Phophosemihydrate Purification from Phosphorus

E. P. LOKSHIN and O. A. TAREEVA

Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,
Kola Science Centre of the Russian Academy of Sciences,
Ul. Fersmana 26A, Apatity184209 (Russia)

E-mail: lokshin@chemy.kolasc.net.ru

Abstract

It has been demonstrated that the main obstacle for phoshosemihydrate use in the manufacture of building materials which is formed due to sulphuric acid processing of the Khibiny apatite concentrate consists in an increased content of phosphorus impurity in water-insoluble form. According to the technology of sulphuric acid extraction of lanthanoid concentrate from phosphosemihydrate developed earlier an efficient lixiviation of water-insoluble phosphorus accumulated in repeatedly used leaching solutions is achieved. We proposed to remove phosphorus from sulphuric acid solutions in the form of hydrated titanyl phosphate through the sedimentation by means of titanyl sulphate. Possibility is demonstrated for titanyl sulphate regeneration via alkaline treatment of hydrated titanyl phosphate to result in obtaining a component of detergents such as $Na_3PO_4 \cdot 12H_2O$. The variants of sulphuric-acid technology for phosphosemihydrate processing are considered wherein the formation of wastes requiring for recycling is excluded.

Key words: obtaining of building materials, phosphosemihydrate, purification

INTRODUCTION

Owing to the processing of phosphate ores into the extraction phosphoric acid, as much as 280 million tons of phosphogypsum is annually formed in the world, only a small part of the substance finding practical use [1]. One of the promising fields of phisphogypsum use is presented by the manufacture of gypsum building materials. Phosphogypsum in Russia is obtained mainly from the Khibiny apatite concentrate which is polluted with radionuclides to an insignificant extent and consequently it can be widely used in the manufacture of building materials.

The Khibiny apatite concentrate use to be processed by means of sulphuric acid method according to semihydrate and hydrate technologies. Phosphosemihydrate and phosphogypsum, respectively, are formed as nonutilizable waste products polluted with of phosphorus and fluorine impurities whose content in manufacture of building materials should be limited.

The engineering requirements for the products based on calcium sulphate utilized in the building industry are established by the Knauf Co. (Germany) which supervises the main enterprises of Russian gypsum industry [2]. In order to use gypsum as a cement setting retarder, as well as for the manufacture of plasterboard, wall board and gypsum blocks the regulated content of insoluble and soluble P_2O_5 and F species amounts to <0.6 and <0.05–0.1 mass % calculated with respect to anhydrite, respectively. Gypsum for wall board is allowed to exhibit the following content of phosphorus and fluorine species, mass %: insoluble P_2O_5 <0.5, insoluble F <0.4, soluble P_2O_5 <0.02, soluble F <0.02.

The residual content of fluorine present within phosphogypsum waste products mainly in the form of SiF_6^{2-} anion and water-soluble P_2O_5 is determined by water consumption for washing. The content of co-crystallized (water-insoluble) P_2O_5 depends on the temperature and molar ratio $CaO : SO_3$ in the solution where-

from calcium sulphate is crystallized [3]. It has been revealed that the rise of the temperature and molar ratio $SO_3 : CaO$ promotes a decrease in the concentration of phosphorus within gypsum crystals. So, as the temperature increased from 55 to 85 °C in the presence of 1 % free H_2SO_4 the mass fraction of P_2O_5 in gypsum crystals decreases from 1.1 to 0.55 %. With the excess of calcium in the decomposed solution equal to 0.2 and 0.4 mass %, the content of P_2O_5 in phosphogypsum at 85 °C amounted to 1.9 and 2.9 mass %, respectively. The presence of water-insoluble phosphorus is determined not only by isomorphic substitution of SO_4^{2-} ions by HPO_4^{2-} ions, but also by entering low-soluble phosphates into products, in particular hydrated lanthanide phosphates those use to bind up to 0.26 mass % of P_2O_5 (calculated with respect to recalculation $CaSO_4$) [4]. The content of impurities depends on the features of the technology under use, varies for phosphogypsum manufactured at various enterprises, and can change in time even for phosphogypsum produced at the same factory. So, phosphogypsum from Minudobreniya JSC (Voskresensk city) with the humidity of 20 % contained 1.06–1.50 mass % of P_2O_5 (including 0.31–0.48 mass % of water-soluble form) and 0.19–0.29 mass % of F [5, 6]. Thus, the content of water-insoluble P_2O_5 calculated with respect to anhydrite can amount up to 0.94–1.29 mass %. In this connection, phosphogypsum waste products of the Russian factories in order to use them in the manufacture of gypsum materials should be purified from phosphorus impurities, whereas fluorine impurities should be converted into the water-insoluble state.

A number of chemical processing methods were proposed for the reduction of phosphorus and fluorine concentration and/or neutralization of their hazardous effect. The treatment with calcium compounds in the form of limy milk or slaked lime [7] provides the conversion of phosphorus and fluorine from soluble species into insoluble forms; however, their content in phoshogypsum does not change.

The reduction of the impurity content can be achieved *via* leaching. For leaching phosphates and fluorides different authors proposed to use water [5], sulphuric [8] and citric acid [9], aqueous solutions of either ammonia [8] or ammonium sulphate [10]. By means of aqueous leaching one could remove only water-soluble part of impurities, therefore the gypsum materials obtained would not meet corresponding requirements. The use of ammonium compounds is inefficient, too. Under acid leaching, both water-soluble and water-insoluble phosphorus can pass into a solution, which allows one to obtain gypsum products of required quality. However thus solutions in which phosphorus will collect are formed. Under a repeated use of solutions the concentration of phosphorus grows until reaching a level whereat the required phosphogypsum purification level becomes impossible. In this connection, the development of methods for acid solution regeneration is necessary for practical realization of the acidic purification technology.

The purpose of the present work consisted in the studies on the possibility of combining the process of sulphuric acid phosphogypsum purification from phosphorus impurities with the process of lanthanide isolation from phosphogypsum according to the method described in [11].

EXPERIMENTAL

The experiments were carried out with phosphosemihydrate produced at Ammophos JSC (Cherepovets city). At this enterprise there is the largest in Russia manufacture realized for sulphuric acid processing the Khibiny apatite concentrate. Under long-term storage in a humid atmosphere, phosphosemihydrate is converted into phosphogypsum that, according to the analysis, contains 1.23 mass % of P_2O_5 as calculated with respect to $CaSO_4 \cdot 2H_2O$, or 1.56 mass % as calculated with respect to $CaSO_4$. For the leaching of phosphorus impurities we used a solution of sulphuric acid with the mass fraction of 26 %, which is optimum for the technology developed for the extraction of lanthanoids. The process of leaching was carried out at a liquid-to-solid ratio $L : S = 2$ (determining the $L : S$ value we took into account the moisture contained within the initial phosphogypsum).

A weighed sample of phosphogypsum (with the humidity of 22 mass %) was treated during 25 min with a solution of sulphuric acid

TABLE 1

Purification of phoshogypsum from phosphorus impurities of with a repeated use of sulphuric acid solution (initial content of P_2O_5 and F amounted to 1.2 и 0.42 mass %, respectively)

Stage of filtrate using	Weighed phospho-gypsum sample, g		Volume, mL		Content in dry phosphogypsum, mass %		Content in filtrate, g/L			
	dry	humid	Filtrate	Washing water	P_2O_5	F	P_2O_5	F	Na_2O	SiO_2
I	200	244	356	40	0.29	0.14	5.49	1.2	1.18	0.45
II	150	182	268	20	0.40	0.06	9.67	1.9	1.96	0.82
III	100	122	178	20	0.41	0.15	13.6	2.5	2.83	0.96

with the mass fraction of 26 %, under stirring at room temperature. The solution was filtered (filtrate), a sediment on the filter was washed out with a preset amount of water (washing water, "scourage") being then dried at 100 ºC. The consumption of washing water did not exceed 20 % of phoshogypsum mass, which prevented forming an excess volume of the sulphuric acid solution. The filtrate and sediment samples were analyzed. The content of fluorine was determined using a potentiometric method (an I-160 ionometer, a fluoride-selective electrode) wherefore fluorine was preliminary distilled out of the sediment and then was absorbed by NaOH solution. Phosphorus in the solutions was analyzed using a spectrophotometric method determining the intensity of colouring for an ammonium-molybdenium complex.

A part of the filtrate remained after sampling was joined with washing water, the concentration of sulphuric acid in the solution was brought up to a preset value; the solution obtained was used for processing the following weighed phosphogypsum sample. The results of the experiments are presented in Table 1.

RESULTS AND DISCUSSION

From the data presented in Table 1 one can see that after triple use of the sulphuric acid solution the residual content of P_2O_5 in phos-phogypsum amounts to 0.41 mass % with respect to dry phosphogypsum, or 0.52 mass % with respect to anhydrite $CaSO_4$. The product obtained meets technical requirements for the content of phosphorus.

The residual content of phosphorus in the product is determined both by non-disclosed water-insoluble forms, and by water-soluble phosphate ion. The amount of the latter depends on the amount of sulphuric-acid solution captured by phosphogypsum and on the concentration of phosphorus therein. The results of the first cycle of phosphgypsum sulphuric acid leaching (see Table 1) show that the solution has been entered with 2.11−2.20 g from 2.4 g P_2O_5 contained in phosphogypsum (the first value was determined from the content of P_2O_5 in phosphogypsum, the second one was determined from the content of P_2O_5 in the filtrate; rather law discrepancy indicates a sufficient accuracy of the method used for P_2O_5 analysis). Hence, the residual content of water-insoluble phosphorus in phosphogypsum amounts only 0.1 mass %, whereas 0.19 mass % of phosphorus has passed into phosphogypsum with the mother solution. With the increase in phosphorus concentration in the solution the contribution of the water-soluble phosphorus remaining in the mother solution to the total content of phosphorus in phosphogypsum under purification would abruptly increase.

The sulphuric acid solution remained within phosphogypsum should be neutralized, which would demand a significant consumption of either limestone or lime. As a result, the impurities contained in the mother solution would remain in phosphogypsum, which could make it unsuitable for using as a building material.

The humidity of the filtered phosphogypsum does not exceed 30 %. With the replacement of this volume of water by equal volume of the sulphuric acid solution, in 1 ton of phosphogypsum there will be $1000 \times 0.3 \times 1.19 \times 0.26 : 0.7 = 65$ kg of 100 % H_2SO_4 (1.19 stands for the density of the solution with sulphuric acid concentration of 26 mass %). Neutralization of this amount of sulphuric acid
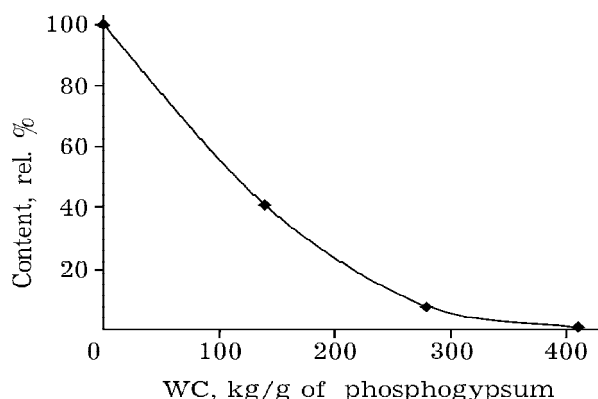
Fig. 1. Residual content of H_2SO_4 (in % with respect to initial content) in phoshogypsum depending on water consumption (WC) for washing (displacement mode).

requires for 37 kg CaO; as the result 113.6 kg of $CaSO_4 \cdot 2H_2O$ is formed. In this connection it is appropriate to carry out a complete separation of the mother sulphuric acid solution whenever possible, and to develop a method for the solution purifying from phosphorus (the regeneration of sulphuric acid solution).

Two methods for reducing the amount of mother solution captured by phosphogypsum have been studied. The first one consists in washing phosphogypsum with water. The efficiency of acid washing removal was simulated in the displacement mode with no counterflow used. From the data presented in Fig. 1 one can see that at the consumption of washing water equal to 100−150 kg per 1000 kg of phoshogypsum the residual content sulphuric acid and water-soluble phosphorus could be 2−2.5-fold reduced. With the use of a counterflow mode the efficiency of washing removal should increase. However, the use of washing is possible only provided that the humidity of phosphogypsum supplied for purification is much less than the humidity of the product obtained after the purification. From the difference of these values one can determine possible consumption of water for washing excluding the formation of the excess of washing solution.

Another method is based on the separation of the mother solution *via* centrifugation [12]. It has been found that at the separation factor $Fr = \omega^2 R/g = 11.8$, where $\omega = 2\pi n R/60$ (a laboratory centrifuge with a radius $R = 0.06$ m, the rotation frequency $n = 7000$ min^{-1}; the industrial analogue being with $R = 1.2$ m,

$n \sim 220$ min^{-1}) the residual content of the sulphuric acid solution amounted to 3.65 % of phoshogypsum mass after the centrifugation during 5 min. In this case 5.4 kg CaO is required for the neutralization of the sulphate solution remained in 1 ton of phosphogypsum, which would result in the formation of 16.6 kg of $CaSO_4 \cdot 2H_2O$. It should be also noted that with the separation of the mother solution *via* centrifugation the loss of rare-earth elements, the consumption of sulphuric acid and the humidity of the product obtained are lowered, which allows one to reduce power input for drying the product, too. In addition, the amount of phosphorus remaining with the mother solution decreases. Due to this fact a higher level of its accumulation could be allowed as well as a less frequent regeneration should be required for the sulphuric acid solution.

When taken into account that the content of water-insoluble P_2O_5 in purified phosphogypsum does not exceed 0.2 mass %, and the residual content of the sulphuric acid solution amounts to 5 mass % of phosphogypsum, the permissible content of P_2O_5 in the mother sulphuric acid solution should not exceed ~75 g/L. Hence, the regeneration could be carried out not earlier than after 15 cycles of the solution use.

We have studied the possibility of phosphate ion sedimentation from the mother sulphuric acid solution according to the reaction
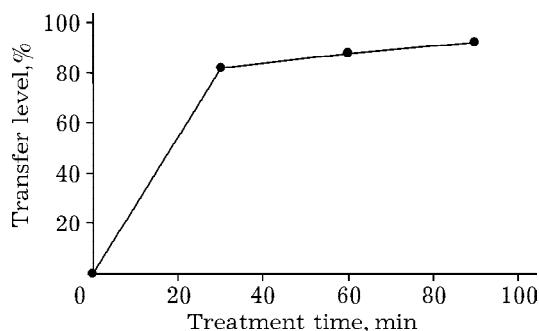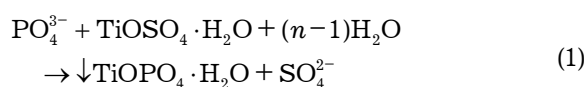
$$PO_4^{3-} + TiOSO_4 \cdot H_2O + (n-1)H_2O \rightarrow \downarrow TiOPO_4 \cdot H_2O + SO_4^{2-} \quad (1)$$

Fig. 2. Level of P_2O_5 transfer into the liquid phase (in % with respect to initial content) depending on the time of $TiOHPO_4 \cdot nH_2O$ treatment with NaOH solution (30 g/L concentration).

To a solution containing 10.45 g/L of P_2O_5, in the presence of polyacrylamide, was added a quantity of $TiOSO_4 \cdot H_2O$ stoichiometrically required for reaction (1); after 25 min passed, a sediment was filtered. The additive of polyacrylamide provides a plausible filtration rate. The residual content of P_2O_5 in the solution was equal to 4.34 g/L which content depends on $TiOHPO_4 \cdot nH_2O$ solubility in the sulphuric acid solution.

Due to the fact that hydrated titanium oxohydrophosphate $TiOHPO_4 \cdot nH_2O$ represents an efficcient sorbent of metal cations, in particular caesium, strontium, uranium radionuclides, it could be used, for example, for the deactivation of liquid radioactive waste products [13]. In addition, in order to establish the potentiality for the regeneration of $TiOHPO_4 \cdot nH_2O$ we have studied the level of phosphorus transfer into the liquid phase depending on the treatment time in the process of interaction between $TiOHPO_4 \cdot nH_2O$ and NaOH solution (30 g/L concentration) (Fig. 2). The experiment was carried out at L : S = 25, which corresponded to NaOH
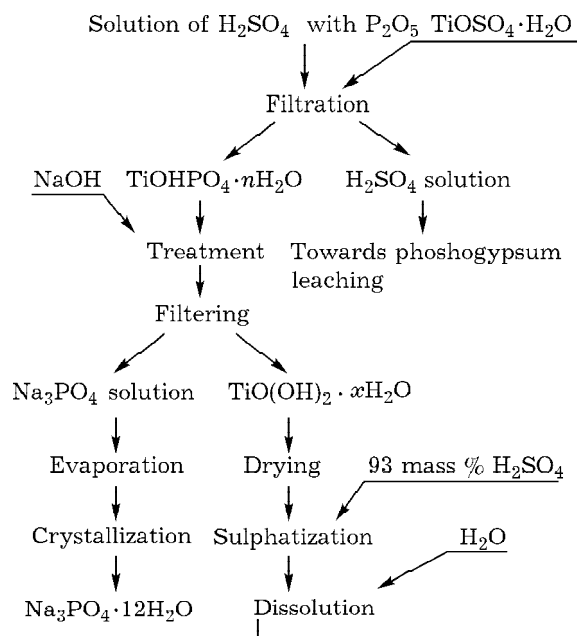

Fig. 3. Schematic diagram for the centrifuging regeneration of sulphuric acid solution contaminated with phosphorus.
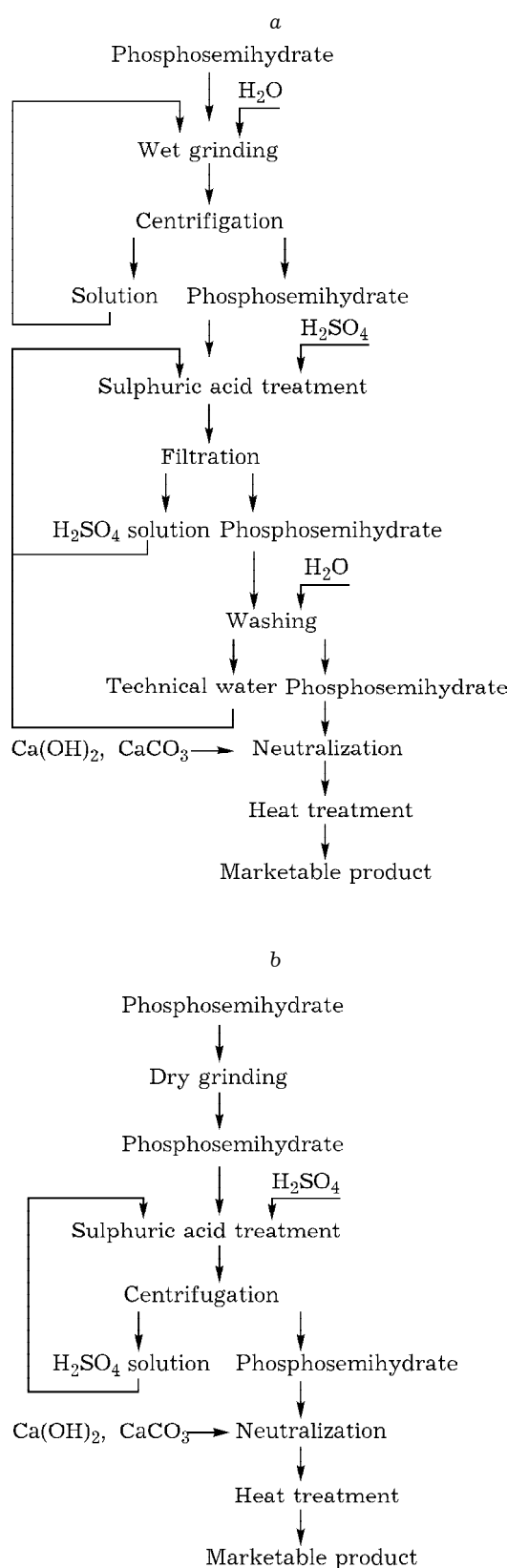

Fig. 4. Process flowsheets for the purification of phosphosemihydrate from phosphorus using water washing of sulphuric acid solution (a) and centrifuging separation of the solution (b).

consumption equal to 112.5 % with respect to the stoichiometry, according to the reaction

$$TiOHPO_4 + 3NaOH \rightarrow Na_3PO_4 + TiO(OH)_2$$
$$+ H_2O \qquad\qquad (2)$$

As one can see from the data presented in Fig. 2, the alkaline hydrolysis of $TiOHPO_4 \cdot nH_2O$ proceeds completely enough. The organization of a counterflow process provides a higher level of phosphorus isolation to yield $Na_3PO_4 \cdot 12H_2O$ which is widely used as a component of detergents. The compound $TiOSO_4 \cdot H_2O$ could be obtained *via* the sulphatization of $TiO(OH)_2 \cdot xH_2O$ using the technique proposed in [13]. A schematic diagram for the purification of sulphuric acid solution from phosphorus with the regeneration of $TiOSO_4 \cdot H_2O$ is presented in Fig. 3.

CONCLUSION

Thus, according to the results of the studies performed, in order to carry out large-scale tests one could recommend process flowsheets presented in Fig. 4. The method including separation of sulphuric acid solution from phosphogypsum by means of centrifugation (see Fig. 4, *b*) is considered to be much more promising. With the use of this pattern, the consumption of the reagents for the leaching of phosphogypsum and the neutralization of acidic solution is reduced; the volume of the sulphuric acid solution supplied to the regeneration can be considerably reduced since one has an opportunity for a much higher phosphorus accumulation level therein before the neutralization. Thus, the consumption of titanyl sulphate decreases to a considerable extent as well as power

inputs for thermal treatment of purified phosphogypsum can be reduced.

However, in order to realize the pattern suggested it is necessary first of all to determine the efficiency of lanthanoid extraction from phosphosemihydrate with the use of sulphuric acid solution with the increased phosphorus content for leaching both them and phosphorus, since the use sulphuric acid solutions is studied only for the content of $P_2O_5 > 20$ g/L. In addition, there can be difficulties observed in the choice of a centrifuge suitable for operation with sulphuric acid media.

REFERENCES

1 P. M. Ruthenford, M. J. Dudas, R. A. Same, *Sci. Total. Environ.*, 149 (1994) 1.
2 L. M. Los', *Stroit. Mat.*, 9 (1999) 43.
3 O. P. Akaev, Yubileynaya Nauch.-Tekhn. Konf. Ivanovskoy Gosudarstvennoy Arkhitekturno-Stroitelnoy Akademii (Proceedings), Ivanovo, 1996, p. 5.
4 E. P. Lokshin, V. N. Lebedev, V. A. Masloboev *et al.*, *Miner. Syrye*, 7 (2000) 122.
5 P. F. Gordashevskiy, A. V. Dolgorev, Proizvodstvo Gipsovykh Vyazhushchikh Materialov iz Gipsosoderzhashchikh Otkhodov, Stroyizdat, Moscow, 1987.
6 M. A. Akhmedov, T. A. Atakuziev, Fosfogips. Issledovaniye i Primeneniye, FAN, Tashkent, 1980.
7 J. H. Potgieter, S. S. Potgieter, R. I. McCrindle, C. A. Strydom, *Cement and Concrete Res.*, 33 (2003) 1223.
8 M. Singh, M. Garg, S. S. Rehsi, *Constr. Build. Mater*, 7 (1993) 3.
9 M. Singh, *Cement and Concrete Res.*, 32 (2003) 1033.
10 M. Singh, S. S. Rehsi, C. A. Taneja, *Ind. J. Technol.*, 22 (1984) 22.
11 RU Pat. No. 2293781, 2007.
12 E. P. Lokshin, V. T. Kalinnikov, Formirovaniye Osnov Sovremennoy Strategii Prirodopolzovaniya v Evpo-Arkticheskom Regione, Apatity, 2005.
13 E. P. Lokshin, V. I. Ivanenko, Kh. B. Avsaragov *et al.*, *Atom. Energiya*, 92 (2002) 118.
14 RU Pat. No. 2264477, 2005.