

INFLUENCE OF THE COMPOSITION OF PHOSPHATE ROCK ON THE AMOUNT OF WATER-INSOLUBLE PHOSPHATE IMPURITIES IN SEMI-HYDRATE PHOSPHOGYPSUM

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Submitted June 13, 2014; accepted March 20, 2015

Keywords: Phosphate rock, Semi-hydrate phosphogypsum, Insoluble impurities, Water-insoluble phosphates

In this work a chemical and mineral composition of phosphate rock and phosphogypsum was investigated in order to identify which impurities of phosphate rock prevent natural phosphates from decomposing in full during the production of phosphoric acid and increase the amount of water-insoluble phosphate impurities in phosphogypsum. The analysis of X-ray diffraction (XRF), X-ray fluorescence (XRD), scanning electron microscopy with energy dispersive X-Ray spectrometry (SEM-EDS) and granulometry was carried out.

The results showed that phosphate rocks (Kovdor and Kirovsk apatites) and the semi-hydrate phosphogypsums differ by their chemical composition. The apatites and phosphogypsums differ in the amount of the major components, as well as other components (MgO, Al₂O₃, SrO, BaO, ZrO₂, Ln₂O₃). In phosphate rock, Ln₂O₃ can be found in the composition of the mineral monazite. The SEM-EDS analysis revealed that the minerals of the apatite group and monazite form aggregate crystals. Monazite dissolves in sulphuric and phosphoric acids very marginal, therefore it prevents the apatites from full decomposition, thus influencing the quantity of insoluble phosphates in semi-hydrate phosphogypsum. The higher is the amount of minerals containing Ln₂O₃ in phosphate rock, the more water-insoluble phosphates remain in phosphogypsum. It was found that influence of Ln₂O₃ impurity is significant higher than influence of particles size of apatite.

INTRODUCTION

Natural gypsum is the main raw material for the production of binding materials. In some cases it could be replaced by the technological waste containing calcium sulphate, for instance, phosphogypsum [1-3]. Phosphogypsum forms in the phosphoric acid production process by decomposing phosphate rock with sulphuric acid and phosphoric acid. However, due to a relatively high amount of phosphate impurities, phosphogypsum is not widely used in the industry of construction materials.

Phosphate impurities in phosphogypsum can exist in three different forms as:

- the water-soluble compounds (H₃PO₄, Ca(H₂PO₄)₂·H₂O) located on the surface of gypsum crystals and inside of crystal agglomerates,
- the compounds of poor water-solubility (CaHPO₄·2H₂O) substituted in the gypsum lattice which has entered in to solid solution with gypsum by substitution of HPO₄²⁻ ions for SO₄²⁻ ions,
- water-insoluble compounds, such as un-decomposed phosphate rock, Ca₃(PO₄)₂.

A number of studies carried out to this day are focused on the study of the influence of water-soluble and water-insoluble phosphate impurities on the physical-mechanical properties of dihydrate and semi-hydrate phosphogypsum. It was determined that water-soluble phosphates retard the setting time and decrease the strength of the plaster and cement [4]. Insoluble phosphates only have influence on the strength parameters of the products. All proposals on enhancing the properties of phosphogypsum are related to the washing or treatment of the phosphate impurities [2, 5-10]. However, most studies omit the analysis of the reasons affecting the amount of phosphate impurities in phosphogypsum.

It is known that the amount of water-soluble phosphate impurities in phosphogypsum depends on the level of their washing-out, which is highly dependent on the morphology and size of phosphogypsum crystals. The morphology and size of phosphogypsum crystals to a large extent depend on the composition of phosphate rock and process conditions [11-16].

Meanwhile, the analysis of the reasons affecting the amount of water-insoluble phosphates in phospho-

gypsum is rather scarce. It is known that the un-decomposed phosphate rock comprises the larger part of water-insoluble phosphates impurities in phosphogypsum [14]. The level of decomposition of phosphate rock is influenced by the fineness of phosphate rock, retention of the pulp in the extractor, processing temperature regime, mixing intensity, amount of free SO₃ in the system, nature of phosphate rock [13]. A data about the influence of the particles' size and amount of SO₃ in the system on the decomposition of phosphate rock can be found in literature [14]. On the other hand, there is no exact data about impurities in phosphate rock which prevent complete decomposition of natural phosphates and thus increase the amount of water-insoluble phosphate impurities in phosphogypsum.

Martin et al. [17] examined the amount of different elements (Al, Si, P, S, K, Ca, Ti, Fe, Ni, Cu, Zn, As, Sr, Y, Pb) in phosphate rocks from different origins (Senegal, Marocco and Togo) and their distribution in dihydrate phosphogypsum. The amount of P in dihydrate phosphogypsum indicate that the natural phosphates are not fully decomposed, while the decomposition itself is considered highly efficient (>90%). Renteria-Villalobos et al. [18] also studied the distribution of different elements in the phosphate rock from Morocco and phosphogypsum extracted from it. They attributed P₂O₅ presence in phosphogypsum to the un-decomposed phosphate rock. However, the afore-mentioned studies omitted to analyse which impurities of phosphate rock prevent natural phosphates from decomposing in full.

The aim of the present work is to identify which impurities of phosphate rock prevent natural phosphates from decomposing in full and increase the amount of water-insoluble phosphates in phosphogypsum.

EXPERIMENTAL

Materials

This study examined Kovdor and Kirovsk apatites (Russia) and industrial semi-hydrate phosphogypsums extracted from them.

Experimental methods

The chemical composition of materials was performed by X-ray fluorescence analysis (XRF) using PW 2404 X-Ray spectrometer.

The amount of P₂O₅ was determined using the yellow phosphor-vanadium-molybdenum complex.

Ignition loss of phosphate rock was determined by heating the substance at 1000°C temperatures and for semi-hydrate phosphogypsum at 400°C temperatures.

The particle size distribution was determined using Coulter Laser Diffraction Analyser LS230.

Scanning electron microscopy (SEM) (OXSFORD ISIS LEO 440i, UK) with energy dispersive X-Ray spectrometry (EDS) of the samples was performed using an accelerating voltage of 20 kV at working distance of 10 mm for SEM observation and a 200 s accumulation time for EDS analysis.

Table 1. Chemical composition of Kovdor and Kirovsk apatites and industrial semi-hydrate phosphogypsums.

Constituents	Origin			
	Kovdor		Kirovsk	
	Apatite (%)	Phosphogypsum (%)	Apatite (%)	Phosphogypsum (%)
CaO	51.92	37.69	50.89	36.51
MgO	1.98	0.26	0.10	0.02
SO ₃	0.14	53.59	0.14	51.88
P ₂ O ₅	38.12	1.13	38.93	2.18
SiO ₂	1.43	0.30	1.22	0.27
Al ₂ O ₃	0.15	0.05	0.96	0.19
Fe ₂ O ₃	0.35	0.04	0.39	0.13
Na ₂ O	0.20	0.08	0.36	0.22
K ₂ O	0.26	0.09	0.18	0.05
F	1.03	0.03	2.78	0.20
TiO ₂	0.03	<0.01	0.21	0.11
SrO	0.35	0.27	1.88	1.63
BaO	<0.01	<0.01	0.13	0.08
ZrO ₂	0.82	0.28	0.23	0.15
Ce ₂ O ₃	0.10	0.07	0.41	0.28
La ₂ O ₃	0.05	0.04	0.35	0.18
Nd ₂ O ₃	<0.01	<0.01	0.14	<0.01
Ign. loss	2.94	5.99	0.60	5.79
other	0.14	0.09	0.11	0.11

X-ray diffraction analysis (XRD) were carried out with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating at 30 kV voltage and 20 mA emission current. The step-scan covered the angular range 5 - 60° (2θ) in steps of 2θ = 0.02°. A program X-fit was used for diffraction profile refinement under the pseudo Void function and for a description of the diffractational background under the 3rd degree Techebyshev polynom [19]. The materials were identified using JCPDS database.

RESULTS AND DISCUSSION

XRF and XRD analysis

The chemical composition of Kovdor and Kirovsk apatites and industrial semi-hydrate phosphogypsums extracted from them is presented in Table 1.

The obtained results show a different amount of the major components (P₂O₅, CaO and F) and other components in the apatites. Impurities, such as MgO, Al₂O₃, TiO₂, SrO, BaO, ZrO₂ and Ln₂O₃ (Ce₂O₃+La₂O₃+Nd₂O₃) indicates the most significant difference of the phosphate rocks.

The X-ray diffraction analysis (Figure 1) shows that Kovdor and Kirovsk apatites contain fluorapatite (Ca₅(PO₄)₃F) and hydroxylapatite (Ca₅(PO₄)₃(OH)). Illite (KH₃O)Al₂Si₃AlO₁₀(OH)₂, ilmenite (FeTiO₃), perovskite (CaTiO₃), dolomite (CaMg(CO₃)₂) and quartz

(SiO₂) were identified in Kovdor and Kirovsk apatites. Forsterite (Mg₂SiO₄) sillimanite (Al₂SiO₅) and calcite (CaCO₃) were only recorded in Kovdor apatite, while the X-ray diffraction pattern of Kirovsk apatite showed traces of nepheline ((Na,K)₂O·Al₂O₃·2SiO₂), titanite (CaTiOSiO₄) and strontianite (SrCO₃).

The results show that Kovdor and Kirovsk apatites differ by their chemical and mineral composition.

It is known that the solubility of minerals-impurities in sulphuric and phosphoric acids is not identical. Thus, the semi-hydrate phosphogypsums forming from different apatites must show a different composition. It is confirmed by the chemical analysis of semi-hydrate phosphogypsums extracted from Kovdor and Kirovsk apatites (Table 1). The afore-mentioned materials do not only differ in the amounts of the major components CaO and SO₃, but also other components such as MgO, P₂O₅, Al₂O₃, Fe₂O₃, Na₂O, F, TiO₂, SrO, BaO, ZrO₂ and Ln₂O₃ (Ce₂O₃+La₂O₃).

The analysis of the difference between total amount of phosphates (P₂O_{5,t}) and water-soluble phosphates (P₂O_{5,w.s.}) shows that water-insoluble phosphates (P₂O_{5,w.ins.}) prevail in both Kovdor and Kirovsk semi-hydrate phosphogypsums (Table 2). The average amount of water-insoluble phosphates in Kovdor semi-hydrate phosphogypsum equals to 0.78 %, while the amount of phosphates in Kirovsk semi-hydrate phosphogypsum is nearly twice as high (1.46 %).

Table 2. The amount of phosphates in Kovdor and Kirovsk semi-hydrate phosphogypsums.

Origin	The range of amount of phosphates (%)		
	total	water-soluble	water-insoluble
Kovdor	1.03–1.27	0.28–0.36	0.72–0.91
Kirovsk	1.30–3.14	0.60–1.21	1.06–1.94

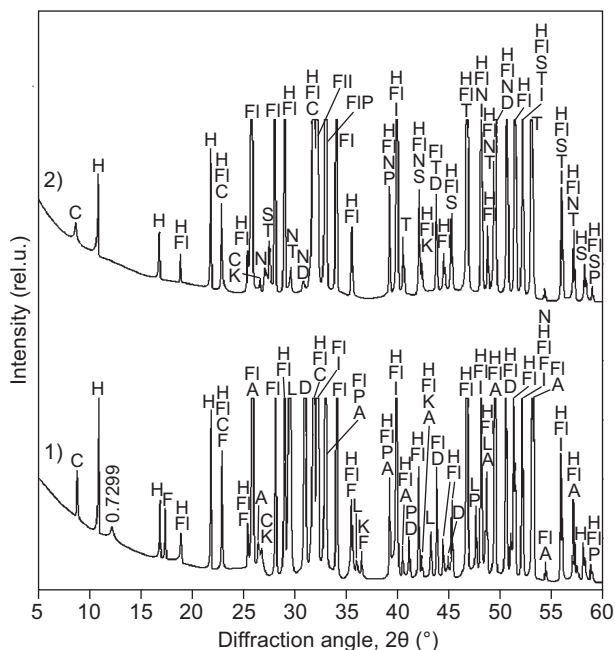


Figure 1. X-Ray diffraction patterns of Kovdor (1) and Kirovsk (2) apatites (Indexes: FI – fluorapatite, H – hydroxylapatite, C – illite, F – forsterite, A – sillimanite, K – quartz, L – calcite, D – dolomite, P – perovskite, I – ilmenite, N – nepheline, T – titanite, S – strontianite).

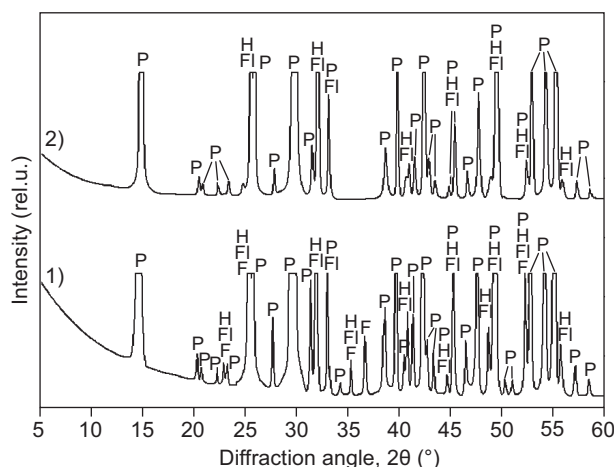


Figure 2. X-Ray diffraction patterns of Kovdor (1) and Kirovsk (2) semi-hydrate phosphogypsums (Indexes: P – semi-hydrate gypsum, FI – fluorapatite, H – hydroxylapatite).

The largest part of water-insoluble phosphates in phosphogypsum is un-decomposed phosphate rock [14]. It is confirmed by XRD of Kovdor and Kirovsk semi-hydrate phosphogypsums (Figure 2). Diffraction maximums characteristic to fluorapatite and hydroxylapatite were recorded.

The impurities contained in phosphate rock are one of the main factors preventing natural phosphates from decomposing in full [13]. A common assumption is that when phosphate rock is decomposed by sulphuric acid during production of phosphoric acid, the impurities contained in phosphate rock preventing from the full decomposition of natural phosphates should not dissolve in sulphuric and phosphoric acids, or their dissolution should be very marginal. It is possible that such impurities should not dissolve in water as well. Therefore, Kovdor and Kirovsk semi-hydrate phosphogypsums were dissolved in water in order to find out the type of those impurities. Then XRD, SEM and EDS analyses were carried out on non-dissolved impurities.

The XRD of insoluble substance in Kovdor and Kirovsk semi-hydrate phosphogypsums (Figure 3) recorded peaks of fluorapatite, hydroxylapatite, illite, as well as the minerals insoluble in sulphuric and phosphoric acids – ilmenite and perovskite. The XRD of insoluble substance in Kovdor semi-hydrate phosphogypsum showed sillimanite insoluble in acids and fully un-reacted forsterite, while the insoluble substance in Kirovsk semi-hydrate phosphogypsum revealed the presence of quartz, titanite and fully un-reacted strontianite. The XRD of insoluble substance of the latter phosphogypsum identified whitrokite ($\text{Ca}_3(\text{PO}_4)_2$), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and calcium fluorite (CaF_2) formed in the process of decomposition of phosphate rock [14].

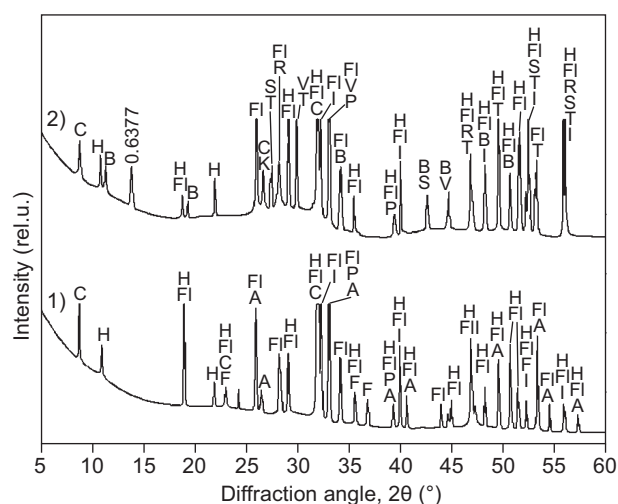


Figure 3. The X-ray diffraction pattern of water-insoluble substance in Kovdor (1) and Kirovsk (2) semi-hydrate phosphogypsums (Indexes: FI – fluorapatite, H – hydroxylapatite, C – illite, F – forsterite, A – sillimanite, K – quartz, P – perovskite, I – ilmenite, T – titanite, S – strontianite, R – calcium fluorite, V – whitrokite, B – brushite).

Solubility of above-mentioned minerals in water also in sulphuric and phosphoric acids was found in references [20-23].

SEM and EDS analysis

The SEM and EDS analysis (Figures 4-7) shows that the insoluble substance is predominated by the crystals containing Ca and P (recalculated to CaO and P_2O_5). Based on the XRD of insoluble substance (Figure 3), the said components may be found in the composition of fluorapatite, hydroxylapatite, whitrokite or brushite. In theory, the ratio of CaO and P_2O_5 in hydroxylapatite is 1.31, fluorapatite is 1.18, whitrokite – 1.18, brushite – 0.79. Therefore, it can be asserted that the crystals containing large quantities of the said components, with $\text{CaO}/\text{P}_2\text{O}_5$ close to 1.31, are un-decomposed hydroxylapatite (e.g. $\text{CaO}/\text{P}_2\text{O}_5$ in the crystal marked by “2” in Figure 4 is equal to 1.29; “A” in Figure 5 – 1.35, etc.).

Therefore, SEM and EDS analysis confirms that the insoluble substance in Kovdor and Kirovsk semi-hydrate phosphogypsums is dominated by the un-decomposed apatite-group minerals.

Particles containing Si (recalculated to SiO_2) were found in the insoluble substance of phosphogypsums (Figures 4, 6-7). The insoluble substance of Kovdor semi-hydrate phosphogypsum (Figure 4) contains a considerable quantity of particles containing Zr (recalculated to ZrO_2). It is most likely that Zr can be found in the composition of the mineral zircon (ZrSiO_4), which is insoluble in acids [23]. A significant part of particles containing La, Ce, Nd (Ln) (recalculated to Ce_2O_3 , La_2O_3 , Nd_2O_3 (Ln_2O_3)) can be found in the insoluble substance of Kirovsk semi-hydrate phosphogypsum (Figures 6-7).

Solache-Rios et al. [24] assert that in the igneous phosphate rocks, lanthanides form their own minerals but it fail to specify these minerals. Santos et al. [25] consider that in phosphate rock lanthanides are found in the composition of the mineral monazite ($(\text{Ce},\text{La},\text{Nd})\text{PO}_4$). Singh and Singh [26] state that lanthanides can be found in various minerals, namely bastnasite, xenotime, monazite.

The examination of the results of SEM and EDS analysis (Figures 4-7) revealed that Ln are present in the same crystals as P. The afore-mentioned components can be found in the mineral monazite ($(\text{Ce},\text{La},\text{Nd})\text{PO}_4$). Monazite, like apatite, is a mineral of igneous origin [27, 28]. It is known that monazite is usually found together with nepheline. Furthermore, the said mineral can occur as an impurity, partially replacing other minerals, such as apatite, titanite, zircon, etc.

The results of X-ray diffraction analysis (Figure 1) show that Kirovsk apatite contains nepheline and titanite. The said mineral is not traced in Kovdor apatite. The SEM and EDS analyses (Figure 4) enable the assumption that zircon can be found in Kovdor apatite. Hence, with

the available results in mind, we may suppose that lanthanides can be found in the mineral monazite in Kovdor and Kirovsk apatites.

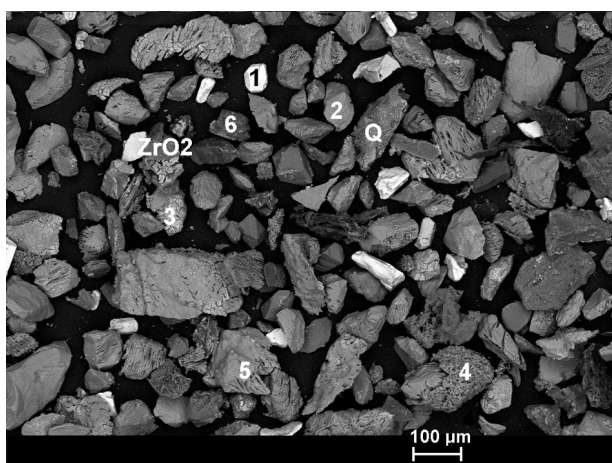
The results of chemical composition (Table 1) show that the amount of Ln_2O_3 ($\text{Ce}_2\text{O}_3+\text{La}_2\text{O}_3+\text{Nd}_2\text{O}_3$) in Kirovsk apatite is up to 6 times higher than in Kovdor apatite. Therefore, Kirovsk apatite should contain more monazite than Kovdor apatite. The results of SEM and EDS analysis (Figures 4-7) confirm this assumption.

The study of results of SEM and EDS analysis of insoluble substance in Kovdor and Kirovsk semi-hydrate phosphogypsums (Figures 4-7) revealed that the minerals of the apatite group and monazite form aggregate crystals. The quantity of apatite-monazite aggregate crystals in Kirovsk semi-hydrate phosphogypsum's insoluble substance (Figures 6 and 7) is considerably higher than in Kovdor semi-hydrate phosphogypsum's insoluble substance (Figures 4 and 5).

To make sure that the minerals of the apatite group and monazite form aggregate crystals, the study of Kirovsk apatite was carried out by means of cut crystals and SEM and EDS analysis. The type of crystal edges (Figure 8) shows that certain apatite grains form crystal aggregates with monazite. EDS analysis (Figure 8, b) confirms the presence of a large quantity of Ce and La in region 3.

In the analysis of phosphate rock from Morocco, Renteria-Villalobos et al. [18] also noted that the particles containing lanthanides are tend to form thin layers or are embedded in the grains of phosphate rock.

Monazite is water-insoluble [20] and it's solubility in sulphuric and phosphoric acids is very marginal [22]. Therefore, we may assume that monazite in forming aggregate crystals with apatites prevents them from full decomposition during extraction process and thus influences the amount of insoluble phosphates in

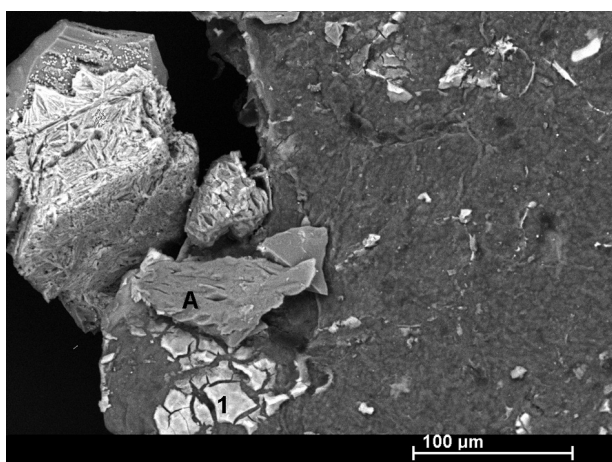


a) SEM

Constituents	Content (%)						
	1	2	3	4	5	6	Q
CaO	–	56.36	33.24	55.06	52.63	2.60	1.42
P ₂ O ₅	–	43.64	37.38	17.37	41.87	1.96	1.06
Al ₂ O ₃	–	–	5.11	3.30	–	–	–
MgO	–	–	–	–	–	54.23	–
SiO ₂	33.21	–	3.52	24.27	–	41.21	97.52
ZrO ₂	66.79	–	–	–	–	–	–
La ₂ O ₃	–	–	6.23	–	–	–	–
Ce ₂ O ₃	–	–	14.52	–	5.50	–	–

b) EDS

Figure 4. SEM (a) and EDS (b) of water insoluble substance in Kovdor semi-hydrate phosphogypsums (300×). Note: Chemical composition of the crystal specified in Figure 4 under a relevant mark.



a) SEM

Constituents	Content (%)	
	1	A
CaO	19.26	57.38
P ₂ O ₅	33.61	42.62
MgO	3.98	–
Al ₂ O ₃	7.91	–
SiO ₂	13.84	–
La ₂ O ₃	6.01	–
Ce ₂ O ₃	11.15	–
Nd ₂ O ₃	4.24	–

b) EDS

Figure 5. SEM (a) and EDS (b) of water insoluble substance in Kovdor semi-hydrate phosphogypsums (1000×). Note: Chemical composition of the crystal specified in Figure 5 under a relevant mark.

phosphogypsum. The chemical analysis can prove the aforesaid; the more lanthanides there are in phosphate rock, the higher amount of water-insoluble phosphates ($P_2O_{5sw.ins}$) remains in semi-hydrate phosphogypsum. In Kirovsk apatite, the average amount of Ln_2O_3 is 0.90 %, while the average amount of $P_2O_{5sw.ins}$ in the semi-hydrate phosphogypsum extracted from it is 1.46 %. Meanwhile, in Kovdor apatite, Ln_2O_3 equals to 0.16 %, while in semi-hydrate phosphogypsum the average value of $P_2O_{5sw.ins}$ is 0.78 %.

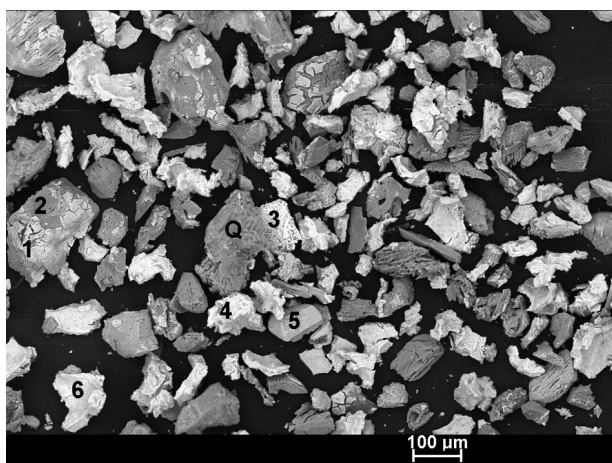
The XRD (Figure 3), SEM and EDS analysis (Figures 4-7) of insoluble substance in Kovdor and Kirovsk semi-hydrate phosphogypsums revealed that the insoluble substance of semi-hydrate phosphogypsums contains minerals, such as perovskite, ilmenite, titanite, zircon, celestine, barite or quartz, which, like monazite, do not dissolve in sulphuric and phosphoric acids [20, 23]. However, SEM and EDS analysis did not showed

the aggregate crystals formed by these minerals with apatites. Therefore, it is probably that they do not have influence on the decomposition of natural phosphates, as well as the amount of insoluble phosphates in semi-hydrate phosphogypsum.

Granulometry

It is known [13] that the decomposition of phosphate rock is influenced by its granulometric composition. The smaller are particles, the faster they are decomposed. In order to compare the particles size of Kovdor and Kirovsk apatites used in the production of phosphoric acid, the study of granulometric composition of these apatites was carried out. The results are presented in Figure 9.

The results show that the particles size in Kovdor and Kirovsk apatites differs. The dominant particles in

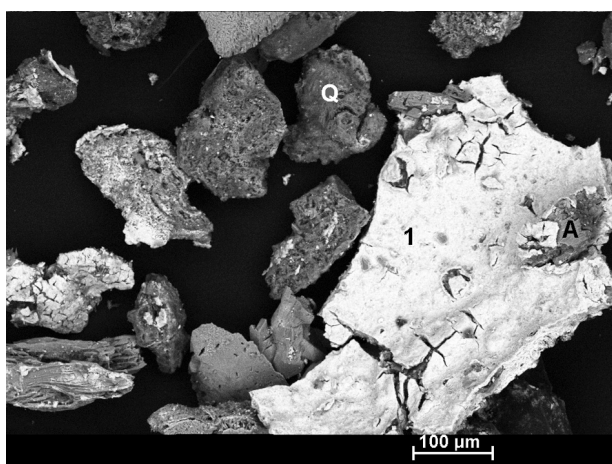


a) SEM

Constituents	Content (%)					
	1	2	3	4	5	6
CaO	8.96	57.13	1.98	6.32	–	5.41
P_2O_5	25.73	42.87	–	40.13	48.25	21.64
Al_2O_3	–	–	–	7.83	–	1.07
Fe_2O_3	–	–	–	–	51.75	1.44
SO_3	–	–	32.75	–	–	–
SiO_2	2.59	–	16.60	4.67	–	36.12
BaO	–	–	36.66	–	–	–
SrO_2	–	–	12.00	–	–	–
La_2O_3	24.12	–	–	15.04	–	9.40
Ce_2O_3	38.60	–	–	26.01	–	24.92

b) EDS

Figure 6. SEM (a) and EDS (b) of water insoluble substance in Kirovsk semi-hydrate phosphogypsums (300×). Note: Chemical composition of the crystal specified in Figure 6 under a relevant mark.

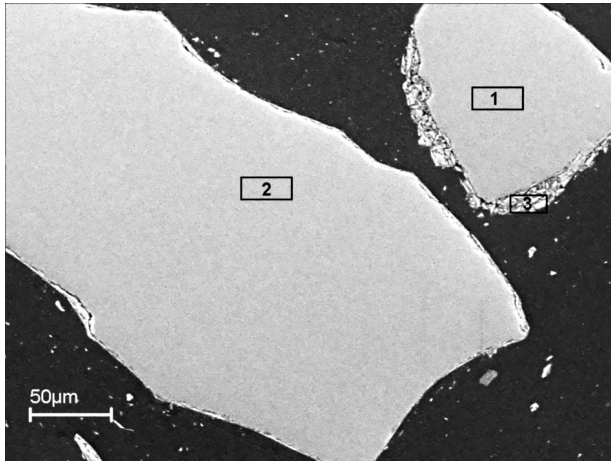


a) SEM

Constituents	Content (%)	
	1	A
CaO	4.66	55.69
P_2O_5	41.52	43.06
Fe_2O_3	3.35	–
SiO_2	3.63	–
La_2O_3	15.06	–
Ce_2O_3	24.42	1.25
Nd_2O_3	7.36	–

b) EDS

Figure 7. SEM (a) and EDS (b) of water insoluble substance in Kirovsk semi-hydrate phosphogypsums (500×). Note: Chemical composition of the crystal specified in Figure 7 under a relevant mark. Note: crystal marked by “Q” in Figures 4-7 is quartz.

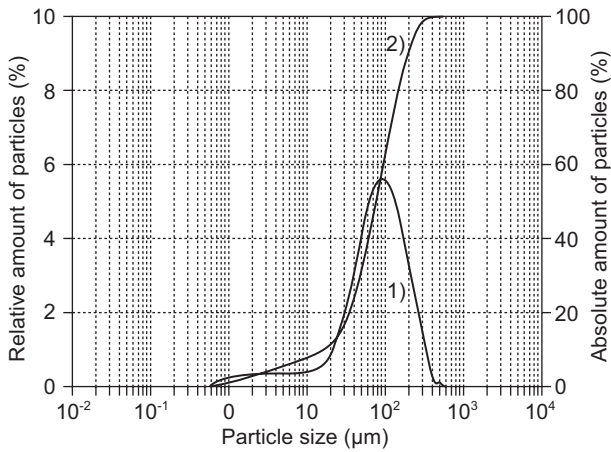


a) SEM

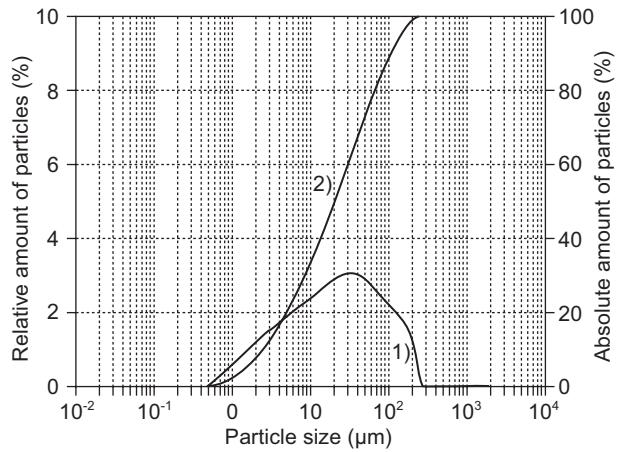
Constituents	Content (%)		
	1	2	3
Ca	38.18	37.45	6.57
P	18.37	18.90	18.56
F	3.44	3.84	0.62
O	39.24	39.48	35.63
La	0.20	0.16	16.20
Ce	0.57	0.17	22.42

b) EDS

Figure 8. SEM (a) and EDS (b) of Kirovsk semi-hydrate phosphogypsum's cut (1000×). Note: Elemental composition of the crystal specified under a relevant mark.

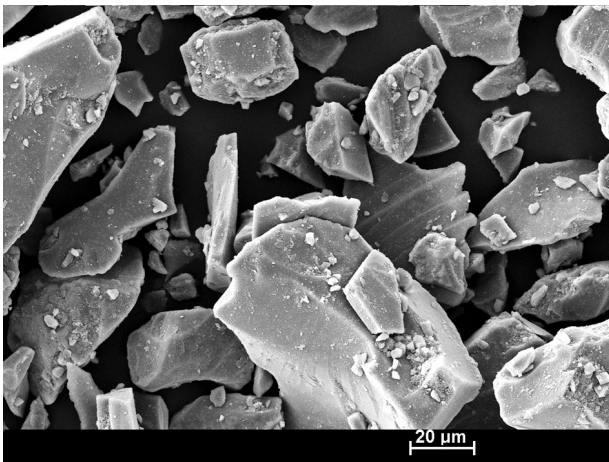


a) Kovdor

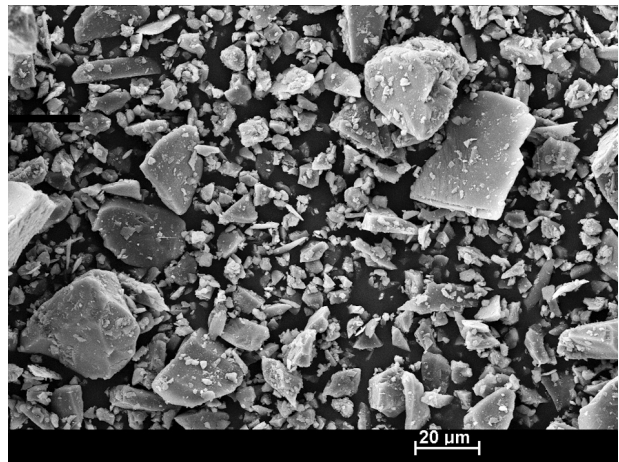


b) Kirovsk

Figure 9. Particles size distribution of Kovdor (a) and Kirovsk apatites (b): 1 – relative amount of particles, 2 – absolute amount of particles.



a) Kovdor



b) Kirovsk

Figure 10. SEM of Kovdor (a) and Kirovsk (b) apatites (2000×).

Kirovsk apatite are more than 2 times smaller than those in Kovdor apatite. The results of the SEM (Figure 10) also confirm that the particles of Kirovsk apatite are tinier than those of Kovdor.

Therefore, the results show that the dominant particles in Kirovsk apatite are more than 2 times smaller than those in Kovdor apatite but the semi-hydrate phosphogypsum extracted from it shows the higher amount of the water-insoluble phosphates, i.e. the undecomposed phosphate rock. Based on such results, it can be concluded that insoluble in sulphuric and phosphoric acids mineral impurities such as mineral monazite has higher influence to the speed of decomposition the Kirovsk apatite rather than the particles size of phosphate rock.

CONCLUSIONS

Kovdor and Kirovsk apatites and the semi-hydrate phosphogypsums extracted from them differ by their chemical composition. Apatites has different amount of the major components P_2O_5 , CaO and F, as well as other components such as MgO, Al_2O_3 , TiO_2 , SrO, BaO, ZrO_2 and Ln_2O_3 . The semi-hydrate phosphogypsums differ in the major components CaO and SO_3 , as well as other components, such as MgO, P_2O_5 , Al_2O_3 , Fe_2O_3 , Na_2O , F, TiO_2 , SrO, BaO, ZrO_2 and Ln_2O_3 .

Ln_2O_3 can be found in phosphate rock in the composition of the mineral monazite. The SEM and EDS analysis of insoluble substance in Kovdor and Kirovsk semi-hydrate phosphogypsums revealed that the minerals of the apatite group and monazite form aggregate crystals. Monazite dissolves in sulphuric and phosphoric acids very marginal, while in the formation of aggregate crystals with apatites, it prevents full decomposition of apatites during extraction process. Thus the quantity of insoluble phosphates in semi-hydrate phosphogypsum is influenced. The higher is the amount of minerals containing Ln_2O_3 in phosphate rock, the more water-insoluble phosphates ($P_2O_{5w.ins}$) remain in semi-hydrate phosphogypsum. The average amount of Ln_2O_3 in Kovdor apatite is 0.16 %, while the semi-hydrate phosphogypsum formed from it contains the average amount of $P_2O_{5w.ins}$ equal to 0.78 %. In Kirovsk apatite, the average amount of Ln_2O_3 equals to 0.90 %, while the remaining average amount of $P_2O_{5w.ins}$ in semi-hydrate phosphogypsum equals to 1.46 %.

The dominant particles in Kirovsk apatite are more than 2 times smaller than those in Kovdor apatite. However, Kirovsk apatite is harder to decompose, thus the higher amount of the water-insoluble phosphates remains in the semi-hydrate phosphogypsum.

Finally, it can be stated that the amount of water-insoluble phosphates in semi-hydrate phosphogypsum is more dependent on the amount of the mineral monazite rather than on the particles size of the phosphate rock.

Acknowledgment

The authors thank to the Institute of Mineral engineering of RWTH Aachen University for performing the SEM investigations.

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