Binders from gypsum-containing waste and products based on them

IOP Conf. Series: Materials Science and Engineering **945** (2020) 012057 doi:10.1088/1757-899X/945/1/012057

Binders from gypsum-containing waste and products based on them

N I Alfimova[1*], S Yu Pirieva[1], M Yu Elistratkin[1], I S Nikulin [2] and A A Titenko[3]

[1]Belgorod State Technological University named after V.G. Shukhov, 46 Kostyukova str., Belgorod, 308012, Russia
[2]Belgorod National Research University, 85 Pobedy st., Belgorod, 308015, Russia
[3]Engineering Center NRU "BelSU", Belgorod, 2a/712, Koroleva st., Belgorod, 308015, Russia

E-mail: alfimovan@mail.ru

Abstract. Gypsum binders are among the most environmentally friendly from the point of view of their production. The raw material base for their production is represented not only by natural raw materials, but also by a wide variety of technogenic materials, phosphogypsum is the most multi-ton and studied of them. At the same time, citrogypsum is also a promising raw material for the production of gypsum binders and, in comparison with phosphogypsum, does not contain toxic impurities that require the development of additional measures for their removal. Synthesis of the binder from gypsum-containing waste is possible with the use of various technologies using autoclaves, chemical reagents and at elevated temperature and atmospheric pressure. Each method has its own advantages and disadvantages. The most acceptable from the point of view of industrial production is the method of calcination at atmospheric pressure, but it does not allow producing high-strength binders and products based on them. It is possible to increase the efficiency of using such binders for the production of small-piece products by applying special molding modes with increased pressing pressure. The possibility of obtaining a binder from the waste of citric acid – citrogypsum production by calcination in a semi-industrial plant is shown. Using standard methods, a complete analysis of the resulting binder was performed: granulometry, grain shape and morphology, normal density and setting time. A comparison was made with construction gypsum (G5) and high-strength gypsum (G16). The possibility of obtaining small – piece products from a synthesized binder with a dry compressive strength of 20 MPa is shown by using the semi-dry pressing method at high pressures.

1. Introduction

Gypsum binders and products based on them have always been very popular in the construction materials market, this is due to the simplicity and environmental friendliness of their production, low energy costs, capital investment and metal consumption of equipment for the production of this type of binders in comparison with cement. However, not all regions have a raw material base for their production. An alternative in this case can be gypsum-containing waste from various industrial productions.

To date, there is a wide range of research in the world aimed at considering ways to dispose of gypsum-containing industrial waste (GCW) [1-4, etc.], including as raw materials for the production of

single- and multi-component binders [5-23]. Prerequisites for this research is the fact that the volume of natural gypsum stone extracted for the production of binders using traditional technology is significantly lower than the volume of GCW of various industries that are annually received in dumps. Currently, there are more than 50 types of technogenic gypsum-containing raw materials, which were considered as objects of research by various scientific groups [1].

The main difficulty in the way of large-scale and widespread use of gypsum-containing waste in the production of binders is the difficulty in applying standard technological modes and equipment used in the production of binders from natural raw materials. This is due to a number of features inherent in GCW, in particular their high humidity, dispersion, the presence of a large number of impurities in their composition, the amount and nature of which varies significantly and depends on the raw material and the technological cycle during which it was formed. Analysis of literature sources has shown the presence of a large number of variations in technologies for obtaining binders from gypsum-containing waste from various industries around the world.

Most of the research is focused on phosphogypsum, which is due to the large-scale nature of this raw material [2-4, 24], but this type of gypsum-containing waste is characterized by an increased content of impurities, including radioactive ones, which determines the need to search for methods of cleaning it before entering the production process. Another by-product of the industry containing calcium sulfate is citrogypsum – a waste of the biochemical production of citric acid. The volume of this raw material is much smaller (0.03-0.04 million tons per year.) [1], however, for a number of regions where there are accumulations of these raw materials, the problem of their processing is relevant not only from the point of view of solving environmental issues, but also from the point of view of expanding the raw material base.

There are studies aimed at considering the possibility of obtaining a binder from citrogypsum under conditions of high atmospheric pressure and temperature [25-27] and by the non-firing method using sulfuric acid as a chemical reagent [17-22]. The first method is characterized by high energy costs and the need for special equipment, the second – less energy, however, its disadvantages include the complexity of the technological process, gradual monitoring and sampling, creating unfavorable working conditions rapid wear of the equipment. Despite the fact that these studies have proved the possibility of obtaining α-modification gypsum binder with strength of up to 30 MPa, these disadvantages do not allow the organization of cost-effective production of gypsum binders by these methods.

As an alternative, we can consider the synthesis of gypsum binders from GCW by calcination, this method is the simplest from the point of view of the arrangement of the production process and equipment, but its disadvantages include the possibility of synthesizing only calcium β-semihydrate with low physical and mechanical parameters of the synthesized binder. First of all, this is due to the high specific surface area of the gypsum-containing waste itself and, as a result, the binder obtained on their basis, as well as the porosity of the particles, which determines increased water absorption and, as a result, a decrease in the compressive and bending strength of both the binder and products based on them.

This problem can be solved by using superplasticizers of different nature [28, 29], which, according to the results of various studies, can increase the strength of the binder obtained from phosphogypsum to an average of 15 MPa, and in some cases up to 29 MPa [29].

Another method of increasing the efficiency of use of such plaster is a cementitious molding with the use of elevated pressures. In particular, a group of researchers proved the possibility of obtaining plaster tiles – an analog of plasterboard. [30, 31] from a gypsum binder ($CaSO4•0.5H2O$) obtained from phosphogypsum. In the first case [30] phosphogypsum was washed and dewatered at a temperature of 150 °C, moistened to produce granules, then repeated pressing was performed in an aqueous medium at a pressure of 20 MPa with a frequency of once every 2 minutes for 24 hours. The bending strength of the resulting tile is 18.9 MPa. In the second [31], phosphogypsum was dehydrated at a temperature of 170 °C. Pressing time – 3 hours, the frequency of application of the load – every 10 minutes. The bending strength of the obtained samples was 14.7 MPa.

In this regard, this paper considers the possibility of obtaining gypsum binders from the waste of the biochemical production of citric acid – citrogypsum (Belgorod, Russia) by calcination and products based on them using the method of semidry molding at high pressures.

2. Materials and methods

The object of research was the waste of the biochemical production of citric acid – citrogypsum Belgorod, Russia.

The element and chemical composition of the studied raw materials is shown in Fig. 1 and table 1, respectively.

Visually citrogypsum is a gray powder with high specific surface area. The analysis of the morphology of citrogypsum particles made with the help of SEM showed that this raw material is mainly represented by large plate-shaped particles with a developed surface, against which the column-shaped particles are visible (Fig. 2).

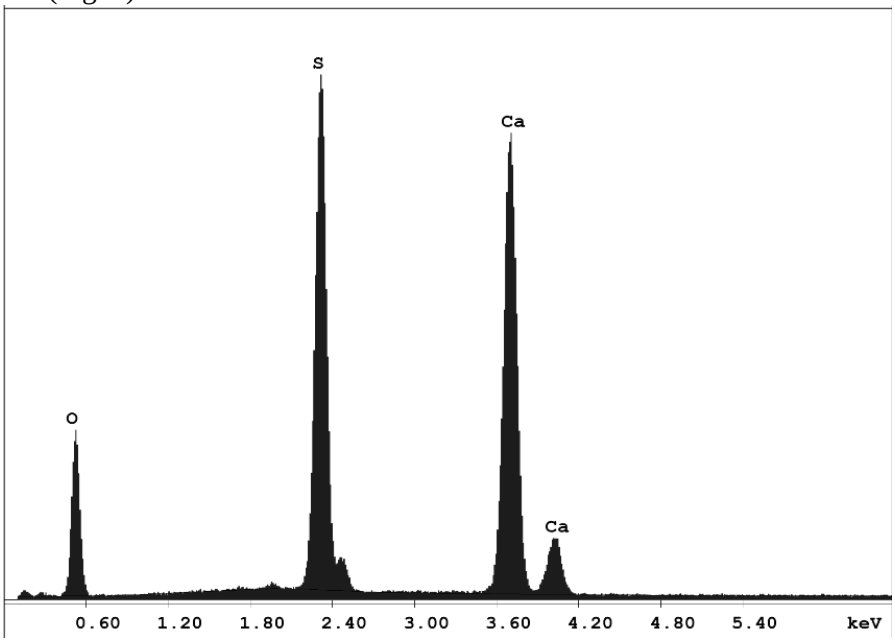

Figure 1. Elementwise composition citrogypsum, Belgorod, Russia.

Table 1. Chemical composition of citrogypsum.

Content of oxides, %				
CaO	SO_3	SiO_2	MgO	o.e.r
29.7–31.5	44.0–45.5	0.3–1.2	0.1–0.4	rest

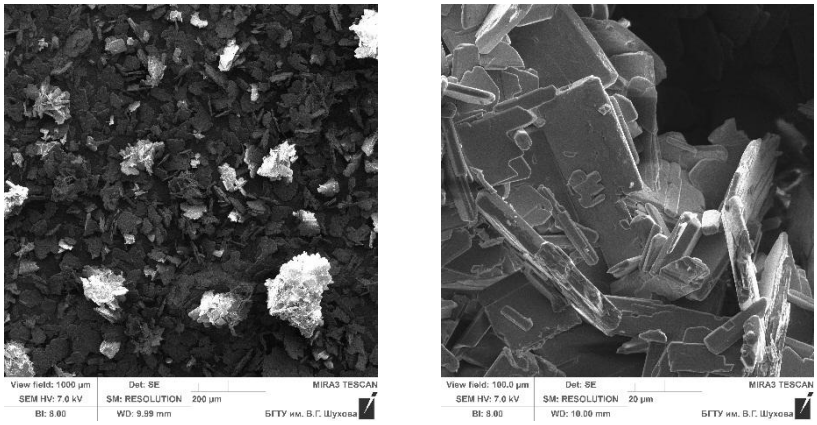

Figure 2. Morphology of the citrogypsum particles.

The process of waste accumulation in the waste storage facility has been carried out for 50 years. The total storage area is about 58.5 thousand m^2, the total reserves according to preliminary estimates – 351.2 thousand m^3. The humidity of waste in its natural state is about 80 % by weight. Their storage was collected by bucket excavators followed by mixing to average the material composition, drying to a humidity of 30 % by weight, carried out in natural conditions in the open air, by periodic mixing.

When producing gypsum stone by semidry pressing, perlite dust with a bulk density of 75 kg/m^3 was used as filler; with a granule size of 5 to 100 microns.

Test methods of gypsum binders were carried out according to GOST 23789-79.

The analysis of the particle surface morphology was performed using a high-resolution scanning electron microscope TESCAN MIRA 3 LMU, which includes an x-MAX 50 Oxford Instruments NanoAnalysis energy-dispersed spectrometer.

Qualitative assessment of the material composition of raw materials was carried out using x-ray phase analysis (RPA). The research was carried out in the range of double angles 2θ 4÷56° using the powder method by means of a general-purpose x-ray diffractometer (DRON-3M) operating in automated mode using the PELDos program.

The granulometric composition of powdered materials was determined using the laser granulometry method on the ANALYSETTE 22 NanoTec plus laser particle analyzer.

Production of the binder by firing was carried out in a semi-industrial installation. Based on the results of numerous studies in this field, a mode was chosen in which the temperature of the binder at the output was about 120 °C.

To obtain the binder in the laboratory, a heat chamber was used.

3. Results

The specific surface area of the resulting binder was 600-650 m^2/kg.

When determining the normal density, it was found that for a gypsum test with a spreading capacity of 180±5 mm, 370 water is needed for 300 g of gypsum binder, thus NG=123%.

According to the terms of setting, the resulting gypsum binder according to GOST 125-79 refers to a normally hardening one (index B, beginning no earlier than 6 min, ending no later than 30 min) (table 2).

Table 2. Setting time of the produced binder.

Water inflow time, h-min	Start of setting time, h-min	End of setting time, h-min	Start of setting, h-min	End of setting, h-min
9-37	9-55	10-07	0-18	0-30

The strength of samples made from gypsum paste of standard consistency is determined 2 hours after the contact of the gypsum binder with water. According to this indicator, the tested sample of gypsum binder does not meet the requirements of GOST 125-79.

The ultimate strength of samples-beams with dimensions of 40 × 40×160 mm at the age of 2 h, formed from gypsum paste with a humidity of 30 % on a vibrating platform (non-standard method), was 2.5 MPa (25 kgf/cm^2) at bending, 3.3 MPa (34 kgf/cm^2) at compression. Gypsum binder conditionally (due to non-standard molding methods and normal density) can be attributed to the G-3 brand.

The analysis of the particle size of the obtained binder and comparison with high-strength gypsum and citrogypsum was carried out (Fig. 3). The graphs show that high-strength gypsum is characterized by a polymodal distribution of particles in a wider range, while the graphs that characterize the granulometry of the original citrogypsum and the binder are single-modal with a distribution of particles in a narrower range. It should also be noted that after high-temperature exposure, the particle size decreases slightly, which is due to the settling of a larger fraction during the passage of citrogypsum through the turbine-type dryer.

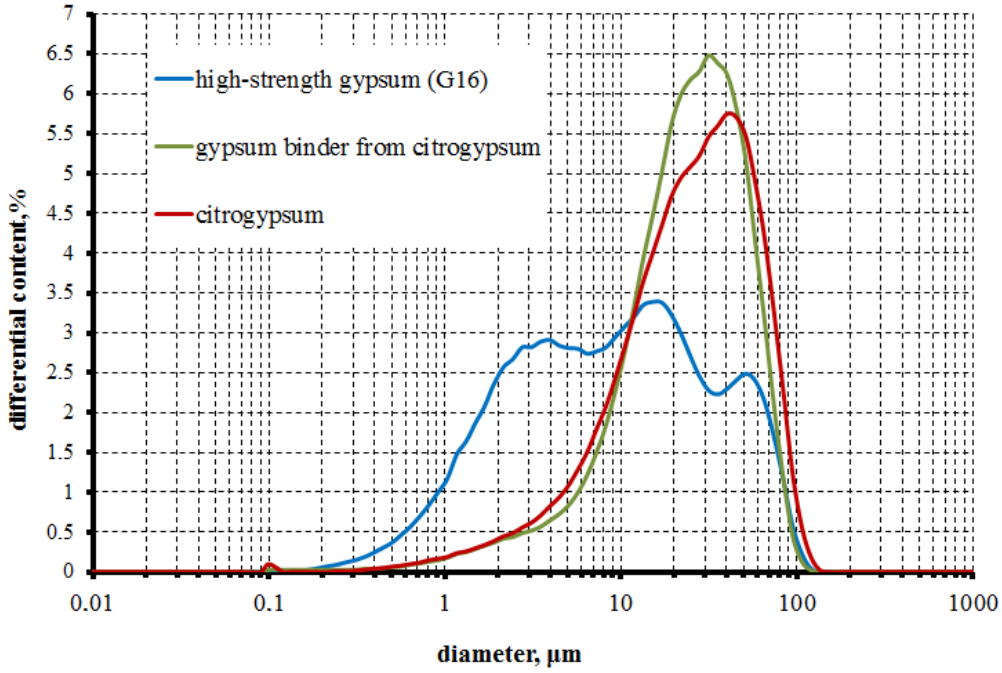

Figure 3. Granulometric composition of citrogypsum and gypsum binders.

Comparative analysis of the obtained binder particles with construction (G-5) and high-strength gypsum (G-16) revealed differences in their morphology and size. Thus, in photos of high-strength gypsum, enlarged columnar crystals stand out clearly against the background of small particles of polydisperse composition (Fig. 4. c). For building gypsum, there is also a significant spread of particles in size and the presence of elongated crystals, but their size is much smaller (Fig. 4, b). At the same time, the crystals of the binder obtained from citrogypsum have a lamellar shape and not a significant size range.

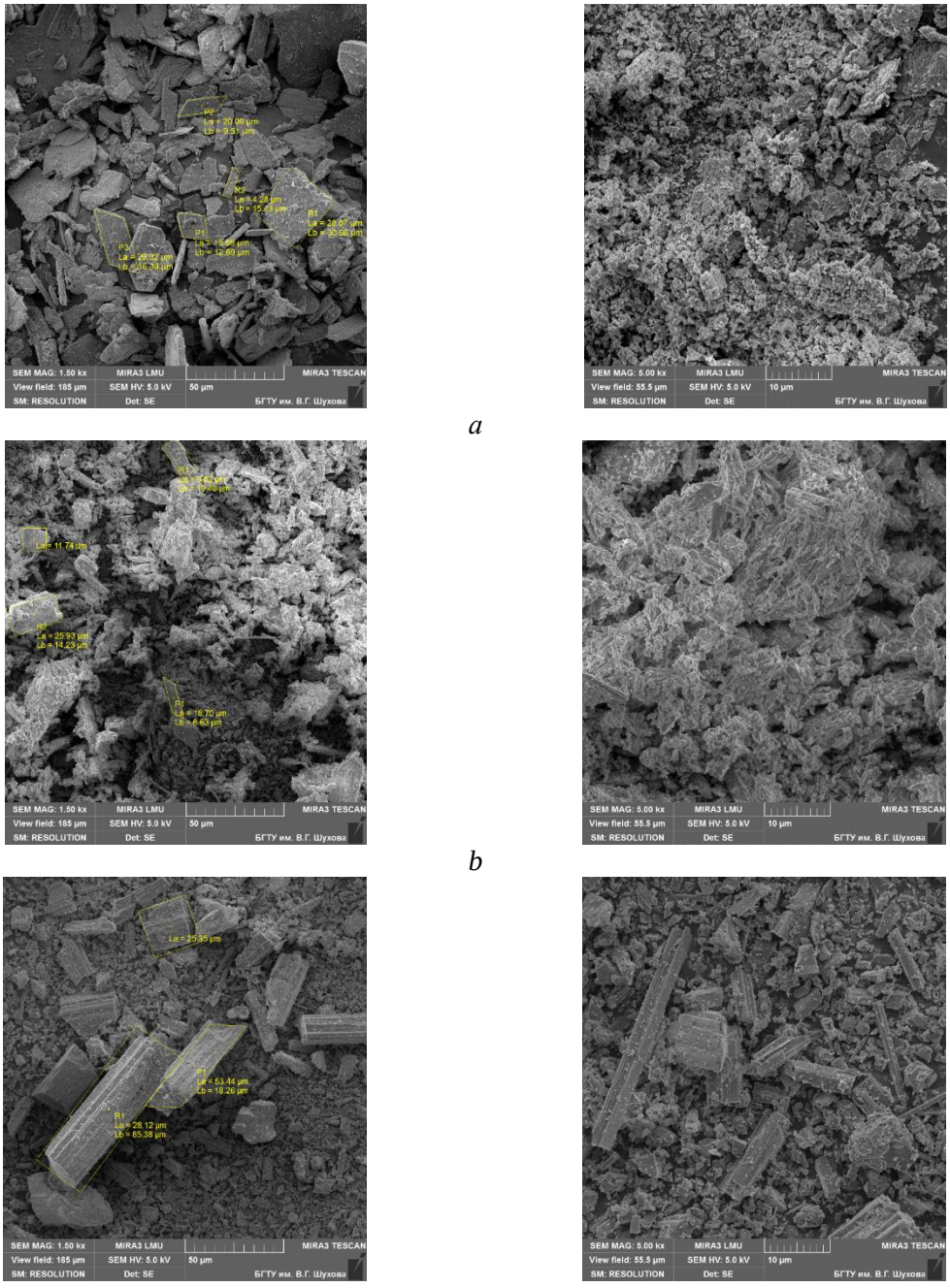

Figure 4. The morphology of the particles of gypsum binders
a – binder from citrogypsum; b – building gypsum (G-5) c – high-strength gypsum (G-16).

4. Discussion

According to the results, the gypsum binder obtained from citrogypsum corresponds to the setting time of normally hardening construction gypsum. However, the determination of the strength of samples made from gypsum paste of standard consistency at the age of 2 hours showed that they do not meet the requirements of the standard.

Production of products using injection molding technology from a synthesized binder is not possible due to its low strength. However, the fact that reducing the water demand of gypsum paste to 30 %

and the use of vibrocompression allowed obtaining samples with a compressive strength of 3.3 MPa, gave reason to believe that the use of non-standard molding methods, in particular, pressing at high pressures, will allow obtaining products with the necessary physical and mechanical characteristics.

In particular, a patent was obtained [32] for the composition of the raw mixture and a method for producing gypsum stone.

The raw mixture consisted of a binder obtained from citrogypsum and perlite dust. Perlite dust was water-saturated before mixing with a gypsum binder made of citrogypsum, which made it easier to mix and obtain a homogeneous mass without the formation of lumps and a uniform distribution of moisture by volume. After that, the molding mass was sent to the mold and held for 30 seconds under a pressing pressure of 10 MPa.

High specific surface of the binder of citrogypsum in conjunction with the proposed method of molding increases the number of contacts between particles, while low water-binder ratio (water is taken in an amount sufficient for the occurrence of a chemical reaction) minimizes the number of pores formed during evaporation of excess moisture and amount of the involved air, which in the aggregate contributes to the strength of the final product.

The composition of the raw material mixture and physical and mechanical characteristics are shown in table 5.

Table 3. Raw mix compositions and physical and mechanical characteristics of products.

Material consumption % by weight			Water-binder ratio	Compressive strength after stripping MPa	Compressive strength 2 hours after pressing, MPa	Compressive strength of dry products, MPa	Water absorption, %
Binder, obtained from citrogypsum	Perlite dust	Water					
83	1.5	15.5	0.18-0.19	2.5	15–16	19–20	No more than 5 %

5. Summary

The principal possibility of obtaining a gypsum binder from the waste of the biochemical production of citric acid – citrogypsum by calcination is shown.

The possibility of increasing the efficiency of the binder obtained from citrogypsum as a raw material for the production of small-piece products using semidry pressing technology is proved. The strength of the products obtained using this technology after stripping was 2.5 MPa, which will significantly reduce the number of defects formed at this stage of product production, and will also allow the production of multi-hollow products. The compressive strength of products in the dry state reached 20 MPa.

6. References

[1] 2004 Plaster materials and products (production and use) *Directory. Edited by A V Ferronskaya. Publishing House ASV* 488 (rus)

[2] Rashad A M 2017 Phosphogypsum as a construction material *Journal of Cleaner Production* **166** 732–743 doi:10.1016/j.jclepro.2017.08.049.

[3] Cánovas C R, Macías F, Pérez-López R, Basallote M D, Millán-Becerro R 2018 Valorization of wastes from the fertilizer industry: Current status and future trends *Journal of Cleaner Production* **174** 678–690 doi:10.1016/j.jclepro.2017.10.293

[4] Klimenko V G 2018 Influence of modifying composition of gypsum binders on the structure of composite materials *Journal of Physics: Conference Series* **1118 (1)** 43285 doi: 10.1088/1742-6596/1118/1/012019

[5] Yang J, Liu W, Zhang L, Xiao B 2009 Preparation of load-bearing building materials from au-

toclaved phosphogypsum *Construction and Building Materials* **23(2)** 687–693 doi:10.1016/j.conbuildmat.2008.02.011
[6] Myasnikov N F, Bershakov N G, Kozlov V P, Naumov E G, Shevchenko N N 2003 Gypsum binder preparation method *Patent RF* 2210540
[7] Semlyov V S, Reutov V A, Kondrikov N B 2008 Method of recycling gypsiferous raw materials *Patent RF* 2324654.
[8] Gubskaya A G, Podluzsky E Ya, Melenko V S 2018 Production of gypsum binder and products from natural and industrial raw materials in the Republic of Belarus *Building Materials* **3** 73–75 (rus)
[9] Ma B, Jin Z, Su Y, Lu W, Qi H, Hu P 2020 Utilization of hemihydrate phosphogypsum for the preparation of porous sound absorbing material *Construction and Building Materials* **234** 117346 doi:10.1016/j.conbuildmat.2019.117346
[10] Li X, Zhang Q, Ke B, Wang X, Li L, Li X, Mao S 2018 Insight into the effect of maleic acid on the preparation of α-hemihydrate gypsum from phosphogypsum in Na_2SO_4 solution, Journal of Crystal Growth **493** 34–40 doi:10.1016/j.jcrysgro.2018.04.025
[11] Li X, Zhang Q, Shen Z, Li L, Li X, Ma S 2019 L-aspartic acid: A crystal modifier for preparation of hemihydrate from phosphogypsum in $CaCl_2$ solution *Journal of Crystal Growth* **511** 48–55 doi:10.1016/j.jcrysgro.2019.01.027
[12] Lu W, Ma B, Su Y, He X, Jin Z, Qi H 2019 Preparation of a-hemihydrate gypsum from phosphogypsum in recycling $CaCl_2$ solution *Construction and Building Materials* **214** 399–412 doi:10.1016/j.conbuildmat.2019.04.148
[13] Ma B, Lu W, Su Y, Li Y, Gao C, He X 2018 Synthesis of α-hemihydrate gypsum from clean-er phosphogypsum *Journal of Cleaner Production* **195** 396e405 doi:10.1016/j.jclepro.2018.05.228
[14] Guan B, Yang L, Wu Z, Shen Z, Ma X, Ye Q 2009 Preparation of α-calcium sulfate hemihydrate from FGD gypsum in K, Mg-containing concentrated $CaCl_2$ solution under mild conditions *Fuel* **88** 1286–1293 doi:10.1016/j.fuel.2009.01.004
[15] Shen Z X, Guan B H, Fu H L, Yang L 2009 Effect of Potassium Sodium Tartrate and Sodium Citrate on the Preparation of α-Calcium Sulfate Hemihydrate from Flue Gas Desulfurization Gypsum in a Concentrated Electrolyte Solution *J. Am. Ceram. Soc.* **92** 2894–2899 doi:10.1111/j.1551-2916.2009.03330.x
[16] Guan B, Kong B, Fu H, Yu J, Jiang G, Yang L 2012 Pilot scale preparation of a-calcium sulfate hemihydrate from FGD gypsum in Ca–K–Mg aqueous solution under atmospheric pressure *Fuel* **98** 48–54 doi:10.1016/j.fuel.2012.03.032
[17] Tarasova G I, Sverguzova S V, Bubnova N Yu, Kozlov V P, Naumov E G 1999 Method of gypsum article making *Patent RF* 2132310.
[18] Sverguzova S V, Tarasova G I, Bubnova N Yu 1998 Promising technologies for the processing of citrogypsum *Ecology and Industry of Russia* **8** 20–24 (rus)
[19] Sverguzova S V, Bubnova N Yu, Tarasova G I 2001 Utilization of gypsum-containing waste by energy-saving technology *Science-production* **3** 41–43 (rus)
[20] Sverguzova S V, Chernysheva N V, Chernysh L I, Shamshurov A V 2010 The in-fluence of the processing conditions of citrogyp-sum on the composition of the obtained gypsum bind-er, *Building Materials* **7** 31–32 (rus)
[21] Sverguzova S V, Tarasova G I, Chernysheva N V, Chernysh L I 2010 Theoretical substantiation of the possibility of non-fired de-hydration of citrogypsum *Bulletin of BSTU named after V. G. Shukhov* **2** 117–121 (rus)
[22] Chernysheva N V, Sverguzova S V, Tarasova G I 2010 Obtaining a gypsum binder from phosphogypsum of Tunisia *Building Materials* **7** 28–30 (rus)
[23] Jin Z, Ma B, Su Y, Lu W, Qi H, Hu P 2020 Effect of calcium sulphoaluminate cement on mechanical strength and waterproof properties of beta-hemihydrate phosphogypsum *Construction and Building Materials* **242** 118198 doi:10.1016/j.conbuildmat.2020.118198

[24] 2020 Mineral Commodity Summaries *Department of the Interior, U S Geological Survey 122*–123 https://minerals.usgs.gov/minerals/pubs/mcs/2016/ mcs2020.pdf
[25] Lukyanova A N, Starostina I V 2013 Building composite materials based on modified gypsum binders obtained from industrial wastes *Fundamental Research* **4(4)** 818–822 (rus)
[26] Edamenko A S, Klimenko V G 2013 About the possibility of using technogenic raw materials in the production of building materials *Internet magazine "Technosphere safety technologies"* **1 (47)** (rus)
[27] Nesterova L L 2016 Possibility of obtaining gypsum binder from citrogypsum *Bulletin of the Yugorsk State University* **2 (41)** 29–33 (rus)
[28] Zheng C, Yu Q, Ning P, Ma J-B, Zheng Y-L 2015 Preparation of β-hemihydrate gypsum with phosphogypsum *Xiandai Huagong/Modern Chemical Industry* **35 (5)** 60–63
[29] Bumanis G, Zorica J, Bajare D, Korjakins A 2018 Technological properties of phosphogyp-sum binder obtained from fertilizer production waste *Energy Procedia* **147** 301–308 https://doi.org/10.1016/j.egypro.2018.07.096
[30] Zhou J., Sheng Z., Li T., Shu Z., Wang Y 2016 Preparation of hardened tiles from waste phos-phogypsum by a new intermittent pressing hydration *Ceram. Int.* **42** 7237–7245 doi:10.1016/j.ceramint.2016.01.117
[31] Zhou J, Li X, Zhao Y, Shu Z, Wang Y, Zhang Y, Shen X 2020 Preparation of paper-free and fiber-free plasterboard with high strength using phosphogypsum *Construction and Building Materials* **243** 118091 doi:10.1016/j.conbuildmat.2020.118091
[32] Alfimova N I, Titenko A A, Nikulin I S, Galdun Yu V, Pirieva S Yu, Elistratkin M Yu 2018 Raw mixture for modified citrogypsum articles and method of their production *Patent RF* 2693808.

Acknowledgments
The work was carried out as part of the implementation of activities of the world-class scientific and educational center “Innovative Solutions in the Agricultural Sector”of Belgorod State University. Agreement #50 of 07.08. 2020; using equipment of High Technology Center at BSTU named after V G Shukhov.