

STUDIES ON THERMOCHEMISTRY AND THERMAL PROCESSING OF APATITE

Mihkel VEIDERMA

Department of Basic and Applied Chemistry, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia; riho@aca.ee

Received 2 November 1999

Abstract. A summary of the results obtained by studies on thermochemistry of synthetic and natural apatites and thermal processing of apatites in the presence of various inorganic compounds or natural minerals is presented. The studies resulted in the development of new methods for thermal processing of phosphate rocks with the purpose of their enrichment or production of feed phosphates and phosphorus fertilizers.

Key words: apatite, synthetic, natural, thermochemistry, thermal processing, defluorinated phosphates, thermophosphates, sulphur dioxide.

INTRODUCTION

Thermochemistry and thermal processing of phosphates, particularly when related to natural and synthetic apatites, have been among the key subjects of the research group of inorganic chemistry and technology at Tallinn Technical University for over 30 years. The research has included studies on the chemical–mineralogical composition of the initial materials and the structure of the main constituents (apatite species), thermal transformations occurring in their composition and structure upon heating, and thermal reactions of apatite with various inorganic compounds and minerals, condensed phosphates included. The basic research has served as a basis for new applied output data both for thermal methods of enrichment and thermal processing of phosphate rock with the view of obtaining feed phosphates for cattle-breeding and phosphate fertilizers, as well as for the utilization of the wastes of the phosphate industry (phosphogypsum and others). The most recent studies of this research cycle dealt with thermal interaction of apatites with sulphur dioxide. In these studies we used natural apatites of different types and deposits as well as apatites with different substitutions in the structure synthesized in our laboratory.

This paper presents a summary of the studies of thermal reactions in the systems containing besides apatites various inorganic compounds and natural minerals in contact with different gaseous mediums. In the field of applied outputs, only references have been presented. Since the reactions comprise changes in the composition and structure of apatites in their great variety, a short overview of apatites and their thermal properties is presented.

In the studies we used different research and analysis methods: thermal analysis (TG, DTG, DTA, EGA, and DEGA coupled with FTIR, GC, or titrimetric equipment) in dynamic and quasi-isothermal-isobaric conditions, XRD, IR, FTIR, Raman spectroscopy, AAS, paper and thin layer chromatography, ion exchange, electrophoresis, SEM, BET, electrical conductivity measurement, chemical analysis, and data processing. Laboratory-scale experiments were often complemented by studies on bench and pilot-scale equipment.

The results of the studies dealt with in this paper have been published in about 80 papers. References are made mainly to the papers published in English and to those in Russian that deal with results not discussed in the English papers.

APATITES AND THEIR THERMAL TRANSFORMATIONS

Apatites are the main resource for the production of phosphorus and its compounds. They are the mineral base of bone and tooth enamel of vertebrates and substances belonging to the natural phosphorus cycle.

Thermal transformations in apatites are of interest for the establishment of their genesis and the structural and compositional peculiarities in order to understand the mechanism and control of their processing, to produce phosphorus fertilizers, feed phosphates, different phosphate based materials (ceramics, cements, fibres, biomaterials for dentifrice and surgery, catalysts, etc.). Thermal processing of phosphate rock also involves interactions between apatite and the accompanying minerals as well as the reagents introduced and the constituents of the gaseous phase.

The structure of calcium apatites is of hexagonal type, the cell corresponding to spatial group $P6_3/m$, with an idealized formula $Ca_{10}(PO_4)_6X_2$, where X represents mainly OH^- , F^- , and Cl^- ions* [1-3]. The structure in the form of Pauling's polyhedrons and their positions in the unit cell are presented in Fig. 1. Calcium atoms occupy two different positions: six of the ten atoms are in position II, four in position I. The atoms CaII form an equilateral triangle, in the centre of which, on the main hexagonal axis, are the atoms X. The atoms CaI are on the trigonal axis, surrounded prismatically by nine oxygen atoms of PO_4 groups. The columns, formed by the prisms of the two kinds of calcium atoms, are joined by isolated PO_4 tetrahedrons, located on the double spiral line. All three ion species (Ca^{2+} , PO_4^{3-} , X^-) in the apatite structure can be replaced by

* At room temperatures OH and Cl apatite can be also monoclinic in structure.

various other ions. The variety of substitutions on the cationic side is numerous, on the anionic side the most important are the replacements of PO_4^{3-} by CO_3^{2-} and HPO_4^{2-} . Apatites (Ap) with substitutions on hexagonal axis are represented by OHAp, FAp, ClAp, OAp. Because of the same charge and similar ion sizes, substitution of OH^- and F^- ions for each other can occur to a continuously variable extent, with a series of OH,F apatites formed. The positions of the ions are somewhat different, the variations of hydrogen bonding $\text{OH}\cdots\text{F}$ depend on their relative content [4, 5]. In case of CO_3Ap , there are two types of carbonate apatites. In type A, CO_3^{2-} is located on the main axis of the structure while in type B PO_4^{3-} is partially replaced by CO_3^{2-} . Substitution of OH^- for F^- causes an increase and of CO_3^{2-} for PO_4^{3-} , a decrease in the apatite lattice parameter a . Besides the widely-spread isomorphism, nonstoichiometry and vacancies in the structure are also characteristic of apatites. Water molecules can also be incorporated into the apatite structure. Substitutions in the structure have a strong influence on the stability, solubility, and other physico-chemical properties of apatites.

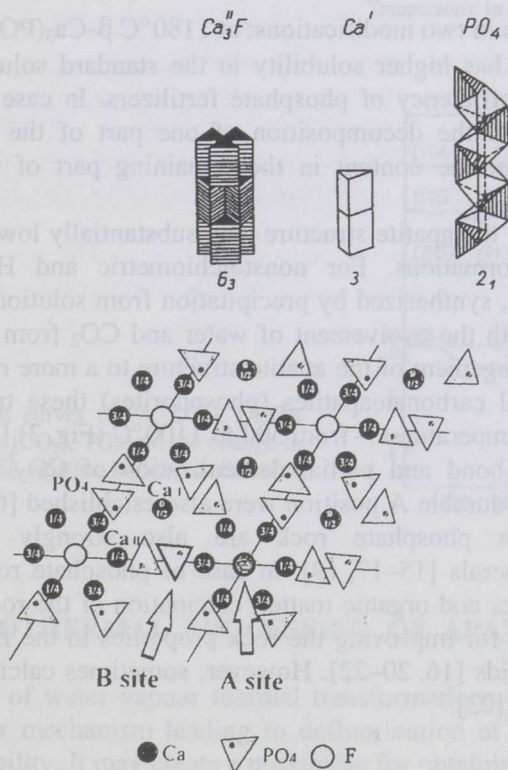
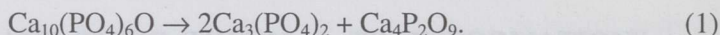


Fig. 1. Structural constituents of the apatite crystal and their projection to the basal plane [1]. A and B sites of CO_3 groups in carbonateapatite are shown.

In endogenous phosphate rock an apatite is represented mainly by F or OH,F apatite. In these apatites OH⁻ and F⁻ are bound by a relatively strong hydrogen bond, while condensation of PO₄³⁻ ions by P–O–P bonds was also revealed. The most widely spread isomorphism in sedimentary apatites (phosphorites) is the B type CO₃²⁻ substitution, at which the degree of substitution of CO₃²⁻ for PO₄³⁻ may reach 25 molar %. An entry of CO₃²⁻ into the structure causes a decrease in the symmetry of the structure and crystallinity, an increase in the porosity of particles, and also an increase in the reactivity and solubility. Substitutions for Ca²⁺ occur to a certain extent (by Na, Mg, Sr, Cd, Mn, U, lanthanoids, etc.) for both endogenous and sedimentary apatites [6–10].

Apatites are relatively thermostable. Thus in an inert gaseous medium fluorapatite does not decompose upon heating up to the melting temperature above 1600°C, the structural changes that occur are negligible. Thermal transformations in stoichiometric OH apatite begin at 900°C with evolvment of water and formation of an oxyhydroxyapatite Ca₁₀(PO₄)₆OH_xO_{1-x/2} and then of oxyapatite Ca₁₀(PO₄)₆O. At temperatures higher than 1200°C oxyapatite decomposes in a reversible manner according to the following reaction:



Ca₃(PO₄)₂ exists in two modifications: at 1180°C β-Ca₃(PO₄)₂ is transferred to an α-form, which has higher solubility in the standard solutions used for the evaluation of the efficiency of phosphate fertilizers. In case of OH,F apatites, simultaneously with the decomposition of one part of the apatite, a gradual increase in the fluorine content in the remaining part of the apatite occurs [9, 11, 12].

Substitutions in the apatite structure may substantially lower the temperature of thermal transformations. For nonstoichiometric and HPO₄²⁻ and CO₃²⁻ containing apatites, synthesized by precipitation from solutions, transformations occur by steps, with the evolvment of water and CO₂ from 150 up to 900°C, followed by rearrangement of the apatite structure to a more regular one (Fig. 2) [13, 14]. In natural carbonateapatites (phosphorites) these transformations are shifted to higher temperatures – from 500 to 1100°C (Fig. 3) [15–17]. Formation of P–O–P bridge bond and partial delocalization of CO₃²⁻ ions from the B position to a more durable A position were also established [6, 16, 18]. Thermal transformations in phosphate rock are also strongly affected by the accompanying minerals [15–17, 19]. In case of phosphate rock containing, for example, carbonates and organic matter, calcination of the rock can be used for its enrichment and for improving the rock properties in the following stages of processing with acids [16, 20–22]. However, sometimes calcination may impair the rock properties [23].

Fig. 2. Thermoanalytical curves (DTA, DEGA-FTIR, EGA-FTIR, TG) of a synthetic apatite with the formula $\text{Ca}_{8.00}\text{Mg}_{1.40}\text{Na}_{0.36}(\text{HPO}_4)_{0.41}(\text{PO}_4)_{5.16}(\text{CO}_3)_{0.43}\text{F}_{1.45}(\text{OH})_{0.55} \cdot 1.83\text{H}_2\text{O}$ obtained by precipitation method [14].

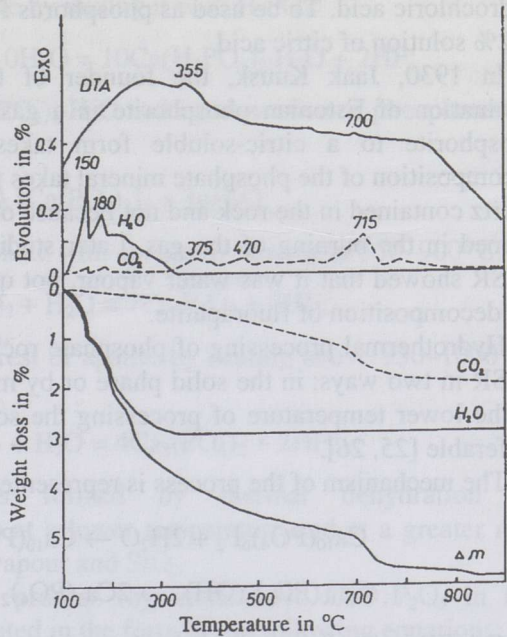
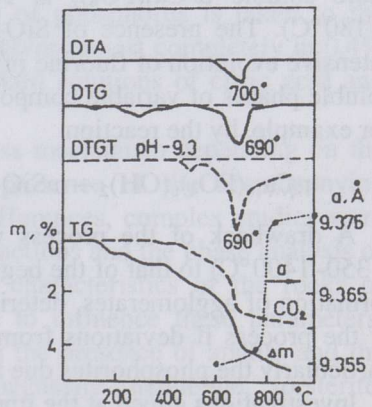


Fig. 3. Thermoanalytical curves (DTA, DTG, DEGA Titr (DTGT), EGA Titr (CO_2), TG) and the change in the parameter a of the apatite lattice of Estonian phosphorite [12].



HYDROTHERMAL PROCESSING OF APATITES

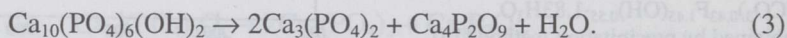
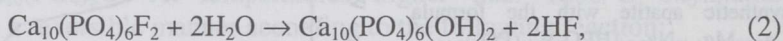
In the presence of water vapour thermal transformations in natural apatites proceed by another mechanism leading to defluorination of apatite and to an increase in its solubility. It may create a possibility for obtaining feed phosphates and phosphorus fertilizers. According to standards feed phosphates must not contain more than 0.1–0.2% fluorine and they must dissolve in 0.4% solution of

hydrochloric acid. To be used as phosphorus fertilizer, the product must dissolve in 2% solution of citric acid.

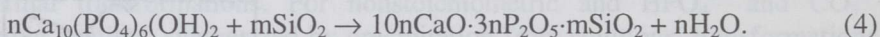
In 1930, Jaak Kuusk, the founder of this method, established that by calcination of Estonian phosphorite in a gas furnace at 1400°C, transition of phosphorite to a citric-soluble form takes place [24]. He assumed that decomposition of the phosphate mineral takes place due to its interaction with the quartz contained in the rock and not because of the influence of the water vapour formed in the burning of the gas. Later studies conducted in the USA and the USSR showed that it was water vapour, not quartz, that played the main role in the decomposition of fluorapatite.

Hydrothermal processing of phosphate rock was applied in the USA and the USSR in two ways: in the solid phase or by means of melting the rock. Because of the lower temperature of processing the solid phase process was considered preferable [25, 26].

The mechanism of the process is represented by the following reactions:



$\text{Ca}_3(\text{PO}_4)_2$ is often present in the product in the form of $\beta\text{-Ca}_3(\text{PO}_4)_2$, since under the influence of the rock admixtures the temperature of its transition to more soluble $\alpha\text{-Ca}_3(\text{PO}_4)_2$ is 100–250°C higher than that of the pure salt (1180°C). The presence of SiO_2 in the rock has an influence upon the more intensive evolution of fluorine in the form of SiF_4 and the formation of the more soluble phases of variable composition on the basis of calcium silicophosphates, for example, by the reaction

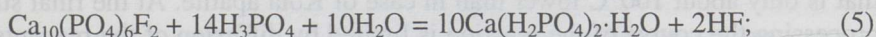


A drawback of the process was the closeness of the process temperature (1350–1400°C) to that of the beginning of the melting of the rock, which caused formation of agglomerates, deterioration of defluorination, and even disturbance of the process if deviations from optimum parameters occurred. This concerns particularly the phosphorites due to their lower melting temperatures.

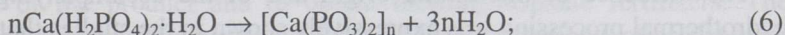
Investigations aimed at the improvement of the process showed the efficiency of the addition of relatively small amounts of phosphoric acid to the rock (3.5–4.5% in the form of P_2O_5). It caused a fall in the process temperature and a rise in the stability and productivity of the process. With Kola apatite, addition of H_3PO_4 is efficient, which has been explained by the decomposition of nepheline (an admixture of the apatite) and the interaction of apatite with the active SiO_2 formed. The application of other acids did not give any similar effect.

A more detailed study of the process carried out by the author in collaboration with fellow-workers showed that the mechanism of the phosphoric acid action is more complicated and can be described as follows [11, 26–28]:

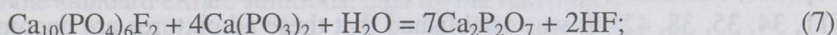
– decomposition of part of apatite by mixing it with H_3PO_4 :



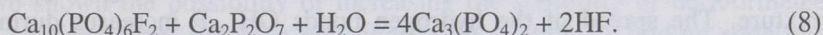
– thermal dehydration of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and condensation of phosphates by heating up to 500–600°C:



– reaction of calcium polyphosphate with apatite by heating at 550–900°C:

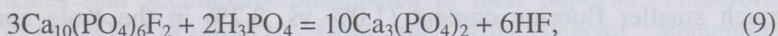


– reaction of $\text{Ca}_2\text{P}_2\text{O}_7$ with the rest of apatite by heating above 950–1000°C, terminating at 1250–1350°C:



Thus, condensed phosphates formed by thermal dehydration of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ react with apatite at a lower temperature and at a greater rate compared to the reaction of water vapour and SiO_2 .

The summary reaction of the process (by molar ratio $\text{CaO}:\text{P}_2\text{O}_5$ in the mixture, equal to 3.0) can be presented in the form of the following equation:



according to which 10% of the total quantity of phosphorus is taken to the product with H_3PO_4 . As a rule, the product dissolves almost completely in 0.4% solution of HCl , but only partially in the standard solutions of citric acid and ammonium citrate.

However, there are differences in the process mechanism depending on the peculiarities of the apatite mineral and the presence of the accompanying minerals in the rock used. To explain these differences, complex studies were carried out, particularly on the kinetics of the reactions and the phase analysis of the formed systems to determine the melting characteristics of the rocks of different composition and to find possibilities to influence these parameters. Dehydration and condensation of phosphates in the presence of apatite and the accompanying minerals (calcite, dolomite, magnesite, nepheline, forsterite, fluorite) and the reactions of condensed phosphates with the components of the rocks were also studied [18, 29–38].

In the presence of phosphate rock, condensation of phosphates proceeds to a smaller extent, depending on the apatite reactivity. In case of the relatively resistant Kola apatite, reaction 7 proceeds at higher temperatures and, therefore, condensation goes further, with the formation of high-molecular polyphosphates ($n > 5$), which may be preserved in the mixtures up to 900–100°C. In processing more reactive Estonian phosphorite, on the contrary, the reactions are shifted to lower temperatures, condensation is inhibited, and polyphosphates occur in the mixture only up to 650°C. When phosphorites are processed, decarbonization and rearrangement of the structure to that of fluorapatite proceed simultaneously.

Nevertheless, defluorination (reactions 7 and 8) is completed at a temperature that is only about 100°C lower than in case of Kola apatite. At the final stage of processing the course of the reaction is limited by diffusion of the reagents [39]. Therefore, the fluidized bed reactors are highly efficient in the realization of the process, which was demonstrated at a pilot plant [40, 41].

The influence of the apatite origin and of the accompanying minerals on hydrothermal processing was expressively shown in the studies that used igneous fluorhydroxyapatites from the Kovdor (North Karelia) and Siilinjärvi (Finland) deposits, containing also carbonates (calcite, dolomite), forsterite, and phlogopite [11, 34, 35, 38, 42]. It was established that these admixtures are decomposed by phosphoric acid to a greater extent than apatite, but not completely. They partly pass over to the following stages of the process, reduce the amount of polyphosphates, reacting with apatite, and lower the melting temperature of the mixture. The spread of the hydrogen bonds OH...F increases during heating, hindering the diffusion along the hexagonal axis of the crystal and defluorination of apatite. The evolution of fluorine proceeds non-synchronously with the decomposition of apatite, leading to the enrichment of the apatite residue with fluor. The changes in the phase composition, the molar ratio F:apatite, and the parameter *a* in the course of Kovdor apatite processing are presented in Fig. 4. Thus, the postulate of easier defluorination of Kovdor apatite as a result of a much smaller fluorine content (1.0% vs. 3.2% in the Kola apatite) was not corroborated by the experimental data. However, industrial production of feed phosphates has been carried out with the temperature kept at 1350–1400°C and an increased amount of H₃PO₄ added (7–8% P₂O₅).

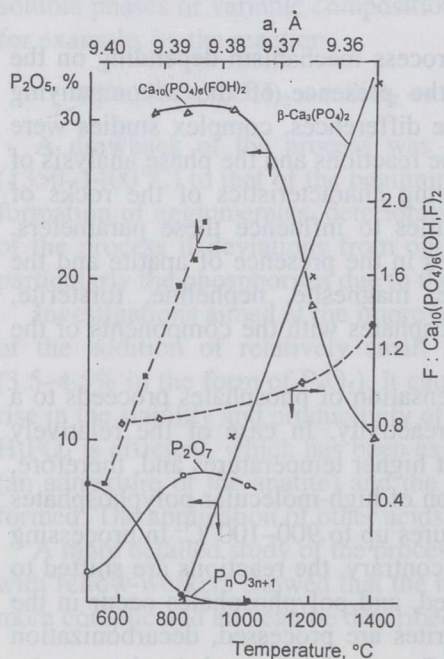
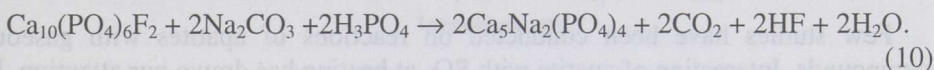


Fig. 4. Changes in the content of different forms of phosphates, in the molar ratio F:apatite, and in the parameter *a* of the lattice of apatite remainder at heating a Kovdor apatite and H₃PO₄ mixture [11, 42].

PREPARATION OF THERMOPHOSPHATE FERTILIZERS

The solubility in 2% solution of citric acid of phosphorus obtained by hydrothermal processing of phosphate rock is usually only 30–40% of its total content. In industry Na_2CO_3 (alone or together with H_3PO_4) is added in order to increase the solubility of the product and to obtain thermophosphate fertilizers. The amounts of the additives have been calculated on the assumption that on the basis of CaNaPO_4 or $\text{Ca}_5\text{Na}_2(\text{PO}_4)_4$ solid solutions can be obtained which are easily soluble in the standard citrate solutions, e.g., by the reaction:



We have shown the possibility of increasing the solubility of defluorinated phosphate obtained from Estonian phosphorite up to 95% by adding soda and phosphoric acid (in amounts corresponding to molar ratios $\text{CaO}:\text{P}_2\text{O}_5$ and $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ 3 and 0.45, respectively) [43].

With a view of lowering the cost of the product, experiments were carried out in which natural aluminosilicates (instead of Na_2CO_3) were added to apatites of the Kola, Kovdor, and Siilinjärvi deposits. Preference was given to the varieties of aluminosilicates that accompany phosphates in their deposits. Therefore, nepheline ($3\text{Na}_2\text{O}\cdot\text{K}_2\text{O}\cdot 4\text{Al}_2\text{O}_3\cdot 8\text{SiO}_2$) from the Kola deposit, glauconite [$\text{K}_2\text{O}\cdot 4(\text{MgO}\cdot\text{FeO}\cdot\text{Fe}_2\text{O}_3\cdot\text{Al}_2\text{O}_3)\cdot 10\text{SiO}_2\cdot 3\text{H}_2\text{O}$] from the Estonian phosphorite deposit, and pseudoleicite (a mixture of $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ and $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) from the Oshurkovo apatite deposit in Siberia as well as shungite (mixture of silica and carbon) from Karelia were chosen for the experiments.

The possibility of obtaining thermophosphate fertilizers, the mechanism and optimal conditions of processing, and the composition of the products were established by experiments in which relatively small amounts of reagents (2.5–3.5% P_2O_5 of H_3PO_4 and 6–8% of aluminosilicates or shungite) were added to apatite also in the respective model systems containing polyphosphates, accompanying minerals, etc. [42, 44–48]. By adding aluminosilicates a liquid phase may be formed at the high temperature stage of processing. It contributes to the decomposition of apatite and in case of limited amounts does not complicate the process. Nepheline proved to be the most suitable additive that guarantees high solubility of the product (up to 99% in 2% citric acid and 85% in neutral ammonium citrate solution) and stability of the sintering process at 1350°C. The product contains $\alpha\text{-Ca}_3(\text{PO}_4)_2$ and its solid solutions with $\alpha\text{-Ca}_2\text{SiO}_4$ or nagelschmidite $\text{Ca}_3(\text{PO}_4)_2\cdot 2\text{Ca}_2\text{SiO}_4$ as phases with a good solubility in the citric acid solution. The high defluorination degree and low Mg and Fe content in raw materials (incorporating into the $\beta\text{-Ca}_3(\text{PO}_4)_2$ structure and preventing its transition to more soluble $\alpha\text{-Ca}_3(\text{PO}_4)_2$) are also an assumption for obtaining a highly soluble product. For that reason glauconite is an additive of little interest. The shortcoming of shungite consists in the formation of resistant

crystalite on heating, leading to a limited reaction with apatite. Addition of pseudoleucite causes partial volatilization of potassium.

The thermophosphate fertilizer obtained should be a good source of phosphorus for plants in acid soils, having an advantage over the water-soluble fertilizers as it contains phosphorus that is less migrating from soils to run-off water.

THERMAL INTERACTION OF APATITE WITH SO₂

Few studies have been conducted on reactions of apatites with gaseous compounds. Interaction of apatite with SO₂ at heating has drawn our attention. In earlier studies the formation of a mixture of CaSO₄ and β -Ca₂P₂O₇ had been established when OH apatite was heated in stationary conditions at 700–800°C in the flow of SO₂. At temperatures over 900°C a mixture was formed of CaSO₄ with a series of calcium phosphosulphates with β -Ca₃(PO₄)₂ structure. The upper limit of the SO₄²⁻ solubility in β -Ca₃(PO₄)₂ corresponds to a compound having the formula Ca₂₀(PO₄)₁₂(SO₄)₂, which is relatively thermostable and does not decompose until 1200°C [49, 50]. Incorporation of SO₄²⁻ into the apatite structure is not excluded as it was assumed in case of calcination of Israeli phosphorite [51].

In our studies we examined transformations in apatites of different composition at dynamic heating up to 1000°C in the flow of air with SO₂ (20% vol.). We used synthetic apatites obtained by precipitation methods with a general formula (Ca,Mg)_{10-n/2}(PO₄)_{6-n}(CO₃)_n(OH,F)₂ differing in Mg:Ca, CO₃:PO₄, and OH:F ratios, and also a sample of Kola fluorapatite [52, 53].

In the presence of SO₂, differently from calcination of apatite in the air alone, thorough transformations take place. Binding of SO₂ by apatite in a wide temperature range – from 400 up to 860–890°C – was established. The amount of SO₂ bound was the highest for OH apatite and the lowest for F apatite. An increase in the CO₃²⁻ content as well as partial replacement of Ca by Mg in apatite structure enhances the SO₂ binding and shifts the beginning of the interactions towards lower temperatures. The maximum amount of SO₃ in the solids obtained has reached 26–27% of the apatite sample mass (3.3–3.4 moles per 1 mole of apatite).

At temperatures higher than 860–900°C intensive evolution of SO₂ from apatites occurs. It comes to an end at 950–980°C and the amount of SO₃ that remains in the solid is 6–11% (Fig. 5).

We established the following phases in the solids: at 750–900°C apatite, CaSO₄, β -Ca₂P₂O₇, or (Ca,Mg)₂P₂O₇; and at 1000°C β -Ca₃(PO₄)₂ or (Ca,Mg)₃(PO₄)₂, CaSO₄, and the remainder of apatite (only when F containing apatite was used).

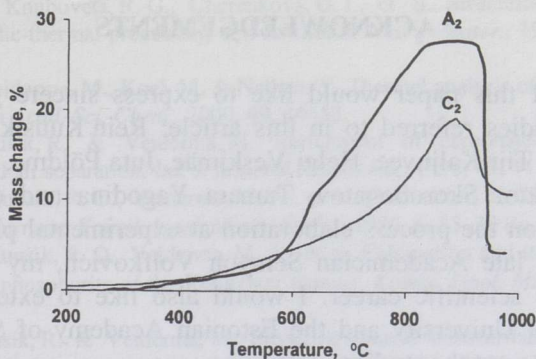
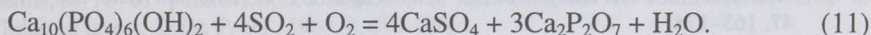


Fig. 5. The mass change in synthetic OH apatite (sample A₂) and OH,F carbonateapatite (sample C₂) at heating in the flow of SO₂-air mixture [53].

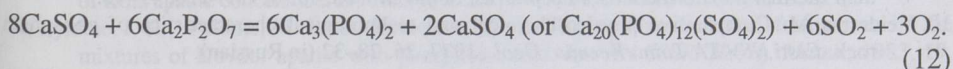
The results obtained enable to distinguish three stages of transformations taking place, one after another, under dynamic heating of apatites up to 1000°C in the presence of SO₂:

1. Dehydration and carbonization of apatites, which proceed at lower temperatures than heating without SO₂.
2. Reaction between apatite and SO₂:

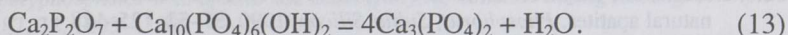


The higher the mole ratios Ca:P and OH:F in the initial apatite, the higher is the amount of SO₂ bound. In case of a sufficient amount of SO₂, OH apatite decomposes fully and F apatite reacts partially due to its more resistant structure.

3. Reaction between CaSO₄ and β-Ca₂P₂O₇ resulting in the evolvment of SO₂ and formation of β-Ca₃(PO₄)₂ or its solid solution with CaSO₄ (calcium phosphosulphate):



A parallel reaction proceeds to a smaller extent:



In the course of decarbonization of apatite, incorporation of SO₄²⁻ into the apatite structure is not excluded. If sulphateapatite is formed it persists shortly upon dynamic heating due to its decomposition at the temperatures of reaction 11, as it was shown by thermal analysis of calcium sulphateapatites, synthesized by the precipitation method [54].

Thermal interaction of apatite with SO₂ is of interest for sorption of SO₂ from exhaust gases and its storing and regeneration (at about 400°C lower than in case of CaSO₄) as well as for obtaining phosphorus fertilizers without production of sulphuric or other acids.

ACKNOWLEDGEMENTS

The author of this paper would like to express sincere gratitude to good colleagues in studies referred to in this article: Rein Kuusik, Meeme Põldme, Kaia Tõnsuaadu, Tiit Kaljuvee, Helgi Veskimäe, Juta Põldme, and Rena Knubovets, also to Viktor Skorobogatov, Tamara Yagodina and others, who have shared the work on the process elaboration at experimental plants. My deepest thanks belong to late Academician Semyon Volfkovich, my supervisor at the beginning of my scientific career. I would also like to extend my thanks to Tallinn Technical University and the Estonian Academy of Sciences for their support in carrying out the studies.

REFERENCES

1. Kanazawa, T. *Inorganic Phosphate Materials*. Kodansha, Tokyo & Elsevier, Amsterdam, 1989.
2. Elliott, J. C. *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*. Elsevier, Amsterdam, 1994.
3. Knubovets, R. G. & Veiderma, M. A. Crystallochemistry and some properties of apatites. In *Physico-chemical Investigations on Monomeric and Polymeric Phosphates*. Nauka, Alma-Ata, 1987, 36–52 (in Russian).
4. Knubovets, R., Veiderma, M. & Tõnsuaadu, K. Application of the peak fitting program "Galactic" for FTIR analysis of OH⁻ ions in apatite. *Proc. Estonian Acad. Sci. Chem.*, 1998, **47**, 163–174.
5. Veiderma, M., Knubovets, R. & Tõnsuaadu, K. Structural properties of apatites from Finland studied by FTIR spectroscopy. *Bull. Geol. Soc. Finland*, 1998, **70**, parts 1 & 2, 69–75.
6. Veiderma, M. A. & Knubovets, R. G. Natural phosphates and phosphate rock. *Izv. AN SSSR. Neorg. Mater.*, 1984, **20**, 991–998 (in Russian).
7. Veiderma, M. A. & Puura, V. A. Phosphorite deposits. *Totals of Science and Technics, ser. Non-metallic Minerals*, VINITI, Moscow, 1988, 6 (in Russian).
8. Veiderma, M. & Knubovets, R. Kiruna apatite. *Scand. J. Metall.*, 1991, **20**, 329–330.
9. Veiderma, M., Knubovets, R. & Tõnsuaadu, K. Fluorhydroxyapatites of Northern Europe and their thermal transformations. *Phosphorus, Sulfur Silicon*, 1996, **109–110**, 43–46.
10. Veiderma, M. Comparative physico-chemical and technological characteristics of phosphate rock. *Eesti NSV TA Toim. Keemia. Geol.*, 1977, **26**, 28–32 (in Russian).
11. Veiderma, M., Põldme, M. & Tõnsuaadu, K. Thermische Entfluorierung von Apatit. *Chem. Techn.*, 1988, **46**, 169–172.
12. Veiderma, M., Kaljuvee, T., Knubovets, R., et al. Thermal transformations in systems based on natural apatites. *Phosphorus, Sulfur Silicon*, 1990, **51–52**, 125–128.
13. Vilbok, H., Knubovets, R. & Veiderma, M. Synthesis and thermal transformations of Ca, Mg-carbonateapatite. *Proc. Estonian Acad. Sci. Chem.*, 1992, **41**, 45–51.
14. Tõnsuaadu, K., Põldme, M., Leskela, T., et al. A thermoanalytical study of synthetic carbonate-containing apatites. *Thermochim. Acta*, 1995, **256**, 55–65.
15. Koel, M., Kudrjashova, M., Tõnsuaadu, K., et al. Evolved gas analysis of apatite materials using thermogase chromatography. *Thermochim. Acta*, 1998, **322**, 25–32.
16. Veiderma, M. & Knubovets, R. Thermal transformations in phosphate rock and their use for the beneficiation of phosphate rock. In *Proc. 2nd Int. Congr. Phosphorus Compounds*. IMPHOS, Boston, 1980, 345–362.
17. Kaljuvee, T., Veiderma, M., Tõnsuaadu, K. & Vilbok, H. Physico-chemical transformations during heating of phosphorites. *J. Therm. Anal.*, 1988, **33**, 839–844.

18. Veiderma, M. A., Knubovets, R. G., Cherenkova, G. I., et al. Structural transformations in apatite by acidic-thermal processing. *Izv. AN SSSR. Neorg. Mater.*, 1987, **23**, 123–126 (in Russian).
19. Tõnsuaadu, K., Veiderma, M., Koel, M. & Nathan, Y. Thermal analysis of Israeli phosphorites. *Proc. Estonian Acad. Sci. Chem.*, 2000, **49**, 44–52.
20. Kaljuvee, T., Kuusik, R. & Veiderma, M. Enrichment of carbonate-phosphate ores by calcination and air separation. *Int. J. Mineral Processing*, 1995, **43**, 113–121.
21. Kaljuvee, T. B., Kuusik, R. O., Veiderma, M. A., et al. Calcination of Chilisai phosphorite in fluidized bed furnace. *Kompl. Ispol. Miner. Syr'ya*, 1985, **6**, 35–39 (in Russian).
22. Kaljuvee, T. B., Kuusik, R. O., Veiderma, M. A., et al. Calcination and its efficiency at acidic processing of phosphorite of the Kokdzhon deposit. *Kompl. Ispol. Miner. Syr'ya*, 1985, **7**, 34–38.
23. Kaljuvee, T., Kuusik, R. & Veiderma, M. Physico-chemical transformations during thermal treatment of phosphorites and solubility of products. *Phosphorus Res. Bull.*, 1999, **10**, 335–341.
24. Kuusk, J. Glühaufschliessung der Phosphorite mit Kieselsäure zu ecks Gewinnung eines citratlöslichen Düngemittels. *Acta Univ. Tartuensis*, 1931, A20, 1–79.
25. Volkovich, S. I. *Hydrothermal Processing of Phosphates to Fertilizers and Feed Supplements*. Khimiya, Moskva, 1964 (in Russian).
26. Volkovich, S. I. & Veiderma, M. A. The progress of hydrothermal processing of phosphate rock. In *Proc. Techn.-Econ. Conf. ISMA*, Orlando, 1978, 49–62.
27. Veiderma, M. A. Acidic-thermal methods for obtaining feed phosphates. In *Studies on Chemistry and Technology of Fertilizers, Pesticides, Salts*. Nauka, Moskva, 1966, 201–210 (in Russian).
28. Veiderma, M. A. Effect of phosphoric acid addition on hydrothermal processing of natural phosphates. *Khim. Prom.*, 1971, **4**, 39–44 (in Russian).
29. Veiderma, M. A. & Volkovich, S. I. Kinetics of defluorination of obolus phosphorite in fluidized layers. *Khim. Prom.*, 1964, **8**, 587–590.
30. Veiderma, M. A. & Volkovich, S. I. Physicochemical analysis of the hydrothermal processing of obolus phosphorite. *Zh. Prikl. Khim.*, 1964, **37**, 937–946 (in Russian).
31. Pyldme, M., Buzagh-Gere, E., Pyldme, J. & Veiderma, M. Thermal analysis of the interaction of phosphorite with condensed phosphates of calcium. *J. Therm. Anal.*, 1976, **10**, 195–204.
32. Veiderma, M., Pyldme, J. & Pyldme, M. The reactions between condensed phosphates and natural phosphates or fluorite by heating. In *Proc. 1st Int. Congr. Phosphorus Compounds*. IMPHOS, Rabat, 1977, 449–456.
33. Veiderma, M. A., Pyldme, M. E. & Pyldme, J. H. Chemism of phosphoric acid-thermal processing of Kola apatite concentrate. *Zh. Neorg. Khim.*, 1979, **24**, 1795–1800 (in Russian).
34. Pyldme, J. H., Pyldme, M. E. & Veiderma, M. A. Thermo-chemical transformations in the mixtures of Kovdor apatite with phosphoric acid. *Izv. AN SSSR. Neorg. Mater.*, 1983, **19**, 978–981 (in Russian).
35. Veiderma, M., Pyldme, M., Tynsuaadu, K. & Utsal, K. Mechanism of reactions in mixtures of calcium polyphosphates with apatite and accompanying minerals during heating. *J. Therm. Anal.*, 1987, **32**, 1093–1103.
36. Tynsuaadu, K. O. & Veiderma, M. A. Thermal transformations in the mixtures of calcium polyphosphate with calcite and forsterite. *Izv. AN SSSR. Neorg. Mater.*, 1987, **23**, 303–306 (in Russian).
37. Tynsuaadu, K. O. & Veiderma, M. A. Thermal transformations in the mixtures of calcium polyphosphate with magnesite and dolomite. *Izv. AN SSSR. Neorg. Mater.*, 1989, **25**, 107–110 (in Russian).
38. Pyldme, M., Utsal, K., Aruväli, I., et al. Investigation of phase transformations in thermal processing of phosphate rock. *J. Therm. Anal.*, 1990, **36**, 1699–1705.
39. Kuusik, R., Luhakooder, E. & Veiderma, M. Diffusion of reagents in granules of phosphorite by hydrothermal processing. *Zh. Prikl. Khim.*, 1971, **44**, 20–26 (in Russian).

40. Veiderma, M. A., Vinkman, A. O., Volkovich, S. I., et al. Defluorination of Maardu phosphorite in pilot plant with fluidized bed reactors. *Khim. Prom.*, 1975, 4, 193–195 (in Russian).
41. Veiderma, M. A., Kuusik, R. O., Yagodina, T. N. & Skorobogatov, V. A. Hydrothermal processing of natural phosphates in fluidized layer. In *Problems in Chemistry and Chemical Technology*. Nauka, Moskva, 1977, 184–192 (in Russian).
42. Veiderma, M. & Tõnsuaadu, K. Thermophosphate fertilizers from Siilinjärvi apatite. *Acta Polytechn. Scand.*, 1996, CH 239.
43. Veiderma, M. A. & Karjus, A. A. On improving of the solubility of defluorinated phosphates from phosphorite. In *Investigations in the Field of Inorganic Technology*. Nauka, Moskva, 1972, 140–144 (in Russian).
44. Veiderma, M., Pyldme, M., Tynsuaadu, K. & Knubovets, R. Search of natural reagents for obtaining thermophosphates. *Phosphorus Res. Bull.*, 1991, 1, 421–426.
45. Tõnsuaadu, K. & Veiderma, M. Composition and properties of the heating products of the mixtures of calcium phosphates and aluminosilicates. *Proc. Estonian Acad. Sci. Chem.*, 1992, 41, 157–163.
46. Veiderma, M., Tõnsuaadu, K., Knubovets, R., et al. Thermophosphates on the basis of apatite and aluminosilicates. *Phosphorus, Sulfur Silicon*, 1993, 76, 187–190.
47. Tõnsuaadu, K., Rimm, K. & Veiderma, M. Composition and properties of thermophosphates from apatite and aluminosilicates. *Phosphorus, Sulfur Silicon*, 1993, 84, 73–81.
48. Tõnsuaadu, K. & Rimm, K. Thermochemical reactions in the systems hydroxyapatite–aluminosilicate or shungite. *Proc. Estonian Acad. Sci. Chem.*, 1994, 43, 137–145.
49. Marraha, M., Heughebaert, I. C. & Heughebaert, M. Action of sulfur dioxide on phosphocalcic hydroxyapatite at different temperatures. *Phosphorus, Sulfur Silicon*, 1993, 79, 181–191.
50. Marraha, M., Heughebaert, I. C. & Heughebaert, M. Étude du Comportement du Phospho-sulfate de Calcium Entre 1100 et 1500 °C. *Ann. Chim. Fr.*, 1991, 16, 619–631.
51. Knubovets, R., Nathan, Y., Shoal, S. & Rabinowitz, I. Thermal transformations in phosphorites. *J. Therm. Anal.*, 1997, 50, 229–239.
52. Tõnsuaadu, K., Peld, M., Bender, V. & Veiderma, M. Binding of SO₂ by synthetic substituted apatites. *J. Therm. Anal. Calorimetry*, 1999, 56, 35–42.
53. Veiderma, M., Tõnsuaadu, K. & Peld, M. Thermal interactions between apatites and SO₂. *Phosphorus Res. Bull.*, 1999, 10, 256–261.
54. Tõnsuaadu, K., Peld, M., Bender, V. & Mikli, V. Characterization of sulphateapatites. Unpublished work.

UURIMUSED APATIITIDE TERMOKEEMIA JA TERMLISE TÖÖTLEMISE ALAL

Mihkel VEIDERMA

On antud ülevaade uurimustest, mis käsitlevad sünteetiliste ja looduslike apatiitide termokeemiat ja termilist töötlemist omaette või mitmete anorgaaniliste ühendite ja looduslike mineraalide manulusel. Saadud tulemuste põhjal on välja töötatud looduslike fosfaatide termilise töötlemise uued meetodid, mille abil on võimalik fosfaate rikastada, sööda- ja väetisfosfaate toota ning vääveldioksiidi siduda.