

Natural and synthetic apatites as sorbents for Cd²⁺ and Cr³⁺ ions from aqueous solutions

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Abstract. The sorption of Cd²⁺ and Cr³⁺ ions from aqueous solutions was investigated on different natural and synthetic apatites. The sorption of Cd²⁺ depends mainly on the apatite specific surface area, it increases with an increase in magnesium and a decrease in carbonate content, reaching 20 and 74 mmol per 100 g of natural and synthetic apatite, respectively. The sorption of Cr³⁺ ions reaches 250 mmol/100 g and depends substantially on the apatite magnesium content, the effect of the specific surface area is less important. The sorption of cadmium proceeds mainly by an ion-exchange mechanism, in the case of chromium also a dissolution–precipitation mechanism is involved.

Key words: apatite, sorption, chromium, cadmium.

INTRODUCTION

Insoluble phosphates such as apatites are considered to be promising materials for immobilization of heavy metals in contaminated waters and soils in order to reduce their solubility and ecological bioavailability [1–6]. As hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] (HAp) is the main component of bones and teeth, incorporation of various metal ions into hard tissues of vertebrates is also of interest in medical and dental sciences concerned with denaturation of bones and accumulation of harmful metal ions [7, 8].

In a HAp structure a large number of substitutions can occur. The most common ones in natural apatites are the substitutions of Mg²⁺ and Na⁺ for Ca²⁺, CO₃²⁻ for PO₄³⁻, and F⁻ for OH⁻ ions. Because of the incorporation of carbonate

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and magnesium into the apatite structure the chemical reactivity of the apatite increases as its structure becomes more irregular. Fluorine and sodium, on the contrary, stabilize the crystal structure of apatite [4, 9–11]. The sorption capacity as well as the other apatite characteristics such as solubility and thermal stability depend substantially on the kind and amount of substitutions and vacancies in the apatite structure, as well as on its crystallinity and specific surface area [12].

The sorption of metal ions on apatite can proceed by different mechanisms such as surface complexation, adsorption, diffusion into the solid, dissolution–precipitation, and ion exchange. Most of the studies on this subject have suggested that ion exchange with Ca^{2+} ions of HAp lattice is the most widely spread mechanism for Cd^{2+} ions sorption [4, 13, 14]. The sorption of Cr^{3+} ions is less studied, but introduction of chromium into the apatite lattice is also considered to be possible [15, 16].

The estimation of the sorption mechanism is based on the analysis of the composition of solutions before and after sorption experiments. Sorption can be characterized by the molar ratio Q – the ratio of the cations bound to the cations released from the apatite. If $Q = 1$, mainly ion exchange between the cations of the apatite and of the solution takes place. $Q > 1$ indicates the domination of the adsorption mechanism, including the filling of cationic vacancies in a non-stoichiometric apatite. When $Q < 1$, usually dissolution of apatite and precipitation of new phases occur. However, different sorption mechanisms often act together and the dominance of one of them is rather hard to distinguish [17].

Most studies on heavy metals binding are carried out on synthetic HAp [1, 2, 12, 13, 16, 17], only a few of them deal with natural apatite minerals [3, 5]. Natural apatites usually contain various anionic and cationic substituents as well as accompanying minerals, which affect their chemical properties. In this study different fractions of Kola apatite and Estonian and Israeli phosphorites were used to evaluate their abilities to bind Cd^{2+} and Cr^{3+} ions from aqueous solutions. Synthetic apatites were examined in order to assess the impact of different apatite characteristics like the content of magnesium, fluorine, and carbonate as well as the specific surface area (SSA) on their sorption capacity and to compare the results obtained with natural apatites. Infrared (IR) spectroscopy, X-ray diffraction (XRD), and thermal analyses were used to study the changes caused by the sorption process in the apatite structure.

MATERIALS AND METHODS

Synthetic apatites

Apatites with different levels of fluoride, carbonate, magnesium, and cadmium substitutions were prepared by precipitation from aqueous solution at 80°C. Two solutions – one containing Ca^{2+} (Mg^{2+} , Cd^{2+}) and NO_3^- ions and the other containing PO_4^{3-} , F^- , CO_3^{2-} , and NH_4^+ ions – were added simultaneously to a NH_4OH – NH_4NO_3 solution with pH 9.7.

Table 1. Chemical composition and SSA of synthetic apatites

Sample	Synthesis conditions	SSA, m ² /g	CaO, %	MgO or CdO, %	P ₂ O ₅ , %	CO ₂ , %	F, %
Ca-HAp							
E11	S	15	54.4	0	36.4	5.0	0
C12	S	18	53.8	0	38.6	2.2	0
A12	S	24	54.1	0	40.4	0.7	0
A13	S	31	53.9	0	41.4	0.3	0
HA1	S	36	54.3	0	39.4	0.6	0
A01	S	79	52.3	0	40.4	0.1	0
HA2	R	85	54.7	0	39.9	1.0	0
HA3	R	86	54.1	0	39.2	0.7	0
Ca-FHAp							
D32	S	10	53.9	0	38.3	2.6	1.8
A42	S	16	54.2	0	39.2	1.1	2.4
C41	S	17	53.7	0	38.7	2.8	3.0
C31	S	19	54.0	0	39.8	1.2	1.7
C42	S	30	53.6	0	39.7	0.8	2.8
A31	S	31	53.8	0	40.1	0.7	1.4
D22	R	55	53.2	0	39.9	1.6	0.7
D21	R	114	53.1	0	36.5	4.2	0.5
MgCa-Ap							
EM12	S	43	44.7	7.0	40.2	1.6	0
EM42	S	14	44.1	7.5	37.5	1.1	2.5
CdCa-Ap							
A1Cd21	S	31	44.2	18.1	35.3	0.14	0
A4Cd22	S	31	44.4	18.9	34.6	0	1.8

S – precipitation with solutions addition at 1 mL/min.

R – precipitation with rapid mixing of solutions.

Different precipitation rates (addition of solutions at 1 mL/min or rapid mixing) were used in order to obtain apatites with different crystallinity and SSA. By adding the NH₄OH solution, the pH was maintained between 9 and 10. The suspension was stirred for 3 h at the precipitation temperature in order to improve the homogeneity and crystallinity of the precipitate, and then kept at room temperature for 24 h. The precipitates were filtered, washed thoroughly with distilled water, and dried at 150 °C.

The synthesized materials were studied by chemical and thermal analyses, IR-spectroscopy, XRD-powder analysis, and specific surface area measurements by the BET method. The synthesized materials were fine powders identified as B-type carbonate apatites, where CO₃²⁻ is substituted for PO₄³⁻. The chemical composition and SSA of the apatites synthesized is given in Table 1.

Natural apatites

Different fractions of Kola apatite and Kabala (Estonia) phosphorite were used. Some of Kabala phosphorite was triboactivated using a planetary mill with

Table 2. Chemical composition and SSA of natural apatites

Sample	Fraction, μm , or treatment	SSA, m^2/g	CaO, %	MgO, %	P_2O_5 , %	CO_2 , %	F, %
Apatite							
Kola-1	100–200	0.3	52.6	0	40.1	0.1	3
Kola-2	71–100	0.2	52.4	0	40.3	0.1	3
Kola-3	45–71	0.6	52.3	0	39.3	0.1	3
Kola-4	25–45	1.1	48.9	0	37.1	0.1	3
Phosphorites							
Kabala-1	100–200	3.8	41.0	0.8	28.3	3.4	2.3
Kabala-2	71–100	4.7	44.2	1.2	29.9	4.8	2.3
Kabala-3	45–71	4.9	45.3	1.6	30.6	5.5	2.3
Kabala-4	25–45	6.3	46.8	2.0	30.1	6.9	2.3
Kabala-T	T	9.1	43.7	1.5	28.3	5.8	2.3
Israel		16.4	54.0	0.3	28.2	10.1	2.9
Israel-G	G	22.7	54.0	0.3	28.2	10.1	2.9
Israel-GC	G, C	21.8	51.4	0.4	33.4	3.9	3.0

T – triboactivated.

G – obtained by grinding.

C – obtained by treatment with ammonium citrate solution.

CrNi balls. For Cd^{2+} ions sorption an Israeli phosphorite sample was additionally used, a part of it was ground and treated with ammonium citrate solution for elimination of carbonates. The chemical composition of natural apatites is shown in Table 2.

Sorption experiments

Sorption experiments were carried out by batch method in aqueous solutions (shaking rate 160 rpm) at room temperature for 24 h. The samples, 100 mg each, were introduced into 50 mL of cadmium or chromium solution.

Sorption solutions were prepared from cadmium and chromium nitrate salts. The concentrations of cations in the solutions were in the range $1.9\text{--}2.4 \times 10^{-3}$ mol/L and $1.9\text{--}5 \times 10^{-3}$ mol/L for Cd^{2+} and Cr^{3+} , respectively. The pH values of the solutions in the case of cadmium were 5 and 6 and for chromium 4 and 5. In order to study the dependence of apatite dissolution and cadmium sorption on the pH of the solution, for some synthetic apatite samples the pH range of sorption experiments was increased from 2 to 7. The pH was adjusted by adding aqueous solution of nitric acid or ammonia.

After sorption the suspensions were centrifuged and the content of Ca, Mg, Cd, Cr, P, and F in the solutions was determined: Ca^{2+} , Mg^{2+} , Cd^{2+} by atomic absorption spectrometry (Carl Zeiss Jena AAS 1N instrument); PO_4^{3-} by spectrophotometry as phosphomolybdate yellow complex (SPEKOL 11, Carl Zeiss

Jena); Cr^{3+} by spectrophotometry [18]; F with ionselective electrode (Fluoride COMB.ISE/BNC). The solid product was washed with distilled water and dried at 105°C . The chemical composition of the solid phases was calculated from the solution analyses results.

The crystal structures of apatites before and after the uptake of Cd^{2+} and Cr^{3+} ions were investigated by powder X-ray diffractometry (DRON-4, CuK_α radiation at 40 kV, 20 mA, step size 0.04°), IR spectroscopy (INTERSPECTRUM 2000, range 400–4000 nm, KBr pellets with sample/KBr mass ratio 1/300), and thermal analysis (SETARAM LabSys instrument, heating rate 10 deg/min, air flow 30 mL/min, Pt crucibles, sample mass 30–60 mg).

According to earlier studies, sorption kinetics depends on the initial cadmium content in the solution, and the main part of sorption takes place within the first 30 min [13, 17]. Our previous studies showed [19] that the major part of the Cd^{2+} uptake proceeds within the first 5 h. To reach a complete equilibrium, 24 h or more is needed. Similar results were obtained for natural apatites. Therefore, the following experiments for establishing the apatite binding capacities and for obtaining comparable data were carried out within 24 h.

Influence of the solution pH

Earlier studies have shown that in pH regions lower than 4, apatite crystals begin to dissolve gradually [20, 21]. We studied the influence of pH on both apatite solubility and cadmium sorption. The results showed that no significant dissolution occurs at pH values 4 and higher; at pH 3 the solubility is 4–7%, then it starts growing and reaches 80–100% at pH 2 (Fig. 1). In cadmium solutions the solubility of calcium is higher, being in correlation with the amount of cadmium bound. The sorption of Cd^{2+} ions has no effect on phosphate solubility.

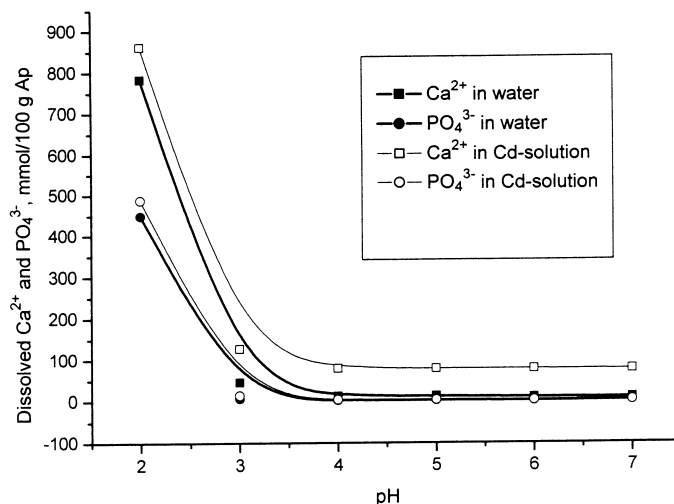


Fig. 1. The dependence of the dissolution of FHCAp D21 on the solution pH.

The sorption of cadmium at pH values lower than 3 is negligible or close to zero, as the apatite begins to dissolve. At pH higher than 3, the sorption is nearing the apatite sorption capacity, not depending on a further pH increase. Based on these results, the sorption experiments were performed at pH values in the range 4 to 6.

INFLUENCE OF THE CHEMICAL COMPOSITION AND THE MORPHOLOGY OF APATITE ON SORPTION

Tables 3 and 4 present sorption capacities of synthetic and natural apatites: the maximum uptake of Cd^{2+} and Cr^{3+} ions from aqueous solutions as well the ion-exchange ratios $Q_{\text{Cd}} = \text{Cd}^{2+}_{\text{bound}} / (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{released}}$ and $Q_{\text{Cr}} = \text{Cr}^{3+}_{\text{bound}} / (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{released}}$.

The sorption capacities for Cd^{2+} ions reached 20 mmol per 100 g of natural apatite and 74 mmol/100 g of synthetic apatite (Tables 3 and 4).

SSA is the main factor affecting apatite cadmium binding capacity (Fig. 2). This explains the higher sorption capacity of synthetic apatites compared to natural

Table 3. Sorption of Cd^{2+} and Cr^{3+} ions on synthetic apatites

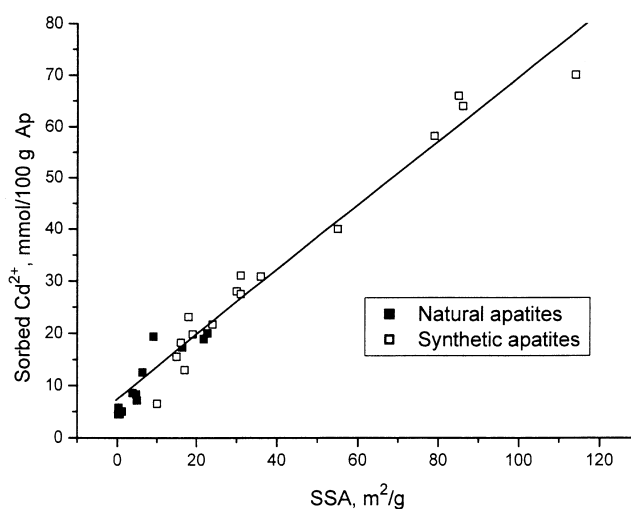
Sample	Cd^{2+} , pH 5–6			Cr^{3+} , pH 4–5		
	mmol/100 g	$\mu\text{mol}/\text{m}^2$	Q_{Cd}	mmol/100 g	$\mu\text{mol}/\text{m}^2$	Q_{Cr}
Ca-HAp						
E11	15.5	10.3	0.7			
C12	23.1	12.7	1.1			
A12	21.7	9.0	1.2	84	35	0.9
A13	31.1	10.0	1.2			
HA1	30.9	8.6	0.9	174	48	0.8
A01	58.2	7.4	1.1			
HA2	66.0	7.8	0.9	201	24	0.9
HA3	64.0	7.4	1.0			
Ca-FHAp						
D32	6.5	6.5	1.1	131	131	0.7
A42	18.2	11.4	1.2	103	64	0.7
C41	13.0	7.7	0.8			
C31	19.8	10.4	0.9			
C42	28.0	9.3	1.0	108	36	0.7
A31	27.5	8.9	1.1			
D22	40.0	7.3	1.0	131	24	0.8
D21	70.0	6.1	0.8	201	18	0.9
MgCa-Ap						
EM12	74.0	17.2	0.7	242*	56	0.9
EM42	25.0	17.9	0.6	242*	173	0.7

* Sorption is limited by Cr^{3+} ions concentration in solution.

Table 4. Sorption of Cd^{2+} and Cr^{3+} ions on natural apatites

Sample	Cd^{2+} , pH 5–6			Cr^{3+} , pH 4–5		
	mmol/100 g	$\mu\text{mol}/\text{m}^2$	Q_{Cd}	mmol/100 g	$\mu\text{mol}/\text{m}^2$	Q_{Cr}
Apatites						
Kola-1	5.7	190	1.0	4.8	160	0.3
Kola-2	4.5	225	0.9	8.0	400	0.5
Kola-3	4.5	75	1.1	8.3	138	0.4
Kola-4	5.0	45	0.8	9.5	86	0.3
Phosphorites						
Kabala-1	8.6	23	1.2	48.4	127	1.1
Kabala-2	8.3	18	1.0	58.1	124	1.1
Kabala-3	7.1	14	0.8	55.8	114	1.0
Kabala-4	12.6	20	1.0	54.4	86	0.9
Kabala-T	19.4	21	0.9	249*	855	1.0
Israel	17.3	11	0.7	n.d.	n.d.	n.d.
Israel-G	20.0	9	0.6	n.d.	n.d.	n.d.
Israel-GC	18.9	9	0.8	n.d.	n.d.	n.d.

* Sorption is limited by Cr^{3+} ions concentration in solution.
n.d. – not determined.

**Fig. 2.** The dependence of Cd sorption on the specific surface area of the apatite.

apatites. The influence of SSA is particularly obvious in natural apatites where no substantial relationship between the chemical composition of the samples and the extent of sorption was observed.

However, SSA is not the only factor affecting the cadmium sorption capacity of apatites, as the amount of Cd^{2+} ions bound per surface unit has no constant value (Tables 3 and 4). For synthetic Ca-apatites it is in the range 6–11 $\mu\text{mol}/\text{m}^2$

and for MgCa-apatites 17–18 $\mu\text{mol}/\text{m}^2$. For natural phosphorites this value is higher, reaching 23 $\mu\text{mol}/\text{m}^2$ for Kabala phosphorite. For Kola apatite, the very small SSA values raise the amounts of bound cadmium per surface unit up to 225 $\mu\text{mol}/\text{m}^2$. Thus, other apatite characteristics beside SSA, such as stoichiometricity (incidence of cationic and anionic vacancies in apatite structure) and the kind and amount of substitutions, should also be taken into consideration.

Our earlier studies on synthetic apatites showed that increasing the carbonate content decreases the sorption of cadmium on apatite [22]. However, this is in contradiction with some other earlier studies [17], in which the higher sorption of cadmium was found to be related to the formation of otavite (CdCO_3). We suppose that as the SSA of apatite depends on the content of CO_3^{2-} in the apatite structure and decreases according to the increase in the carbonate substitution level, the relationship between the apatite sorption capacity and carbonate content may as well be an effect of the SSA. Carbonate substitution causes also a compression in the apatite structure (a decrease in unit cell parameter a), which can make the diffusion of Cd^{2+} ions through the channels on the hexagonal axes more difficult. Compared to other substitutions, the influence of fluorine is less important [22].

The sorption of chromium is higher than that of cadmium. For Cr^{3+} ions the maximum binding was up to 242 and 249 mmol per 100 g apatite for magnesium containing synthetic apatites and the triboactivated natural phosphorite sample, respectively. In these cases the sorption was limited due to the insufficient content of chromium in the sorption solution, as 98% of Cr^{3+} ions from the solution were bound (Tables 3 and 4). For other samples the extent of bound Cr^{3+} ions from the solution was lower and the apatite sorption capacities were reached.

For chromium sorption, compared to cadmium, the influence of substitutions is greater. No direct relationship between the sorption capacity and SSA of apatites was found, except for HAp samples, where the sorption grows with increasing SSA. For fluorapatites, an increase in the carbonate content causes an increase in the chromium sorption capacity.

From the studied substitutions in the apatite structure, magnesium has the most important influence, causing an increase in both the cadmium and chromium sorption capacity. For HAp the sorption of cadmium increases from 30.9 to 74 mmol/100 g and for FHAp from 18.2 to 25 mmol/100 g. The increase in the case of chromium is particularly obvious as then 98% of the chromium was bound from the solution in the concentration range studied. The higher sorption capacity of MgCa-apatites can be attributed to the deformations in the apatite crystal structure, caused by substitution of Ca^{2+} ions (0.99 Å) with a smaller Mg^{2+} ions (0.66 Å), which facilitates sorption, making the structure more available for the introduction of additional substitutions. As the ionic radius of Cr^{3+} (0.63 Å) is closer to Mg^{2+} than that of Cd^{2+} (0.97 Å), it explains the bigger effect of Mg-substitution on chromium sorption in the case sorption takes place by the ion-exchange mechanism. On the other hand, the higher reactivity of magnesium substituted apatites may promote the dissolution of apatite and formation of new phases, which can be both apatitic and non-apatitic chromium containing phosphates [16].

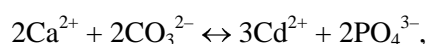
SORPTION MECHANISM

The estimation of the sorption mechanism is based on the molar ratio (Q) of the cations bound with the apatite to the cations released from the apatite during sorption as well as on the structural changes caused by the sorption process.

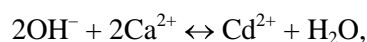
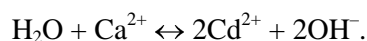
The dissolution of Ca^{2+} and Mg^{2+} ions resulting from the sorption process depends on the amount of Cd^{2+} and Cr^{3+} ions bound. The concentration of fluoride and phosphate in the solution after the sorption was negligible.

Cadmium sorption

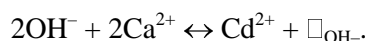
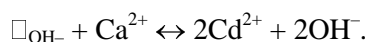
For cadmium sorption the value of Q is close to one, which allows an assumption that sorption takes place mainly by cation exchange. The deviations from the exact value of $Q = 1$ can be caused by changes in the level of other substitutions, mainly carbonate:



or simultaneous changes in the structure (content of structural water):



or the incidence of cationic or anionic vacancies (\square) in the structure:



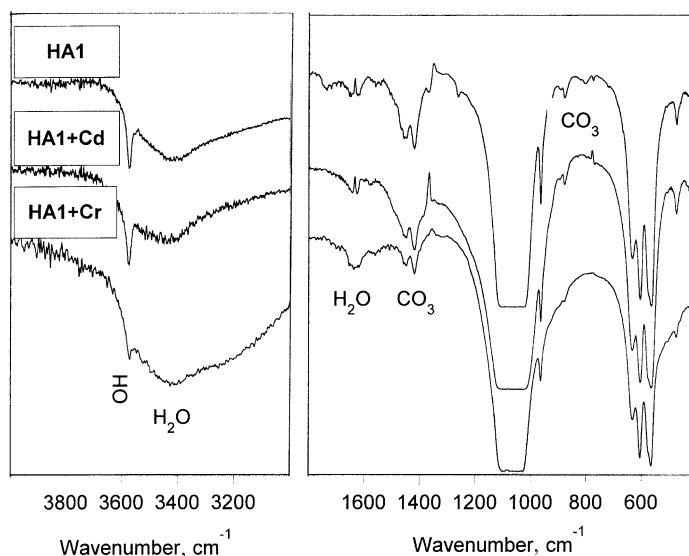
In the case of fluorcarbonate-apatites the molar ratio Cd/Ca in sorption products is in the range 0.013–0.024, for HAp it is up to 0.069, and for apatites with a large SSA (FHAp D21 and MgCa-apatites) it reaches the value of 0.082. Compared to synthetic CdCa-apatites (Table 5), where the Cd/Ca ratio is 0.18–0.19, these values are lower. Previous studies [8, 16, 23] showed that introduction of small quantities of Cd^{2+} ions into an apatite takes place mainly on Ca(2) sites in the apatite structure, placed in a triangular form on the planes around hexagonal axes [23]. Thus, the limitations on sorption, compared with precipitation, can be caused by the difficulties on the diffusion of Cd^{2+} ions into the apatite structure via channels along the hexagonal axis, which is supposed to be the probable migration path for cations in the apatite structure.

According to thermal analysis the sorption of cadmium causes a small decrease in the structural water content in apatite and a shift in the evolvement of crystalline water towards lower temperatures, followed by a shift of the top of an exotherm, indicating the reorganizations in the apatite structure [24].

Table 5. Influence of cadmium on apatite cell parameters

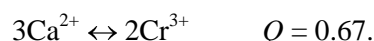
Sample	Cell parameters, Å		Sample	Cd/Ca molar ratio in apatite	Cell parameters, Å	
	<i>a</i>	<i>c</i>			<i>a</i>	<i>c</i>
Synthetic Ca-apatites			Synthetic CaCd-apatites			
A13	9.428	6.887	A1Cd21	0.18	9.409	6.843
A31	9.397	6.888	A4Cd22	0.19	9.373	6.844
Synthetic Ca-apatites before Cd ²⁺ sorption			Synthetic Ca-apatites after Cd ²⁺ sorption			
HA1	9.423	6.889	HA-1 + Cd ²⁺	0.03	9.415	6.885
HA2	9.425	6.888	HA-2 + Cd ²⁺	0.07	9.405	6.872
HA3	9.419	6.883	HA-3 + Cd ²⁺	0.07	9.418	6.870
Natural apatites before Cd ²⁺ sorption			Natural apatites after Cd ²⁺ sorption			
Kola-4	9.388	6.898	Kola-4 + Cd ²⁺	0.01	9.385	6.894

The ion-exchange mechanism of cadmium sorption is also confirmed by the results of XRD analysis and IR spectroscopy (Fig. 3) – the solid products retain their apatitic structure and there is no indication of any appearance of new phases beside the apatitic one. The changes in the XRD spectra become noticeable when the Cd/Ca molar ratio in the sorption product exceeds 0.07, corresponding to the cadmium sorption level 64 mmol/100 g Ap. A decrease in the cell parameters as a result of cadmium sorption is observed (Table 5). This is in accordance with the smaller values of the cell parameters of synthetic partly Cd-substituted Ca-apatites, compared to Ca-apatites. The sorption of cadmium on natural apatites is too small to induce any structural changes.

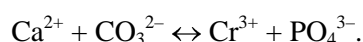
**Fig. 3.** IR spectra of Ca-HAp HA1 before and after Cd²⁺ and Cr³⁺ ions sorption.

Chromium sorption

The molar ratio Q is in the range 0.7–0.9 for synthetic apatites, close to 1 for Kabala phosphorite, and 0.3–0.5 for Kola apatite. Considering the electro-neutrality in the case of Cr^{3+} sorption if it occurs by an ion-exchange mechanism, the value of Q should be less than 1:



However, a higher Q value can be obtained when simultaneously with Cr^{3+} sorption carbonate is released and a restructuring takes place in the apatite structure:



This can explain the higher Q values for Kabala phosphorite (CO_2 content 3.4–6.9%) and low Q values for Kola apatite (CO_2 content 0.1%).

The Cr/Ca ratio in sorption products of natural apatites is usually less than 0.1. It reached 0.44 only for the triboactivated phosphorite sample, which is higher than in synthetic apatites (0.27 and 0.34 for Ca-apatites and MgCa-apatites, respectively).

Thermal analysis showed that the evolution of water as a result of chromium sorption in CaMg-apatites was shifted towards higher temperatures and did not proceed in clearly defined steps like in the initial apatite. When in FAp EM42 (Fig. 4) water evolved in two steps with maximums at 178 and 290°C and was followed by exothermic effects at 335 and 558°C, indicating structural reorganizations, then after the sorption of chromium water evolved in one step in the temperature range 150–300°C, with maximum at 205°C, followed by one exotherm at 333°C, and without other thermal effects at higher temperatures. The behaviour of HAp EM12 was similar (Fig. 4), as a result of chromium sorption the exothermic effect at 618°C disappeared and the exotherm at the end of the water evolution at 333°C increased, indicating that the structural rearrangements took place at lower temperatures.

The essential change in the thermal behaviour of apatites as a result of chromium sorption indicates that although the apatite structure remained, it was substantially rearranged. Therefore, considering also the high amount of Cr^{3+} ions sorbed per surface unit of an apatite, the probable sorption mechanism is dissolution–precipitation, although the new phase can also be an apatitic one.

IR spectra reveal that sorption of chromium causes an increase in the Ca-apatite water content (larger absorption band in the range 3000–3400 and 1659 cm^{-1}). A decrease in the absorption peaks at 876, 1420 and 1457 indicates the diminishing of the carbonate content in both Ca- and CaMg-apatites (Figs. 3 and 5), indicating the changes in the apatite structure taking place as a result of chromium sorption. In the IR spectra of CaMg-HAp, an emergence of absorption peaks in the range 560–600 cm^{-1} appeared (Fig. 5), indicating some improvement in the apatitic structure.

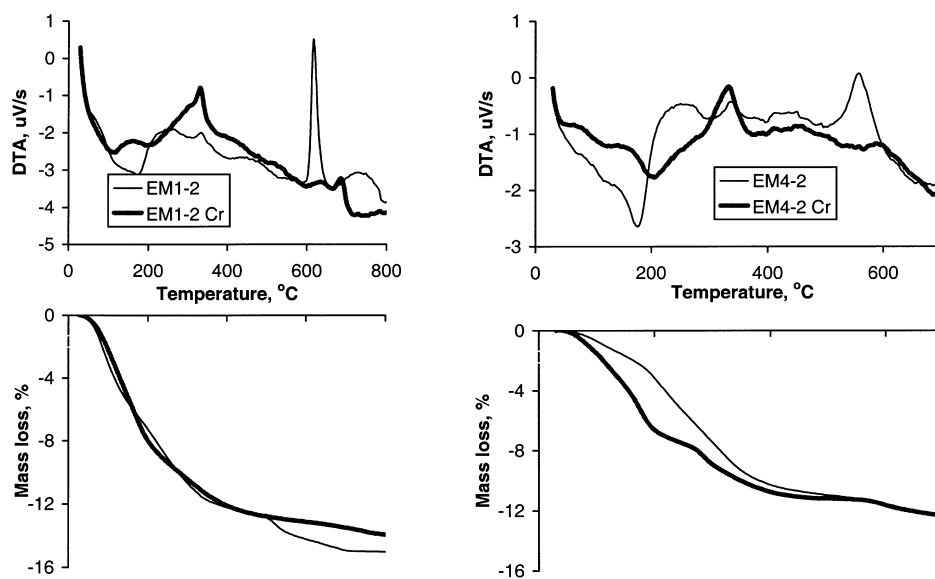


Fig. 4. Thermal analysis curves of MgCa-apatites before and after Cr^{3+} ions sorption.

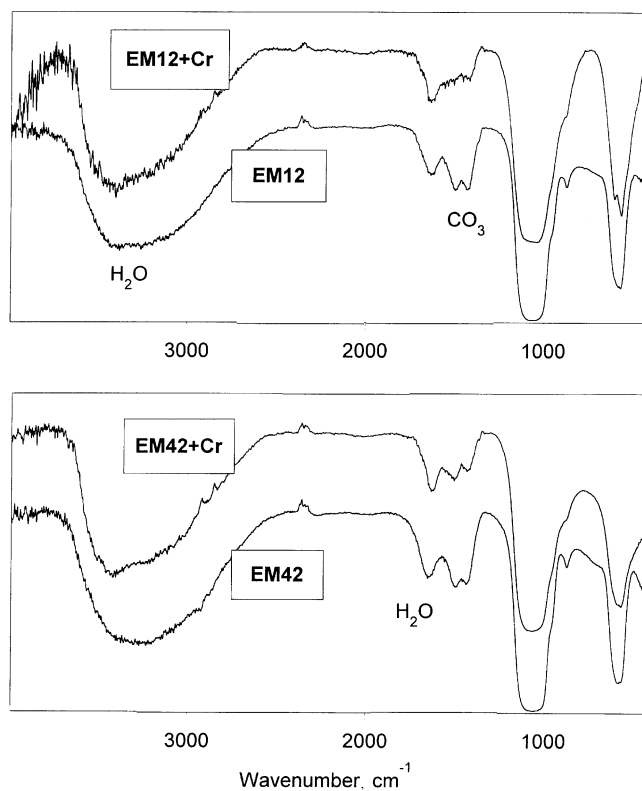


Fig. 5. IR spectra of MgCa-apatites.

Table 6. Influence of chromium on apatite cell parameters

Sample	Cell parameters, Å		Sample	Cr/Ca molar ratio in apatite	Cell parameters, Å	
	<i>a</i>	<i>c</i>			<i>a</i>	<i>c</i>
Synthetic Ca-apatites before Cr ³⁺ sorption			Synthetic Ca-apatites after Cr ³⁺ sorption			
HA1	9.423	6.889	HA1 + Cr ³⁺	0.23	9.409	6.878
D22	9.391	6.882	D22 + Cr ³⁺	0.17	9.395	6.882
Natural apatites before Cr ³⁺ sorption			Natural apatites after Cr ³⁺ sorption			
Kola-4	9.388	6.898	Kola-4 + Cr ³⁺	0.01	9.390	6.894
Kabala-4	9.347	6.889	Kabala-4 + Cr ³⁺	0.07	9.346	6.890

The changes in the cell parameters caused by Cr³⁺ sorption are given in Table 6.

In FHAp sample D22 with a higher carbonate content the sorption of chromium caused an increase in the cell parameter *a*. This can be explained by a decrease in the carbonate content and an increase in the content of structural water in the apatite structure, as the location of CO₃²⁻ groups in B-position in the apatite structure diminishes the value of the cell parameter *a*. In HAp sample HA1 with a lower carbonate content, on the contrary, as a result of chromium sorption a decrease occurred in the value of both cell parameters, which can be due to an introduction of smaller Cr³⁺ ions than Ca²⁺ into the apatite structure.

In the XRD spectra of poorly crystallized CaMg-HAp (EM12) as a result of Cr³⁺ sorption the peaks of both HAp and brushite (CaHPO₄ · 2H₂O) appear (Fig. 6).

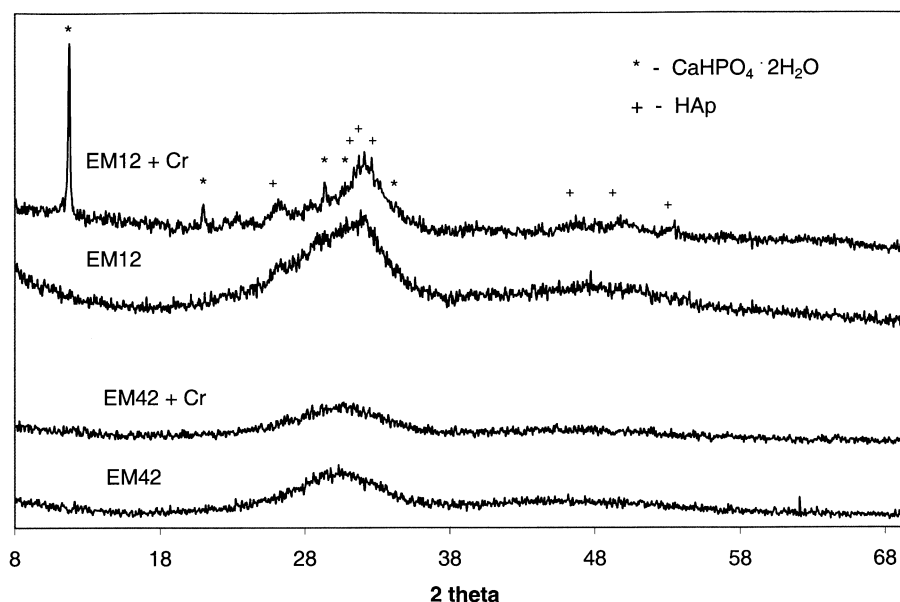


Fig. 6. XRD spectra of MgCa-apatites.

In the case of FAp (EM42) there is no evident influence of chromium on XRD spectra – probably the stabilizing effect of fluorine on the apatite structure prohibits the formation of additional phases beside apatite. Considering the release of Ca^{2+} and Mg^{2+} ions as a result of chromium sorption, in the case of CaMg-FAp their relative amounts are similar (both about 30% of their total content), while in the case of CaMg-HAp the release of Mg^{2+} is considerably higher than that of Ca^{2+} (53% and 23%, respectively). Therefore, although the amount of the sorbed chromium on both apatites is equal, the sorption mechanisms can differ according to the chemical composition of the apatite – in FAp the sorption proceeds mainly by ion-exchange, in HAp by the dissolution–precipitation mechanism.

The strong influence of triboactivation in the case of Kabala phosphorite on chromium sorption, compared to cadmium sorption (Table 4), also indicates different sorption mechanisms. As the structural defects created during activation increase the reactivity of a material [25], the results obtained support the dissolution–precipitation mechanism of chromium sorption.

CONCLUSIONS

The study of cadmium and chromium sorption on apatites revealed that the sorption capacity of apatites for Cr^{3+} ions is substantially higher than that for Cd^{2+} ions.

The sorption of cadmium depended mainly on the specific surface area of apatites. The number of sorbed ions per surface unit remained in a certain range, referring to an ion-exchange process, which was limited with the size of the apatite specific surface. The molar ratio Q and changes in apatite cell parameters also confirmed an ion-exchange process. The changes in thermal behaviour indicate that the sorption process affected directly the apatite structure.

The sorption of chromium had no direct dependence on the surface area. The main factors enhancing the chromium sorption capacity of apatites were their magnesium content and triboactivation, which both increased apatite reactivity. Although according to the values of the molar ratio Q the sorption may correspond to an ion-exchange process, the number of Cr^{3+} ions bound per surface unit was very high and the mechanism of dissolution–precipitation seemed to be more likely. No formation of other crystalline phases beside apatite was observed, except for MgCa-HAp, where in addition to the apatite a brushite structure also appeared. Simultaneously with chromium sorption, carbonate was partly dislodged from the apatite structure, and in Ca-apatites the content of water also increased. Considering the changes in the apatite unit cell parameters the sorption of chromium was assumed to take place mainly by reprecipitation of apatite.

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Looduslikud ja sünteetilised apatiidid Cd²⁺ ja Cr³⁺ ionide sidujatena vesilahustest

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On uuritud Cd²⁺ ja Cr³⁺ ionide sorptsiooni erineva koostise ja eripinnaga looduslikel ja sünteetilistel apatiitidel. Cd²⁺ ionide sorptsiooni ulatus sõltub peamiselt apatiidi eripinnast. See suureneb apatiidi magneesiumi sisalduse suurenemisel ja karbonaadi sisalduse vähenemisel, ulatudes vastavalt 20 ja 74 mmol 100 g apatiidi kohta looduslike ja sünteetiliste apatiitide korral. Cr³⁺ sorptsioon ulatub 250 mmol 100 g apatiidi kohta ning see sõltub oluliselt magneesiumi sisaldusest apatiidis. Kaadmiumi sidumine lahusest toimub peamiselt ioonivahetuse teel, kroomi puhul kaasneb ka lahustumis-sadenemisprotsess.