

CADMIUM IMMOBILIZATION BY HYDROXYAPATITE

The contamination of air, soil and water by cadmium is a great environmental problem. If cadmium occurs in nature in ionic form, soluble in water, it easily enters into the food chain. Hydroxyapatite (HAP), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is a sparingly soluble salt and an excellent matrix for the removal of heavy metals from solutions. Considerable research attention has been paid to the bond between Cd^{2+} ions and synthetic hydroxyapatite of known composition. The sorption mechanism is complex. The dominant process is ion exchange, but surface adsorption, surface complexation and coprecipitation can also contribute to the overall mechanism. The sorption capacity depends on the characteristics of hydroxyapatite itself and on the experimental conditions. Under optimum conditions a maximum capacity of 0.8 mol Cd^{2+} /mol HAP can be achieved. HAP is a potential sorbent for the remediation of contaminated water and soil, for industrial waste treatment, and it is also referenced as a material that can be used as a barrier around waste depositories.

Cadmium is a silver-blue metal and its compounds are widespread in nature in low concentrations. Due to anthropogenic activity the cadmium concentration in the environment, especially in urban and industrialized areas, has become significantly higher in the last century. It is much less mobile in soils than in air and water. The major factors governing cadmium adsorption and distribution in soils are: the composition of the soil, pH, the soluble organic matter content, the presence of organic and inorganic ligands and competition from other metal ions. The immobilization of Cd^{2+} may be achieved by attachment to solid matrixes, with low solubility, through coprecipitation or sorption processes. Apatite remediation of heavy metals is an emerging technology for the stabilization of metals, including cadmium, in order to prevent them from migrating or leaching.

CADMIUM IN THE ENVIRONMENT

Distribution of cadmium in the environment

Natural cadmium levels in the

The average natural abundance of cadmium is presented in Table 1. Cadmium ores are rare. Greenockite (CdS) is the only mineral of any importance, which contains cadmium. Zinc, lead and copper ores (sulfides and oxides) contain high levels of Cd^{2+} . Sedimentary rocks, such as marine phosphates, and phosphorites, may also accumulate cadmium (up to 500 ppm) [1,2]. Levels from 10 ng/L to 4000 ng/L have been reported for rainwater, fresh waters, and surface waters in urban and industrialized areas [3]. Ambient air cadmium concentrations have been estimated to range from 2 to 15 ng/m³ in urban areas, and from 15 to 150

Table 1. The average natural abundance of cadmium

Earth crust	0.1–0.5 ppm
Atmosphere	0.1–5 ng/m ³
World oceans	10–100 ng/l
Zinc ores	200–14000 ppm
Lead and copper ores	200–500 ppm
Fossil fuels	0.5–1.5 ppm

ng/m³ in industrialized areas [3]. The average exposure levels have decreased markedly in the past 40 years due to national occupational exposure standards.

Cadmium emission

Cadmium emission arises from both natural sources and anthropogenic activity. It can be emitted to all three major components of the environment – air, water and soil, and then transferred between them.

The most important natural emission of cadmium occurs during the weathering and erosion of rocks, volcanic activities and forest fires.

Anthropogenic emissions arise from:

1. The manufacture, use and disposal of cadmium products (Ni–Cd batteries, cadmium pigments, cadmium stabilizers, cadmium coatings, cadmium alloys and cadmium electronic compounds).

2. The presence of cadmium as an impurity in non-cadmium products (non-ferrous metals and alloys of zinc, lead and copper, iron and steel, fossil fuels, cement, phosphate fertilizers).

The influence of cadmium exposure on human health

For non-smokers, the major route for cadmium intake is ingestion [3]. The presence of trace levels of cadmium in foodstuffs can be attributed to the use of phosphate fertilizers and sludge on agricultural soils [3].

Cadmium mainly accumulates in the kidneys and, at high levels, it may lead to serious kidney failure. Many

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other adverse effects may occur in the bones and stomach. This was observed in a syndrome known as "itai-itai" in Japan, as a result of consuming cadmium-contaminated rice. The symptoms were severe bone pain and the disease was characterized as osteomalacia. The hydroxyapatite phase of bones has a high affinity for cadmium, and as a result a disease similar to osteoporosis (softness of the bones) occurs. Stomach irritation leading to vomiting and diarrhea are also often associated with the ingestion of high levels of cadmium in food and drinking water. If it is inhaled, cadmium can cause serious lung problems, including lung cancer. Smoking of tobacco is an important source of air cadmium exposure for smokers, since one cigarette contains about 0.5 – 2 µg of cadmium and about 10% of the cadmium content is inhaled [3].

HYDROXYAPATITE

Hydroxyapatite (HAP) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ has been one of the most popular phosphate materials in the last decade due to its importance in the environment and biological systems, and numerous applications in various fields of science and technology.

HAP is a naturally occurring mineral, present in phosphate rocks and sediments, together with other members of the such as the "apatite family" (fluoro, chloro and carbonated apatites), and non-apatite minerals such as calcite (CaCO_3) and gypsum (CaSO_4) [4]. Furthermore, about 40% of an adult human bone is Ca-deficient HAP, which together with collagen and other organic substances, has an important role in both the biological and structural aspects of bone [5].

HAP crystallizes in a hexagonal $\text{P6}_3/\text{m}$ space group. A significant detail of the crystal structure is that Ca^{2+} ions occupy two different crystallographic sites. Ca(I) is found on the ternary axes $x = 1/3$ and $y = 2/3$, while Ca(II) is found at sites with m symmetry at $z = 1/4$, $z = 3/4$. Per unit cell of HAP, 4 atoms of Ca occupy the Ca(I) position, and 6 Ca-atom occupy the Ca(II) site [5].

The solubility of HAP is low and it decreases with increasing solution pH and with increasing temperature (retrograde solubility) [6]. HAP solubility is also incongruent, which means that the solubility product, K_{sp} , is not constant, and the Ca/P ratio of a saturated solution of HAP differs from the Ca/P ratio of a solid phase. The main theoretical explanation is that HAP, as a salt of a weak acid, undergoes hydrolysis in aqueous solutions, yielding solid surface complexes. Stoichiometric HAP samples have high thermal stability and no phase transformation occurs by heating the HAP powder up to 1200°C [7]. HAP also has a high surface area. Bone mineral surface range from 100–200 m²/g HAP, while the specific surface area of synthetic samples varies from 20–200 m²/g HAP, according to preparation conditions [4].

The ability for various cationic and anionic substitutions leads to the formation of solid solutions or

isomorphic compounds [5]. Bivalent metal ions such as Sr^{2+} , Ba^{2+} , Mg^{2+} , Cd^{2+} , Pb^{2+} , can substitute Ca^{2+} in the apatite crystal lattice. The most significant anionic substitutions are replacements of OH^- by F^- and Cl^- , and PO_4^{3-} by AsO_4^{3-} and VO_4^{3-} . All these properties make HAP a powerful material for the reduction of the concentration of many organic and inorganic substances from aqueous solutions. It is especially useful for the immobilization of heavy metals such as Pb^{2+} , Cd^{2+} , Zn^{2+} , U(VI) etc., through coprecipitation and sorption processes [8–14].

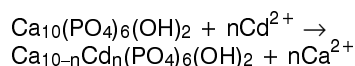
HAP almost never occurs in nature in its pure form. It is usually synthesized in the laboratory, under defined conditions, by means of wet, dry and hydrothermal procedures [5].

HAP affinity towards cadmium, the nature of their interaction under various conditions, has been studied in detail [9, 10, 13–28].

REACTIONS BETWEEN HYDROXYAPATITE AND Cd^{2+} IONS

Coprecipitation of cadmium by HAP

A series of Ca–Cd HAP solid solutions may be synthesized over the entire compositional range by coprecipitation in aqueous solutions [15]. Stoichiometric quantities of ammonium dihydrogen phosphate and solutions of Ca^{2+} and Cd^{2+} ions were mixed in CO_2 -free atmosphere at 37°C. Chemical, X-Ray diffraction and SEM analyses have confirmed that homogeneous solid solutions were obtained according to the reaction:



The process leads to the formation of pure cadmium hydroxyapatite $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$. The replacement of Ca^{2+} ions by smaller Cd^{2+} ions contracts the unit cells of apatite, and, consequently, decreases in the crystal dimensions were observed.

Sorption of cadmium by HAP

In order to identify the sorption mechanism, the sorption of Cd^{2+} ions was studied under various conditions and using HAP samples of different origin and characteristics.

The sorption kinetic experiments have revealed that the sorption of cadmium ions on HAP is a two step process. Under experimental conditions similar to freshwater environments [16], the sorption kinetics were not concentration dependent in the range 1–20 µg/l, more than 90% of the cadmium was sorbed within a few hours, but the final equilibrium was not reached within 28 days of equilibration. Two straight lines can describe the dependence of the distribution coefficients K_d versus $\log(\text{time})$, one for sorption time intervals shorter than one day and the other for longer equilibration periods.

For much higher initial concentrations of cadmium (10^{-3} mol/dm³) [14], 62% of the total cadmium from the solution was sorbed in the first 6 hours. After 48 hours of equilibration, 79% was removed, but equilibrium was reached. It was also shown that temperature in the range 25–50°C, had no significant influence on the sorption kinetics. M. Fedoroff, et al. [17] found, that at an initial concentration of $3.96 \cdot 10^{-3}$ mol/dm³, at all temperatures (18, 28 and 75°C) the first step of the sorption process was very fast. After 2 minutes of equilibration 50% of the final value was achieved at 18 and 28°C, and 25% at 75°C. Afterwards, the rates were much slower. A constant concentration of cadmium in the solid phase (0.6 mol Cd/mol HAP) at 18°C was observed from 24 to 192 hours, but for higher temperatures no steady state was reached after more than 300 hours of equilibration. They assumed that the quasi-constant value at 18°C was more likely a very slow uptake than real equilibrium.

The influence of pH on cadmium sorption on HAP was also studied. Cadmium forms insoluble hydroxide in solutions at pH > 9 and therefore, its removal from an aqueous environment in the absence of a sorbent is due to precipitation. Even at lower pH values (in the range 7–9), a considerable percent of the hydrolyzed species, Cd(OH)⁺, was present in the solution. On the other hand, the solubility of HAP was significant at pH < 5 and, therefore, a decrease in the sorption capacity and precipitation of new solid phases could be expected [18].

For an initial concentration of $5 \cdot 10^{-4}$ mol Cd/dm³, no effect of pH in the pH initial range 5–7 was observed in respect to cadmium sorption on HAP [19]. This may be explained by the large buffer capacity of the HAP surface. In the initial pH range 4–10, the final pHs of the HAP suspensions, without cadmium ions, were the same and equal to pH_{pzc}, which was between 6 and 7 for most synthetic HAP samples [19–21]. Consequently, no real pH-gradient could be achieved, and all the pH values, measured after equilibration with cadmium solutions, were the same. The experimental results of Jeanjean et al. [4,18] are in the good agreement with previous results. The amount of sorbed cadmium remarkably increases in the pH range 3–5, due to a decrease in HAP solubility with increasing pH.

The experimental results of sorption from solutions of different initial concentrations of cadmium, followed typical adsorption isotherms of the Langmuir type [11,14,16,22], but the maximum (equilibrium) sorption capacities were quite different. Literature data about the amount of Cd²⁺ sorbed by HAP are systematized in the Table 2. First, it may be noticed that all the experiments were performed with HAP samples of different origin, chemical composition and specific surface area, at different temperatures, time of equilibration and initial cadmium concentrations. It can be expected that the amount of sorbed cadmium increases with increasing initial cadmium concentration, amount of HAP in the

suspension, specific surface area, time of equilibration and the Ca-deficiency of the sample.

The amount of sorbed cadmium increased from 0.697 [23] to 0.831 mol/g [24], with an increasing solid/solution ratio from 1:500 to 1:250. These results are comparable, because the same HAP powder was used, and the other experimental conditions were almost the same. If the results from references [14] and [24], are compared it may be noticed that the amount of sorbed Cd²⁺ is lower for the HAP of better stoichiometry. When the solid to solution ratio was much lower than in the other experiments (1:2000) [22], the sorbed amount was 0.432 mmol/g. The Ca/P ratio in the HAP used in reference [22] was 1.37. The low Ca/P ratio, e.g. crystal lattice defects, led to better sorption of the cadmium ions.

The influence of solution temperature was studied in the range 24.4–40°C [22], and 25–50°C [14]. In both studies, the increase in temperature led to a slight decrease in the maximum sorption capacity. The sorption was exothermal and weak sorption forces were predominant in the overall sorption process.

A maximum sorption capacity of ~ 0.8 mol Cd/mol HAP was achieved in standard, batch equilibration experiments. But, S. McGrellis, et al. [25], have shown that greater capacities can be reached if another sorption protocol is used. They studied the influence of the rate of Cd-ion introduction into the HAP suspension in water. As the time of introduction of 0.02 M Cd(NO₃)₂ solution increases from 0 to 2 minutes, the sorbed quantity of cadmium increases from 0.8 to 1.13 mol/mol HAP and reaches 1.22 mol/mol HAP for an introduction time of 35 minutes. This is an indication that if HAP were used as a barrier placed in the pathway of contaminated water coming from waste depositories, slow percolation of water would lead to higher sorption capacities than those observed in standard batch experiments.

In respect to other natural inorganic sorbents such as riverine suspended particles, illite, montmorillonite and kaolinite, HAP has a much higher affinity for Cd²⁺. It can be predicted that cadmium will be enriched in apatite layers in multiple adsorbent systems (sediments and soils) [16].

The desorption of cadmium from HAP has also been studied under various conditions. Xu et al. [11] examined the desorption process in two different matrixes, 0.5 M KCl and 0.5 M CaCl₂, for an initial concentration of Cd²⁺ in the solid phase of 0.595 mmol/g. The suspensions were shaken for 30 hours. The results indicated that there was no significant desorption in KCl solutions (1.2 %), but in CaCl₂ solutions up to 75% of the cadmium ions were released. The experiments of Mandjiny et al. [18], on the reversibility of sorption, showed that sorption did not proceed as a reversible equilibrium. Samples containing 0.8 molCd/molHAP were equilibrated with a solution containing 4 molCa/molHAP for 48 days. Only 15% of

the initially present cadmium was released into the solution. In the work of Smičiklas [14], after the sorption of Cd^{2+} from solutions containing 10^{-4} – 10^{-2} mol/dm³ Cd^{2+} the solids were dried and then equilibrated with $\text{Ca}(\text{NO}_3)_2$ solutions of the same concentration of Ca^{2+} as that of Cd^{2+} in the sorption experiments (10^{-4} – 10^{-2} mol/dm³). For the highest concentration of Cd^{2+} in the solid phase (0.653 mmol/gHAP), 20–25 % was desorbed after 24 hours of equilibration. Only 2 % was desorbed and in the case of the lowest concentration (0.019 mmol/gHAP).

The mechanism of Cd^{2+} sorption on HAP

By definition, sorption is a broad term, which describes the attachment of dissolved species to the surface of a solid sorbent. Generally, sorption may occur through three types of processes:

1. Surface adsorption, accumulation of the sorbate on the surface of the solid phases (physical adsorption, ion exchange, and surface complexation).
2. Absorption, or diffusion of the sorbate species into the solid phase.
3. Precipitation and coprecipitation, e. g. dissolution of the existing solid phase and precipitation of a new phase, containing the sorbate in its structure.

The experimental conditions of the synthetic procedure determine the most important sorption properties of HAP (purity, crystallinity, stoichiometry, specific surface area, porosity, shape and size of the HAP particles). HAP samples used for sorption experiments in the literature, are all synthetic, but derived by different synthetic methods and, thus with different characteristics. This makes a comparison of the results rather difficult, yet the comparison would be even more difficult if natural apatite were used. The nature of the sorbed cation (valence, electronegativity, ionic radius and the tendency of forming insoluble compounds or hydrolytic products) also has a great influence on the sorption mechanism. Finally, two or more mechanisms can be involved in the overall sorption process.

The mechanism of Cd^{2+} sorption on HAP is a complex process. It was suggested that more than one

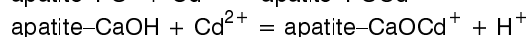
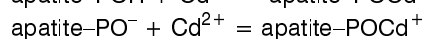
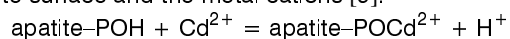
mechanism might be simultaneously responsible to some extent of the removal process:

- ion exchange [26,27],
- diffusion and ion exchange [18],
- adsorption, ion exchange and recrystallisation [16],
- adsorption, ion exchange, surface complexation, coprecipitation [22],
- adsorption, ion exchange [14].

According to the sorption kinetics, the first rapid step corresponds to the ion-exchange processes. The radii of Ca^{2+} and Cd^{2+} ions are very similar (0.099 and 0.097 nm), therefore heteroionic substitution is expected in the HAP lattice.

The ratio between the amount of cations released from the apatite surface into the solution (Ca^{2+} – ions, or Ca^{2+} and Na^+ , in cases where sodium cations were present in the sample as an impurity) and Cd^{2+} – ions sorbed on HAP, is close to 1 [26,27]. That is an indication of a pure ion exchange process. However, in some cases [14, 9], the Ca/Cd ratio was found to be < 1. The larger amount of sorbed cadmium in respect to the amount of calcium released from the HAP surface to the solution, suggests that other processes may be involved beside ion exchange.

In the experiments with constant initial pH and different amounts of cadmium in the solution, especially when larger cadmium concentrations were used, the final pH values were lower than the pH_{PZC} of HAP (Table 2, references [11] and [14]), as an indication of specific cation sorption. The chemistry of the HAP surface is pH dependent. In the presence of Cd^{2+} , the following reactions may occur between the active groups of the apatite surface and the metal cations [9]:



The release of H^+ into the solution leads to the better solubility of HAP, therefore Ca^{2+} ions may be present in the solution, not only due to ion exchange, but also due to the dissolution of HAP.

The maximum sorption capacity decreases with increasing temperature and this is an indication of weak sorption forces (physical sorption and ion exchange)

Table 2. The amounts of Cd^{2+} sorbed by hydroxyapatite

Solid to solution ratio	S_p (m ² /g)	$\frac{\text{Ca}}{\text{P}}$	t (°C)	Time of equilibration	Cd^{2+} Initial conc. (ppm)	Cd^{2+} Final conc. (ppm)	pH _i	pH _f	$\frac{\text{mmolCd}^{2+}}{\text{g HAP}}$	Ref.
1:200	21	1.67	25	24 h	11.24–1124	0.64–757	~ 4.5	5.7–4.1	0.653	14
1:250	–	1.52	25	48 h	896	523	7	–	0.831	24
~1:300	77	–	26	20 h	0–281	214.5	~ 6.7	~ 5.3	0.592	11
1:400	63	1.65	20	30 min	50 and 100	66.8	5.7	6.0	0.295	26
1:500	–	–	20	48 h	896	739	2–8	–	0.697	23
1:2000	52	1.37	24	15 min	0–100	75	7	6–6.5	0.432	22

[14, 22]. The Langmuir sorption isotherms are also an indication of the ion exchange between cadmium and the HAP surface.

The HAP surface charge is a result of the dissolution and/or adsorption of potential determining ions such as lattice ions (Ca^{2+} , P^{3-} , OH^-), their hydrolytic products, or some other ions from the solution. Measurement of the ζ -potential of the HAP particles before and during the sorption of Cd^{2+} , shows that the HAP surface becomes less negative in the presence of Cd^{2+} [22]. This fact is attributed to the attachment of cadmium cations onto the surface of HAP.

As opposed to the surface accumulation model, after further structural analysis, a new sorption model was proposed [18,23,28]. The concentration and distribution of cadmium in HAP crystals were measured by the Proton Induced X-ray Emission (PIXE) and Rutherford Backscattering (RBS) techniques. Different incident proton energies were used (in the range 500 KeV–2 MeV), in order to obtain the cadmium depth distribution profile. The absence of a characteristic peak in the RBS spectrum showed that there was no accumulation of cadmium on the surface of HAP. Cadmium is distributed through the bulk of the particle, but the concentration was lower in the middle of the particle than in the superficial part by a factor of 2. Diffusion coefficients ranging from 10^{-10} to 10^{-12} cm^2/s were calculated, depending on the contact time between the solution of Cd^{2+} and HAP. Diffusion could be influenced by the porosity of the sample. The smallest values of the diffusion coefficient corresponded to the longest contact times, suggesting that the coefficient decreased with increasing cadmium concentration. Furthermore, after cadmium fixation, XRD analyses and SEM imaging showed no variation of the unit cell parameters and no change in the morphology of the starting apatite material.

The sorbed Cd^{2+} ions were exclusively located in the Ca (II) sites, adjacent to the channels centered on the hexagonal screw axes containing OH^- ions. The limitation of the sorption capacity to 0.8 molCd/mol HAP was explained by the tendency of cadmium not to occupy a site close to another that had already been occupied by the same cation.

In Ca–Cd HAP solid solutions, Cd^{2+} ions occupy both the Ca(I) and Ca(II) sites, so it seems that sorption and coprecipitation lead to a different distribution of cadmium in the apatite crystal lattice. It was suggested based on all these results, that diffusion followed by ion exchange was the main mechanism of cadmium removal by HAP [18, 23, 28].

Recrystallization is the dissolution of smaller crystals at the expense of the growth of larger ones. Consequently, some Cd^{2+} ions from the surrounding solution may occur in the new surface layers of HAP. This may be attributed to the slow phase of cadmium uptake, but the extent of this process must be very small

[16]. However, in the case of Ca-deficient apatites a dissolution–precipitation mechanism was detected, and it was confirmed by the occurrence of new solid phase, cadmium hydrogen–phosphate, $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$. This process plays a major role in the pH region 2–4, due to the high solubility of HAP at low pH. A similar dissolution–precipitation process was observed in the case of a "slow introduction method" [25], when a much higher sorption capacity was reached, compared to the standard batch technique.

CONCLUSION

Apatites show a great affinity towards metal cations. A capacity of 0.7 – 0.8 mol/mol HAP (~ 0.7 mmol/g HAP, or ~ 80mg/g HAP) for cadmium was reached and this amount is sufficient for the use of HAP in water decontamination processes. Therefore, HAP is a potential sorbent for the remediation of contaminated water and industrial wastes. The mechanism of cadmium sorption on HAP is complex. The mechanism of Pb^{2+} and U (VI) sorption on HAP is defined with much more certainty, because XRD analyses clearly shows the existence of a new solid phases on the surface of HAP. The most recent investigations of the cadmium removal mechanism have suggested that diffusion and ion exchange are dominant, but other mechanisms may attribute to the overall sorption process, according to the physico–chemical properties of the HAP sample used and the experimental conditions. The desorption of Cd^{2+} ions from HAP is low, especially for low initial concentrations of cadmium in the solid phase.

The high sorption affinity of HAP towards cadmium is an advisable property from the aspect of wastewater treatment, but it has a negative effect regarding cadmium retention in the human body or the commercial use of natural apatite that contains Cd^{2+} as an impurity.

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IZVOD

IMOBILIZACIJA KADMIJUMA HIDROKSIAPATITOM

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Zagađivanje vode, vazduha i zemljišta kadmijumom predstavlja jedan od velikih ekoloških problema. Ukoliko se u prirodi nalazi u jonskom obliku, rastvorljiv u vodi, kadmijum lako ulazi u lanac ishrane. Imobilizacija Cd^{2+} jona se može ostvariti vezivanjem za čvrste matrikse, male rastvorljivosti, putem koprecipitacije ili sorpcije. Hidroksiapatit, $Ca_{10}(PO_4)_6(OH)_2$, je slabo rastvorna so, koja se pokazala kao odličan sorbent za uklanjanje teških metala iz vodenih rastvora. U literaturi, posebna pažnja je posvećena izučavanju veze između sintetičkog hidroksiapatita, poznatog sastava i jona kadmijuma. Mehanizam sorpcije Cd^{2+} jona je složen. Preovlađujući proces je jonska izmena, ali površinska adsorpcija, površinsko kompleksiranje i koprecipitacija takođe mogu doprineti ukupnom mehanizmu. Sorpcioni kapacitet zavisi od osobina samog hidroksiapatita i od eksperimentalnih uslova. Maksimalni kapacitet sintetičkog hidroksiapatita prema kadmijumu iznosi 0,8 mol Cd^{2+} /mol HAP-a. HAP je zbog toga potencijalni sorbent za prečišćavanje zagađenih voda i zemljišta, za obradu industrijskog otpada, a takođe nalazi primenu i kao reaktivna barijera, oko odlagališta radioaktivnog i drugog opasnog materijala.

Key words: Cadmium • Hydroxyapatite • Sorption •
Ključne reči: Kadmijum • Hidroksiapatit • Sorpcija •