

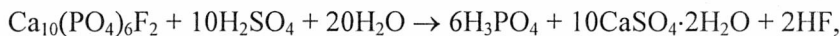
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A NEW PROCEDURE OF PHOSPHOGYPSUM PURIFICATION IN ORDER TO DIMINISH THE CONTENT OF RADIONUCLIDES

Phosphogypsum obtained by "wet procedure" for phosphoric acid production is actually calcium-sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which contains a high percentage of impurities as well as radionuclides originating from the basic raw material used for the production, i.e., phosphate. In the technology of phosphoric acid production by "wet procedure", phosphogypsum is intended to be a "sponge" that absorbs all impurities from phosphoric acid (except uranium) and to be left in deposits as the unnecessary burden. Since enormous amounts of phosphogypsum result from phosphoric acid production (the ratio is 5:1), phosphogypsum deposits are the problem per se, as far as environmental protection is concerned, because they occupy large areas and may contaminate the air, underground waters, as well as water flows that receive phosphogypsum in the form of 2% suspension. In the procedure proposed, phosphogypsum is transformed into hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, which corresponds to natural gypsum, and the impurities which are present in this compound are in accordance with natural gypsum composition. By removing radionuclides with barium-sulphate, ^{226}Ra isotope content decreases below the maximum permissible concentration, but this process is directly dependent on the type of the phosphate utilized in phosphoric acid production.

1. INTRODUCTION

Phosphogypsum is a by-product of the phosphate fertilizer which is produced in large quantities worldwide during the production of phosphoric acid [1], [2]. The "wet" process is most commonly applied in production of phosphoric acid, and it can be summarized by the following equation [3]:



e.g., according to the scheme in figure 1 [8].

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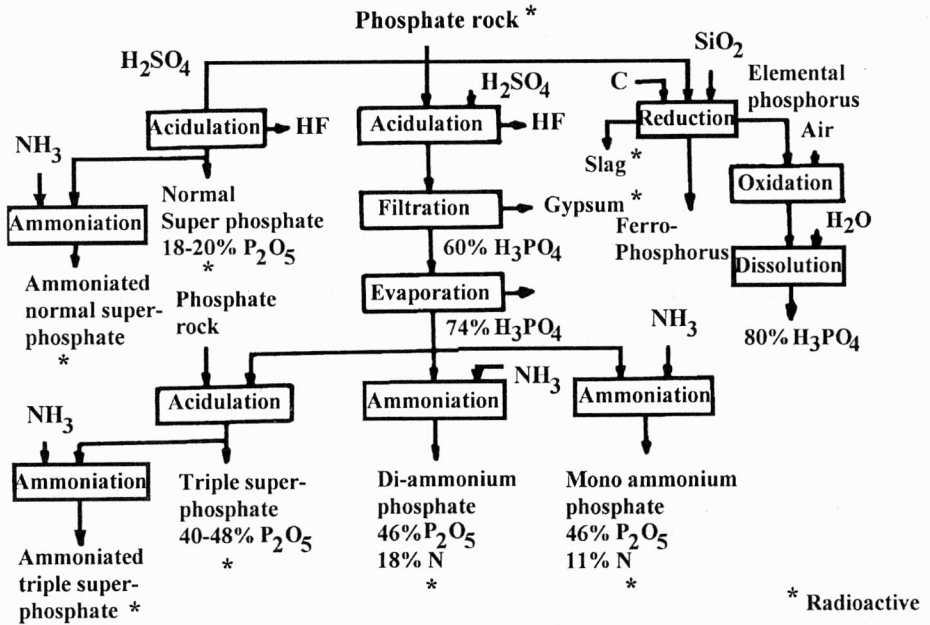


Fig. 1. The production of phosphatic fertilizers

As can be seen from figure 1, phosphogypsum is separated in filters from phosphoric acid, which is then concentrated and subsequently utilized for mineral fertilizer production, while the phosphogypsum is kept in deposits (figure 2) [5], or in areas intended for this purpose (mines, opencasts), or is (temporarily) discarded as a much diluted (2 wt.%) suspension into water-courses.

Phosphogypsum in raw condition, that is, immediately after filter separation, creates a great problem to phosphoric acid producers. It arises as soon as the first factory of phosphoric acid was established, in which "wet" technology was used, and no ultimate solution to this problem has been found yet. The CaO/P_2O_5 ratio in the phosphates utilized for phosphoric acid production is 1.35–1.65, which means that the mass of dried phosphogypsum per 1 t of P_2O_5 obtained is between 4 and 5 t, making thus phosphogypsum, and not phosphoric acid, the *main product* of the plant [6].

Phosphogypsum mainly consists of gypsum ($CaSO_4 \cdot 2H_2O$), but it also contains smaller quantities of impurities that may have harmful influence on the environment, as, for instance, heavy metals [7] and natural radionuclides [8]. The presence of impurities in phosphogypsum, especially of radionuclides, may prevent further utilization of it. Thus, additional purification is necessary before its application [9], [10].

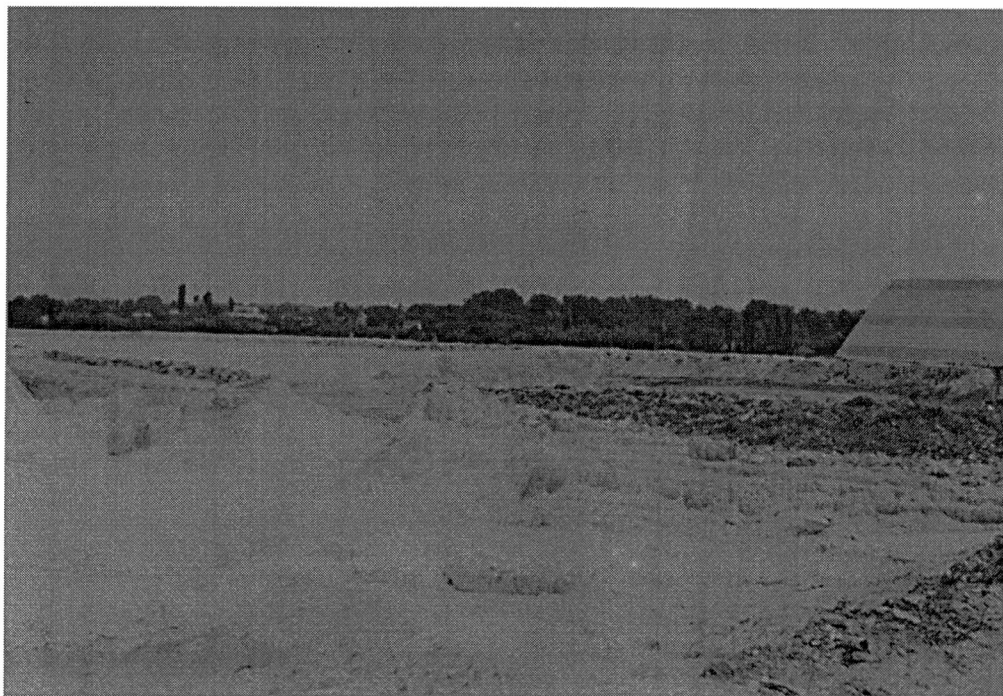


Fig. 2. Appearance of phosphogypsum deposit – “white dead sea”

Phosphogypsum components, originally present in phosphate, which are not found in natural gypsum, occur in active forms and pollute the soil (as well as underground waters) and natural water flows [5]. Insoluble particles are, sooner or later, sedimented along the banks and shallows of the river bed, forming bigger accumulations, lessening the insolation of the bottom of the river and covering river flora and fauna with a thin layer of sediment. Apart from occupying large areas and preventing further development of flora and fauna, phosphogypsum, due to the radionuclides which originate from phosphates, represents also a further source of radionuclides and their radioactive daughters, which may additionally contaminate the environment [11].

For that reason, worldwide investigations are in progress with the objective of exploiting phosphogypsum as a raw material for the production of various materials applicable mainly in construction industry, which is represented schematically (optionally) in figure 3.

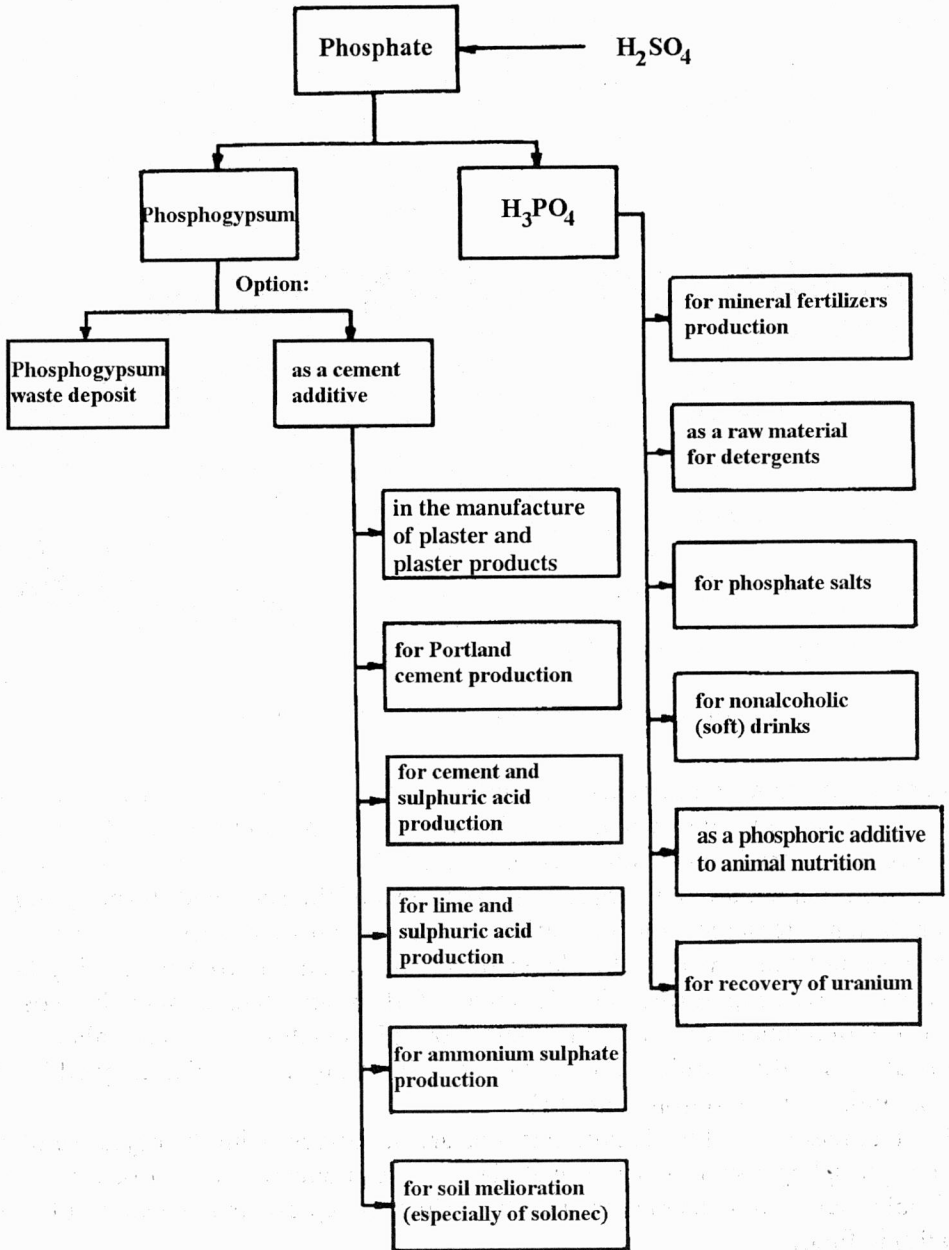


Fig. 3. Scheme of application of phosphoric acid and optionally of phosphogypsum

All this made it necessary to undertake investigation in order to purify phosphogypsum and bring it closer to natural gypsum by its composition. To this end, a new method has been applied of phosphogypsum purification, and testing of the quality, chemical composition and physicochemical properties have been performed by standard silicate analysis, by the method of alkaline melting, X-ray diffraction analysis and thermogravimetric analysis.

To compare the structure of natural gypsum with phosphogypsum obtained immediately after filter separation in the plant for phosphoric acid production, as well as after application of purification procedure, the scanning electron microscopy has been applied.

As the initial raw material, i.e., *phosphates* contain radionuclides (figure 1), they are also found in the phosphogypsum. For that reason, gamma spectrometric analysis of phosphogypsum has been performed, before and after purification, and the equation has been given for calculating the coefficient of radon liberation from phosphogypsum.

2. EXPERIMENTAL

All investigations were performed with phosphogypsum obtained from chemical industry in IHP Prahovo by a technological procedure in which raw phosphates are treated with H_2SO_4 . Phosphogypsum purification was carried out by the new procedure, which will be described in further part of the paper.

Gamma spectrometric analysis of phosphogypsum samples was performed as follows: phosphogypsum samples were homogenised, dried at 105 °C (for 6 hours) and put into a container (Marinelli) of appropriate geometric shape and kept closed airtight (for 30 days) in order to achieve radioactive equilibrium. Gamma spectrometric measurements were performed by three pure germanium detectors manufactured by EG&G "ORTEC", Germany, with the efficiency of 25–30% and energy resolution of 1.75–1.95 keV. The detectors were connected to a multichannel analyser by the same manufacturer and to corresponding computer equipment. Energy calibration, as well as calibration of detector efficiency, was performed by radioactive standard supplied by Amersham. The measurement time for one sample was 60.000 to 100.000 s, and the basic radiation was measured after 250.000 s.

Measurements of the total activity were performed by α - β anticoincidental proportional gas counter ("COUNTERMASTER") with basic radiation of 1 imp/min. Planchet radius was 2.3 cm. Counter efficiency amounted to 24% and was determined by a standard of ^{90}Sr .

Phosphogypsum and natural gypsum samples were analysed using scanning electron microscope (SEM), JSM-840A, JEOL, Japan.

X-ray diffraction analysis was carried out using the diffractometer for powder Siemens D-500 with Ni-filtered CuK_{α} radiation. Identification of crystalline phases in

the samples recorded has been carried out by position and intensity comparison of diffraction profiles with JC PDS data.

Thermogravimetric analysis of phosphogypsum was performed on Dermatograph STANTON, England, with the speed of heating up to 7 °C/min in air stream in mixture with Al_2O_3 , samples were analysed in ceramic crucible at a temperature of up to 500 °C.

3. RESULTS AND DISCUSSION

Thermogravimetric analysis of phosphogypsum sample was performed in air stream with the speed of heating of 7 °C/min. The results obtained are presented in figure 4, showing the change of sample mass in wt.% versus temperature. The mass loss for phosphogypsum is 17.53 wt.% (gypsum loses 2 molecules of water), which would correspond to gypsum portion of 84 wt.% in the sample. For natural gypsum, which is hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), the mass loss is 5.75 wt.%, which would correspond to gypsum portion of 93 wt.%.

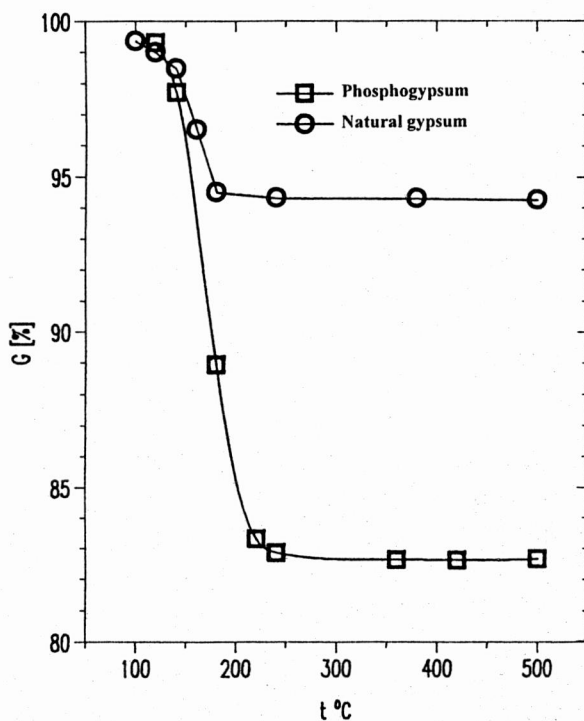


Fig. 4. Thermogravimetric analysis of phosphogypsum samples

It is essential for phosphogypsum purification that temperature be elevated. The following conditions: temperature around 90 °C and sulphuric acid concentration of 28 wt.% were necessary for phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – dihydrate) to be transformed into a hemihydrate – $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, which corresponds to natural gypsum, see the state diagram of calcium sulphate in figure 5. It can be seen that only under these conditions phosphogypsum is situated within region II, where the form of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is dominant over $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

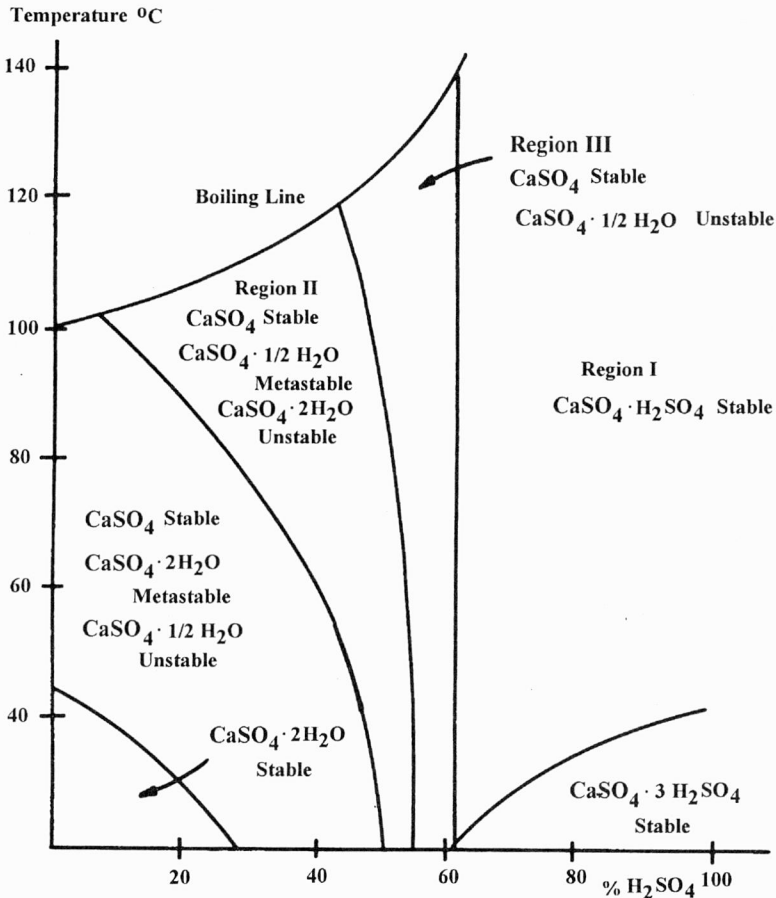


Fig. 5. Stability diagram – CaSO_4 in $\text{CaSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system

Phosphogypsum purification was carried out by solution of H_2SO_4 in water, with concentration of 28 wt.%, which was heated up to the temperature of 90 °C. Phosphogypsum was added to the solution and an emulsion was made by continual stirring. Next, barium sulphate was added and the mixture was stirred until the temperature reached

85 °C. It was cooled afterwards, and then filtered through a special Buchner funnel, separating the solid from the liquid phase. After drying and calcination, the grinding of the purified phosphogypsum was carried out in a laboratory mixer to the particle size mainly between 100 and 200 µm, with only 12% particles bigger than 200 µm.

The results of the analysis of chemical and mineralogical composition of natural gypsum, phosphogypsum taken from the filter in the process of phosphoric acid production by "wet procedure", and previously processed and purified phosphogypsum by the new procedure are given in table 1.

Table 1

Chemical and mineralogical composition of natural gypsum, phosphogypsum taken from plant's pipe and purified phosphogypsum

| Chemical composition | Natural gypsum (in wt. %) | Phosphogypsum taken from plant's pipe (in wt. %) | Purified phosphogypsum (in wt. %) |
|---|------------------------------|--|---|
| CaSO ₄ ·2H ₂ O | — | 74.16 | 11.54 |
| CaSO ₄ ·0.5H ₂ O | 81.34 | — | 77.26 |
| CaSO ₄ , anhydride | 6.16 | — | — |
| Bonded (fixed) water, H ₂ O | 5.38 | 18.02 | 7.21 |
| CaSO ₄ , total | 82.12 | 56.14 | 81.59 |
| | Excess: | | |
| Free CaO | 0.70 | 0.77 | 0.29 |
| SO ₃ | — | — | — |
| Sum: | 88.20 | 74.93 | 89.09 |
| | Impurities: | | |
| Free water, at 45 °C | 1.30 | 0.34 | 1.03 |
| Calcination loss | 0.98 | 2.18 | 0.60 |
| SiO ₂ + insoluble residue | 4.15 | 21.75 | 4.55 |
| MgCO ₃ | — | — | — |
| Na ₂ O | — | — | — |
| K ₂ O | — | — | — |
| Al ₂ O ₃ + Fe ₂ O ₃ | 0.06 | 0.04 | 0.17 |
| MgO | — | — | — |
| CaCO ₃ | 5.09 | — | 4.48 |
| P ₂ O ₅ | — | 0.84 | 0.09 |
| Sum: | 11.58 | 25.15 | 10.92 |
| Total: | 99.78 | 100.08 | 100.01 |

It can be seen that phosphogypsum is in the form of dihydrate immediately after being separated from filters (74.16 wt.%), while the natural gypsum is hemihydrate in essence (81.34 wt.% CaSO₄·0.5H₂O). Using the purifying procedure proposed, phosphogypsum is transformed into hemihydrate (77.26 wt.% CaSO₄·0.5H₂O), and all the remaining parameters are far closer to natural gypsum than to phosphogypsum.

To determine morphological composition and structure, homogeneity and the presence of faults in their structure, an inspection was performed by scanning electron microscope (SEM) of the natural gypsum and various phosphogypsum samples, and the photographs are given in figures 6 through 9.

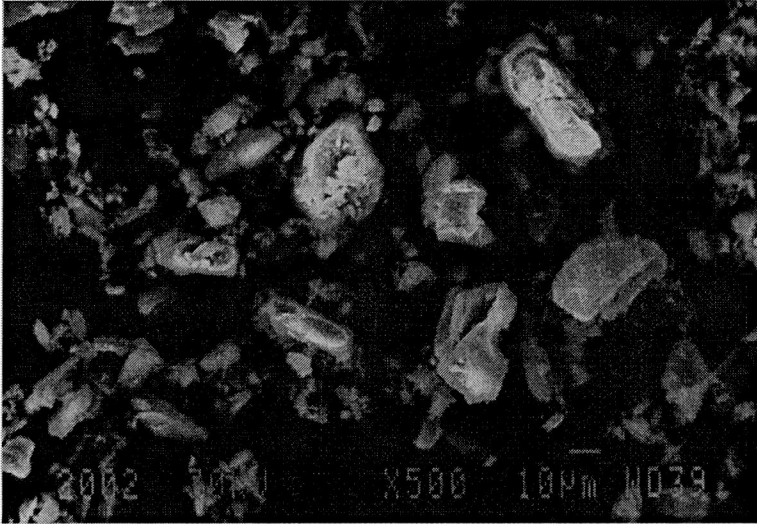


Fig. 6. SEM photograph of crystalline structure of natural gypsum ($\times 500$)



Fig. 7. SEM photograph of crystalline structure of phosphogypsum taken from plant's pipe ($\times 1,000$)

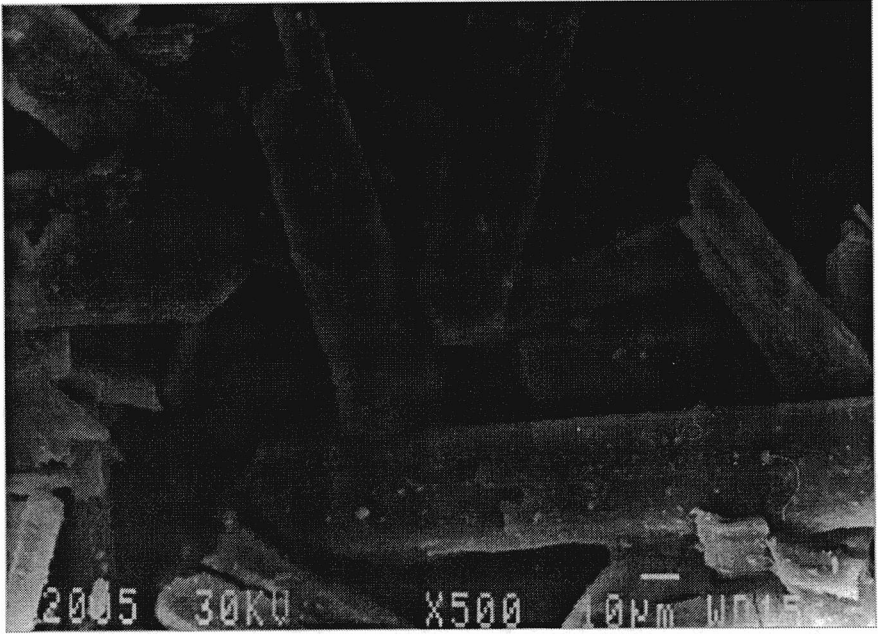


Fig. 8. SEM photograph of crystalline structure of purified phosphogypsum ($\times 300$)

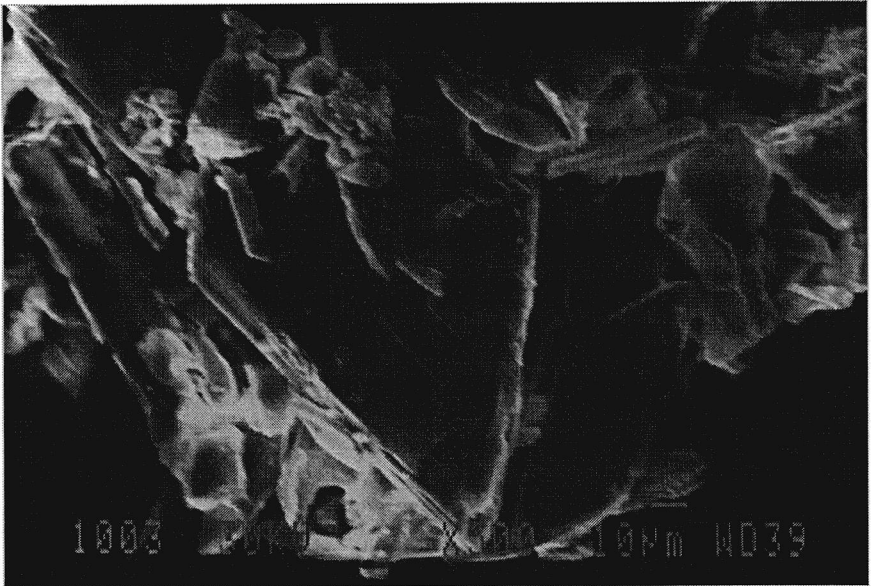


Fig. 9. SEM photograph of crystalline structure of mixture of 75 wt.% natural gypsum and 25 wt.% phosphogypsum ($\times 500$)

SEM photographs of natural gypsum and phosphogypsum show that these two materials, regardless of having the same chemical composition, have different structures: natural gypsum has more poorly expressed crystal structure, and phosphogypsum has a marked crystal structure, mostly of rhombic and hexagonal forms, which indicate its more complex composition than that of the natural gypsum. This has also been confirmed by earlier investigations [12], [13].

An X-ray diffraction analysis of natural gypsum and phosphogypsum indicated the presence of impurities in phosphogypsum. The results confirm that the two materials are the same, however, phosphogypsum contains ingredients not found in natural gypsum.

The X-ray diffractograms obtained for natural gypsum and phosphogypsum are presented in figures 10 and 11.

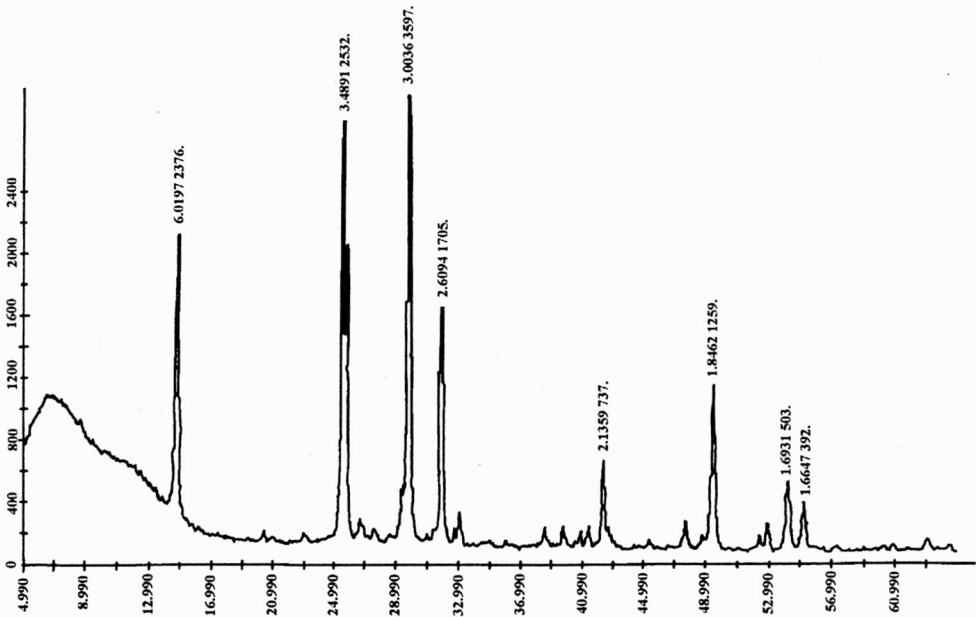


Fig. 10. Characteristic X-ray diffractogram of natural gypsum

The X-ray diffraction analysis was carried out by comparing the position and intensity of diffraction profiles with JC PDS data. The following crystalline phases were identified: for natural gypsum $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (33–310) – *identification number from standard*; for phosphogypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (33–311); $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (33–310) spectra corresponded to natural gypsum, CaHPO_4 (9–80) or $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (9–77) spectra also corresponded to natural gypsum [14].

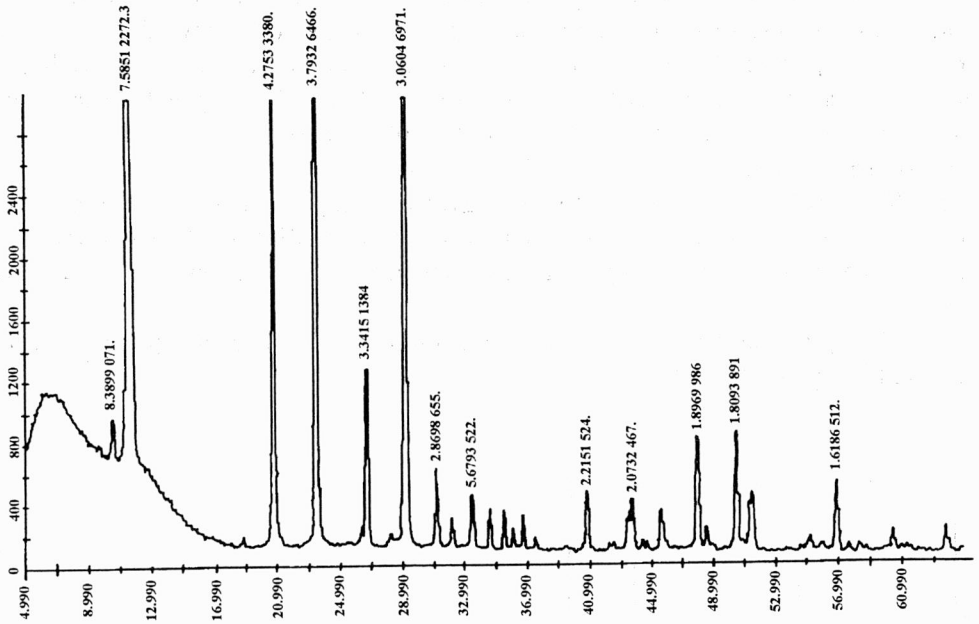


Fig. 11. Characteristic X-ray diffractogram of phosphogypsum

The main difference between natural gypsum and phosphogypsum is in radionuclide content. This content is variable, as it depends on the initial raw material – phosphate; namely, phosphates formed from sediment phosphates (Florida, Morocco, Tunisia, Senegal) contain uranium in higher concentrations, while phosphates of volcanic origin (Cola, Caratau) either contain radionuclides in traces, or do not contain them at all. During technological processing of phosphates by wet procedure, due to degradation with H_2SO_4 , 14 wt.% of uranium from phosphates pass into phosphogypsum (and the residue into H_3PO_4), while almost 80 wt.% of the radium from the phosphate pass into phosphogypsum. Uranium in phosphate is in equilibrium with radium. The quantity of radium may be calculated according to the equation:

$$N_u/t_{1/2,U} = N_{Ra}/t_{1/2,Ra},$$

where: N – number of atoms submitted to radioactive degradation; $t_{1/2}$ – half-life of radioactive isotope. The oxidation state of uranium in phosphates and the mode of ore treatment determine uranium distribution between acid and phosphogypsum. Passage of uranium from phosphoric acid is in direct dependence with the amount of P_2O_5 used if ore dissolution is performed under oxidation conditions [15]. In phosphates from Florida, which contain U(IV) form as uranium dominant form under normal conditions of processing by “wet procedure”, between 60 and 80 wt.% uranium passes into the acid, and the residue into phosphogypsum, while for phosphates of African

origin, where uranium is mostly in the form of U(VI), its share in the acid may be almost 90 wt.% [16].

3.1. PROCESS OF URANIUM REMOVAL FROM PHOSPHOGYPSUM

In the literature available, various procedures can be found for decreasing the radionuclide content in phosphogypsum [17]–[20], but none of them allows complete removal of the main “fault” of phosphogypsum, in comparison with natural gypsum, because it is variable and in direct relation with the type of phosphate used as a raw material [7].

The process for reducing radionuclide contamination in phosphogypsum, applied in this paper, is our primary objective. Our further aim is to obtain a purified gypsum product from phosphogypsum containing radioactive contaminants (radionuclides).

It has now been discovered that the foregoing objectives are accomplished for reducing the radioactive contamination (radionuclides) in phosphogypsum in a process which comprises:

- admixing phosphogypsum containing radionuclides with dilute sulphuric acid containing barium sulphate at an elevated temperature to form an acid slurry, having a solid component comprised of a fine fraction and a coarse fraction, and
- separating the said fine fraction of solid from the coarse fraction,
- whereby the fine fraction predominates in the barium sulphate and the radionuclides, and
- whereby the coarse fraction predominates in phosphogypsum of reduced radioactive contamination.

In the first step of purification, a thermal decomposition of phosphogypsum, from dihydrate to semihydrate (see figure 5), may generally be accomplished by dry kettle calcination at atmospheric pressure and temperature of about 115–160 °C or by thermal dehydration of dilute acid such as in nearly an aqueous sulphuric acid solution having a concentration of 28 wt.% at atmospheric pressure and temperature of about 90 °C, which is used to digest the phosphogypsum.

In the second step of this process, sufficient barium sulphate is added to the slurry of phosphogypsum and sulphuric acid to concentrate a barium sulphate in the resulting slurry. Greater amounts of barium sulphate could be used, but it is generally unnecessary since such an excess adds to the cost of carrying out the process without significantly improving the reduction of radioactive contamination (radionuclides). Barium sulphate is preferably added as a concentrated sulphuric acid solution containing from about 0.10 to about 10 wt.% of barium sulphate. Fuming sulphuric acid may be employed to dissolve the barium sulphate, if desired.

Phosphogypsum was being agitated with the solution of sulphuric acid and barium sulphate for 12 minutes, while maintaining the temperature of the resulting slurry at

about 85 °C. After the desired elevated temperature is obtained, the slurry is agitated for a sufficient time to effect solubilization of the radioactive contaminations (radionuclides), followed by absorption and/or co-precipitation of radium sulphate crystals with barium sulphate crystals in finely divided form. This digestion period ranges from 5 to 250 minutes.

After the reaction of the acid slurry has been completed, the slurry is preferably cooled at a temperature of 30–35 °C and then filtered. If desired, the hot acid slurry may be washed without a separate cooling step. The acid slurry with or without prior cooling is subjected to a solid–liquid separation, such as filtration or cyclone separation, and the clarified acid is recovered. It may be recycled, after reconstruction, for use in reacting with additional impure phosphogypsum or used in other parts of the fertilizer process.

The filter cake was washed with water and the solids were dried at a temperature of 60 °C. The dried solids were mixed with water and then wet screened on a 100 micron screen. The solid phosphogypsum retained on the 100 micron screen was collected and dried at 60 °C.

The results of gamma spectrometric analysis of natural gypsum and phosphogypsum purified by the procedure proposed are given in table 2.

Table 2

Gamma spectrometry results of the samples of unpurified and purified phosphogypsum by new process [21]

| Radionuclides | Radioactivity (Bq/kg) | |
|------------------------------------|--------------------------------------|------------------------------------|
| | Activity of unpurified phosphogypsum | Activity of purified phosphogypsum |
| ^{226}Ra | 439±20 | 379±20 |
| ^{232}Th | 8.7±0.5 | 7.1±0.5 |
| ^{40}K | < 8.7 | 7.8±0.5 |
| Radionuclides of artificial origin | < 1.0 | < 1.1 |

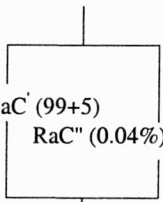
As one can see from table 2, the activity of phosphogypsum purified by this procedure is decreased by approximately 10 wt.% in comparison with raw phosphogypsum. It should be emphasized that the original raw material, that is phosphate, determines much the content of radionuclides, which ought to be primarily taken into consideration when choosing the phosphate.

The results of the analysis of radionuclide content in raw phosphogypsum are in accordance with literature data obtained by investigation of ^{226}Ra isotope contents in various types of phosphogypsum, which range from 430 to 790 Bq/kg. The presence of thorium, as well as the presence of the products of degradation of thorium sequence, is not of any importance, because the activity originating from thorium is not high.

The presence of ²²⁶Ra isotope is dangerous because of liberation of (the only) radioactive gas radon (Rn-222), which is a daughter of radium degradation sequence (table 3).

Table 3

Radioisotopes in the radium series

| Radioisotope (historical name) | Element | Half-time | Particle energies ^a (MeV) | γ-ray energies (MeV) |
|--|-------------------|------------|--|----------------------|
| Radium | ²²⁶ Ra | 1620 years | α, 4.78 (94.3%) α, 4.59 (5.7%) | 0.187 (5.7%) |
| Radon | ²²² Rn | 3.82 days | α, 5.49 (99+%) α, 4.98 (<0.1%) | 0.51 (0.075) |
| RaA | ²¹⁸ Po | 3.05 min | α, 6.00 (99+%) | |
| RaB | ²¹⁴ Pb | 26.8 min | β ⁻ , 0.67–1.03 | 0.053–0.352 |
| RaC | ²¹⁴ Bi | 19.7 min | β ⁻ , (99+%) 0.4–3.18 α, (0.04%) | |
|  | ²¹⁴ Po | 160 μsec | α, 7.68 | |
| | ²¹⁰ Tl | 1.32 min | β ⁻ , 1.96 | 0.32–2.36 |
| RaD | ²¹⁰ Pb | 21.4 years | β ⁻ , 0.017 (85%) β ⁻ , 0.064 (15%) | 0.047 (85%) |
| RaE | ²¹⁰ Bi | 5.0 days | β ⁻ , 1.16 (99+%) | |
| RaF | ²¹⁰ Po | 138.4 days | α, 5.30 (99+%) | |
| RaG | ²⁰⁶ Pb | stable | | |

^a The β⁻ or γ⁻ spectra contain many lines, only ranges of energy without abundances are given RaG – unradioactive lead (isotope ²⁰⁶Pb) or radium lead.

The daughter product of ²²⁶Ra, ²²²Rn, is having a half-life of 3.82 days, and the extent to which this escapes from any biological system in which ²²⁶Ra is deposited profoundly affects the dose. Radiation danger upon the contact of human organism with radon is connected with its radioactive “short-lived radon descendents”: ²¹⁸Po, ²¹⁴Pb, ²¹⁴Bi and ²¹⁴Po, which mostly damage the lungs. A disintegration product later in series is RaD (²¹⁰Pb) with a half-time of 21 years; this element and those derived from it will not reach equilibrium amounts in the life-time of a man but, for example, may be present in a person who has acquired an accidental body burden of ²²⁶Ra.

3.2. DETERMINATION OF ²²²Rn EMANATION COEFFICIENT [22]

After the equilibrium period of 30 days, the total activity of ²²²Rn is in secular equilibrium with ²²⁶Ra. The activity of the total gaseous ²²²Rn in phosphogypsum (or sample)

was calculated, taking into consideration the volume of the vessel with the sample, the porosity of the phosphogypsum, and the volume removed during sampling. Porosity (P), i.e., fraction of total volume of phosphogypsum, was calculated by:

$$P = 1 - (D_b/D_p),$$

where D_b is the bulk density (g/cm^3 , phosphogypsum (solids+porosity) and D_p is the density of phosphogypsum particle, and was assumed to be 2.32 g/cm^3 , which is the value of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [23]. The efficiencies of the scintillation cells were determined with a calibrated ^{222}Rn source, which quantitatively delivered 3 Bq in an unspecified volume.

The ^{222}Rn emanation coefficient (ε) was calculated by:

$$\varepsilon = \frac{\text{total activity (Bq) of } ^{222}\text{Rn in the gaseous phase}}{\text{total activity (Bq) of } ^{226}\text{Ra in the sample}} \cdot 100\%.$$

Radioactivity is investigated as the contents of three radioactive isotopes: K-40, Ra-226 and Th-232. The biological harmfulness evaluated for these three isotopes has the following relations:

$$^{40}\text{K} : ^{226}\text{Ra} : ^{232}\text{Th} = 1 : 12.5 : 16.50$$

which is not the case with phosphogypsum, because several times higher radioactivity originates from ^{226}Ra isotope than from other isotopes (table 2).

It can be seen from table 2 that by using the procedure proposed, the activity of ^{226}Ra isotope is decreased below the maximum permissible concentration (400 Bq/kg) [24].

Upper permissible limits of radioactivity are calculated according to so-called summary formula established by the National Commission for Protection from Radiation in the former USSR, and according to our currently valid regulations it has the following form [24]:

$$\begin{aligned} \text{Index for interiors} &= \frac{^{226}\text{Ra (Bq/kg)}}{200} + \frac{^{232}\text{Th (Bq/kg)}}{300} + \frac{^{40}\text{K (Bq/kg)}}{3000} \\ + \frac{V_{\text{interiors}} (\text{Bq/kg})}{4000} &\leq 1, \\ \text{Index for exteriors} &= \frac{^{226}\text{Ra (Bq/kg)}}{400} + \frac{^{232}\text{Th (Bq/kg)}}{300} + \frac{^{40}\text{K (Bq/kg)}}{5000} \\ + \frac{V_{\text{exteriors}} (\text{Bq/kg})}{4000} &\leq 1, \\ \text{Index for roads} &= \frac{^{226}\text{Ra (Bq/kg)}}{700} + \frac{^{232}\text{Th (Bq/kg)}}{500} + \frac{^{40}\text{K (Bq/kg)}}{8000} \\ + \frac{V_{\text{for roads}} (\text{Bq/kg})}{2000} &\leq 1. \end{aligned}$$

In the opinion of the majority of experts, there is no negligible level of radioactive rays; only one radioactive disintegration is enough to cause mutagenic change, that is, appearance of cancer cells. Lowering the dose only brings about the lowering of the probability of illness appearing.

The results of the investigation of radionuclide content indicate a significant presence of Ra-226 isotope of 439 Bq/kg. This fact is in accordance with literature data on the values of Ra-226 isotope content in various forms of phosphogypsum, which range between 430 and 790 Bq/kg. The presence of Ra-226 isotope is dangerous because of the liberation of radioactive gas radon Rn-222 isotope. Radon, which is produced by radium degradation and the half-life of which is 3.8 days, gets accumulated in the atmosphere of closed rooms. Radon is an α -emitter and induces much more serious damage to living tissue when it is inhaled and the radioactive products of its decay are deposited in lungs. At radioactivity equilibrium, 1 g of Ra corresponds to $3.7 \cdot 10^{10}$ Bq. During decay, radon yields at first a sequence of solid radioactive particles which emit α -, β -particles and γ -quant. Radiation danger upon the contact of human organism with radon is connected with its radioactive "short-lived radon descendants": ^{218}Po , ^{214}Pb , ^{214}Bi and ^{214}Po , which mostly damage the lungs. These isotopes are responsible for the dose of radiation received by human lungs. Radon is inhaled and expired by people, it does not remain in breathing system, but the products of its radioactive decay adhere to all materials, and even to air particles. When they are inhaled, they remain in lungs and constantly emit the radiation.

There is no one generally accepted scientific view on how small quantities of radon affect human health, but one thing is sure: radon in high quantities is certainly harmful, but for the small quantities, there are no valid data. This is a fundamental scientific problem that has not still been solved. It actually amounts to the question on the risk from "small doses". It is an old scientific controversy: according to some authors – each dose is harmful, even the smallest dose received may have disastrous consequences. With the lowering of the dose, the probability of a harmful effect decreases, but does not disappear, until the dose decreases down to zero.

4. CONCLUSIONS

Phosphogypsum obtained by "wet procedure" for phosphoric acid production is actually calcium-sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which contains a high percentage of impurities as well as radionuclides originating from the basic raw material for the production, i.e., phosphate.

In the technology of phosphoric acid production by "wet procedure" it is intended for phosphogypsum to be a "sponge" that absorbs all impurities from phosphoric acid (except uranium) and to be left in deposits as the unnecessary burden.

Since enormous amounts of phosphogypsum result from phosphoric acid production (the ratio is 5:1), phosphogypsum deposits are the problem per se, as far as environmental protection is concerned, because they occupy large areas and may contaminate the air, underground waters, as well as water flows that receive phosphogypsum in the form of 2 wt.% suspension.

In the procedure proposed, phosphogypsum is transformed into hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, which corresponds to natural gypsum, and the impurities present are in accordance with natural gypsum composition. Removing radionuclides with barium-sulphate, ^{226}Ra isotope content decreases below the maximum permissible concentration, but this process is directly dependent on the type of the phosphate utilized in phosphoric acid production.

ACKNOWLEDGEMENTS

The work carried out in our laboratory was supported by the Ministry for Science, Technology and Development of Serbia (Project 1941). The authors are grateful to the Ministry for Science, Technology and Development for partial financial support.

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NOWA METODA OCZYSZCZANIA FOSFOGIPSU Z RADIONUKLIDÓW

Fosfogips to dwuwodny siarczan wapnia ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) otrzymywany podczas produkcji kwasu fosforowego „metodą mokrą”. Fosfogips zawiera znaczne ilości zanieczyszczeń, a wśród nich radionuklidy pochodzące z podstawowego surowca – fosforanu (fosforytu). W technologii produkcji kwasu fosforowego „metodą mokrą” fosfogips powinien mieć strukturę gąbczastą, aby absorbować wszystkie zanieczyszczenia (poza uranem). Fosfogips jest składowany jako nieprzydatny odpad. Ponieważ w czasie produkcji kwasu fosforowego powstają znaczne ilości fosfogipsu (w stosunku 5:1), więc składowiska tej substancji, zajmujące olbrzymie tereny, stanowią poważny problem w ochronie środowiska. Dodatkowo mogą być przyczyną zanieczyszczenia powietrza, wód podziemnych i powierzchniowych, do których fosfogips może dostawać się w postaci 2% zawiesiny. W proponowanej metodzie oczyszczania fosfogips jest przekształcany w półwodzian, ($\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O}$), który odpowiada naturalnemu gipsowi, jego zanieczyszczenia zaś są charakterystyczne dla naturalnego gipsu. Usunięcie radionuklidów za pomocą siarczanu baru obniża zawartość izotopu ^{226}Ra poniżej dopuszczalnego stężenia, jednakże proces ten jest bezpośrednio zależny od rodzaju fosforanu (fosforytu) użytego do produkcji kwasu fosforowego.

The first part of the book is devoted to a general history of the United States from its discovery to the present time. It is divided into three periods: the first, from the discovery to the establishment of the first colonies; the second, from the establishment of the first colonies to the declaration of independence; and the third, from the declaration of independence to the present time.

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