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

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Phosphogypsum obtained by "wet procedure" for phosphoric acid production is actually calcium-sulphate dihydrate, $CaSO_4 \cdot 2H_2O$, which contains a high percent of impurities as well as radionuclides, originating from the basic raw material. Technology of phosphoric acid production by "wet process" intends for phosphogypsum to be a "sponge" that absorbs all impurities from phosphoric acid (except uranium) and to be left in deposits as an unnecessary burden. As an enormous amount of phosphogypsum results from phosphoric acid production (the ratio is 5:1), phosphogypsum deposits are a burden per se, from the view of environmental protection, because they occupy large areas and may contaminate the air, ground water, but also surface water that receive phosphogypsum in the form of dilute suspension. By the proposed procedure, phosphogypsum is transformed into hemihydrate, $CaSO_4 \cdot ½H_2O$. Im the process of removing radionuclides with barium-sulphate, ^{226}Ra isotope content decreases below the permitted concentration, but this process is directly dependent on the type of the phosphate utilized in phosphoric acid production.

Keywords: phosphogypsum, scanning electron microscopy (SEM), X-ray diffraction analysis, gammaspectrometric analysis, thermogravimetric analysis

Introduction

Phosphogypsum is the by-product of the phosphate fertilizer which is produced in large quantities worldwide [1,2]. The "wet" prosphoric acid process is the most common one, used to produce phosphoric acid, it can be shown by the following reaction equation: [3]

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow$$

$$\rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF$$

e.g. by scheme on *Fig.1* [8].

As it may be seen in *Fig.1*, phosphogypsum is separated on filters from phosphoric acid, which is then concentrated and subsequently utilized for fertilizer production. The phosphogypsum is disposed (*Fig.2*) [5], in the areas intended for this purpose (mines, opencasts) or is (temporarily) discarded as a very diluted (2 wt.%) slurry into natural water streems.

Phosphogypsum represents a great problem for phosphoric acid producers. The problem of phosphogypsum arised at the moment as the first plant of phosphoric acid was established, working with "wet process" technology, and the final solution of this problem could not be found yet. Namely, CaO/P_2O_5 ratio in the phosphates used for phosphoric acid production, is 1,35-1,65, which means that the mass of dried phosphogypsum per 1 t of obtained P_2O_5 is between 4 and 5 t. This means that phosphogypsum, and not phosphoric acid, is the main product of the plant [6].

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

The components of phosphogypsum, originally present in raw phosphate, but are absent in natural gypsum, pollute the soil (as well as ground waters) and natural water streems [5]. Insoluble particles, sooner or later, are sedimented along the banks and shallows of the river bed, forming bigger accumulations, lessening the isolation of the bottom of the river and covering river flora and fauna with a thin layer of sediment. Besides occupying large areas and preventing further development of flora and fauna, phosphogypsum, due to

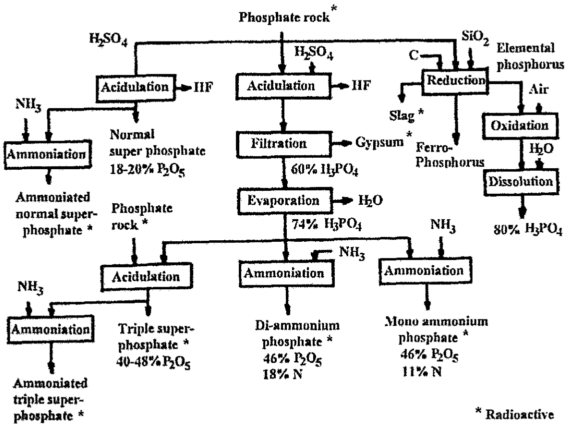

Fig.1 The production of phosphate fertilizers

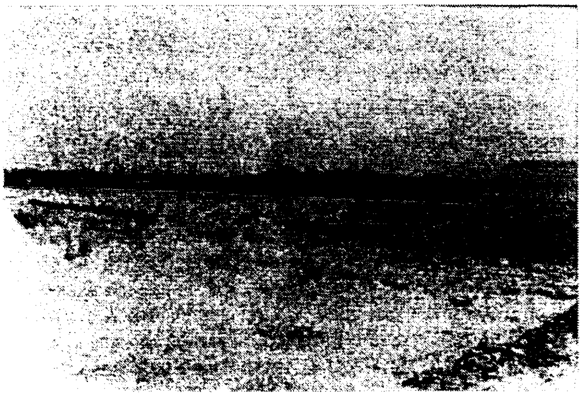

Fig.2 Appearance of a phosphogypsum deposit - "white dead sea"

the radionuclides which originate from phosphates, represents also a further source of radionuclides and their radioactive daughters, which may additionaly contaminate the environment [11].

For that reason, there are investigations in progress worldwide with the objective of exploitation of phosphogypsum as a raw material in construction industry This is represented schematically (optionally) in the *Fig.3*.

All these were reasons to undertake investigations in order to purify phosphogypsum and bring its composition. closer to natural gypsum. To achieve the given objective, a new method was applied in phosphogypsum purification, and testing the quality. Chemical composition and physico-chemical analyses were performed using standard silicate analyses, as the method of alkaline melting, X-ray diffraction and thermo-gravimetric analysis.

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

As the raw material - *natural phosphates* - contain radionuclides (*Fig.1*), they are also found in the phosphogypsum. For that reason, gamma spectrometric analysis of phosphogypsum was performed, before and after the purification, and an equation is given for calculating the coefficient of radon liberation from phosphogypsum.

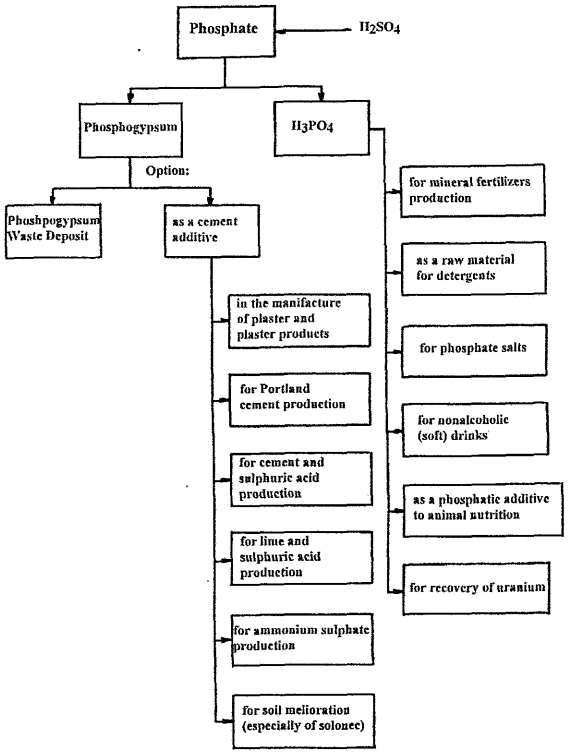

Fig.3 Scheme of application of phosphoric acid and optionally of phosphogypsum

Materials and Methods

All investigations were performed with phosphogypsum, obtained from chemical plant 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 discussed in further part of this 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 (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 1,75-1,95 keV. The detectors were connected to a multi-channel analyser by the same manufacturer and to corresponding computer equipment. Energy calibration, as well as calibration of detector efficiency were 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.

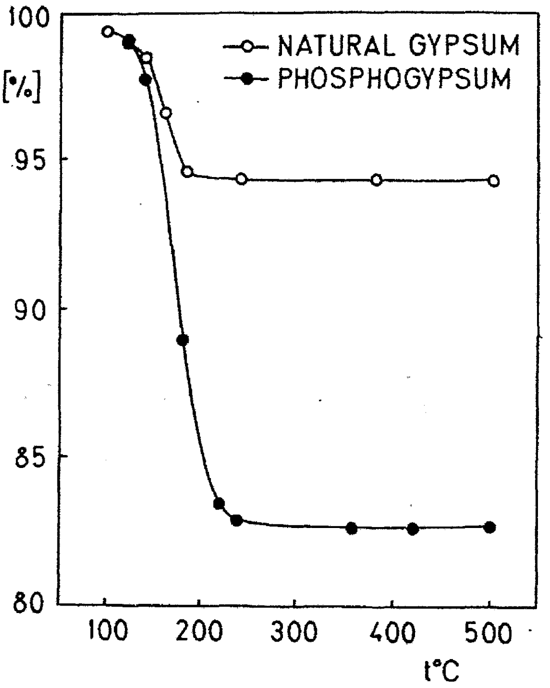

Fig.4 Thermogravimetric analysis of phosphogypsum samples

Measurements of 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 microscopy SEM, JSM-84OA, JEOL, Japan.

X-ray diffraction analysis was carried out using the diffractometer for powder SIEMENS D–500 with Ni-filtered CuK$_a$ radiation. Identification of crystalline phases in recorded samples was carried out by position and intensity comparison of diffraction profiles with JC PDS data.

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

Results and Discussion

Thermogravimetric analysis of phosphogypsum samples were performed in air stream with speed of heating of 7°C/min, and the obtained results are presented at *Fig.4*, showing the change of sample mass in wt.% in dependence on temperature. The mass loss for phosphogypsum is 17.53 wt.% (gypsum loses 2 molecule of water), that would correspond to gypsum portion of 84 wt.% in sample. For natural gypsum, which is hemihydrate ($CaSO_4 \cdot ½H_2O$) the mass loss is 5.75 wt.% that would corresponds to gypsum portion of 93 wt.%.

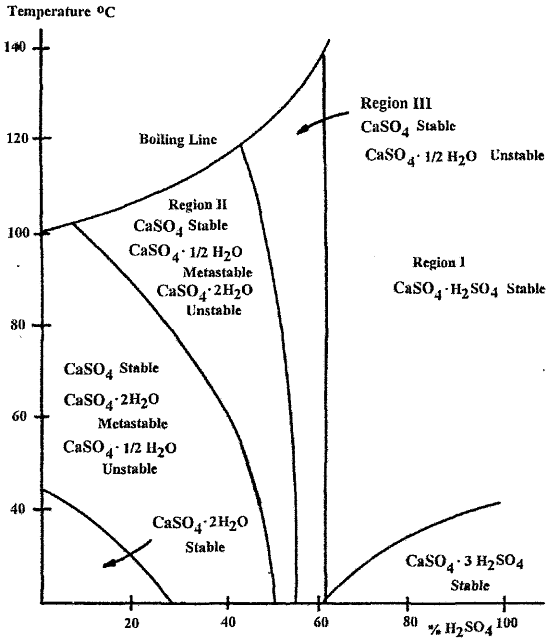

Fig.5 Stability diagram - $CaSO_4$ in $CaSO_4 \cdot H_2SO_4 \cdot H_2O$ system

The procedure of phosphogypsum purification is based on enhanced temperature. The conditions, temperature around 90°C and sulphuric acid concentration of 28 wt.%, were necessary for phosphogypsum ($CaSO_4 \cdot 2H_2O$ - dihydrate) to be transformed into a hemihydrate - $CaSO_4 \cdot ½H_2O$, that corresponds to natural gypsum This is represented in *Fig.5*, the state diagram of calcium sulphate. From *Fig.5* it can be seen that only under these conditions phosphogypsum is situated within region II, where the form $CaSO_4 \cdot ½H_2O$ is dominant over $CaSO_4 \cdot 2H_2O$.

Phosphogypsum purification was carried out by solution of H_2SO_4, with concentration of 28 wt.%, which was heated up to 90°C. Phosphogypsum was added to the solution and an emulsion was made with intensive stirring. After the addition of phosphogypsum, barium sulphate was added also with continuous stirring, until the temperature reached 85°C. Then the mixture was cooled. After cooling, it was 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 by laboratory mixer. until the particle size reached 100 to 200 µm, only 12 % of the particles were bigger than 200 µm.

The results of analyss of chemical and mineralogic composition of natural gypsum, phosphogypsum taken from filter from the process of phosphoric acid production by "wet procedure" and previously processed and purified phosphogypsum by the new procedure, are presented in *Table 1*.

From *Table 1* it can be seen that phosphogypsum is in the form of dihydrate, immediately after separation from filters (74.16 wt.%), while the natural gypsum is hemihydrate in essence (81.34 wt.% $CaSO_4 \cdot ½H_2O$). By the proposed purifying procedure, phosphogypsum is tranformed into hemihydrate (77.26 wt.%

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.%)
$CaSO_4 \cdot 2H_2O$	–	74.16	11.54
$CaSO_4 \cdot ½H_2O$	81.34	–	77.26
$CaSO_4$, anyhidride	6.16	–	–
Bonded (fixed) water, H_2O	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**
	Impurties:		
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_2O	–	–	–
K_2O	–	–	–
$Al_2O_3+Fe_2O_3$	0.06	0.04	0.17
MgO	–	–	–
$CaCO_3$	5.09	–	4.48
P_2O_5	–	0.84	0.09
Sum:	**11.58**	**25.15**	**10.92**
Total:	**99.78**	**100.08**	**100.01**

Fig.6 SEM photograph of crystalline structure of natural gypsum (x500)

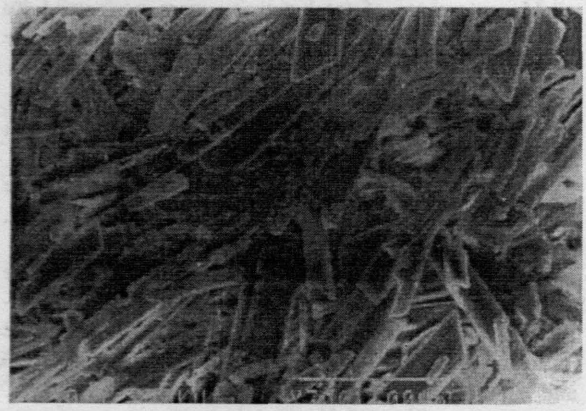

Fig.7 SEM photograph of crystalline structure of phosphogypsum taken from plant's pipe (x1,000)

$CaSO_4 \cdot ½H_2O$), and all the remaining parameters are far closer to natural gypsum than to phosphogypsum.

To establish morphological composition and structure, their homogeneity and the presence of faults in the structure, an inspection was performed by scanning electronic microscopy (SEM) of the natural gypsum and various phosphogypsum samples, and the photographs are represented in *Figs.6* to *9*.

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 poorly expressed crystal structure, and phosphogypsum has a marked crystal structure, mostly of rhombic and hexagonal forms, which indicates its more complex composition than that of the natural gypsum. This has also been confirmed by previous investigations [12,13].

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, but that phosphogypsum contains ingredients being absent in natural gypsum.

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

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 $CaSO_4 \cdot ½H_2O$ (33-310) – *identification number from standard*; for phosphogypsum: $CaSO_4 \cdot 2H_2O$ (33-311); $CaSO_4 \cdot ½H_2O$ (33-310) spectra corresponded to natural gypsum, $CaHPO_4$ (9-80) or $CaHPO_4 \cdot 2H_2O$ (9-77) spectra also corresponded to natural gypsum [14].

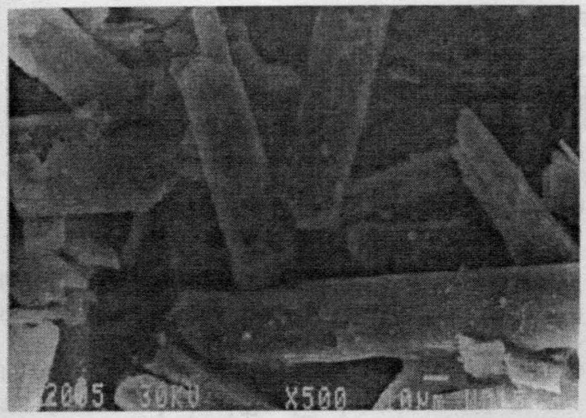

Fig.8 SEM photograph of crystalline structure of purified phosphogypsum (x300)

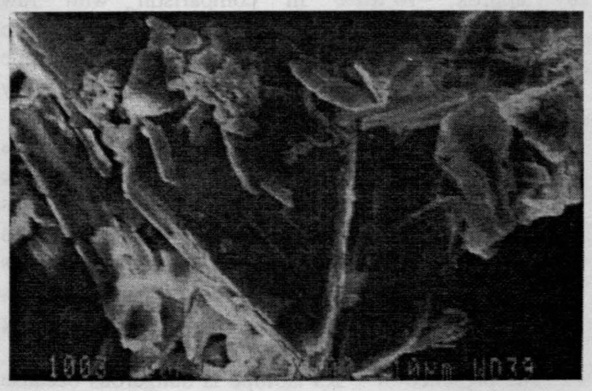

Fig.9 SEM photograph of crystalline structure of mixture of 75 wt.% natural gypsum and 25 wt.% phosphogypsum (x500)

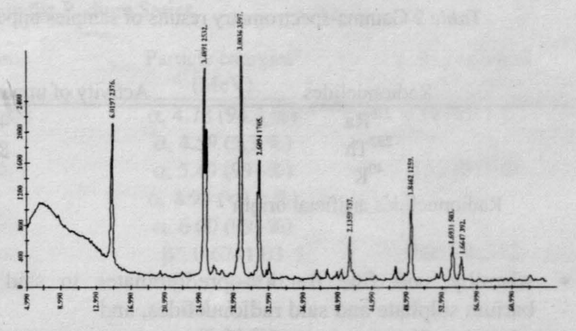

Fig.10 Characteristic X-ray diffractogram of natural gypsum

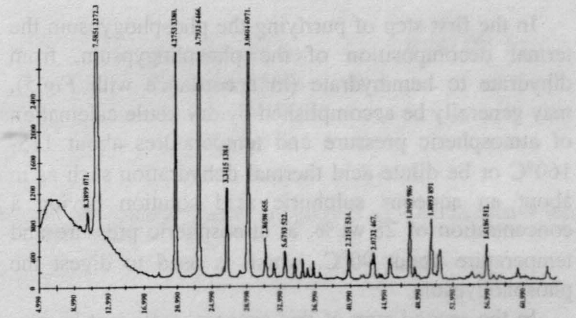

Fig.11 Characteristic X-ray diffractogram of phosphogypsum

The main difference between natural gypsum and phosphogypsum lies in their radionuclide content, although this content is variable, because it depends on the initial raw material - phosphate. Namely, phosphates formed from sediment phosphates (Florida, Marocco, 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.% od the present radium from the phosphate passes into phosphogypsum. Uranium in phosphate is in equilibrium with radium. Radium quantity may be calculated according to the equation:

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

where: N = number of atoms submitted to radioactive degradation; $t_{\frac{1}{2}}$ = half-life of radioactive isotope. 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 proportion with the use of P_2O_5 if ore dissolution is performed under oxidation conditions [15]. In phosphates from Florida, which contain U(IV) form as uranium dominant form at normal conditions of processing by "wet process", 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 participation in the acid may be almost 90 wt.% [16].

Process of uranium removal from phosphogypsum

In the available literature there are presented various procedures for decreasing of radionuclide content in phosphogypsum [17-20], but no one could remove completely that main "fault" of phosphogypsum, in comparision with natural gypsum, because it is variable and is in direct relation with the type of phosphate used as raw material [7].

The process for reducing radionuclide contamination in phosphogypsum, applied in this paper, it is a primary object of our idea. It is a further object of this idea to provide a course purified gypsum product from phosphogypsum containing radioactive contaminants

It has now been discovered that the foregoing objects 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 acidic slurry, having a solid component comprised of fine fraction and a coarse fraction, and
- separating the said fine fraction of solid from the coarse fraction,

Table 2 Gamma-spectrometry results of samples 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 artificial origin	< 1.0	< 1.1

- whereby said fine fraction predominates in said barium sulphate and said radionuclides, and
- whereby the coarse fraction predominates in phosphogypsum of reduced radioactive contamination.

In the first step of purifying the phosphogypsum the termal decomposition of the phosphogypsum, from dihydrate to hemihydrate (in accordance with *Fig.5*), may generally be accomplished by dry kettle calcination of atmospheric pressure and temperatures about 115-160°C or be dilute acid thermal dehydration such as in about an aqueous sulphuric acid solution having a concentration of 28 wt.%. at atmospheric pressure and temperature 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 provide a barium sulphate concentration in the resulting slurry. Excess barium sulphate may be employed, 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 to a concentrated sulphuric acid solution containing from about 0.10 to 10 wt.% by weight of barium sulphate. Fuming sulphuric acid may be employed to dissolve the barium sulphate, if desired.

Phosphogypsum was agitated with the solution of sulphuric acid and barium sulphate for a period of 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 period to effect solubilization of the radioactive contaminations (radionuclides), followed by absorption and/or co-precipitation of radium sulphate crystals with barium sulphate crystals in fine divided form. This digestion period ranges from 5 to 250 minutes.

After the reaction of the acid slurry was completed, the slurry is preferably cooled, at a temperature of 30-35°C and then filtered. If desired, the hot acid slurry can be washed without a separate cooling step. The acidic slurry with or without prior cooling is subjected to a solid–liquid separation step, 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 was slurried with water and then wet screened on a 100 micron screen. The solid phosphogypsum retained on the 100 micron was collected and dried at 60°C.

The results of gamma spectrometric analysis of natural gypsum and phosphogypsum purified by the proposed procedure are represented in the *Table 2*.

As it can be seen from the *Table 2*, activity of phosphogypsum purified by this procedure is decreased by approx. 10 wt.% in comparison with raw phosphogypsum. It is necessary to stress that the original raw material - phosphate determines much the content of radionuclides, which should be primarily taken into consideration when choosing the phosphate.

The obtained results of radionuclide content analysis 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 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 ^{226}Ra isotope is dangerous because of liberation of (the only) radioactive gas radon (isotope-222), which is a daughter of radium degradation sequence (*Table 3*).

The daughter product of ^{226}Ra, ^{222}Rn, having a half–life of 3.82 days, and the extent to which this escapes from any biological system in which ^{226}Ra is deposited profoundly affects the dose. Radiation danger at the contact of human organism with radon is connected with its radioactive "short–lived radon escendents": $^{218}_{84}$Po, $^{214}_{82}$Pb, $^{214}_{83}$Bi and $^{214}_{84}$Po, which mostly damage the lungs. A disintegration product later in series is RaD (^{210}Pb) with a half–life of 21 years; this element and those derived from it will not reach equilibrium amount in the life–time of a man but, for example, may be present in a person who has acquired an accidental body burden of ^{226}Ra.

Determination of ^{222}Rn emanition coefficient [22]

After the 30 days equilibrium period, the total activity of ^{222}Rn in secular equilibrium with ^{226}Ra. The activity of the total gaseous ^{222}Rn in phosphogypsum (or sample) was calculated, taking into consideration the volume of the vessel in which sample exist, the porosity of the phosphogypsum, and the volume removed during sampling. Porosity (P), fraction of total phosphogypsum was calculated by:

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

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 %)	
RaC' (99+5)	^{214}Po	160 ?sec	α, 7.68	
RaC'' (0.04 %)	^{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] Where the β^- or γ^- spectra contain many lines, only ranges of energy without abundances are given RaG – unradioactive lead (isotope ^{206}Pb) or (radium's lead or RaG)

where D_b is bulk density (g/cm^3, phosphogypsum (solids+porosity) and D_p is particle density of phosphogypsum was assumed to be 2.32 g/cm^3, the value fos $CaSO_4 \cdot 2H_2O$ [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 coeficient (ε) was calculated by:

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

Radioactivity is investigated as the contents of three radioactive isotopes: K–40, Ra–226 and Th–232. Biologically harmful evaluation of 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).

From the *Table* 2, it may be noticed that by the proposed procedure, isotope ^{226}Ra activity is decreased below tha maximal permitted concentration (400 Bq/kg) [24].

Upper permitted limits of radioactivity are calculated according to so-called Summary formula which has been formulated by National commission for protection from radiation in former USSR, and according to our currently valid regulations it has the following form [24]:

$$\textbf{Index for interiors} = \frac{^{226}\text{Ra (Bq/kg)}}{200} + \frac{^{232}\text{Th (Bq/kg)}}{300} + \frac{^{40}\text{K(Bq/kg)}}{3000} + \frac{V_{\text{interiors}}\text{(Bq/kg)}}{4000} = 1$$

$$\textbf{Index for exteriors} = \frac{^{226}\text{Ra (Bq/kg)}}{400} + \frac{^{232}\text{Th (Bq/kg)}}{300} + \frac{^{40}\text{K(Bq/kg)}}{5000} + \frac{V_{\text{exteriors}}\text{(Bq/kg)}}{4000} = 1$$

$$\textbf{Index for roads} = \frac{^{226}\text{Ra (Bq/kg)}}{700} + \frac{^{232}\text{Th (Bq/kg)}}{500} + \frac{^{40}\text{K(Bq/kg)}}{8000} + \frac{V_{\text{for roads}}\text{(Bq/kg)}}{2000} = 1$$

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 of the dose only brings about the lowering of the probability of the illness appearance.

The obtained 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 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 at the contact of human organism with radon is connected with its radioactive "short–lived radon descendents": $^{218}_{84}$Po, $^{214}_{82}$Pb, $^{214}_{83}$Bi and $^{214}_{84}$Po, which mostly damage the lungs. These isotopes are called, which 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 a 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 ones, there are no valid data. This is one 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 received dose 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.**

Conclusions

Phosphogypsum obtained by "wet procedure" for phosphoric acid production is actually calcium-sulphate dihydrate, $CaSO_4 \cdot 2H_2O$, which contains a high percent of impurities as well as radionuclides originating from the basic raw material for the production - phosphate.

Technology of phosphoric acid production by "wet procedure" intends for phosphogypsum to be a "sponge" that absorbs all impurities from phosphoric acid (except uranium) and to be left in deposits as an unnecessary burden.

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

By the proposed procedure, phosphogypsum is transformed into hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$, which corresponds to natural gypsum, and the present impurities are in accordance with natural gypsum composition. By process of removing radionuclides with barium-sulphate, ^{226}Ra isotope content decreases below the maximal permitted concentration, but this process is directly dependent on the type of the phosphate utilized in phosphoric acid production.

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