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RESEARCH ARTICLE

Technology for processing phosphogypsum into a fluorescent dye based on calcium sulfide

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Abstract

Objectives. *There is considerable economic demand for products obtained by processing phosphogypsum. In particular, calcium sulfide-based materials having luminescent properties are the object of intensive study due to the wide range of possibilities for their use. The alloying of the structure of calcium sulfide with cations of rare earth elements leads to the appearance of a glow having various colors. However, the high cost of such phosphorescent materials is due to the high chemical purity of the reagents required for their synthesis. The development of efficient methods for obtaining calcium sulfide-based luminescent materials from phosphogypsum is part of an integrated approach to solving the problem of synthesizing economically demanded materials from production waste.*
Methods. *The synthesized materials were studied using X-ray phase analysis and scanning electron microscopy. Photos of the samples were taken under illumination with an incandescent lamp or a fluorescent ultraviolet lamp.*
Results. *According to X-ray phase analysis, phosphogypsum is mainly comprised of calcium sulfate dihydrate and calcium sulfate hemihydrate. Heat treatment of a phosphogypsum sample at a temperature of 1073 K is accompanied by the formation of anhydrous calcium sulfate. In the presence of a reducing agent, a composite material is formed containing a phase of anhydrous calcium sulfate and calcium sulfide. Due to the calcium sulfide content, phosphogypsum has luminescent properties when heat-treated in the presence of various reducing agents, including activated carbon, wood charcoal, vegetable oil, citric acid, starch, and sucrose.*

Conclusions. *Optimal technological conditions for obtaining a composite material exhibiting luminescent properties are revealed. The successful synthesis of phosphor from without non-pretreated phosphogypsum is demonstrated. Optimal technological conditions for obtaining a composite material exhibiting luminescent properties are as follows: heat treatment temperature is 1073–1173 K; isothermal holding time is 60 min; reducing agent quantity is 37–50% (mol). The study results are widely applicable to processing wastes obtained from large-scale chemical production involving the production of a highly demanded inorganic product.*

Keywords: *phosphogypsum, thermal reduction, luminescent materials, calcium sulfide*

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НАУЧНАЯ СТАТЬЯ

Технология переработки фосфогипса в люминесцентный краситель на основе сульфида кальция

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Аннотация

Цели. *Материалы с люминесцентными свойствами на основе сульфида кальция являются объектом интенсивного изучения ввиду широкого круга возможностей их использования. Легирование структуры сульфида кальция катионами редкоземельных элементов приводит к появлению свечения различной окраски. Синтез подобных материалов осуществляют из химически чистых реактивов, что приводит к высокой стоимости люминофоров. Разработка способа получения люминесцентного материала на основе сульфида кальция из фосфогипса является актуальной задачей химической технологии, позволяющей осуществить комплексный подход к решению проблемы получения экономичных востребованных материалов из отходов производства.*
Методы. *Синтезированные материалы были изучены с помощью рентгенофазового анализа, растровой электронной микроскопии. Фотографии образцов выполняли при освещении лампой накаливания или люминесцентной ультрафиолетовой лампой.*
Результаты. *Согласно данным рентгенофазового анализа, фосфогипс представляет собой двуводный сульфат кальция и полуводный сульфат кальция. Термообработка при температуре 1073 K образца фосфогипса сопровождается образованием безводного сульфата кальция, в присутствии восстановителя происходит образование композиционного материала, содержащего фазу безводного сульфата кальция и сульфида кальция. Термообработанный в присутствии ряда восстановителей — активированного угля,*

березового угля, растительного масла, лимонной кислоты, крахмала, сахарозы — фосфогипс обладает способностью к люминесценции, обусловленной наличием сульфида кальция.

Выводы. *Выявлены оптимальные технологические условия получения композиционного материала, проявляющего люминесцентные свойства. Показано, что для синтеза люминофора наиболее удачным является использование фосфогипса без предварительной обработки. Оптимальные технологические условия получения композиционного материала, проявляющего люминесцентные свойства: температура термообработки 1073–1173 K, продолжительность изотермической выдержки 60 мин, количество восстановителя – 37–50 мол. %. Проведенное исследование открывает широкие возможности переработки отхода многотоннажного химического производства с получением востребованного неорганического продукта.*

Ключевые слова: *фосфогипс, термическое восстановление, люминесцентные материалы, сульфид кальция*

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INTRODUCTION

Modern technologies for extracting inorganic materials exert increasing environmental pressures. One of the most actively developing industries involves the production of mineral fertilizers. In particular, phosphogypsum is formed from apatite raw materials during the production of phosphoric acid for further processing into phosphorus-containing fertilizers. However, large-scale phosphogypsum dumps occupying significant areas involve a serious burden on the ecosystem [1, 2]. Thus, developing the foundations of methods for processing such inorganic production wastes is an urgent chemico-technological task. Currently, phosphogypsum byproducts are mainly reused for building materials—wall panels, dry mixes, etc. [3–5]—and in the production of fertilizers [6, 7]. The accumulated reserves of phosphogypsum can be equated to natural resources with zero extraction costs. In this regard, it is relevant to study the possibility of processing phosphogypsum to obtain demanded inorganic products.

Calcium sulfide serves as a matrix for the production of inorganic phosphors [8–10]. In the contemporary world, materials with luminescent properties are the object of intensive study due to a wide range of possibilities for their use [11–13]. One widely used material is calcium sulfide-based phosphor [14–17]. Doping of the calcium sulfide structure with europium cations leads to the appearance of a red [14–16] or orange [14] glow; the presence of cerium in the composition produces a green and yellow-green glow [16]; cations of some d-elements can be used in the production of materials having a purple, blue [9], or yellow [17] glow. As a rule, the synthesis of such materials is carried out from chemically pure reagents, which leads to a high cost of phosphors (EUR 50–70 per kg).

In this regard, the purpose of this study is to develop a method for obtaining calcium sulfide from phosphogypsum as part of an integrated approach to synthesizing valuable materials from production wastes.

MATERIALS AND METHODS

In order to study the possibility of obtaining an inorganic luminescent material, phosphogypsum containing $CaSO_4 \cdot 2H_2O$ of at least 99 wt % was used. Sucrose (*PTO OSNOVA*, Russia), A grade birch activated carbon (*SBV GRUPP*, Russia), wood charcoal (*PKF SISTEMA*, Russia), vegetable oil (*GK YUG ROSSII*, Russia), citric acid (*Standart*, Russia), and starch (*KF Bogorodskaya*, Russia) were used as reducing agents.

The following phosphogypsum samples were used to assess the ability to recover to the target product:

1) pre-heat-treated at 1073 K for 60 min;

2) dried in a drying cabinet at a temperature of 473 K for 5 h to a constant weight;

3) without preliminary heat treatment, with the addition of water in an amount of 10 wt % by weight of phosphogypsum;

4) without pretreatment.

The study of the possibility of recovery was carried out as follows. A reducing agent was added to phosphogypsum according to the formulation. The samples were homogenized in a 0.45 kW mixer with a speed of 1500 rpm, after which they were placed in alund crucibles in the working space of a muffle furnace and heat-treated according to the following regime: heating rate is 13 K/min; treatment temperature is 1073 K; time at this temperature is 60 min. Following heat treatment, the samples were cooled to a furnace temperature of 293 K, weighed and crushed in a mortar.

For each sample, the relative luminous flux emitted by the surface of the sample of a fixed area was measured using an original installation (Fig. 1) comprising an ultraviolet (UV) radiation source, light filters, and a recording sensor. A sample and reference sample used as a phosphor yellow YAG:Ce were placed in the installation and illuminated with a radiation having a wavelength of 380 nm. The luminous flux from the surface of the sample and the reference sample was recorded through a light filter that excludes ultraviolet rays. The relative luminous flux was obtained as the ratio of the luminous flux from the surface of the test sample to the luminous flux from the surface of the reference sample.

In order to determine the optimal heat treatment time, the phosphogypsum samples and reducing agent were homogenized in a manner similar that described above. Next, the samples were heat-treated according to the following regime: heating rate is 13 K/min; heat-treatment temperature is 1173 K. After reaching the heat-treatment temperature, the sample batches were moved every 10 min to a cooling chamber made of thermal insulation material and cooled slowly to a temperature of 293 K. After weighing the samples and crushing them in a mortar, the relative luminous flux emitted by the surface of the sample of a fixed area was measured.

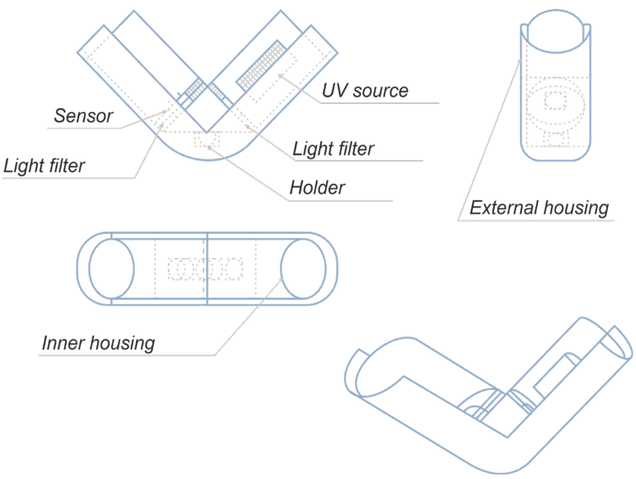

Fig. 1. Diagram of the installation for measuring the luminous flux from the surface of the irradiated UV sample.

In order to select the reducing agent and the heat treatment temperature, phosphogypsum weighing 17.20 g and the reducing agent were weighed with an accuracy of 0.01 g on technical electronic scales according to the ratios indicated in Table 1, homogenized in a 0.45 kW mixer with a speed of 1500 rpm, after which they were placed in alund crucibles in the working space of a muffle furnace, where they were produced heat treatment according to the following modes: samples were heated at a rate of 13 K/min to the calcination temperature, which was 1073 K, 1173 K, and 1273 K. Upon reaching the calcination temperature, the samples were kept at this temperature for 60 min. At the end of the heat treatment, the samples were cooled together with the furnace to a temperature of 293 K. After that, the samples were crushed in a mortar to a powdery state. The relative luminous flux emitted by the sample surface of a fixed area was measured.

Phase composition was studied on an ARL X'TRA X-ray diffractometer (*ARL*, Switzerland) using monochromatized Cu-Kα radiation by point-by-point scanning (step 0.01°, accumulation time at point 2 s) in the range of values 2θ from 15° to 80°. The qualitative phase composition was determined using PDF-2 in the Crystallographica software[1].

Micrographs of the samples were obtained using a Quanta 200 scanning electron microscope (*FEI*, USA). The images were taken at an accelerating voltage of up to 30 kV.

Photos of the samples were taken under illumination with an incandescent lamp or a fluorescent ultraviolet lamp FT5 BLACK LIGHT (*Camelion*, Russia).

RESULTS AND DISCUSSION

According to X-ray phase analysis, phosphogypsum is a dihydrous calcium sulfate (Calcium Sulfate Hydrate gypsum low, PDF Number: 010-70-7008) and semi-aqueous calcium sulfate (Calcium Sulfate Hydrate, PDF Number: 010-80-1235) (Fig. 2a). Heat treatment at a temperature of

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[1] PDF-2. The Powder Diffraction File™. International Center for Diffraction Data (ICDD), PDF-2 Release 2012, www.icdd.com (2014).

Table 1. Ratio of phosphogypsum and reducing agents

Reducing agent	Reducing agent mass, g	Molar fraction of the reducing agent, %
A grade birch activated carbon	0.30	12.5
	0.60	25
	1.20	50
	1.80	75
	2.40	100
	3.00	125
	3.60	150
	4.80	200
Sugar	0.70	12.28
	1.40	24.56
	2.90	50.88
	4.30	75.44
	5.70	100.00
	7.10	124.56
	8.60	150.88
	11.40	200.00
Vegetable oil	0.30	13.64
	0.60	27.27
	1.10	50.00
	1.70	77.27
	2.20	100.00
	2.80	127.27
	3.40	154.55
	4.40	200.00
Citric acid	1.10	6.40
	2.10	12.21
	4.30	25.00
	6.40	37.21
	8.50	49.42
	10.70	62.21
	12.80	74.42
	17.10	99.42
Starch	0.70	12.96
	1.40	25.93
	2.70	50.00
	4.10	75.93
	5.40	100.00
	6.80	125.93
	8.10	150.00
	10.80	200.00

1073 K of a phosphogypsum sample is accompanied by the formation of anhydrous calcium sulfate (PDF Number: 010-74-2421) (Fig. 2b). Heat treatment at a temperature of 1073 K of a phosphogypsum sample in the presence of a reducing agent leads to the formation of a composite material containing a phase of anhydrous calcium sulfate (Calcium Sulfate, PDF Number: 010-70-0909) and calcium sulfide (Calcium Sulfide, PDF Number: 000-08-0464) (Fig. 2c) (data for phosphogypsum reduced in the presence of sucrose are given as an example).

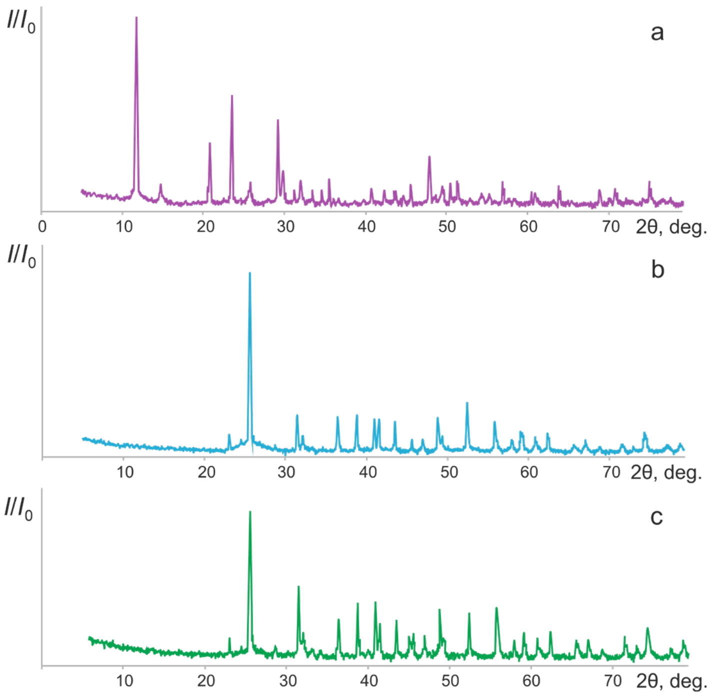

Fig. 2. X-ray diffraction patterns of the phosphogypsum samples: (a) dried at a temperature of 473 K, (b) heat-treated at a temperature of 1073 K, (c) heat-treated in the presence of a reducing agent at a temperature of 1073 K.

Various micrographs of phosphogypsum were also obtained: dried at a temperature of 473 K (Fig. 3a); heat-treated at a temperature of 1073 K (Fig. 3b); heat-treated in the presence of a reducing agent at a temperature of 1073 K (Fig. 3c), where data for phosphogypsum reduced in the presence of sucrose are given as an example.

Figure 3 represents samples of phosphogypsum, heat-treated at temperatures of 473 K and 1073 K as lamellar crystals. Cracks appearing on the crystals at increased heat treatment temperatures may be due to the processes of removing crystallization water. Heat treatment in the presence of a reducing agent is accompanied by partial destruction of the structure: plate crystals lose boundary clarity, while clusters of the reduced material form on their surface. Figure 4 schematically represents the process of transition of the original structure to the restored one.

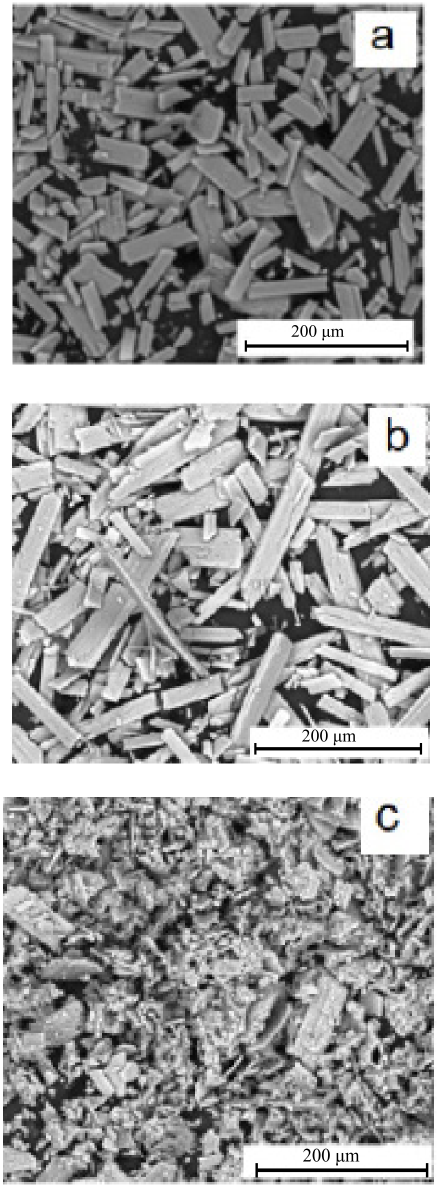

Fig. 3. Micrographs of phosphogypsum: (a) dried at a temperature of 473 K, (b) heat-treated at a temperature of 1073 K, (c) heat-treated in the presence of a reducing agent at a temperature of 1073 K.

The luminescent properties of phosphogypsum heat-treated in the presence of a reducing agent (Fig. 5) are due to the presence of calcium sulfide. Figure 5 shows photos of samples under visible illumination (Fig. 5a) and ultraviolet illumination (Fig. 5b and 5c); a light filter is used to remove the UV part of the radiation (Fig. 5b).

Results of studying the effect of pretreatment

The results of measuring the relative luminous flux from the surface of the studied phosphogypsum

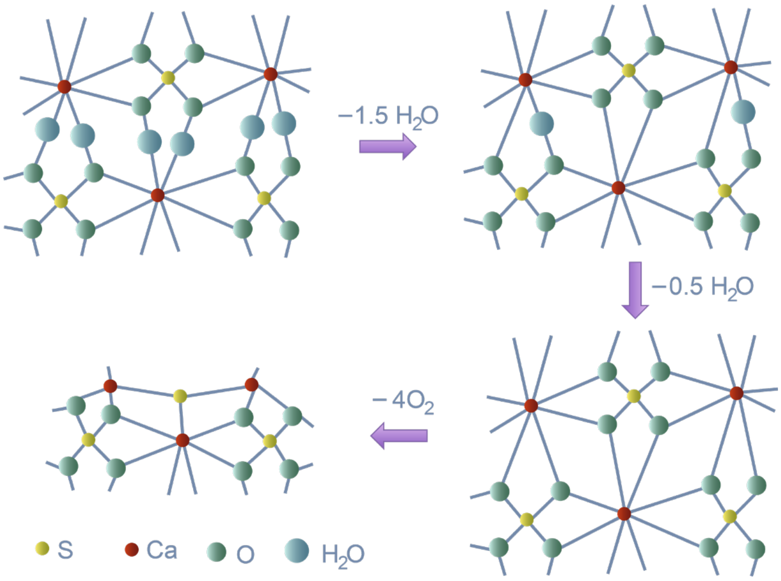

Fig. 4. Schematic representation of the formation of the composite material $CaSO_4$/CaS.

sample obtained with various preliminary preparations are shown in Table 2.

From the results shown in Table 2, it follows that phosphogypsum without pretreatment is more suitable for the synthesis of phosphor.

Determination of the optimal heat treatment time

When calculating the change in the mass of the sample, the final mass of the sample, the mass of the reducing agent and the mass of water were subtracted from the initial mass of the sample. The results of these calculations and measurements are shown in Table 3.

The data obtained indicate that at a given temperature, the exposure time of 60 min was optimal for obtaining a luminescent material. It can be assumed that a shorter holding time is not enough for the recovery process to proceed, which is also evidenced by the insufficient loss of mass, compared with the calculated one, and traces of unreacted coal in the calcined samples. A longer calcination time leads to the reverse oxidation reaction of the compounds obtained during the reduction process.

Selection of reducing agent

The following reducing agents were selected for the recovery process: A grade birch activated carbon, sugar, vegetable oil, citric acid, and starch.

The following reduction reactions of phosphogypsum to calcium sulfide (1)–(5) have been proposed for these reducing agents.

For coal (1):

$$CaSO_4 \cdot 2H_2O + 2C \rightarrow CaS + 2H_2O + 2CO_2. \qquad (1)$$

Fig. 5. Samples of reduced phosphogypsum under illumination:
ordinary light (a), ultraviolet light (b, c), and ultraviolet light with a light filter (b).

Table 2. Results of the recovery of phosphogypsum that has undergone various pretreatment

Phosphogypsum samples	Average mass loss, g	Relative luminous flux
Pre-heat treated at 1073 K for 60 min	0.24	0.36
Dried in an oven at 473 K for 5 h	0.27	0.51
Without pre-heat treatment with the addition of water	0.23	0.52
Without pretreatment	0.21	0.88

Table 3. Determination of the optimal heat treatment time

Time, min	Mass change, g	Relative luminous flux
0	−0.48	0.10
10	−0.02	0.15
20	0.03	0.24
30	0.12	0.34
40	0.14	0.68
50	0.18	0.71
60	0.21	**0.88**
70	0.21	0.85
80	0.18	0.81
90	0.12	0.80
100	0.11	0.75
110	0.05	0.69

For sucrose (2):

$$C_{12}H_{22}O_{11} + 6CaSO_4{\cdot}2H_2O \rightarrow 6CaS + 12CO_2 + 23H_2O. \quad (2)$$

For vegetable oil, it was assumed that sunflower oil is glycerin oleodilinoleate (3):

$$79CaSO_4{\cdot}2H_2O + 2C_{57}H_{100}O_6 \rightarrow 79CaS + 258H_2O + 114CO_2. \quad (3)$$

For citric acid (4):

$$9CaSO_4{\cdot}2H_2O + 4C_6H_8O_7 \rightarrow 9CaS + 34H_2O + 24CO_2. \quad (4)$$

For starch (5):

$$C_6H_{10}O_5 + 3CaSO_4{\cdot}2H_2O \rightarrow 3CaS + 6CO_2 + 11H_2O. \quad (5)$$

Based on the proposed reactions, 2.40 g of coal, 5.70 g of sucrose, 2.20 g of vegetable oil, 8.50 g of citric acid and 5.40 g of starch were taken as 100%.

In order to check the effect of heat treatment conditions on pure reducing agents, samples of reducing agents were placed in crucibles in a muffle furnace and calcined for 60 min at a temperature of 1073 K. At the end of the heat treatment, the crucibles were empty, the reducing agents were completely burned.

Table 4 shows data on the study of the effect of various reducing agents on the process of obtaining the target material. In all experiments, the mass of the phosphogypsum sample was 17.20 g.

To test the possibility of using wood charcoal instead of A birch activated carbon, the cost of which is lower, phosphogypsum samples weighing 17.20 g and a reducing agent, which is A grade birch activated carbon and wood charcoal of various weights, were heat treated at a temperature of 1173 K, the same as described above. The results of the study are shown in Table 5.

Table 5 data indicates that birch activated carbon and wood charcoal are equally well suited for use as phosphogypsum reducing agents; however, the price of wood charcoal makes it more economically attractive.

According to Tables 4 and 5, the best values of the relative luminous flux were noted for phosphogypsum samples with sucrose and starch as a reducing agent at a molar fraction of the reducing agent of 50% and a heat treatment temperature of 1173 K. For samples with reducing agents—vegetable oil and citric acid—the optimal

Table 4. Results of heat treatment of phosphogypsum with various reducing agents at different temperatures

Reducing agent	Reducing agent mass, g	Mole fraction of the reducing agent, %	Relative luminous flux at heat treatment temperature, K		
			1073	1173	1273
A grade birch activated carbon	0.30	12.5	0.12	0.12	0.10
	0.60	25	0.15	0.14	0.25
	1.20	50	0.20	**0.88**	0.61
	1.80	75	0.11	0.73	0.55
	2.40	100	0.10	0.68	0.48
	3.00	125	0.09	0.59	0.30
	3.60	150	0.06	0.25	0.16
	4.80	200	0.05	0.05	0.06
Sugar	0.70	12.28	0.17	0.14	0.10
	1.40	24.56	0.49	0.38	0.14
	2.90	50.88	0.38	**1.13**	0.86
	4.30	75.44	0.33	1.00	0.88
	5.70	100.00	0.24	0.85	0.81
	7.10	124.56	0.19	0.82	0.92
	8.60	150.88	0.14	0.77	0.83
	11.40	200.00	0.10	0.72	0.38
Vegetable oil	0.30	13.64	0.20	0.12	0.10
	0.60	27.27	0.29	0.14	0.10
	1.10	50.00	**0.80**	0.22	0.10
	1.70	77.27	0.79	0.40	0.10
	2.20	100.00	0.78	0.65	0.10
	2.80	127.27	0.73	0.59	0.20
	3.40	154.55	0.70	0.42	0.10
	4.40	200.00	0.74	0.42	0.20

Table 4. Continued

Reducing agent	Reducing agent mass, g	Mole fraction of the reducing agent, %	Relative luminous flux at heat treatment temperature, K		
			1073	1173	1273
Citric acid	1.10	6.40	0.24	0.10	0.10
	2.10	12.21	0.39	0.12	0.10
	4.30	25.00	0.86	0.35	0.15
	6.40	37.21	**0.93**	0.75	0.15
	8.50	49.42	0.91	0.90	0.15
	10.70	62.21	0.90	0.88	0.10
	12.80	74.42	0.84	0.80	0.26
	17.10	99.42	0.63	0.60	0.21
Starch	0.70	12.96	0.20	0.14	0.14
	1.40	25.93	0.37	0.33	0.19
	2.70	50.00	0.52	**1.00**	0.62
	4.10	75.93	0.52	0.97	0.81
	5.40	100.00	0.36	0.92	0.92
	6.80	125.93	0.27	0.82	0.83
	8.10	150.00	0.27	0.69	0.79
	10.80	200.00	0.27	0.41	0.60

Table 5. Comparison of A grade birch activated carbon and wood charcoal

Reducing agent	Reducing agent mass, g	Mole fraction of the reducing agent, %	Relative luminous flux
A grade birch activated carbon	1.2	50	**0.88**
	1.8	75	0.73
	2.4	100	0.68
	4.8	200	0.05
Wood charcoal	1.2	50	**0.86**
	1.8	75	0.77
	2.4	100	0.70
	4.8	200	0.10

temperature was 1073 K, at which the maximum value of the relative luminous flux was reached with a reducing agent molar fraction of 37–50%.

CONCLUSIONS

A comprehensive study of the possibility of obtaining the demanded inorganic luminescent material from the multi-tonnage waste of orthophosphoric acid production was carried out. The following main results were obtained:

1) The study of the effect of preliminary preparation of phosphogypsum in the form of heat treatment at different temperatures, humidification of samples, allowed us to establish that for the synthesis of phosphor the most successful is the use of phosphogypsum without pretreatment.

2) Heat treatment at a temperature of 1073 K of a phosphogypsum sample is accompanied by the formation of an anhydrous compound – calcium sulfate. Heat treatment in the presence of a reducing agent leads to the formation of a composite material containing a phase of anhydrous calcium sulfate and calcium sulfide.

3) When the temperature of the heat treatment increases, cracks appear on the crystals, which may be due to the processes of removing crystallization water. Heat treatment in the presence of a reducing agent is accompanied by partial destruction of the structure, plate crystals lose the clarity of the boundaries, clusters of the reduced material form on their surface.

4) Heat-treated phosphogypsum in the presence of a number of reducing agents – A grade birch activated carbon, wood charcoal, vegetable oil, citric acid, starch, and sucrose – has the ability to luminescence due to the presence of calcium sulfide.

5) The optimal technological conditions for obtaining a composite material exhibiting luminescent properties were revealed: the heat treatment temperature is 1073–1173 K, the duration of isothermal exposure is 60 min, the amount of reducing agent is 37–50 mol %.

6) The conducted research opens up wide possibilities for processing waste from multi-tonnage chemical production to obtain a sought-after inorganic product.

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Authors' contributions

O.A. Medennikov – synthesis and experimental study of sample properties, interpretation of experimental results, writing the text of the article;

N.P. Shabelskaya – interpretation of experimental results, writing the text of the article.

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