The use of phosphoric acid waste product for calcium sulfide production

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Abstract. The article studies the technological features of calcium sulfide production from phosphogypsum. To ensure the environmental safety of industrial enterprises, closed production cycles creation is necessary. One of the criteria for "green" technologies is industrial waste recycling. Phosphogypsum formed during the orthophosphoric acid production from apatite raw materials by sulfuric acid method can be classified as large-tonnage waste. Phosphogypsum can be considered a mineral with zero mining costs and zero feedstock to produce valuable products. The synthesized materials are characterized using a complex of modern methods such as X-ray phase analysis, and electron microscopy. An environmentally friendly precursor, sucrose, is used as a reducing agent for calcium sulfate. The recovered material is a mixture of calcium sulfate and sulfide. When illuminated with ultraviolet light, it glows yellow-orange. The article presents an integrated approach to the problem of phosphoric acid production waste disposal by marketable products production.

1. Introduction
To ensure the environmental safety of industrial enterprises, closed production cycles creation is necessary. One of the criteria for "green" technologies is industrial waste recycling. Phosphogypsum formed during the orthophosphoric acid production from apatite raw materials by sulfuric acid method can be classified as large-tonnage waste. Phosphogypsum storage leads to the formation of dumps that occupy significant areas, thus, damaging the ecosystem [1, 2]. Phosphogypsum can be considered a mineral with zero mining costs and zero feedstock to produce valuable products such as rare earth elements [3-5], and composite materials to remove chromium ions from aqueous solutions [6]. At present, a significant amount of phosphogypsum is deployed for the production of construction materials: cement [7-9], non-combustible wall panels [3, 10, 11], and glass ceramics [12].

In the modern world, materials with luminescent properties become increasingly popular. They can be used not only traditionally for the production of dyes in the polymer materials industry, but also as chemo sensors for a number of metals. Silicates, phosphates, sulfides and other compounds of alkaline earths and transition elements are used as luminescent materials. Calcium sulfide is one of the most widespread luminophore [13-15]. A number of publications are devoted to the problem of the reduction of calcium sulfide, which is the main component of phosphogypsum [16-19].
The purpose of the study is to investigate the technological features of calcium sulphide production from phosphogypsum, which will allow an integrated approach development to solving the problem of production wastes by recycling them into marketable products.

2. Materials and methods
For the synthesis, agricultural phosphogypsum (FG) and calcium sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were used. Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) was used as a reducing agent.

Phosphogypsum and calcium sulphate were pre-dried at the temperature of 100° C to constant weight.

To prepare the samples, phosphogypsum (calcium sulphate) and sucrose (in terms of carbon) were used in the molar ratio of $\text{CaSO}_4 / \text{C} = \frac{1}{2}$; as shown in [17], this ratio of calcium sulfate / reducing agent is optimal.

Phosphogypsum (or calcium sulphate) and the reducing agent were weighed with an accuracy of 0.01 g on a technical electronic balance, homogenized for 20 s in a 0.3 kW mixer at the speed of 1500 rpm, placed in alundum crucibles in the working space of a muffle furnace and subjected to heat treatment at the temperature of 1073 K for 1 hour. Cooling of samples to room temperature was slow and performed with an oven.

To study luminescence of the samples, they were illuminated with a Camelion FT5 BLACK LIGHT fluorescent ultraviolet lamp.

The phase composition was studied with an ARL X'TRA X-ray diffractometer (using Cu-Kα radiation); micrographs of the samples were obtained using Quanta 200 scanning electron microscope. The material composition was determined using scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

3. Experiment and discussion
The obtained samples were of white powder. Figure 1a shows an X-ray diffraction pattern of dried phosphogypsum. The sample is Calcium Sulfate Hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, PDF # 010-70-7008). Figure 1b shows an X-ray diffraction pattern of phosphogypsum heat-treated at the temperature of 1073 K. The sample contains anhydrous calcium sulfate (Calcium Sulfate, PDF # 010-71-4906). In the process of heat treatment, calcium sulfate dihydrate first transforms into semi-aqueous, and then into anhydrous calcium sulfate:

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 1.5\text{H}_2\text{O},$

$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} = \text{CaSO}_4 + 0.5\text{H}_2\text{O}.$

Figure 1c shows an X-ray diffraction pattern of phosphogypsum reduced at the temperature of 1073 K, it is a mixture of calcium sulfate and calcium sulfide (Calcium Sulfide, PDF # 010-77-2011).

![Figure 1](image_url)

**Figure 1.** X-ray diffraction photos of samples: a – phosphogypsum dried at the temperature of 373 K, b – phosphogypsum heat treated at the temperature of 1073 K, c – phosphogypsum reduced at the temperature of 1073 K.
Lines characterizing the CaS phase appear on the X-ray image in 2θ regions of 32 and 45 degrees, the 56 degree line is enhanced due to the superimposition of reflections from calcium sulfate and sulfide.

Figure 2 shows a micrograph of reduced phosphogypsum. Plate-like crystals typical of calcium sulfate and crystals of irregular shape are visible in the sample, which confirms the X-ray phase analysis data on calcium sulfate and sulfide mixture presence in the sample.

![Figure 2](image1.png)

**Figure 2.** Micrograph of a phosphogypsum sample reduced at the temperature of 1073 K.

The following mechanism of the calcium sulfide formation reaction can be assumed:

\[ \text{CaSO}_4 + \text{C}_{12}\text{H}_{22}\text{O}_{11} + 10\text{O}_2 = \text{CaS} + 12\text{CO}_2 + 11\text{H}_2\text{O} \]

or, in terms of pure carbon:

\[ \text{CaSO}_4 + 2\text{C} = \text{CaS} + 2\text{CO}_2 \]

The thermodynamic ability and the highest probability of the latter reaction were appropriated by the authors of [17].

Under the action of exciting ultraviolet radiation, the samples emit in the yellow-orange region of the spectrum with the maximum radiation length of 550-600 nm (figure 3).

![Figure 3](image2.png)

**Figure 3.** Photographs of phosphogypsum samples exposed to illumination: sunlight (a, b), ultraviolet radiation (c, d); a, c – original phosphogypsum, b, d – reduced phosphogypsum.
Figures 3a, b show photographs of phosphogypsum exposed to sunlight (figure 3a – original phosphogypsum, figure 3b – reduced phosphogypsum). Figures 3c, d show photographs of phosphogypsum exposed to ultraviolet illumination (figure 3c – original phosphogypsum, figure 3d – reduced phosphogypsum). After reduction, the sample is presented in the form of sintered material or a cake. This may be due to the transition of sucrose when heated to the liquid phase, which envelops the phosphogypsum particles, and contributes to the uniform distribution of the reducing agent throughout the system. As data in figure 3c show, the original phosphogypsum does not exhibit luminescent properties.

Analysis of X-ray phase, microscopic and elemental data suggests that as a result of calcium sulfate reduction, calcium sulfide is formed, which exhibits the properties of a luminescent material when irradiated with ultraviolet radiation.

4. Conclusion
A simple method of obtaining a luminescent material from orthophosphoric acid production waste by the sulfate method is proposed. The way of converting the main part of phosphogypsum – calcium sulfate – into a luminescent material based on calcium sulfide is shown. The obtained results open up massive opportunities for production waste recycling into cheap marketable products.

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