

## Cd<sup>2+</sup> and Zn<sup>2+</sup> sorption on apatite in the presence of EDTA and humic substance

K. Viipsi<sup>1</sup>, S. Sjöberg<sup>2</sup>, K. Tõnsuaadu<sup>1</sup> and A. Shchukarev<sup>2</sup>

<sup>1</sup> Laboratory of Inorganic Materials, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, ESTONIA, karin.viipsi@ttu.ee

<sup>2</sup> Department of Chemistry, Umeå University, SE-901 87 Umeå, SWEDEN

**Abstract.** The sorption of Cd<sup>2+</sup> and Zn<sup>2+</sup> on hydroxyapatite [HAP- Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] and fluorapatite [FAP- Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(F)<sub>2</sub>] with different specific surface area and stoichiometry was investigated in batch experiments in the pH range 4 to 11 (25 °C; 0.1 M KNO<sub>3</sub>). The impact of different conditions was concerned: solution pH, the presence of complexing ligands (EDTA and humic substance) and competing metal ions, as well as reaction kinetic and equilibrium conditions. To evaluate the reversibility of Cd<sup>2+</sup> sorption onto HAP, desorption characteristics in water, Ca, EDTA, and HUM-solutions were determined. Additionally to solution analysis the surface composition of solid phases was analysed by X-Ray Photoelectron Spectroscopy (XPS). The information from the chemical analyses was used to design an equilibration model that takes into account dissolution, surface potential, solution and surface complexation, as well as possible phase transformations. It was revealed that apatites effectively sorb Cd<sup>2+</sup> and Zn<sup>2+</sup> by ion exchange reactions on surface by formation of new surface phases. Using XPS the formation of a Me-enriched HAP surface was found, which was interpreted as the formation of a solid solution with the general formula: Ca<sub>8.4-x</sub>Me<sub>x</sub>(HPO<sub>4</sub>)<sub>1.6</sub>(PO<sub>4</sub>)<sub>4.4</sub>(OH)<sub>0.4</sub>. In a binary solution (Cd+Zn) the competition of metals reduced individual sorbed amount compared with the single component solutions but the total adsorption maximum was approximately constant. The presence of EDTA reduces the metal sorption on apatite due to [CdEDTA]<sup>2-</sup> and [ZnEDTA]<sup>2-</sup> complexes and increases apatite solubility due to [CaEDTA]<sup>2-</sup> complex formation. The dissolved humic substance was bound on apatite in suspensions but the amount of Cd<sup>2+</sup> bound was not changed. The results showed that the solution pH and the presence of complexing ligands have a significant effect on heavy metal sorption on apatite and must be considered if apatites are used as remediation agent. The proposed model can be used to predict apatite dissolution and surface phase transformations in the presence of metal ions and EDTA.

**Key words:** apatite, heavy metals, sorption, complexing ligands, XPS, modelling

### Introduction

Contaminated soil and water presents an unacceptable risk to human and ecological health and must be remediated. The removal of heavy metals from natural waters and soils needs special attention because their variety of toxic effects. Among different treatments the adsorption technology is attractive due to its efficiency, economical and simple operation.

Phosphate materials like hydroxyapatite [HAP- Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH] and fluorapatite [FAP-Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F] has a strong ability to fix toxic metals and has been applied for wastewaters purification and *in situ* soil remediation.

Cd<sup>2+</sup> and Zn<sup>2+</sup> are studied as typical heavy metals widely present in surface and ground waters, soils and

sediments due to anthropogenic activity. If these metals occur in nature in ionic form, they easily enter the food chain, causing various toxic effects on living organisms. The main sources of Cd<sup>2+</sup> in natural waters are industrial wastes and phosphate fertilisers. Zinc plays an important role in essential biological functions but, at high concentrations, causes gastrointestinal distress and diarrhoea. Main sources of Zn<sup>2+</sup> are atmospheric pollution, farm manures, sewage sludge, fertilisers, agro chemicals, limes and industrial wastes (Mirsal, 2008).

The metal ion binding process on apatite (AP) is controlled by number of factors including pH, contact time, type of metal ions in a solution, apatite physico-chemical properties, solution composition etc. (Sljivic *et al.*, 2009). The fixation of metal ion on AP surface may

take place through one or more simultaneous mechanisms of: ion exchange, surface complexation, dissolution of apatite to form new metal phosphates, and substitution of  $\text{Ca}^{2+}$  ions in apatite by other metal ions during recrystallization.

The mobility of metal ions in environment is controlled by the number of factors including natural (humic compounds) and synthetic (EDTA) chelating agents. The effect of the ligands on the uptake of metal depends on the stability and charge of the complex formed (Wang *et al.*, 2009).

Although the sorption of heavy metals on apatites has been extensively studied, the dominating sorption mechanism is under discussion and much less attention has been paid to the effect of the complexing ligands on the uptake.

The purpose of the present study was to investigate  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  sorption on hydroxy- and fluorapatite in the absence/presence of ethylenediaminetetraacetic acid (EDTA) and humic substance (HUM) and to explain the sorption mechanism.

## Materials and Methods

In experiments synthetic hydroxy- and fluorapatites was used. The specific surface area varied from 26.5 to 85.5  $\text{m}^2/\text{g}$ . The detailed description of apatite characteristics, synthesis procedure and methods can be found at Viipsi, 2012a.

The HAP/FAP dissolution and  $\text{Cd}^{2+}/\text{Zn}^{2+}$  sorption (in the presence and absence of EDTA and humic substance) experiments were performed in batch experiments at room temperature within the final pH range 4–11. An ionic medium of 0.1 M  $\text{KNO}_3$  and solid/solution ratio 2 g/L was used. Reaction time varied from 5 min to 1 week. Sorption solutions with different components contained of 2.1 mM Cd, 2 mM Zn, 2 mM EDTA and were prepared from analytical grade  $\text{Cd}(\text{NO}_3)_2$ , metallic Zn (dissolved in  $\text{HNO}_3$ ) and  $\text{Na}_2\text{EDTA}$ . Humic substances (Flucka, Switzerland, Tech.) 10 mg/L were used.

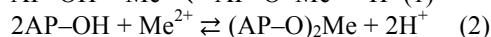
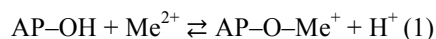
## Results and Discussion

The kinetic studies were performed to estimate the time period required to establish equilibrium between the AP phase and the solution.

The results revealed that the  $\text{Cd}^{2+}$  sorption process on HAP is, at first, very fast. Due to plenty of “free” surface area of the sorbent being available for the sorption of  $\text{Cd}^{2+}$ , the majority was bound within the first five minutes. This rapid step was followed by a slower increase within 5 h until equilibrium was reached. The first step was characterised as the dissolution of HAP and the formation of a new stable Cd–apatite phase on its surface. In the second step, the stability of a new phase was further increased by the diffusion of  $\text{Cd}^{2+}$  ions inside the HAP crystal lattice (Raicevic *et al.*, 2005). The time necessary for achieving equilibrium depends on the

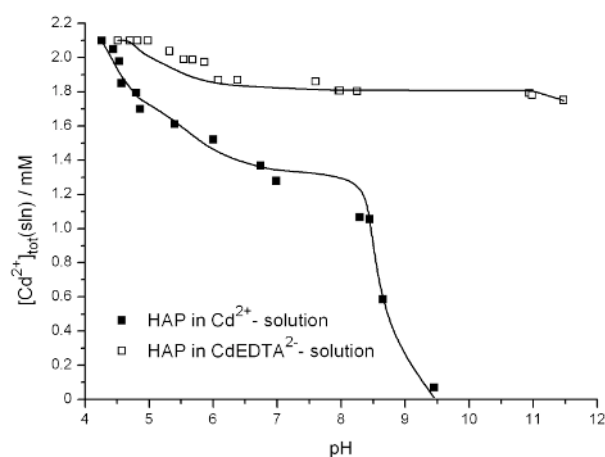
amount of non-complexed metal ions in solution.

The sorption of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  shifted the equilibrium pH of solutions to lower values. The higher the amount of sorbed metal ions is, the greater is the deviation of the equilibrium pH from pure AP suspension pH. The drop in equilibrium pH suggests that  $\text{H}^+$  ions are liberated from the solid surface into the aqueous phase as a result of the exchange with metal cations:



Therefore, decrease in final pH value suggests the formation of surface complexes (Smiciklas *et al.*, 2006; Xu *et al.*, 1994).

The amount of metal ions sorbed increased with pH, and reached 100% due to precipitation of hydroxides at pH 9.5 for  $\text{Cd}^{2+}$  (Fig. 1) and at pH 8.5 for  $\text{Zn}^{2+}$ . In an equimolar binary cation solution (Cd+Zn), the competition of metal ions reduced the amounts of individual ions bound by up to 20 % compared with the single component solutions. At the same time the total adsorption extent was approximately constant. The amount of adsorbed  $\text{Zn}^{2+}$  in single- and binary- metal solutions was higher than that of  $\text{Cd}^{2+}$  (Viipsi, 2012a).



**Fig. 1.** Experimental (symbols) and calculated (lines) results of  $\text{Cd}^{2+}$  sorption on HAP in Cd- and Cd-EDTA-solution.  $[\text{Cd}^{2+}]_{\text{tot(sln)}}$  denotes  $\text{Cd}^{2+}$  in a solid phase.

The presence of EDTA increased the dissolution of apatite and decreased the amounts of Me ions sorbed (Fig. 1) because of the formation of Ca/Cd/ZnEDTA<sup>2-</sup> complexes (Viipsi, 2012a). It was found that the EDTA and Cd/ZnEDTA<sup>2-</sup> complexes do not adsorb on AP at any measurable amounts. Therefore, the possible amount of metal ions bound with AP in solution depends also on EDTA concentration. Contrary to EDTA, the dissolved HUM was bound to apatite, but the amount of  $\text{Cd}^{2+}$  bound to apatite was not affected by HUM (Viipsi *et al.*, 2010).

Comparison of the solutions' chemical and solid surface XPS analysis results indicated that the apatite

surface layer differs from the bulk. The XPS analysis revealed a Me/P ratio ( $\text{Ca}+\text{Cd}+\text{Zn}$ )/P=  $1.4 \pm 0.1$  which was the same in the absence as well as in the presence of  $\text{Cd}^{2+}$  and/or  $\text{Zn}^{2+}$  ions. This observation implies that the sorption of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions on AP occurs mainly by ion exchange reactions with  $\text{Ca}^{2+}$  ions. An equilibrium model was designed to describe proton- and ligand-(EDTA) promoted dissolution of HAP as well as surface phase transformations in the presence of  $\text{Cd}^{2+}$  and  $\text{CdEDTA}^{2-}$  (Viipä *et al.*, 2012b). The total concentration of protons, calcium, phosphate and cadmium in solution were used to calculate a model for the dissolution and surface complexation of HAP. In the different calculations the computer code WinSGW which based on the SOLGASWATER algorithm was used.

The model obtained describes well experimental results (Fig. 1) and reveals that metal ions are sorbed by formation of a new, less soluble metal-substituted surface layer with the composition  $\text{Ca}_{8.4-x}\text{Me}_x(\text{HPO}_4)_{1.6}(\text{PO}_4)_{4.4}(\text{OH})_{0.4}$ .

In the desorption process it was found that  $\text{Cd}^{2+}$  sorbed in the presence of EDTA and HUM are more easily removed from apatite in comparison with  $\text{Cd}^{2+}$  that are sorbed in the absence of ligands. HUM impact on  $\text{Cd}^{2+}$  bonding with apatite emerges in the different  $\text{Cd}^{2+}$  desorption levels, depending on the presence or absence of HUM. The desorption level of bound  $\text{Cd}^{2+}$  depends on the composition of the leaching solution. For instance,  $\text{Ca}^{2+}$  ions are quite readily readsorbed by apatite, increasing  $\text{Cd}^{2+}$  ions desorption. The presence of EDTA may cause complete  $\text{Cd}^{2+}$  ions desorption from apatite (Tõnsuaadu *et al.*, 2008; Viipä *et al.*, 2010).

## Conclusions

Apatite, a stable mineral in a wide range of environmental conditions, has significant potential for remediation of toxic metal-contaminated waters and effluents and as a barrier to reduce metal migration from contaminated soil or solid waste. Heavy metal binding with minerals and plant uptake in environmental conditions is affected by natural (humic compounds) and synthetic chelating agents like diamine tetraacetic acid (EDTA). The present study was performed in order to establish the influence of EDTA and humic substance on the sorption and desorption of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions on apatite and the sorption process mechanism. As a result of this investigation the following conclusions have been made:

- Sorption character and extent of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  by apatite depends not only on the specific surface area of apatite and pH of solution, but also on apatite stoichiometry, cationic composition of solution, as well as on the presence of chelating compounds.
- Due to the sorption of cations on apatite surface the equilibrium pH of the solution decreases in correlation with the sorbed amount.
- In the solution containing both  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  cations, the amounts of individual ions bound with

apatite are reduced in comparison with the single component solutions. The total adsorption extent is approximately the same. The amount of  $\text{Zn}^{2+}$  ions adsorbed is slightly higher than that of  $\text{Cd}^{2+}$  ions in single- as well as in binary- cation solutions.

- The amount of  $\text{Cd}^{2+}$  removed with apatite from solution is not inhibited by soluble humic compounds in the initial pH range of the solution from 5 to 8.
- The amount of metals sorbed in the presence of EDTA is dependent on the content of non-complexed cations in solution. Cations sorption on apatite occurs in the pH interval 5-7 by ion exchange reaction at the surface of apatite crystals by formation of a new metal-substituted surface layer. The composition of the formed layer differs from the bulk and initial surface of apatite. The sorption mechanism of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions in the presence of EDTA is also ion exchange and the sorption kinetics is not affected.
- A thermodynamic model was designed that supports ion exchange mechanism at surface and the formation of metal-substituted apatite surface layer.
- $\text{Cd}^{2+}$  sorbed in the presence of EDTA and humic compounds is more easily removed from apatite at desorption. The strength of  $\text{Cd}^{2+}$  ions fixation in apatite structure depends also on apatite structure and on the composition of desorption solution. Soluble humic compounds in desorption solution do not increase desorption, but EDTA may cause complete  $\text{Cd}^{2+}$  desorption from apatite.
- Hydroxy- and fluorapatites have similar sorption properties and therefore the natural apatites, which are mostly fluorapatites, could also be used for heavy metal sorption in remediation.
- Hydroxy- and fluorapatites are effective sorbents in processing soil or wastewater contaminated by toxic metals but the reduced efficiency in relation to specific cations in multi-component systems and in the presence of EDTA should be carefully considered.

## Acknowledgements

This research was supported by European Social Fund's Doctoral Studies and Internationalisation Programme DoRa and by the Estonian Ministry of Educations and Research (SF0140082s08) and the Estonian Science Foundation (Grant No 8207).

## References

- Mirsal IA. Soil Pollution: Origin, Monitoring & Remediation. Springer 2008.
- Raicevic S, Kaludjerovic-Radoicic T & Zouboulis AI, In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification. 2005; 117(1): 41-53.
- Sljivic M, Smiciklas I, Plecas I & Mitric M, The influence of equilibration conditions and hydroxyapatite physico-chemical properties onto retention of  $\text{Cu}^{2+}$  ions. 2009; 148(1): 80-88.

- Smiciklas I, Dimovic S, Plecas I & Mitric M, Removal of  $\text{Co}^{2+}$  from aqueous solutions by hydroxyapatite. 2006; 40(12): 2267-2274.
- Tõnsuaadu K, Viipsi K & Trikkel A, EDTA impact on  $\text{Cd}^{2+}$  migration in apatite-water system. 2008; 154(1-3): 491-497.
- Wang Y-J, Chen J-H, Cui Y-X, Wang S-Q & Zhou D-M, Effects of low-molecular-weight organic acids on Cu(II) adsorption onto hydroxyapatite nanoparticles. 2009; 162(2-3): 1135-1140.
- Viipsi K, Impact of EDTA and Humic Substances on the Removal of Cd and Zn from Aqueous Solutions by Apatite. Tallinn University of Technology 2012a; Doctoral Thesis.
- Viipsi K, Sjöberg S, Shchukarev A & Tõnsuaadu K, Surface phase transformations, surface complexation and solubilities of hydroxyapatite in the absence/presence of Cd(II) and EDTA. 2012b; 27(1): 15-21.
- Viipsi K, Tõnsuaadu K & Peld M, Impact of soluble humic substance on  $\text{Cd}^{2+}$  sorption on apatite in aqueous solutions. 2010; 26(sup2): 77-85.
- Xu Y, Schwartz FW & Traina SJ, Sorption of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  on Hydroxyapatite Surfaces. 1994; 28(8): 1472-1480.