23789-2018 «Gypsum binders. Test methods» were accepted in order to define setting time, normal consistency, ultimate resistance of test-beams in bending and compressing. Grade was defined after 28 d of air-hardening according to the resistance of air-hardening synthanite.

In order to determine the field of application for the developed air-hardening synthanite, the researches were carried out to develop dry mix mortars based on it, in particular, dry plaster for finishing works. Fluoro-Anhydrite: hardening activator (caustic lime) ratio, mass %, is 90 : 10. Synthanite chemical composition is following (mass, %): CaO – 3.1; $SO_3$ – 45.3; $Fe_2O_3$ – 0.1; LOI – 0.2. The employed synthanite had the following characteristics: true specific gravity – 2.5 g/$cm^3$, bulk density – 850 kg/$m^3$, specific surface – 550 $m^2$/kg, grade according to resistance – M100, softening coefficient – 0.4, beginning of setting time - 2 h 35 mins, the end of setting time - 5 h 20 mins. The sand was preliminarily subjected to thorough size grading 0-0.16; 0.16-0.63; 0.63-1.25; 1.25-2.5 (2.0) mm with their further dosing for selecting the optimal grain size composition taking into account the requirements for grains fineness depending on the purpose of mortars. Full screening residues, %: 0.315 -50; 0.16 – 90; less 0.16 – 100, fineness modulus FM=1.4. Dry plaster was produced when mortar components were mixed, binder: filler ratio was accepted 1:2 to 1:4. Water was mixed for producing mortar mix with StroiCNIL cone slump 10 cm in accordance with the requirements in order to provide remoldability when there are hand method and mechanical method of plaster application.

To develop the composition of dry plasters, interstate standard procedures GOST 5802-86 «Mortars. Test methods» were accepted. In order to define the optimal composition of dry plasters, samples 7.07x7.07x7.07 cm in size were formed, that hardened under air-dry conditions at the temperature (20±2) °C. Grade of dry plasters was defined according to compressive resistance at the age of 28 d.

## 3. Results and discussion

As a result of studies on the neutralisation of acid Fluoro-Anhydrite, the effect of the dispersion of the neutralising reagent and its amount on the completeness of the neutralisation reaction was established (Figure 1). Lime of different specific surface (from 400 $m^2$/kg to 800 $m^2$/kg was introduced in the amount 10-30 % of the product mass.

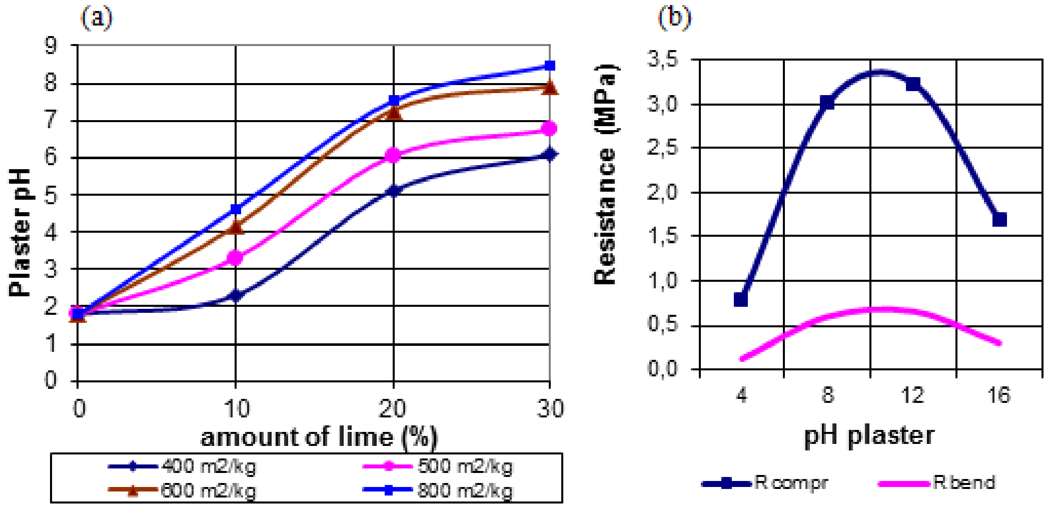



*Figure 1: Influence of (a) lime specific surface and amount on plaster pH, (b) pH of plaster on the resistance of samples at the age of 7 d*

It was found that when specific surface is increased from 400 $m^2$/kg to 800 $m^2$/kg, plaster pH level increases too. This positive tendency is observed when $CaCO_3$ content is different. It can be seen from Figure 1, that optimal specific surface of lime is within 550-600 $m^2$/kg. Optimal amount of lime in the plaster for neutralisation is 20 % (when the initial level of material acidity pH = 1.81). The optimal pH level was ~7-8, and intensive gain of resistance characteristics is observed before it. When pH level is changed lower or higher than the optimal one, resistance characteristics are decreased or neutralising agent is overconsumed (Figure 1). When mixed with water, the neutralised Fluoro-Anhydrite showed up weak binding properties: specific surface was 400-420 $m^2$/kg, true specific gravity - 2.5 g/$cm^3$, bulk density was 816 kg/$m^3$, normal consistency 36.5 %, pH=7.3, the beginning of setting time was 19-55 h-min., the end of setting time was 29-34 h-min., ultimate compressive resistance at the age of 28 d – 3.5 MPa, ultimate bending resistance – 0.7 MPa. So the further work was devoted to activation of neutralised Fluoro-Anhydrite. In order to activate neutralised Fluoro-Anhydrite, the influence of plaster mechanical activation in a vibrating mill on its properties was studied, as well as impact of hardening activators-additives (chemical activation) both separately, and in combination (mechanical and chemical activation). The results are provided in Table 1.

*Table 1: The influence of activation method on the properties of neutralised Fluoro-Anhydrite*

| The type of neutralised Fluoro-Anhydrite activation | Specific surface, $m^2$/kg | Setting time, h-min (begin. / end) | Ultimate compressive resistance at the age of 7 d, MPa | Ultimate bending resistance at the age of 7 d, MPa | pH |
|---|---|---|---|---|---|
| --- | 420 | 19-50 / 29-10 | 2.7 | 0.5 | 7 |
| Mechanical | 600 | 11-10 /16-15 | 8.1 | 1.8 | 7 |
| Chemical | 350 | 2-50 / 4-40 | 3.5 | 0.8 | 10 |
| Mechanical-chemical | 600 | 1-16 / 3-09 | 9.6 | 2.0 | 10 |

The control indicators were resistance and setting time, that enabled to increase material resistance considerably up to 8.12 and 1.83 respectively (2.5-3.5 times) and to reduce setting time up to 11-10 and 16-15 respectively (beginning – 1.5-2 times, end – 1-1.5 times). Granulated structure of the waste slows down neutralisation process. Fine grinding enables to decompose calcium fluoride that covers granules of the waste and to carry out neutralisation process more completely thus increasing the substance activeness and reducing setting time. However, setting time is still too long.

During chemical activation material resistance and setting time remained test items. Chemical activation enables to reduce setting time of technogenic anhydrite considerably while its strength properties are hardly changed. It is shown that if setting time is reduced up to 8-10 times (the beginning is from 19-50 to 2-50 h-min, the end is from 29-10 to 4-40 h-min), strength properties are increased only 1-1.2 times. Mechanical and chemical activation enables to increase the substance activeness optimally by combining positive aspects of either mechanical or chemical activation. Combination of mechanical and chemical activation enables to heighten each other's effect that contributes to considerable improvement of material physical-technical properties, in particular, setting time reduction, and increase of binder resistance (Table 1). In this regard the following additives were used as additives-activators during chemical and mechanical activation: CaO – 10 %, $K_2SO_4$ – 1.0 %.

The results of determining the optimal degree of grinding of synthanite are as follows. As synthanite dispersiveness (specific surface) was increased, setting time reduction and strength properties improvement were observed (Figure 2).

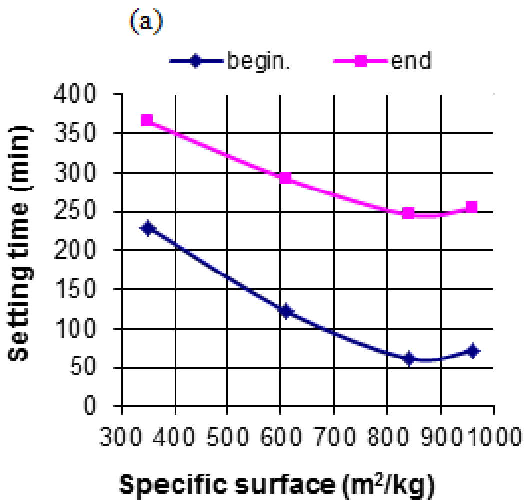
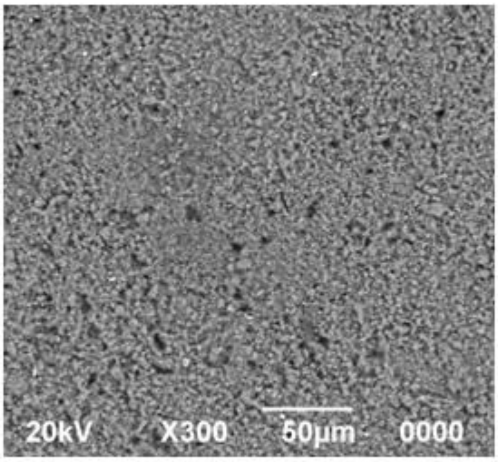



*Figure 2: Dependence of binder dispersiveness (a), setting time, (b) resistance*

It can be seen in Figure 2 that as the binder specific surface is increased from 350 $m^2$/kg up to 900 $m^2$/kg, resistance increase and setting time reduction are observed, and further increase of specific surface more than 900 $m^2$/kg causes increase of water demand and consequently causes setting time extension and resistance decrease. It was found out that within the range of binder dispersiveness from 350 to 550-600 $m^2$/kg, its physical and technical properties are intensively improved, so setting time is considerably reduced, and its resistance properties are increased. Then while the binder is further ground from 550-600 to 850-900 $m^2$/kg, the curve flattening is observed – insufficient improvement of the indicated properties. Finally, when specific surface is increased more than 900 $m^2$/kg, a negative tendency is observed, and water demand of the plaster sharply grows, setting time is increased and binder resistance is decreased. It was observed that despite of the fact that more water was required for unmilled binder in comparison with ground one. Further, when samples were formed, water segregation was observed. Basing on the analysis of the obtained dependences, the optimal specific surface of the developed synthanite was accepted Ssp = 500-600 $m^2$/kg.

The optimal conditions for hardening were defined in this work. As synthanite is similar to gypsum, air-dry conditions and samples drying were tested. Besides, samples holding above water was applied (wet conditions of hardening). The most favourable medium for synthanite hardening is air-dry, when resistance in compression and bending at the age of 28 d is 15.7 and 3.0 MPa. When samples were dried, their resistance was 8.2 and 1.8 MPa, after hardening in wet conditions – 6.7 and 1.1 MPa. Synthanite is hardened slowly, so during intensive drying when samples are dewatered quickly, and process of hydration slows down. In wet conditions calcium sulfate dihydrate (cementing binder) is dissolved when there is excess of water, and that causes resistance decrease. Hardening in air-dry conditions contributes to creation of the required prerequisites for synthanite hardening and for its structure formation. The structure of synthanite at the age of 28 d is shown in Figure 3.



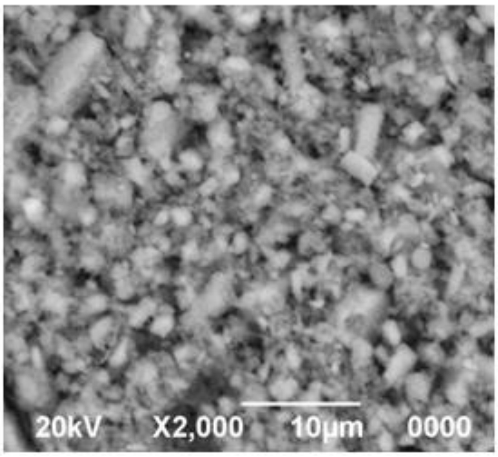




*Figure 3: The structure of synthanite at the age of 28 d*

The results of defining physical-technical properties of air-hardening synthanite with the optimal composition (Fluoro-Anhydrite neutralised with lime up to pH 7-8 - 80-90 % mass; caustic lime - 10-20, % mass.) are provided in Table 2. The obtained binder based on air-hardening Fluoro-Anhydrite corresponds to grades according to resistance 100; 125; 150.

*Table 2: The outcomes of the research on optimisation of synthanite composition*

| Specific surface, $m^2/kg$ | pH | Normal consistency, % | Setting time, h-min (begin. / end) | Ultimate resistance at the age of 28 d, MPa (in compression / in bending) | Grades according to resistance | Softening coefficient |
|---|---|---|---|---|---|---|
| 500-600 | 10-12 | 40.5-41.5 | 2-10 – 2-50 / 4-10 – 5-40 | 10.5-15.1 / 2.0-3.4 | 100-150 | 0.46 |

There are the results of the selection of the composition of dry plaster. It was found out that when binder : filler ratio is varied in the range of the following values - from 1:2 to 1:4, the binder consumption is reduced considerably and that causes a decrease of operational characteristics of the mortar (Table 3). The optimal binder : filler ratio in the plaster of the grade not lower than M50 is 1:2.5 (composition 2, Table 3).

*Table 3: Influence of binder: sand ratio on the properties of dry plaster*

| Composition | Binder : sand ratio | Water : binder ratio | Ultimate compressive resistance of the mortar, MPa | Plaster adhesion strength, MPa |
|---|---|---|---|---|
| 1 | 1:2 | 0.52 | 8.8 | 0.41 |
| 2 | 1:2.5 | 0.55 | 8.0 | 0.35 |
| 3 | 1:3 | 0.61 | 6.6 | 0.28 |
| 4 | 1:3.5 | 0.66 | 5.4 | 0.16 |
| 5 | 1:4 | 0.72 | 3.8 | 0.08 |

Filler consumption decrease from the optimal one causes overconsumption of the binder, filler consumption increase causes some decrease of physical-technical properties. Besides, binder : filler ratio increase more than 1:2.5 causes plaster adhesion strength decrease lower than it is required for pasters of specified level, that equals 0.35 MPa. Binder : filler ratio that equals 1 : 4 can be recommended for the dry plaster of the grade lower than M50. Then methyl- hydroxyethyl-cellulose – Tylose MH 60010 P4 produced by Clariant (Germany) was used as water-retaining admix to dry plasters. The use of tylose additive in the amount 0.2 % of mortar mass increased water-retaining capability up to the required specified one (for plasters not less than 95 %) (Table 4).

Test results concerning main physical-technical properties of mortar samples made from dry plasters of optimal composition (for strength class grade M50 / M25, mass %: synthanite – 33.27-24.95 / 20-19.5; sand – 66.55-74.83 / 79.82-80.28; cellulose ester – 0.18-0.22 / 0.18-0.22; water – 59.5-61.5 / 75.5-77.5) are provided in Table 5. The obtained plasters are of good remoldability and low delaminatability. The surfaces are easy to float during plastering, visible shrinkage cracks are not formed. The developed compounds of mix mortars can be recommended for refurbishment of premises (inside surfaces of walls and ceilings) under normal and dry operation conditions.

*Table 4: Influence of MH 60010 P4 admix on the properties of dry plaster*

| Additive content, in % of mass | Water/binder ratio | Water-holding capacity, % | Ultimate compressive resistance of the mortar, MPa | Plaster adhesion strength, MPa |
|---|---|---|---|---|
| 0 | 0.54 | 84 | 8.1 | 0.35 |
| 0.15 | 0.59 | 93 | 7.3 | 0.40 |
| 0.20 | 0.60 | 96 | 6.7 | 0.42 |
| 0.25 | 0.62 | 98 | 6.2 | 0.46 |

*Table 5: Comparative characteristics of synthesized dry plasters*

| Property | Grade according to resistance | |
|---|---|---|
| | M50 | M25 |
| Indicator of mortar properties | | |
| Service life, h | 2.5 | |
| Grade according to consistency | Pk3 | |
| Water-holding capacity, % | 95-97 | |
| Delaminatability | 1.5 | |
| Remoldability | Composition is plastic | |
| Indicator of hardened mortar properties | | |
| Ultimate compressive resistance, MPa, | 5.5-7.4 | 2.7-3.2 |
| Adhesional strength in mechanical separation, MPa | 0.4 | - |
| Average density, kg/m$^3$ | 1800 | |
| Softening coefficient | 0.3-0.4 | |

## 4. Conclusions

It has been established that during mechanical-chemical activation in the presence of an activating component, acid pre-neutralisation, acceleration of the processes of hydration and hardening synthanite are provided, due to the complementary and mutually reinforcing effect of chemical and mechanical activation.

- The nature of the influence of the dispersion of the neutralising agent on the completeness of the neutralisation reaction of Fluoro-Anhydrite, which is manifested in a more complete neutralisation process due to the intensification of chemical reactions, which allows reducing the consumption of the neutralising component, is revealed.
- Optimal parameters of mechanical-chemical activation of Fluoro-Anhydrite are substantiated. Ensuring that the pH level of the binder mixture reaches 10-12 leads to an improvement in the physical and technical properties of the synthanite: an increase in strength by 3.5-4 times, a reduction in the setting time by up to 9-12 times.

– The possibility of involving a secondary product in the production of building materials-the waste hydrofluoric production, which will ensure the environmental safety of the environment of the region under consideration and the rational use of industrial waste in construction, is shown.

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