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Recycling and disposal of gypsum-containing waste generated in the production of citric acid

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Abstract. The cycle of citric acid production with the formation of gypsum-containing waste was considered and options for processing and utilization of citrogypsum were proposed. The methods obtained include: the use of citrogypsum in the production of building materials, the extraction of rare earth metals, as well as the creation of a high-quality organic-mineral fertilizer, during the creation of which it is possible to reduce the negative effect not only from the accumulation of citrogypsum, but also from manure stored in the filtration fields. In the future, the resulting fertilizer can be used for reclamation of technologically disturbed territories.

1. Introducton

The production of edible citric acid results in an industrial by-product called citrogypsum. The problem of utilization of gypsum-containing waste, including the processing of citrogypsum, is one of the most important and difficult to solve all over the world. The total amount of gypsum-containing waste in the world is estimated at about 7-8 billion tons, the annual increase is 100-280 million tons per year. According to the state report "On the state and use of mineral resources of the Russian Federation in 2011", more than 500 thousand tons of citrogypsum have accumulated in territory of the Russian Federation.

Citrogypsum is stored in open areas, which can cause serious environmental problems caused by the presence of toxic elements [1–3]. Washing with water removes soluble impurities of citrogypsum, heat treatment leads to optimization of unwanted volatile impurities. Minimizing the negative impact on the environment requires the adoption of cleaner manufacturing processes and appropriate treatment technologies, as well as the disposal of solid waste.

One of the ways to utilize citrogypsum is to transport it after additional moistening to filtration fields and mixing with animal waste [4]. Due to the fact that the slurry tank cannot be isolated from the environment, during storage and as a result of biochemical degradation of organic impurities contained in citrogypsum and manure, substances with an unpleasant odor are released, for example, hydrogen sulfide, which negatively affects the quality air at the landfill and in the surrounding area.

Under the influence of atmospheric precipitation, organic acids and other soluble impurities are washed out, and filtration fields become a source of ground and surface water pollution.

2. Results

The criteria set in environmental regulations vary widely from country to country, and there may be different waste management strategies around the world [3]. Thus, the development of effective methods for processing citrogypsum is an urgent task.

Currently, citric acid is obtained by citric acid fermentation of sugar beet and cane molasses using certain strains of the mold fungus *Aspergillus niger*. Further separation of crystalline citric acid is based on the low water solubility of its calcium salts. As a result, the acid turns into poorly soluble tricalcium citrate:

$$2C_6H_8O_7 + 3Ca(OH)_2 = Ca_3(C_6H_5O_7)_2 \downarrow + 6H_2O,$$

$$2C_6H_8O_7 + 3CaCO_3 = Ca_3(C_6H_5O_7)_2 \downarrow + 3H_2O + CO_2 \uparrow.$$

The crude calcium citrate taken from the sludge tank is decomposed by concentrated sulfuric acid, resulting in the reaction forming citric acid and calcium sulfate dihydrate (citrogypsum). The chemical formula of the reaction is as follows [5]:

$$Ca_3(C_6H_5O_7)_2 \cdot 4H_2O + 3H_2SO_4 + 2H_2O = 2C_6H_8O_7 + 3CaSO_4 \cdot 2H_2O.$$

Citrogypsum is a gray or light gray finely dispersed mechanical mixture with a moisture content of 48% (when stored in filtration fields for up to 6 months) to 33% (with longer storage). The chemical composition of citrogypsum is presented in Table 1.

Table 1. The chemical composition of citrogypsum, mass. %

SO_3	CaO	H_2O	CaC_2O_4	Al_2O_3	$Na_3C_6H_5O_7$	CO_2	Fe_2O_3	MgO
45.69	31.7	21.23	8	0.12	0.1–0,15	0.05	0.04	0.04

By the content of $CaSO_4{\cdot}H_2O$ (97.1%), citrogypsum belongs to the 1st grade of gypsum raw material [6].

Methods for utilization of citrogypsum are shown in Figure 1. Citrogypsum is used in agriculture and the construction industry. In the future, in order to reduce the cost of the technology for the utilization of citrogypsum, it is planned to use the methods of associated extraction of rare earth elements. There are various techniques for extracting rare earth elements from gypsum-containing wastes, for example, phosphogypsum [7–8]. The team of authors plans in the future to develop and implement methods for the associated extraction of rare earth elements from citrogypsum: lanthanum, cerium, neodymium, and praseodymium.

Citrogypsum is used in agriculture as a fertilizer component and to improve the quality of soils, for example, as an ameliorative additive in sodium or acidic soils, as well as during composting of manure. Various studies show that citrogypsum is an effective alternative for the improvement, desalination, and desodification of saline sodium soils [9–10], and organo-mineral fertilization with the addition of citrogypsum increases crop yields [11–12].

Due to the large amount of calcium and sulfur, the use of citrogypsum improves the yield of agricultural crops of some species. In gray forest soils of Russia [11–12], two different amounts (15 and 30 tons per hectare) of organo-mineral fertilizer containing 30% citrogypsum were added to soybean and winter wheat fields and a significant increase in yield was obtained when fertilizing 15 tons per hectare. The increase affected not only the yield per unit area, but also the individual grain weight, the number of spikelets, the percentage of filled spikelets. Figure 2 shows an increase in yield in three crops: wheat, corn and soybeans, after the application of organic-mineral fertilizer based on citrogypsum to the soil.

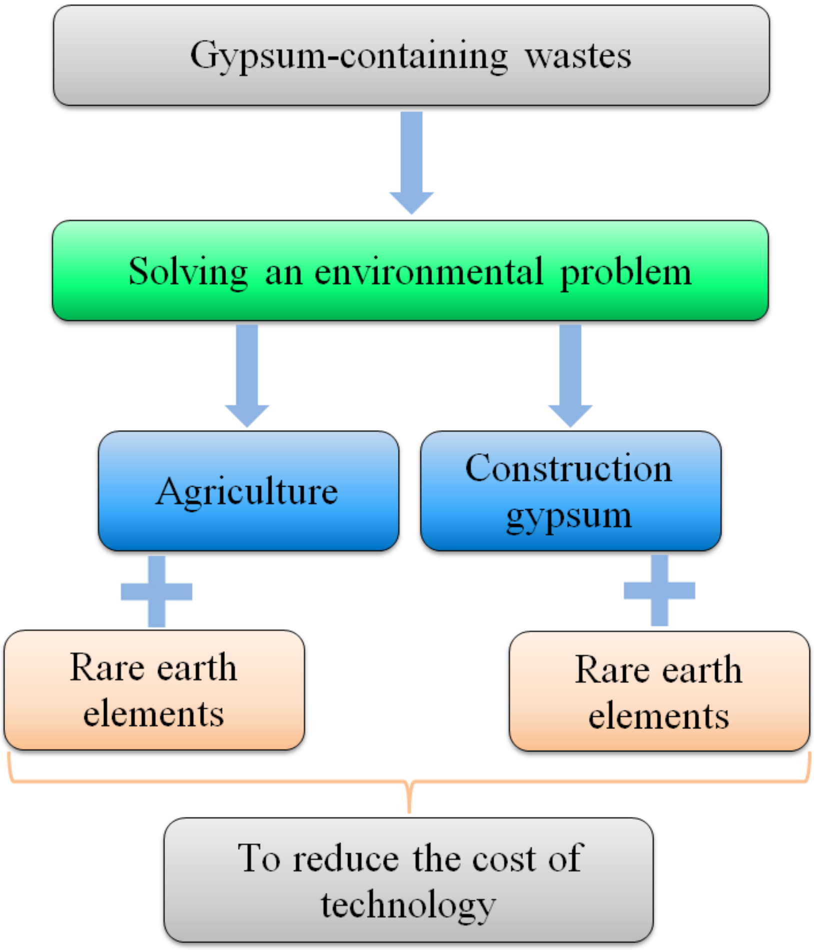

Figure 1. Utilization options for citrogypsum

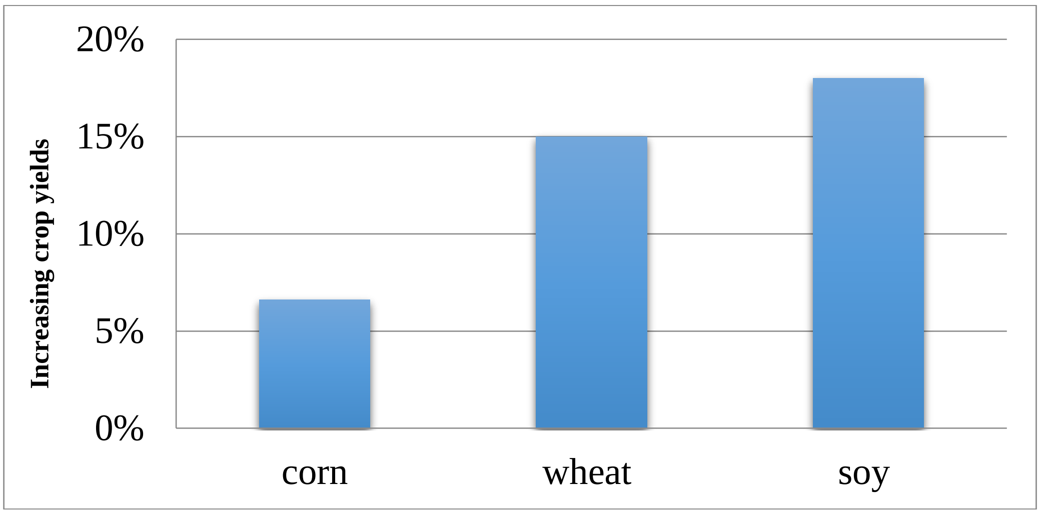

Figure 2. Increase in yield after applying organic-mineral fertilizer based on citrogypsum to the soil

The use of citrogypsum in acidic soils can be used to control the harmful effects of acidity in the subsoil, which promotes root growth and efficient use of water and nutrients by plants. The addition of citrogypsum to the soil improves its plasticity and shrinkage characteristics, and also leads to soil stabilization [13].

3. Conclusions

The production of citric acid results in the formation of large quantities of citrogypsum as a by-product, usually stored in open areas, entering the soil or groundwater. This causes serious problems for the environment and human health.

However, citrogypsum is a valuable product in some areas such as agriculture, used to improve soil quality or as fertilizer, in the construction field in the production of cement, building blocks, etc. An important issue remains the relationship between costs (pollution damage and negative environmental consequences) and benefits from disposal.

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