Biosafety binder based on gypsum-bearing waste

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Abstract. Gypsum-based binders and obtained gypsum materials and products are widely used in the world-building materials market. However, not everywhere there is a natural raw material base for their production. In connection with this feature, gypsum-containing wastes from different industries are of particular interest, which can potentially be used as an analogue to natural gypsum stone. One of these alternative options is gypsum-containing waste – citrogypsum. Citrogypsum is a by-product of the biochemical synthesis of citric acid. Based on the fact that 95–97 % of citrogypsum is represented by calcium sulfate dihydrate, it can be considered as an alternative replacement for natural gypsum stone in gypsum binder production. Citrogypsum is stored in open dumps, contacting with the environment medium. The fungus *Aspergillus niger* can be found in cytogypsum, which is used as a culture for the microbiological synthesis of molasses in the production of citric acid. *Aspergillus niger* is a species of higher molds of the genus *Aspergillus* and can cause disease in humans and animals. In this connection, biotesting of the raw material (citrogypsum) and gypsum binders obtained by sintering citrogypsum using oats (*Avena sativa L*) and cladocerans (*Daphnia magna*) was carried out. Gypsum plaster grade G5 was used as control samples. The results of the research allowed concluding that the binder based on citrogypsum meets environmental safety standards. It does not contain a fungus *Aspergillus niger* that is dangerous to human health. So, it can be used for the production of building products.

1 Introduction

Gypsum-based binders and obtained gypsum materials and products are widely used in the world-building materials market. Howe – ver, not everywhere there is a natural raw material base for their production. In connection with this feature, gypsum-containing wastes from different industries enterprises are of particular interest, which can potentially be used as an alternative to natural gypsum stone. One of these alternative options is gypsum-containing waste – citrogypsum.

In respect thereof, products based on gypsum binders are in great demand. This is primarily due to their environmental safety. The production of gypsum binders is realized by dehydration of $CaSO_4 \cdot 2H_2O$. Natural gypsum stone is used as the main raw material [1]. Such gypsum-containing waste from various industries as phosphogypsum, FGD-gypsum, citrogypsum, borogypsum, etc., can be used as an alternative to natural stone. The effectiveness of their use for the production of gypsum binders has been proven by numerous studies around the world. This approach allows not only expanding the raw material resources of the region but also solving the problem of accumulation of gypsum-containing waste, the volumes of which are significant throughout the world [1–3].

However, the use of gypsum-containing waste for the production of gypsum binders has some features that are associated with the specifics of raw materials, namely, their unstable material and granulometric composition, the presence of impurities, the type and amount of which depends on the production technology. All of this must be taken into account when developing technology and choosing a technology for production [3].

Cytrogypsum is a gypsum-containing waste that is formed as a result of the biochemical synthesis of citric acid. Unlike phosphogypsum, CG does not contain heavy metal impurities and does not require the search additional ways for their removal, and therefore, it is preferable as an alternative to natural gypsum stone for the production of binders.

Citrogypsum storage facility is located on the territory of Belgorod (Russia). The waste accumulation process was realized for 50 years. The storage area is about 58500 m^2 where the waste was accumulated during a fifty years. The total reserves are 351200 thousand m^3 (Fig. 1). At present time, the technology has been developed for processing this waste into a binder by sintering it in drum dryers [4].

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Fig. 1. General view of the citrogypsum storage

However, when using citrogypsum-based binders to priduce construction materials and products, it is necessary to take into account special aspects of the synthesis of $C_6H_8O_7$-acid. $C_6H_8O_7$ is found in significant quantities in the fruits of various fruits and berries (strawberries, raspberries, etc.). Initially, citric acid was extracted chemically from citrus fruits, but this method has many of the following significant disadvantages that make this technology economically inefficient, such as:

- high cost of raw materials;
- multi-stage technology;
- the need to use toxic chemicals;
- low yield of the final product.

Due to a large number of disadvantages of the chemical method, citric acid is currently obtained from sugar-containing products using the activity of microorganisms. The use of this method greatly simplifies the technological process, since it includes only one technological operation – fermentation. At the same time, the yield of the final product vs. the chemical method is much higher, which positively affects the cost of the final product [5].

The most valuable source of raw materials for the synthesis of citric acid is currently considered molasses. It should also be noted that in outfits with a high content of fructose and sucrose, molasses contains substances necessary for the life of the fungus. It is when using molasses that the maximum yield of citric acid is achieved. Synthesis of $C_6H_8O_7$ is schematically demonstrated in Figure 2.

The main microorganism used to produce citric acid is *Aspergillus niger*. This is associated with easy to handle, ferments various cheap raw materials, and provides a high yield [5–7]. However, it should be noted that *Aspergillus niger* is a species of higher molds from the genus *Aspergillus*. With increased humidity on the premises and the presence of a nutrient medium, this fungus can multiply intensively with the release of microtoxins, the action of which adversely affects the health of humans and animals [8, 9].

Although the production of citrogypsum-based binders is realized by sintering at a temperature of 120–150 °C [1] that is sufficient to ensure the death of the spores of this fungus, the openness of production does not provide a full guarantee.

Thus, given the constant contact of cytrogypsum with an open atmosphere, as well as the possibility of the presence of spores of the microscopic fungus *Aspergillus niger* in the initial raw material (cytrogypsum) and citrogypsum-based binder since this fungus is a producer of citric acid in the technology of its production, the need to assess the microbiological contamination of the binder takes place. It was the purpose of the studies presented in this article.

2 Materials and Methods

Cytrogypsum (CG) is a by-product of biochemical synthesis («Citrobel LLC», Russia). It is a white powder with a SSA about 220–250 m^2/kg. Cytrogypsum is 95–97% represented by calcium sulfate dihydrate, which is represented on the X-ray spectrum by peaks in Å: 7.628; 4.291; 3.069; 2.88; 2.69; 2.087; 3.809; 2.22 (Fig. 3). The main oxides of citrogypsum are SO_3 and CaO, respectively (Table 1).

The binder obtained by sintering citrogypsum is a white powder with a specific surface area (SSA) of the order of 350–400 m^2/kg [4].

The gypsum plaster grade G5 was used as a reference sample (All-Union State Standard 125-79).

Samples of aqueous extracts of materials were cultured in nutrient media of meat infusion agar-agar (MPA) and modified Czapek-Dox agar (CZA) in triplicate.

MPA is a solid phase or semi-liquid nutrient medium for growing microbes. It consists of meat-peptone broth in the amount of 0.5% and agar in the amount of 2%.

CZA is a semi-synthetic solid-phase nutrient medium containing sodium nitrate as a source of nitrogen ions. This medium was created for the synthesis of chlamydospores and the cultivation of fungi.

Synthesis of citrogypsum-based binder was carried out by citrogypsum dehydration under a heating process in a laboratory oven. This synthesis consists of the following technical steps:

- the first stage: the implementation of natural drying of citrogypsum in ambient conditions (at 22 °C and RH is 56-63%);
- the second stage: in the volume of citrogypsum. reached the minimum possible humidity, large stony and clay inclusions were removed;

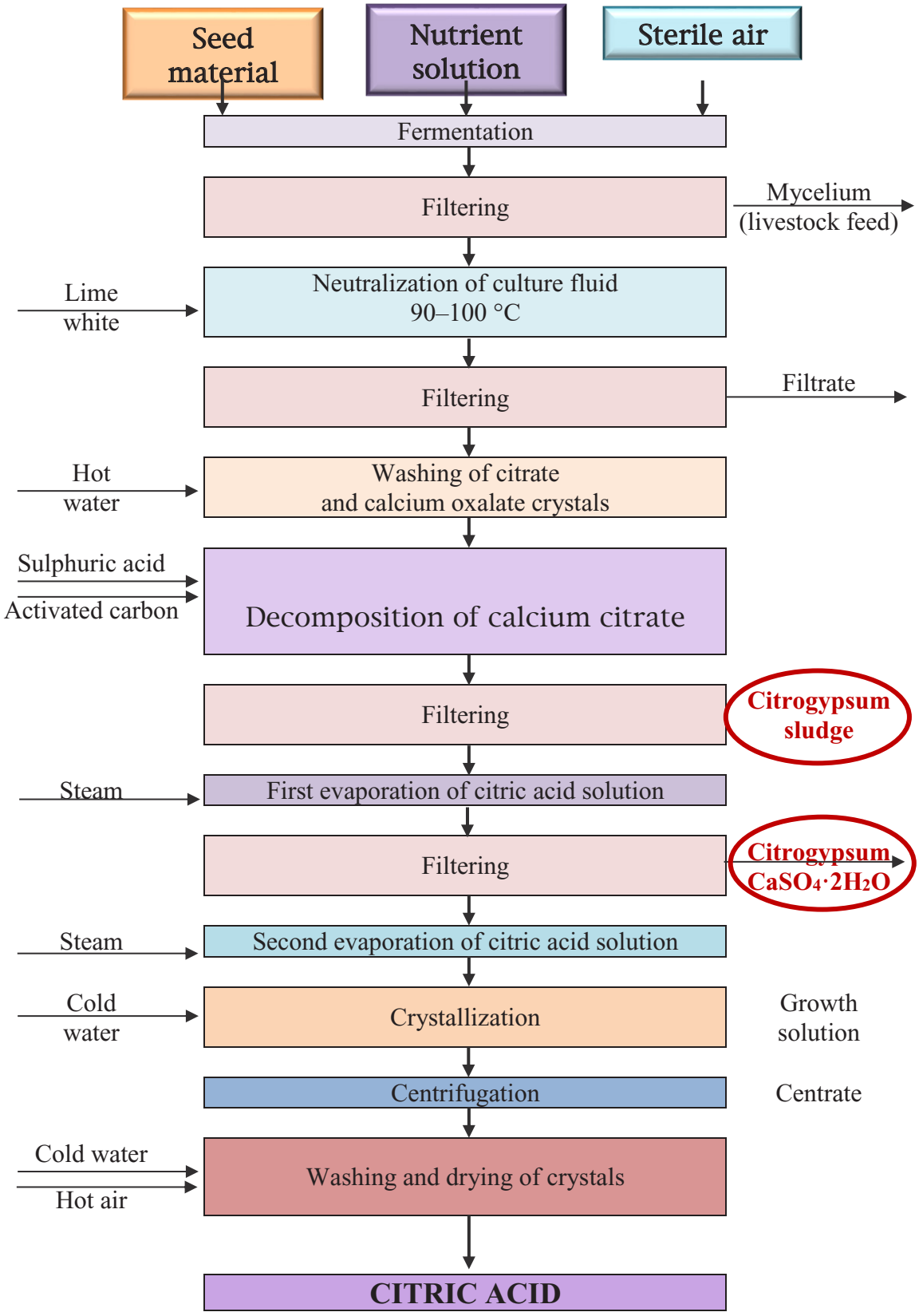

Fig. 2. Scheme of synthesis of $C_6H_8O_7$

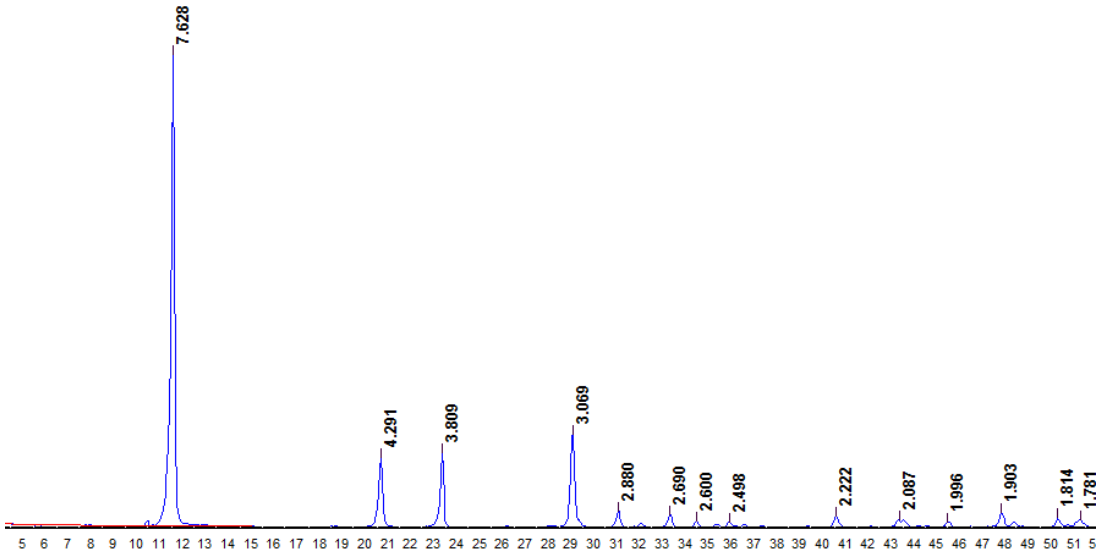

Fig. 3. X-ray spectrum of citrogypsum

Table 1. Oxide content of citrogypsum

Oxide	SO_3	CaO	SiO_2	FeO	SrO	Al_2O_3	MgO	Na_2O	P_2O_5	K_2O
Fraction of total mass, %	55.47	43.36	0.54	0.15	0.14	0.13	0.06	0.04	0.08	0.03

- the third stage: citrogypsum was poured onto a baking sheet in a volume of 2 kg and sent to a drying laboratory cabinet. To control the change in the temperature of citrogypsum, a thermocouple was immersed in its mass. The set temperature of the drying cabinet was 175 ºC. Heating was carried out until the citrogypsum reached a temperature as close as possible to the temperature of the oven (160–165 ºC);
- fourth stage: exposure of citrogypsum in an oven at a given temperature for 1 hour, followed by cooling and exposure in natural conditions (at 22 °C and RH is 56–63%) for 2 days until the mass of citrogypsum stabilizes.

The control media were an aqueous extract of G-5 commercial building gypsum, made from natura gypsum stone according to standard technology, and ordinary tap water.

Cultured in MPA

The MPA is heated in a water bath, then cooled to 40–50 °C. Sterile Petri dishes were taken; 2 ml of an aqueous extract were added, then + 10 ml of MPA. The contents were mixed gently followed by freezing, and then they were put in a thermostat for 24 hours. Then the number of colonies was counted under a magnifying glass.

Cultured in CZA

Cultivation of a sample of aqueous extracts of materials on CZA was carried out in the same sequence as inoculations for MPA under a temperature of 28–30 °C.

Biotesting with daphnids

A water extract of 100 ml was poured into the vessels; 10 individuals of Daphnia were placed there with a glass tube. Special survivors were counted after 1, 6, 24, 48, 72, and 96 sec. Individuals are considered survivors if they move freely in the water column and float to the surface no later than 15 seconds after it is lightly rocked.

Biotesting with oat

The filter paper was placed in a Petri dish. Water extract was added there and seeds were placed. Then the dish was left for 3-4 days. On the 3–4th day, germination of seeds begins, germination was assessed, and the length of the root and the ground part of the sprout is certified with accuracy in mm. The same procedure was carried out in 7 days. Further, according to such parameters as germination, condition, and length of shoots, the toxicity was assessed.

3 Results and Discussions

Biotesting of materials. Establishing class of hazard. The biotesting results using common oats (*Avena sativa L*) and cladocerans (*Daphnia magna*) are presented in Tables 2–4.

Table 2. Assessment of fungal and bacterial contamination

No.	Material name	Control indicators	
		Total colony-forming units (CFU), g	
		bacterial	fungi
1	Citrogypsum (feedstock)	66900	2100
2	Citrogypsum-based binder	56000	Not found
3	Gypsum plaster grade G5 (reference sample)	65600	800

Table 3. Biotesting results using seed oats

No.	Material name	Control indicators at the test object *Avena sativa L.*	
		Root length, cm	Student t-test value
1	Citrogypsum (feedstock)	7.2±0.7	2.07
2	Citrogypsum-based binder	5.9±0.5	0.8
3	Gypsum plaster grade G5 (reference sample)	5.0±0.5	0.4
4	Control (water)	5.3±0.6	–

Table 4. Biotesting results using cladocerans

No.	Material name	Control indicators at the test object Daphnia magna	
		Survival at 48 h, %	Survival at 96 h, %
1	Citrogypsum (feedstock)	100	100
2	Citrogypsum-based binder	100	100
3	Gypsum plaster grade G5 (reference sample)	100	90
4	Control (water)	100	90

All extracts of gypsum-containing materials with a 95% probability do not adversely affect the growth of the roots of the test object *Avena sativa L*. and the survival rate of *Daphnia magna*, and by Order No. 536 of 04.12.2014 can be classified as waste practically non-hazardous to the environmental medium (Class 5), with a very low degree of harmful effects.

4 Conclusion

It has been established that water extracts from citrogypsum and gypsum-containing materials do not have a negative effect on the growth of the roots of the *Avena sativa L.* test object, as well as the survival of the planktonic crustacean *Daphnia magna* in the studied media. The experimental data have been demonstrated, the citrogypsum-based binder, according to environmental safety standards, is not inferior to building gypsum. There is no fungus in its composition, and, therefore, it can be applied to produce construction materials and products.

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