Development of technology for processing solid waste from the production of orthophosphoric acid into an inorganic composite material

O A Medennikov, N P Shabelskaya, E A Sidash, V A Ulyanova and A N Yatsenko
Platov South-Russian State Polytechnic University (NPI), 132, St. Prosveshcheniya, Novocherkassk, Rostov region, 346430, Russian Federation

E-mail: nina_shabelskaya@mail.ru

Abstract. The article considers the processes of processing solid waste from the production of phosphoric acid - phosphogypsum - into composite inorganic materials. It is shown that heat treatment at a temperature of 1073 K leads to the formation of inactive calcium sulfate. Carrying out the heat treatment process under similar conditions in the presence of an organic reducing agent is accompanied by the formation of a composite material with a luminescent ability. A simple method for the disposal of large-tonnage production waste with the production of a demanded product is proposed.

1. Introduction
Modern production puts ever-increasing environmental pressure on the environment. In the process of obtaining phosphoric acid, a large-tonnage waste is formed - phosphogypsum. The economic damage that occurs as a result of the formation and storage of phosphogypsum is very significant. The cost of storing phosphogypsum in individual countries can be estimated at $4.5 million. More than 85% of all produced phosphogypsum is disposed of without processing [1-6]. In this case, phosphogypsum is used as a fertilizer [1-2;7], the production of binders [6;8]. Extensive studies show the relevance, prospects and high efficiency of the use of phosphogypsum. At the same time, the environmental significance of phosphogypsum utilization should be noted, since not only thousands of hectares of fertile land occupied by dumps are released, but also in the case of its use as fertilizers, the soil is enriched with calcium, silicon, phosphorus, sulfur and a complex of microelements. However, it is more rational to process this production waste in order to obtain valuable products from it. Phosphogypsum is a safe secondary source of lanthanides, since its total radioactive background does not exceed admissible values [9-10]. The content of rare earth metals in phosphogypsum is in the range of 0.4–0.6%. Analysis of the elemental composition of rare earth elements that make up phosphogypsum indicates a significant content of Ce, Pr, Nd, Sm, Eu, Gd, Dy, and Y. [13] - for binding carbon dioxide. Composite materials are increasingly used in modern production, as they allow obtaining materials with improved characteristics [14–19]. It is noted in [18-19] that the use of a composite material based on phosphogypsum makes it possible to obtain road surfaces with increased strength. The development of a method for the utilization of phosphogypsum will allow organizing an efficient and environmentally friendly production.
The aim of the study was to develop a method for processing solid waste from the production of phosphoric acid - phosphogypsum - to obtain an inorganic composite material with a luminescent ability.

2. Materials and methods
For the study, phosphogypsum was used, which contains at least 99% (mass.) calcium sulfate dihydrate. The main method for obtaining a composite material was the process of reducing a part of calcium sulfate to calcium sulfide. Vegetable oil was used as a reducing agent.

The inorganic composite material was prepared as follows: vegetable oil was added to the precisely measured amount of phosphogypsum in various proportions. The mixture was thoroughly mixed until completely homogeneous. This preform was placed in an alundum crucible in a furnace. To remove crystallization water, the temperature was slowly raised at a rate of 13 K/min, heating was carried out to 1073–1273 K, then the sample was kept in the oven at this temperature for 60 minutes. Upon completion of heat treatment, the sample was slowly cooled to room temperature.

In order to establish the phase composition of the samples, they were studied using X-ray phase analysis using an ARL X'TRA device. The morphology of the samples was studied using scanning electron microscopy (SEM). The studies were carried out at the Center for Collective Use "Nanotechnologies" SRSPU (NPI).

The luminosity of the samples was determined using an original setup consisting of a radiation source, a light filter, and a recording sensor. The sample was placed in a setup, illuminated with radiation at a wavelength of 380 nm, and the luminosity of the sample was recorded through a light filter that did not transmit ultraviolet rays.

3. Results
According to known literature data, heat treatment of phosphogypsum at a temperature of 1073 K leads to the formation of inactive gypsum, which is not capable of hydration.

The heat treatment at 1023 K is accompanied by the production of a material identified by X-ray phase analysis as calcium sulfate (figure 1a).

![Figure 1. Radiographs of fired (a) and reduced (b) phosphogypsum.](image)

On fig. figure 2 shows a micrograph of a calcined phosphogypsum sample. The sample is lamellar crystals.
Heat treatment in the presence of a reducing agent is accompanied by the formation of a composite material containing a mixture of calcium sulfate and calcium sulfide (figure 1b). The microphotograph of the composite material (figure 3) shows that some of the lamellar crystals are destroyed, and clusters of irregular shape are formed on their surface.

Calcium sulfide, which is the basis of the phosphor, can be obtained by reducing calcium sulfate with a carbon-containing reagent [20]. The work [21] provides information on the reduction of phosphogypsum by a number of organic compounds (waste of olive oil production, citric acid, sucrose).

![Figure 2. Micrograph of a phosphogypsum sample heat-treated at 1073 K.](image)

![Figure 3. Micrograph of a phosphogypsum sample heat-treated at a temperature of 1073 K in the presence of a reducing agent.](image)

Table 1 lists the luminosity values of a sample heat-treated in the presence of a reducing agent at a temperature of 1073 K.

| Indicator            | Meaning |
|----------------------|---------|
| Weight of reducing agent, % | 0 10 25 50 75 100 125 150 200 |
| Relative luminosity  | 0 0.20 0.30 0.80 0.80 0.75 0.70 0.70 |
4. Discussion
During heat treatment at a temperature of 1073 K, the process of dehydration of calcium sulfate dihydrate proceeds with the formation of lamellar crystals according to reaction (1):

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}. \quad (1) \]

In the presence of vegetable oil, the process of reducing calcium sulfate to sulfide proceeds according to reaction (2):

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{reducing agent} \rightarrow \text{CaS} + \text{CO}_2 + \text{H}_2\text{O}. \quad (2) \]

As is known, one of the widely used inorganic phosphors is a material based on calcium sulfide [20]. Heat-treated in the presence of a reducing agent, phosphogypsum has the ability to luminescence due to the presence of a calcium sulfate/calcium sulfide composite material.

According to the results obtained, the highest luminosity was established for samples with a molar ratio of phosphogypsum : reducing agent = 1 : 0.5 - 1.0. With an increase in the amount of reducing agent in the system, the luminescent ability decreases. This may be due to the incomplete oxidation of organic matter during heat treatment: the samples with a high content of the reducing agent were contaminated with carbon.

5. Conclusion
As a result of the study, the process of processing waste from the production of phosphoric acid was studied to obtain a composite material calcium sulfate/calcium sulfide. The resulting material has luminescent properties. The optimal ratios of phosphogypsum and reducing agent have been established. A simple method for processing waste into demanded inorganic materials is proposed.

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References
[1] Huang L, Liu Y, Ferreira J F S, Wang M, Na J, Huang J and Liang Z 2022 Long-term combined effects of tillage and rice cultivation with phosphogypsum or farmyard manure on the concentration of salts, minerals, and heavy metals of saline-sodic paddy fields in Northeast China. *Soil and Tillage Research* 215 105222

[2] Costa R F, Firmano R F, Colzato M, Crusciol C A C and Alleoni L R F 2022 Sulfur speciation in a tropical soil amended with lime and phosphogypsum under long-term no-tillage system. *Geoderma* 406 115461

[3] Wu S, Yao X, Yao Y, Ren C, Wu C, Zhang C and Wang W 2021 Recycling phosphogypsum as the sole calcium oxide source in calcium sulfoaluminate cement production and solidification of phosphorus. *Science of the Total Environment* 80820 152118

[4] Wu F, Liu X, Wang C, Qu G, Liu L, Chen B, Zhao C, Liu S and Li J 2022 New dawn of solid waste resource treatment: Preparation of high-performance building materials from waste-gypsum by mechanical technology. *Construction and Building Materials* 3187 126204

[5] Cao W, Yi W, Peng J, Li G and Yin S 2022 Preparation of anhydrite from phosphogypsum: Influence of phosphorus and fluorine impurities on the performances. *Construction and Building Materials* 3187 126021

[6] Cao W, Yi W, Peng J, Li J and Yin S 2022 Recycling of phosphogypsum to prepare gypsum plaster: Effect of calcination temperature. *Journal of Building Engineering* 45 103511

[7] Yang R, Howe J A, Harris G H and Balkcom K B 2022 Reevaluation of calcium source for runner-type peanut (Arachis hypogaea L.). *Field Crops Research* 2771 108402

[8] Du M, Wang J, Dong F, Wang Z, Yang F, Tan H, Fu K and Wang W 2022 The study on the effect of flotation purification on the performance of α-hemihydrate gypsum prepared from
phosphogypsum. Scientific Reports 12(1) 95

[9] Rödel T, Kiefer S and Borg G 2022 Rare-earth elements in phosphogypsum and mineral processing residues from phosphate-rich weathered alkaline ultramafic rocks, Brazil. Industrial Waste: Characterization, Modification and Applications of Residues 505 – 54028

[10] Wei Z and Deng Z 2022 Research hotspots and trends of comprehensive utilization of phosphogypsum: Bibliometric analysis. Journal of Environmental Radioactivity 242 106778

[11] Yang J, Ren Y, Lu J, Liu H, Zhang Z, Pang H and Boukh K 2021 Chemical looping gasification with a CuFe$_2$O$_4$-enhanced phosphogypsum oxygen carrier during reduction in a fluidized bed reactor. Chemical Engineering Journal 42615 131346

[12] Pan Q, Ma L, Du W, Yang J, Ao R, Yin X and Qing S 2022 Hydrogen-enriched syngas production by lignite chemical looping gasification with composite oxygen carriers of phosphogypsum and steel slag. Energy 24115 122927

[13] He H, Hao L, Fan C, Li S and Lin W 2022 A two-step approach to phosphogypsum decomposition: Oxidation of CaS with CO$_2$. Thermochimica Acta 708 179122

[14] Mittova I Ya, Sladkopevtsev B V and Mittova V O 2021 Nanoscale semiconductor and dielectric films and magnetic nanocrystals - new directions of development of the scientific school of Ya. A. Ugai "Solid state chemistry and semiconductors". Condensed Matter and Interphases 23(3) 309-336

[15] Tomina E V, Pavlenko A A and Kurkin N A 2021 Synthesis of bismuth ferrite nanopowder doped with erbium ions. Condensed Matter and Interphases 23(1) 93-100

[16] Smolii V A, Kosarev A S, Yatsenko E A and Gol'tsman B N 2018 Structure Formation in Cellular Glass Based on Novocherkassk CHPP Ash-Slag Wastes. Glass and Ceramics 75 303-307

[17] Yatsenko E A, Goltsman B M, Klimova L V and Yatsenko L A 2020 Peculiarities of foam glass synthesis from natural silica-containing raw materials Journal of Thermal Analysis and Calorimetry 142 119-127

[18] Xie L, Zhou Y, Xiao S, Miao X, Murzataev A, Kong D and Wang L 2022 Research on basalt fiber reinforced phosphogypsum-based composites based on single factor test and RSM test. Construction and Building Materials 31617 126084

[19] Meskini S, Remmal T, Eijaouani H and Samdi A 2022 Formulation and optimization of a phosphogypsum – fly ash – lime composite for road construction: A statistical mixture design approach. Construction and Building Materials 31510 125786

[20] Tong X, Yang J, Wu P, Zhang X and Seo H J 2019 Color tunable emission from CaS:Cu$^+$, Mn$^{2+}$ rare-earth-free phosphors prepared by a simple carbon-thermal reduction method. Journal of Alloys and Compounds 779 399 – 403

[21] Medennikov O A, Shabelskaya N P, Gaidukova Yu A, Astakhova M N and Chernysheva G M 2021 The use of phosphoric acid waste product for calcium sulfide production. IOP Conf. Series: Earth and Environmental Science 677 052049