THESIS ON NATURAL AND EXACT SCIENCES B122

Impact of EDTA and Humic Substances on the Removal of Cd and Zn from Aqueous Solutions by Apatite

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Declalaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

Karin Viipsi

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EDTA ja humiinaine mõju Cd ja Zn eraldamisele vesilahusest apatiidiga

KARIN VIIPSI

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K. Tõnsuaadu, *K. Viipsi*, A. Trikkel, EDTA impact on Cd^{2+} migration in apatite – water system. *Journal of Hazardous Materials*, 2008, 154, 491–497.

Paper II:

K. Viipsi, K. Tõnsuaadu, M. Peld, Impact of soluble humic substance on Cd^{2+} sorption on apatite in aqueous solutions. *Chemistry and Ecology*, 2010, 26(2), 77–85.

Paper III:

K. Viipsi, S. Sjöberg, A. Shchukarev, K. Tõnsuaadu, Surface phase transformations, surface complexation and solubilities of hydroxyapatite in the absence/presence of Cd(II) and EDTA, *Applied Geochemistry*, 2012, 27(1), 15–21.

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K. Viipsi, S. Sjöberg, K. Tõnsuaadu, A. Shchukarev, Hydroxy- and fluorapatite as sorbents in Cd- Zn- multicomponent solution in the presence of EDTA. Manuscript submitted to *European Journal of Soil Science*, under review.

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THE AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

I The author fulfilled the experiments and analyses, interpretated the results, prepared tables and figures and started manuscript writing.

II The author analysed and interpretated the results and wrote the paper. The results were presented by the author at the 12th Nordic-Baltic IHSS Symposium on Natural Organic Matter in Environment and Technology in Tallinn, Estonia, in 2009.

III The author carried out the experiments, performed calculation work and wrote the manuscript. The applicant performed the process modelling in collaboration with prof. S. Sjöberg. The results were presented by the author at 20th annual meeting of Society of Environmental Toxicology and Chemistry (SETAC) Europe: Science and Technology for Environmental Protection in Seville, Spain, in 2010 and at 7th International Symposium on Inorganic Phosphate Materials in Argonne, Illinois, USA, in 2011.

IV The author was responsible for planning and conducting the experiments, calculation work, interpretation of results, and writing the paper. The results were presented by the author at SETAC Europe 21st Annual Meeting-Ecosystem Protection in a Sustainable World: A Challenge for Science and Regulation in Milan, Italy, in 2011 and at 6th International Symposium of Interactions of Soil Minerals with Organic Components and Microorganisms: Soil Interfaces in a Changing World in Montepellier, France, in 2011.

INTRODUCTION

Nowadays toxic metals are one of the most important pollutants in source and treated water as well as in soils and are becoming a severe public health problem. Heavy metal contamination exists in aqueous waste streams of many industries.

Soil remediation techniques based on the excavation, transport and landfilling of metal-contaminated soils and wastes are effective, but can also be disruptive to ecosystems due to the vast size of the contaminated areas and the high costs involved. A cheaper alternative for soil remediation is *in situ* remediation techniques that avoid transportation and landfilling costs by treating the respective contaminants in place. In situ stabilisation of metals means forming insoluble compounds, thus decreasing their mobility and reducing bioavailability in order to reduce the risks of groundwater contamination, plant uptake, and exposure of other organisms.

Cadmium (Cd) is regarded as one of the most toxic metals commonly present in contaminated soils and is relatively soluble and bioavailable in comparison to other trace metals. Zinc (Zn) plays an important role in essential biological functions but, at high concentrations, causes gastrointestinal distress and diarrhoea. If these metals occur in nature in the ionic form, they easily enter the food chain, causing various toxic effects on living organisms.

Calcium phosphates with apatite structure [$Ca_{10}(PO_4)_6(OH/F)_2$] (AP) possess an ability to bind metal ions from solutions and are, therefore, considered to be prospective materials for the immobilisation of toxic metals from polluted soils, sediments, and waters, allowing rehabilitation of soils and re-vegetation of highly polluted industrial sites. The addition of apatite has been shown to lower the mobility of Cd, Zn, Pb, Cu, Co, Mn, Ni, Al, Ba, Mn, Fe and U in sediments and soils inhibiting their uptake by plants (Xu *et al.*, 1994; Mandjiny *et al.*, 1998; Perrone *et al.*, 2001; Ohnuki *et al.*, 2004; Smiciklas *et al.*, 2006; Corami *et al.*, 2007; Oliva *et al.*, 2010). Apatite is a preferred material for long-term containments because of its relatively high sorption capacity for heavy metals, low water solubility, high stability under reducing and oxidising conditions, availability and low cost. Apatite amendment does not have implications on the environment contrary to alum (aluminium sulfate), phosphogypsum, bauxite, and fly ash, for example, that had a detrimental effect on soil and water quality after pollutants immobilisation (Udeigwe *et al.*, 2011).

Heavy metal bonding with minerals and plant uptake in environmental conditions is affected by natural (humic compounds) and synthetic chelating agents (Grcman *et al.*, 2001; Kos & Lestan, 2004; Smiciklas *et al.*, 2006). The amount of synthetic ethylenediaminetetraacetic acid (EDTA), a strong chelating compound, increases continuously in the environment (Grundler *et al.*, 2005). In agricultural practice EDTA is introduced into soil as a common ingredient of fertilisers or for increasing heavy metal ion bioavailability in phytoextraction. It is found that if apatite amendment to Pb, Zn, Cd, and Cu-contaminated soil reduces their bioavailability, then addition of EDTA enhances heavy metal uptake by plants (Grcman *et al.*, 2001; Kos & Lestan, 2004). The amount of metal ion removed from solution decreases significantly with the increase in the concentration of chelating ligands.

It is evident that the mechanism of metal interaction with apatites varies depending on system conditions, particularly on the environmental pH, the properties and composition of the metal ions and the presence of complexing ligands in solution. Relatively few studies have concerned the sorption mechanism of heavy metals in the presence of chelating compounds.

The hydroxy- and fluorapatite structure is known to incorporate Cd and Zn in calcium (Ca) sites by processes of surface complexation, co-precipitation, diffusion and substitution (Xu *et al.*, 1994; Valsami-Jones *et al.*, 1998; Smiciklas *et al.*, 2008; Dybowska *et al.*, 2009). Different investigations have increasingly insisted that the sorption is determined by apatite surface. They show that Cd sorption on HAP occurs by forming the new less soluble surface layer and not through the bulk (Marchat *et al.*, 2006; Yasukawa *et al.*, 2007; Zhang *et al.*, 2009).

Crystal structure investigations show that there are minor modifications of the crystallite morphology after cadmium (Jeanjean *et al.*, 1996; Yasukawa *et al.*, 2007) and zinc fixation (Chen *et al.*, 1997b). The concentrations of sorbed cations in the solid phase (atomic ratio of heavy metal/Ca ≈ 0.05) are too small to induce significant changes of cell parameters and therefore the XRD and FTIR analyses, particularly in the case of a multi-component solution, do not reveal changes in the solid phase. Spectroscopic techniques, such as X-ray photoelectron spectroscopy (XPS), have the potential to provide valuable information about the interactions between metal ions, organic ligands, and surfaces.

A study on the removal of Cd and Zn ions from aqueous solutions in the presence of ethylenediaminetetraacetic acid (EDTA) and humic substance (HUM) by synthetic hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) and fluorapatite ($Ca_{10}(PO_4)_6(F)_2$, FAP) was conducted in batch conditions. The influence of different sorption parameters, such as equilibration time, pH value of solution, and the specific surface area, on the sorption amount of Cd^{2+} and Zn^{2+} were studied and discussed. To get a better insight into the sorption mechanism the information from the chemical analyses and XPS data was used to design an equilibrium model that takes into account dissolution, solution and surface complexation, as well as possible phase transformations.

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LIST OF ABBREVATIONS AND SYMBOLS

HAP – hydroxyapatite
FAP – fluorapatite
AP – hydroxy- as well as fluorapatite
EDTA – ethylenediaminetetraacetic acid
HUM – humic substance
FTIR – Fourier transform infrared spectroscopy
XRD – powder X-ray diffractometry
XPS – X-ray photoelectron spectroscopy
SEM – scanning electron microscope
SSA – specific surface area
pH_{PZC} – pH of point of zero charge, describes the condition when the electrical charge density on a surface is zero
pH_{in} – initial pH of solution
pH_{fin} – final or equilibrium pH of solution
sln – solution
sld – solid phase
Me^{2+} – Cd^{2+} as well as Zn^{2+}
Q_{sorb} – the mole ratio of metal ions bound by AP to Ca^{2+} ions released from apatite

1 LITERATURE OVERVIEW

1.1 Heavy metals and environment

Metal ions entrained into the environment as a consequence of anthropogenic activity are often not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. The toxic elements discharged in the effluents will be absorbed and accumulated by microorganisms. Eventually, the toxic element will get transferred to humans via the food chain.

For this study, Cd and Zn were chosen as typical metals ions, with wide presence in surface and ground waters, soils and sediments caused by anthropogenic activity. They belong to the most common heavy-metal pollutants listed by the US Environment Protection Agency and European Environment Agency.

1.1.1 Cadmium

Cadmium is an element that occurs naturally in the earth's crust and is usually present in the environment as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulphur (cadmium sulphate, cadmium sulphide). Although it occurs naturally in the environment, due to anthropogenic activity excessive amounts of cadmium are released to the environment and there has been a sharp rise in the global use of cadmium. Cd is released into the aqueous system from atmospheric pollution, industrial activities (metal plating, smelting, mining, cadmium-nickel batteries, phosphate fertilisers, lime, agrochemicals, fossil fuel combustion, pigments, stabilizers, compost industrial wastes, paint and alloy industries) as well as from sewage sludge (biosolids). The EU environmental quality standards for cadmium in inland waters is 0.25 µg/L (Manahan, 2005; Lewinsky, 2007).

Cd is almost always divalent in all stable compounds, and it forms hydroxides and complex ions with ammonia and cyanide, and also a variety of complex organic amines, sulphur complexes, chlorocomplexes, and chelates. Cadmium forms precipitates with carbonates, arsenates, phosphates, oxalates, and ferrocyanides. It is readily soluble in nitric acid. The mobility and bioavailability of Cd depends mainly on its chemical species. Cd in soils and sediments appears mainly in the exchangeable fraction. Several studies implicated that Cd in soils contaminated by anthropogenic activities such as mining and smelting seems to be more bioavailable than Cd from unimpacted soils. In the soil solution, most of the Cd is present as free Cd^{2+} and $CdHCO_3^+$. Most of the Cd added to calcareous soils adsorbs rapidly or precipitates in the solid phase. As complexation of Cd with organic matter is weak because of the competition for binding sites with Ca, only small amounts of Cd occur complexed with organic ligands. Adsorption is the main operating mechanism of the reaction of Cd at low concentrations with soils (Bradl, 2005).

Cadmium has no physiological function, it is a highly toxic element and is considered as a carcinogen. Since the body has no mechanism to keep Cd at a safe level, it accumulates in the body, causing several health problems, like kidney damage, itai-itai disease (Nogawa & Suwazono, 2011) and calcium loss in bones that might lead to the bone disease osteoporosis (Bhattacharyya *et al.*, 2008).

1.1.2 Zinc

Zinc is the 24th most abundant element in the Earth's crust. The element is normally found in association with other base metals such as copper and lead in ores. The most common zinc ore is sphalerite (zinc blende), a zinc sulfide mineral, which is the most heavily mined zinc-containing ore because its concentrate contains 60–62 % zinc. The largest mineable amounts are found in Australia, Asia, and the United States.

The industrial use of Zn comprise galvanising of iron and steel for corrosion protection, alloys, vulcanisation of rubber, photocopying paper, paints, rayon glass, enamel and plastic industries, fertilisers, medicine and cosmetics (Fosmire, 1990; Manahan, 2005). Zinc concentrations are rising unnaturally through human activities. Some soils are heavily contaminated with zinc, and these are to be found in areas where zinc has to be mined or refined, or where sewage sludge from industrial areas has been used as fertiliser. The EU environmental quality standards for zinc are 8-125 µg/L (depends on the hardness of the water) and 40 µg/L in fresh and saltwater, respectively.

Zinc has a low affinity for oxides and prefers to bond with sulphides. It is a moderately reactive metal and strong reducing agent. Zinc reacts readily with acids, alkalis and other non-metals. In aqueous solution an octahedral complex, $[Zn(H_2O)_6]^{2+}$ is the predominant species. The total concentration of zinc in soils depends on the composition of the parent material and soil mineralogy, especially the concentration of quartz, which tends to dilute most elements. Zinc can react with clay minerals, with organic matte and with metal oxides. Only a small fraction of the total zinc is exchangeable or soluble. About one-half of the dissolved zinc exists as the free hydrated cation. Zinc forms complexes with many of the common organic acids potentially found in soils (citric, malic, oxalic, etc.) and also with humic substances (Robson, 1994).

Zinc is one of the most important trace ions for humans and animals necessary for the proper function of over 80 different enzymes, several of them involved in bone metabolism. Even though zinc is an essential requirement for a healthy body, excess zinc can be harmful, and cause zinc toxicity. Excessive absorption of zinc can suppress copper and iron absorption and can cause damage to the stomach lining due to the high solubility of the zinc ion in the acidic stomach (Bothwell *et al.*, 2003).

1.2 Heavy metals remediation

A number of technologies are accessible to curtail the problem of heavy metals in the environment, for example chemical precipitation, ion exchange, chemical oxidation or reduction, solvent extraction, reverse osmosis, electrolytic recovery, coagulation, adsorption and so on. The selection of the treatment methods depends on the concentration of waste and the cost of treatment. The need for safe and economical methods for removing heavy metals, even in a very small concentration, from polluted wastewaters has resulted in the search for alternative techniques (Lewinsky, 2007). The *in situ* treatment techniques, in which soil is remediated without the need for removal of the soil from its initial location, have the potential to be relatively cheap compared to engineering-based approaches such as physical isolation or separation of contaminated material (e.g. capping, soil washing) or *ex situ* techniques (e.g. excavation and dumping of soil elsewhere) (Wood, 1997).

Adsorption has been shown to be an economically feasible alternative method in comparison with the above cited ones. It is the only method that is available for the removal, recovery and recycling of toxic heavy metals from waste water. Many kinds of sorbents have been reported for Cd and Zn removal, such as activated carbon, mesoporous materials, fly ash, clay, calcite, zeolite, vermiculite, kaolinite, chitosan, gibbsite, goethite, alumina, montmorillonite, ferrihydrite and apatite (Lewinsky, 2007; Elkady *et al.*, 2011; Udeigwe *et al.*, 2011).

Phosphate stabilisation resulting in formation of highly insoluble phosphates which are stable over almost the entire pH range found in the natural environment represents an efficient strategy for reducing heavy metals toxicity by decreasing their mobility and bioavailability (Elkady *et al.*, 2011). Stötzel *et al* (Stötzel *et al.*, 2009) showed that nanocrystalline hydroxyapatite (SSA=168 m^2/g) outperforms activated carbon regarding Zn adsorption with 420%. The results suggested that HAP and FAP amendment could significantly reduce the bioavailability and increase the geochemical stability of soil Cd and Zn in contaminated soils (Chen *et al.*, 2007). The ability of apatite to reduce heavy metal uptake by plants has been well documented by many authors (Xu *et al.*, 1994; Valsami-Jones *et al.*, 1998; Peld *et al.*, 2004; Raicevic *et al.*, 2005; Corami *et al.*, 2008; Smiciklas *et al.*, 2008).

1.3 Apatite mineral

Apatite is a group of phosphate minerals which includes: fluorapatite, hydroxylapatite, chlorapatite, and bromapatite. The general chemical formula is usually presented as $Ca_{10}(PO_4)_6X_2$ ($X=F^-$, OH^-, Cl^-, Br^-). Hydroxyapatite, also known as hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the major component of tooth enamel and bone mineral. Fluorapatite, $Ca_{10}(PO_4)_6(F)_2$, is the most common phosphate mineral in the Earth's crust. Apatite is found in igneous, metamorphic and sedimentary rocks. Extensive deposits of igneous mineral are found in Kola

Peninsula, Russia. Massive sedimentary apatite deposits are mined for industrial purposes in regions of Morocco, Tunisia, Israel and Egypt. The primary use of apatite is in the manufacture of phosphorous fertiliser and acid.

Apatite has a hexagonal crystal structure that belongs to space group $P6_3/m$. Crystals are generally formed as well-shaped, elongated or stubby hexagons. The structure of apatite can be visualised as a series of phosphate 'tubes' internally lined by calcium ions. This first calcium site is half-surrounded by five oxygens, and half-exposed to the central space into which the fluoride ion is inserted. A second calcium site - surrounded by six oxygens - provides the link to join these 'tubes' together (Figure 1). This type of structure allows different substitutions to a certain extent at the Ca site as well as at the phosphate and hexagonal axis site. The colour of apatites ranges from colourless, white, yellow to red, brown, pink or purple depending on additive ions.

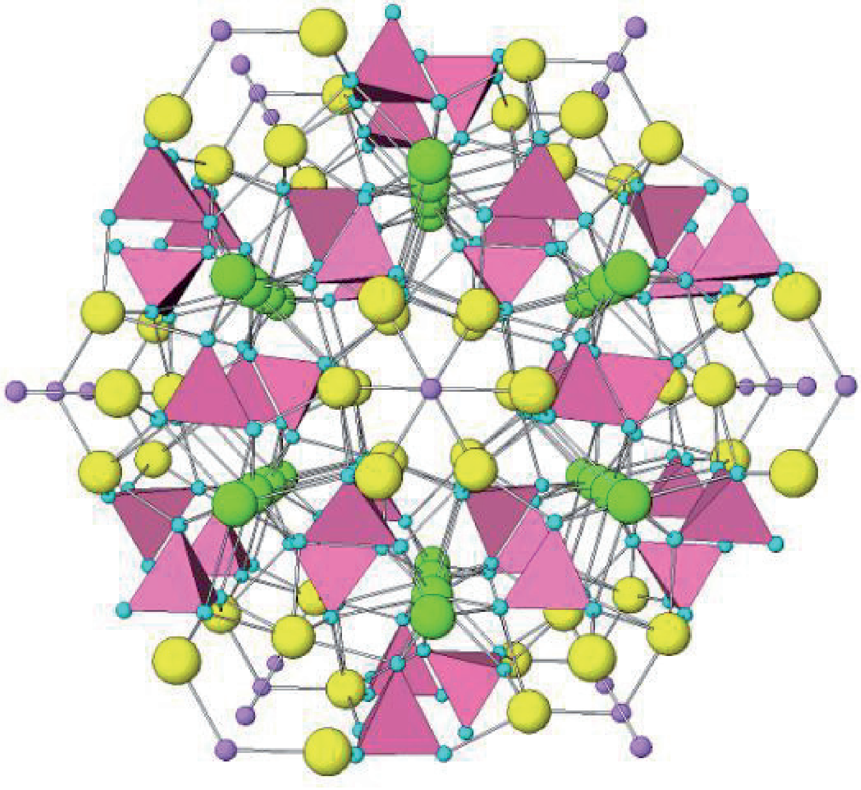

Figure 1 Apatite structure (viewed down the [0001] crystallographic axis). The structure consists of $(PO_4)^{3+}$ groups (pink tetrahedra), monovalent anions like F^- and $(OH)^-$ (purple spheres) in the "tunnels" parallel to [0001], and Ca^{2+} cations in two coordinations: colored yellow, Ca(2) and green, Ca(1), respectively (Chakhmouradian, 2011).

1.4 Metal sorption mechanism on apatite

The results of kinetic studies revealed that Cd and Zn removal takes place in two different steps; the first involves a rapid metal removal and the second one exhibits a subsequent removal until equilibrium is reached, which is a slow and quantitatively insignificant step (Xu *et al.*, 1994; Valsami-Jones *et al.*, 1998; Fedoroff *et al.*, 1999; Bailey *et al.*, 2005; Lee *et al.*, 2005; Corami *et al.*, 2007; Sheha, 2007; Corami *et al.*, 2008; Smiciklas *et al.*, 2008; Feng *et al.*, 2010). The experimental results were successfully analysed using the two most widely applied kinetic models for fitting sorption kinetic data: pseudo-first-order equation and pseudo-second-order model (Smiciklas *et al.*, 2008; Sljivic *et al.*, 2009; Feng *et al.*, 2010).

Depending on the metal ion and apatite characteristics, the sorption process can proceed via different mechanisms. The following mechanisms have been proposed to explain the binding of metal ions with apatites (Xu *et al.*, 1994; Jeanjean *et al.*, 1996; Fedoroff *et al.*, 1999; Perrone *et al.*, 2001; Somasundaran, 2006; Corami *et al.*, 2007; Smiciklas *et al.*, 2008; Sljivic *et al.*, 2009; Elkady *et al.*, 2011):

- superficial sorption: adsorption, surface complexation;
- diffusion into the solid, filling cationic vacancies in nonstoichiometric apatite (absorption);
- exchange with apatite lattice cations (ion exchange);
- dissolution of apatite and precipitation of new, apatitic or non-apatitic phosphates (dissolution-precipitation method).

The thermodynamic calculations indicate that the Cd and Zn sorption process is thermodynamically favourable, spontaneous and endothermic in nature (Sljivic *et al.*, 2009; Elkady *et al.*, 2011). It is found that the Cd-Ca-apatite phase has higher stability in comparison with the pure stoichiometric HAP, with the highest being ~5.5 Ca–substituted atoms by Cd (Raicevic *et al.*, 2005).

Several investigations show that the main mechanism of Cd removal by hydroxyapatite is the ion exchange with Ca^{2+} (Mandjiny *et al.*, 1995; Jeanjean *et al.*, 1996; da Rocha *et al.*, 2007; Smiciklas *et al.*, 2008) and partial dissolution of apatite with subsequent precipitation of a Cd-containing hydroxyapatite with the formula $Cd_xCa_{10-x}(PO_4)_6(OH)_2$ (Raicevic *et al.*, 2005; Marchat *et al.*, 2007; Corami *et al.*, 2008).

The mechanism of Zn sorption on apatites is less clear. To explain Zn immobilisation on apatite, many concurrent processes mentioned above are also proposed (Xu *et al.*, 1994; Lee *et al.*, 2005; Charlet *et al.*, 2006; Sheha, 2007; Smiciklas *et al.*, 2008; Oliva *et al.*, 2010). According to Corami *et al.* (Corami *et al.*, 2007), Zn immobilisation takes place through a two-step mechanism: the first step is the surface complexation on specific sites of HAP surface; the second step is ion exchange with Ca^{2+} and the formation of a heavy metal-containing hydroxyapatite. Xu *et al.* (Xu *et al.*, 1994) suggested that the surface complexation and the calcium–zinc hydroxyapatite co-precipitation were the primary processes in the immobilisation of Zn by HAP, while the ion exchange and the solid diffusion might be secondary processes. Furthermore, desorption data suggest that Zn is held strongly to the solid phase, because Zn diffusion into the mineral interior is promoted by the relatively small size and ionic radius of Zn (0.74 Å). According to Raicevic *et al.* (Raicevic *et al.*, 2009) Zn-FAP is less stable than pure FAP. This indicates that the possible mechanism of Zn immobilisation by FAP might be the direct incorporation of Zn ions into the solid phase, but this would be limited by the higher FAP stability and will strongly depend on FAP crystallinity and structural properties.

Additional information about sorption mechanisms can be revealed by crystallographic structure analysis and by spectroscopic techniques. XRD analysis by Zhu *et al.* (Zhu *et al.*, 2008) supports the ion-exchange mechanism with Cd, because the lattice parameters (*a* and *c*) of original HAP (9.422 Å and 6.870 Å) slightly decreased after sorption (9.401 Å and 6.851 Å). The ionic radius of Cd^{2+} (0.97 Å) is smaller than that of Ca^{2+} (0.99 Å).

Terra *et al.* (Terra *et al.*, 2010) interpreted the Cd sorption mechanism as ionic-covalent interaction and the more covalent character of Ca(2) site determines its preferential occupation by Cd. Although other investigations insist that Cd prefers the Ca(2) site in the apatite structure (Jeanjean *et al.*, 1994; Jeanjean *et al.*, 1996), according to diffraction studies by Nounah *et al.* and Srinivasan *et al.* (Nounah *et al.*, 1992; Srinivasan *et al.*, 2006) and the extended X-ray absorption fine structure spectroscopy (EXAFS) studies by Sery (Sery *et al.*, 1996), Lanfranco *et al.* (Lanfranco *et al.*, 2003) and Bailey *et al.* (Bailey *et al.*, 2005) it is suggested that Cd partially occupies both the Ca(1) and Ca(2) sites, with a slight preference for the Ca(2) site.

Different investigations have increasingly insisted that the sorption is determined by apatite surface and the apatite specific surface area is the limiting factor (Peld, 2005; Zhu *et al.*, 2008). The X-ray adsorption spectroscopy (XAS) results from Bailey *et al.* (Bailey *et al.*, 2005) indicates that a relatively high proportion of the Cd sorbed to hydroxylapatite remained as kinetically active surface species. Badillo-Almaraz *et al.* (Badillo-Almaraz *et al.*, 2003) and Marchat *et al.* (Marchat *et al.*, 2007) concluded that Cd diffusion occurs in the superficial layer of the crystallites and not into the bulk. XPS studies have revealed that Cd sorption on HAP occurs by forming the new less soluble surface layer and not through the bulk (Marchat *et al.*, 2006; Yasukawa *et al.*, 2007; Zhang *et al.*, 2009). Mechanistic models from Gómez del Rio proves also that surface complexation has an important contribution to the adsorption process (Gómez del Rio *et al.*, 2004).

1.5 Heavy metals and organic complexes in soil

There is a growing acceptance that the lability or chemical reactivity of sorbed soil metals is an important aspect of soil metal status, especially with respect to remediation technologies and consideration of long term hazards.

Metals introduced into soil through anthropogenic sources could be dissolved in soil solution, associated with soil organic matter, adsorbed onto inorganic constituents, and/or precipitated as solids. The mobility and bioavailability of metals in soil systems are controlled by organic matter, clay minerals, pH, redox potential, and Fe/Al oxides (Udeigwe *et al.*, 2011). However, the impact of trace metals on soil and the surrounding environment often cannot be predicted simply by measuring the total concentration because only the soluble and mobile fraction has the potential to leach or to be taken up by plants and enter the food chain.

It is found that Cd bound together with organic compounds is a major source of soluble Cd in most of the soil solutions (Krishnamurti & Naidu, 2003). Therefore, metal ions bonding with minerals and plant uptake in environmental conditions is affected by natural (humic compounds) and synthetic (EDTA) chelating agents (EDTA) (Grcman *et al.*, 2001; Kos & Lestan, 2004; Smiciklas *et al.*, 2006).

1.5.1 EDTA

Ethylenediaminetetraacetic acid (EDTA) is a strong complexing ligand (Fig. 2). In agricultural practices EDTA is applied to the soil as a common ingredient of fertilisers to improve micronutrient availability. Widespread use of EDTA as a chelate for agricultural and industrial applications increases its concentrations in various water sources and in wastewaters (Darban *et al.*, 2000). Moreover, in a phytoextraction different mobilising agents (incl. EDTA) are used to artificially enhance heavy metal solubility in soil solution from the soil solid phase and thus to increase heavy metals phytoavailability. Indeed, there is growing concern that EDTA may complex with free heavy metal ions in solution, thus preventing precipitation and sorption of metals in sorbing material barriers in landfills and/or purification systems (Bradl, 2005; Malandrino *et al.*, 2006).

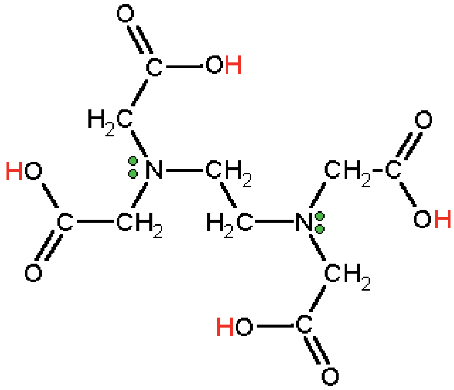

Figure 2 EDTA or ethylenediaminetetraacetic acid is a polyprotic acid containing four carboxylic acid groups and two amine groups with lone pair electrons (Sinex, 2004)

It is found that if apatite amendment to Pb, Zn, Cd, and Cu-contaminated soil reduces their bioavailability and lowers plant uptake, then subsequent addition of EDTA enhances heavy metal uptake by plants (Grcman *et al.*, 2001; Kos & Lestan, 2004). In batch experiments the effect of EDTA concentration on Cd, Zn, Cu, Co and Pb sorption characteristics on apatite was studied (Ma, 1996; Kos & Lestan, 2004; Smiciklas *et al.*, 2006; Maxted *et al.*, 2007; Wang *et al.*, 2009) and the negative effect to the immobilisation was shown.

1.5.2 Humic acid

Humic substances are a very complex organic material possessing various functional groups (carboxylic, amino, phenolic groups, groups involving sulphur atoms) and moieties (aliphatic chains and aromatic rings) which characterises its composition and properties (Fig. 3). They can significantly alter the characteristics of mineral surfaces. Organic acids adsorbed onto mineral particles produce a net negative charge on the surface. Humic acids are highly negatively charged and organic matter contributes towards the lowering of the point of zero charge (pzc) of soils. Low pH conditions are favourable for humic acid and metal complexation because the pzc of humic acid is below pH 0.5, and at higher pHs humic acid begins to dissolve. Kretzschmar *et al.* (Kretzschmar *et al.*, 1997) showed the impact of humic acid on kaolinite surface pzc, which changed from pH≈ 4.8 to the same kaolinite containing only 0.25 wt.% humic acid to $pH_{pzc} \approx 2.0$.

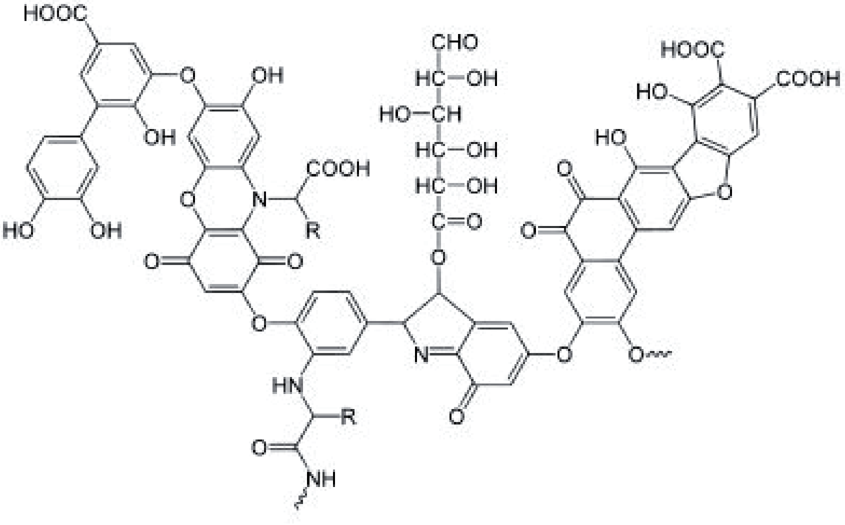

Figure 3 Example of a typical humic acid, having a variety of components including quinone, phenol, catechol and sugar moieties (Stevenson, 1994)

The oxygen containing functional groups in humic acid represent a quarter of the total molecular weight of humic acids. The carboxyl (COOH) group increases in abundance with humification, reacts readily with metals, and gradually dissociates between pH 2.5 and 7 to form the carboxylate (COO^-). The phenolic hydroxyl (OH) group is derived from lignin in woody plants, reacts less with metals, and dissociates between pH 8 and 13.5. The COOH and phenolic OH groups account for the total acidity of humic acid while the alcoholic OH group is only weakly acidic and reacts minimally with metals. Therefore, humic acid may remove metals from solution at low pH but at high pH metal bonding with dissolved humic acid results in the formation of soluble metal humate species (Coles & Yong, 2006).

According to the literature, the dissolution of HUM at pH values of 3.7–8.4 found in soils (Weng *et al.*, 2001; Krishnamurti & Naidu, 2003; Bailey *et al.*, 2005) makes the formation of soluble metal–humic complexes possible, retaining metal in solution even at a pH at which a hydroxide can form (Varrault & Bermond, 2002). At the same time, organic ligands can enhance metal sorption to mineral surfaces through the formation of ternary complexes (Arias *et al.*, 2002). General findings about HUM adsorption–desorption indicate that retention of HUM by solid surfaces decreases as pH increases. This is the combined effect of decreased specific interactions between the functional groups of HUM and the solid surface, and increased electrostatic repulsion between HUM molecules and the solid surface, and among HUM molecules themselves (Avena & Koopal, 1998). Calcium ions can promote the coagulation and precipitation of humic acids (Weng *et al.*, 2002).

Malandrino *et al.* (Malandrino *et al.*, 2006) considered carboxylic acids present in soils, sediments and aerosols as analogs for functional groups in humic acids, in order to observe the behavior of heavy metals on mineral surfaces in the presence of macromolecules. Results showed that the presence of these carboxylic acids did not affect sorbed amounts of metals on clay. Contrary to this, Bois *et al.* (Bois *et al.*, 2003) showed that humate ions enhance chromium(III) adsorption on apatite in the low pH range. This increase may be explained by the formation of a surface ternary complex. At high pH ($pH>6$), Cr(III) adsorption is decreased. This is the result of aqueous Cr(III)-humate complexation which competes with Cr surface complexes and the ternary surface complexes. Additionally, a shift of the adsorption edge is observed. However, it is proved that humic acid adsorbs on the mineral surface and therefore affects metal sorption and these processes are highly correlated with pH (Coles & Yong, 2006).

In conclusion, metal uptake by minerals may be reduced in the presence of ligands due to competition between the ligand and metal ions for surface sites, or through the formation of soluble complexes that do not adsorb onto the surface.

1.6 Modelling of interactions between minerals, metal ions and complexing ligands

In order to obtain better explanations of reaction mechanisms, modelling in conjunction with spectroscopic techniques is used. Many authors are concerned with apatite surface modelling because the surface determines the apatite dissolution and sorption behaviour. The approaches used were based on first-principles simulations and calculated surface energies (Astala & Stott, 2008), quantum mechanical calculations based on the density functional theory coupled with interatomic potential methods (Almora-Barrios *et al.*, 2009; de Leeuw, 2010), results of surface state analysis, passed through the logic of chemical equations (Dorozhkin, 1999).

The adsorption of Cd onto goethite in the presence of citric acid is successfully modelled by an extended constant-capacitance surface complexation model by Lackovic *et al.* (Lackovic *et al.*, 2004). Perrone *et al.* (Perrone *et al.*, 2001) obtained a good agreement between experimental and calculated values for nickel sorption on carbonate fluorapatites with the nonelectrostatic model and constant capacitance model. Interactions between humics, ions, and minerals surfaces are also successfully modelled. Electrostatic interactions (van Riemsdijk *et al.*, 2006), metal mobility in exchangeable and non-exchangeable mode (Bryan *et al.*, 2007) and Cd, Zn, and Cu adsorption on bidentate chelate of the carboxyl groups on HUM (Jeong *et al.*, 2007) was clarified by electrostatic models.

Bengtsson *et al.* (Bengtsson, 2007) studied surface complexation reactions with the solubility/surface complexation equilibrium model (constant capacitance model). They insisted that apatites form surface layers different than the bulk when they equilibrated in aqueous solutions and that carboxylic acids, malonate, citrate and mellitate, adsorbed as outer-sphere complexes. The surface composition of apatites is given as well as the complexation and ion exchange reactions on the surface are attached to fully describe the dissolution behaviour of apatites.

1.7 Summary of the literature review

The removal of toxic metals from contaminated soils and waters is one of the most important issues of environmental remediation. Reducing trace elements' solubility, mobility, and bioaccumulation *in situ* is an effective, low-cost way of remediation that does not require drastic disturbance of the site.

Apatites are suitable sorbent materials for remediation of contaminated soil and water because of their low solubility and ability to bind toxic metals from solutions into their structure. The sorption mechanism in simple artificial conditions is thoroughly studied for AP, including the influence of reaction conditions, apatite chemical and physical characteristics, metal type and solution composition. Different investigations have increasingly insisted that the apatite dissolution and metal sorption is determined by apatite surface. Despite the large number of investigations in this area, the sorption mechanism elucidation is complicated, since different mechanisms can often act together. Using spectroscopic and calculation techniques, it is showed that Cd sorption on AP occurs by forming the new less soluble surface layer and not through the bulk.

It is very common for several contaminants to occur simultaneously in polluted environments such as soils, wastewater or mine water effluents. It is thus important to test the effectiveness of any remediation agents in contact with multi-contaminant solutions. The presence of several metals in a solution may affect the overall metal removal rate due to, for example, competition effects. It is also possible to test if a preferential uptake of metal occurs from such solutions.

At the same time, there is a growing acceptance that the mobility or chemical reactivity of soil metals is an important aspect of soil metal status. Whereas in real systems different complexing ligands are present, it is important to examine how these ligands impact the metal sorption process on apatite. To solve this problem a whole complex of methods must be used, starting with chemical analyses, followed by structural analytic methods supplemented by mathematical modelling.

2 THE PURPOSE OF THE PRESENT STUDY

The purpose of the present study was to investigate cadmium and zinc sorption on hydroxy- and fluorapatite in the absence/presence of EDTA and humic substance. The impact of apatite properties, solution cationic composition, presence of complexing ligands and reaction parameters like solution pH and equilibration time were considered. The reaction mechanism was elucidated with the help of XPS-analysis and thermodynamic modelling.

3 EXPERIMENTAL

3.1 Materials

In the experiments synthetic apatites were used (Table 1). Apatites HA-5, 6, 9, and FA-1, 2 were prepared by precipitation from aqueous solution. Two solutions, one containing $Ca(NO_3)_2$, the other containing NH_4^+, PO_4^{3-} and F^- ions, were added simultaneously to NH_4OH-NH_4NO_3 solution under N_2 flow. Different solution addition rates and temperatures were used in order to obtain apatites with different crystallinity and SSA. The suspension was stirred for 3 hours at the precipitation temperature in order to improve the homogenity and crystallinity of the precipitate, and then kept at room temperature for 24 hours. The precipitates were filtered, washed thoroughly with distilled water and dried at 110°C. Apatite HAL-16F is prepared at the Institute of Inorganic Chemistry in Riga Technical University (Palcevskis *et al.*, 2006) and HA-ff is a commercial apatite (Fluka, fast flow).

Table 1. The characteristics of APs used

Sample	SSA, m^2/g	CaO, %	P_2O_5, %	F, %	Ca/P (bulk)	Ca/P (surface)	pH_{PZC}
HAL-16F	82.5	55.9	36.6	–	1.94	–	–
HA-5	85.5	52.4	40.0	–	1.66	–	6.8±0.1
HA-ff	37.9	48.5	42.8	–	1.44	–	6.0±0.1
FA-1	26.5	54.2	41.3	3.4	1.66	–	5.9±0.1
HA-6	37.5	51.1	41.3	–	1.57	1.40	6.9±0.1
HA-9	40.2	52.9	41.9	–	1.59	1.24	–
FA-2	39.0	54.0	40.7	3.1	1.66	1.29	–

The Ca/P molar ratio of stoichiometric apatite is 1.67 (10:6). Apatites used in this study included materials with calcium deficiency (Ca/P<1.67) as well as calcium excess (Ca/P>1.67). The specific surface area, analysed by the BET-method, varied from 26.5 to 85.5 m^2/g.

Different characterisation techniques have been used to identify the prepared APs. The chemical composition of the synthesised APs was determined by dissolving 0.25 g of the sample in 100 ml of HCl. The material was analysed for calcium and phosphorus. The apatitic structure of obtained materials was confirmed by X-ray diffractometry (XRD) and Fourier transform-infrared (FT-IR) analyses. In order to determine the morphological features and surface characteristics of the adsorbent materials, a scanning electron microscope was used.

The materials synthesised were fine powders identified by IR spectroscopy. An XRD analysis showed that all synthesis products had well crystallised AP structures. For example, the unit cell parameters of HA-6 are presented in Table 6. The size of prismatic crystals varied up to 200 nm in length (Figure 13).

3.2 Experimental procedures

The influence of pH, contact time and complexing agents on Cd^{2+} and Zn^{2+} removal from aqueous solutions was studied in a batch experiments. The conditions under which experiments were conducted are given in Table 2.

Sorption solutions were prepared from analytical grade $Ca(NO_3)_2$, $Cd(NO_3)_2$, metallic Zn (dissolved in HNO_3) and Na_2EDTA. The ionic media 0.1 M KNO_3 was used. Humic substances (Flucka, Switzerland, Tech.) with an 18 % ash content and 49.8 % C content were used. The water-soluble Ca content was 0.19 %, and was determined in an experiment in which 200 mg of HUM was mixed with 100 mL of water at pH 6.5. The pH of solutions was adjusted by adding different amounts of NH_4OH, KOH or HNO_3.

Experimental results of Cd and Zn sorption on apatite depend on many factors, whereby, for studying a new factor, the background experiments must also be repeated with the apatite used in the experiment. For that reason the solubility of apatites in water, EDTA and HUM was also studied in addition to the Cd/Zn binding experiments in metal- and ligand-containing solutions.

The main sets of experiments included:

1) sorption kinetic study, where the initial pH of sorption solution was fixed (pH_{in} = 4, 5, 6, 7) before AP addition and the pH was determined after certain time moments during 24 h (P I, II);
2) sorption equilibrium study, where the initial solution composition was varied adding different amounts of H^+ or OH^- ions to get the final pH on a large scale (pH_{fin} = 4–11), equilibration time of 3–7 days (P III, IV).
3) desorption, where samples which came out from sorption experiments were put into contact with leaching solutions with different compositions for 5–24 h.

To estimate the desorption of bound metal ions from APs obtained in sorption experiments, different desorption solution combinations were used (Table 2). Ca solutions were used because Ca^{2+} ions are supposed to exchange with bound and exchangeable metal ions in the solid AP phase (Hodson *et al.*, 2001; Peld *et al.*, 2004).

The solubility, adsorption and desorption experiments were carried out by mixing the suspensions on a rotating stirrer or by shaking in closed flasks at room temperature (23 ± 2 °C). The solid/solution ratio was 2 g/L. After mixing, the suspension pH was measured and the solid phase was separated from the solution by centrifugation (SIGMA 2-16PK) and filtration (blue-band filter paper). The amount of the sorbed metal was calculated as the difference between the solution concentrations before and after the sorption.

Table 2. Experimental conditions

Paper	Effect of…	pH_{in}	pH_{fin}	Contact time	Ionic medium (KNO_3)	Sorption solution composition*	AP	Desorption solution composition*
I	Initial pH; EDTA	Adjusted 4, 5, 6, 7	no Cd: 6.9-7.2 with Cd: 5.0-6.1	5 min, 15 min, 30 min, 1 h, 3 h, 5 h	–	Cd; Cd+EDTA (for desorption samples each comp. 3mM)	HAL-16F; HA-5; HA-ff	H_2O; 3 mM Ca; 3 mM Ca + 3 mM EDTA(time: 5h, pH_{in}=6, 7)
II	Initial pH; HUM	Adjusted 4, 5, 6, 7	no Cd: 6.4-6.5 with Cd: 5.1-5.6	24 h	–	Cd; Cd+HUM; Cd+Ca; Cd+Ca+HUM	FA-1; HA-6	H_2O; HUM; Ca+HUM (time: 24h, pH_{in}=6.3)
III	Equilibrium pH; EDTA	Not determined	3-11	Min 3 days	0.1 M	Cd; Cd+EDTA	HA-6	–
IV	Equilibrium pH; competing cation; EDTA	Not determined	4-11	1 week	0.1 M	Cd; Cd+EDTA; Zn; Zn+EDTA; Cd+Zn; Cd+Zn+EDTA	HA-9; FA-2	–

*if not noted, the concentration of Ca, Cd, Zn and EDTA 2 mM, HUM 10 mg/L

3.3 Analytical methods

The concentrations of Ca^{2+} as well as Cd^{2+} and Zn^{2+} in solution were determined by atomic absorption spectrometry (Carl Zeiss Jena AAS 1N; VARIAN Spectra AA 55B). The flame type was air/acetylene, while absorption wavelengths (λ) were 422.7 nm for Ca, 228.8 nm for Cd and 213.9 for Zn. The concentration of PO_4^{3-} was determined spectrophotometrically (SPEKOL 11, CARL Zeiss Jena; SpectroDirect) as the phosphomolybdate yellow complex (λ=430 nm). F^- concentration was measured using an ion-selective electrode (Fluoride COMB.ISE/BNC). The pH was measured with Mettler Toledo electrode DG-112 Pro calibrated with Mettler Toledo pH buffer solutions (4.01; 7.00; 9.21) and connected to an automatic titrator T90 under N_2 flow. The surface area of the AP particles was measured by the BET method (adsorptive gas N_2, carrier gas He, heating temperature 150°C) using sorptometer KELVIN 1040/1042 software (Costech International)[1].

X-ray powder diffraction (XRD) was carried out using an X-ray diffractometer (DRON-4) with CuKα radiation at 40 kV, 20mA, step size 0.04°[2].

The crystal structures of apatites were investigated by Fourier transform infrared spectroscopy (FT-IR) by INTERSPECTRUM 2000 in the wavenumber range 400–4000 cm^{-1} at room temperature. In the KBr pellets the sample/KBr mass ratio 1:300 was used[3].

Thermal analysis was performed by the SETARAM LabSys 2000 instrument (heating rate 10 deg/min, air flow 30 mL/min, sample mass 30-60 mg in Pt crucibles)[3].

A scanning electron microscope was used to identify the morphology of solid samples and estimate the particle diameter. All samples were studied in SEM Zeiss EVO-MA15. Both SE (secondary electron) and BE (back-scattered electron) regimes were used[4].

The centrifuged (4000 rpm, 15 min) wet pastes of AP suspensions were used for cryogenic XPS measurements. The fast-freezing procedure applied to wet pastes is described in detail elsewhere (Shchukarev & Sjöberg, 2005; Shchukarev, 2006). The XPS spectra were recorded with a Kratos Axis Ultra DLD electron spectrometer using a monochtomated Al K_α source operated at 150 W, a hybrid lens system with magnetic lens, providing an analysis area of 0.3 x 0.7 mm^2, and a charge neutraliser. The binding energy (BE) scale was referenced to the C 1s line of aliphatic carbon contamination, set at 285.0 eV. Processing of the spectra was accomplished with Kratos software[5].

pH_{pzc} measurements of APs were performed in the pH range 6.4–7.6, using a Malvern Instruments Zetasizer 4 instrument (Department of Chemistry, Umeå University).

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[1] Performed by M. Uibu at the Laboratory of Inorganic Materials, TUT

[2] Preformed by R. Traksmaa at the Center of Materials Research, TUT

[3] Performed by K. Tõnsuaadu at the Laboratory of Inorganic Materials, TUT

[4] Performed by V. Mikli at the Center of Material Research, TUT

[5] Performed by A. Shchukarev, Department of chemistry, Umeå University

4 RESULTS AND DISCUSSION

Metal ion sorption on apatite is controlled by many different factors simultaneously and therefore for evaluation some of them the comparative experiments in different solutions are needed keeping other factors constant. In present experiments reaction time, apatite composition, solution pH and cationic composition, as well the presence of EDTA and HUM, was varied.

4.1 Metal sorption, apatite dissolution and pH change kinetics

To elucidate the sorption mechanism in the presence of chelating compounds their impact on the Cd ions sorption kinetics was studied at certain initial pH values (P.I). In these experiments with apatites HAL-16F, HA-5 and HA-ff, Cd sorption and Ca release as well as pH change were observed. The kinetic studies were performed to estimate the time period required to establish equilibrium between the AP phase and the solution.

The results (Fig. 4) revealed that the cadmium 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 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. Due to gradual occupancy of active sites and decreasing Cd^{2+} concentration in the liquid phase, sorption in a second phase became less efficient. This is in accordance with the results from other research, revealing a two-step sorption process (Xu *et al.*, 1994; Smiciklas *et al.*, 2006; Corami *et al.*, 2007; Sheha, 2007; Corami *et al.*, 2008; Smiciklas *et al.*, 2008; Feng *et al.*, 2010). 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 Cd ions inside the HAP crystal lattice (Raicevic *et al.*, 2005). Addition of EDTA into the solution did not affect Cd sorption kinetics considerably, but the sorbed amount of Cd decreased.

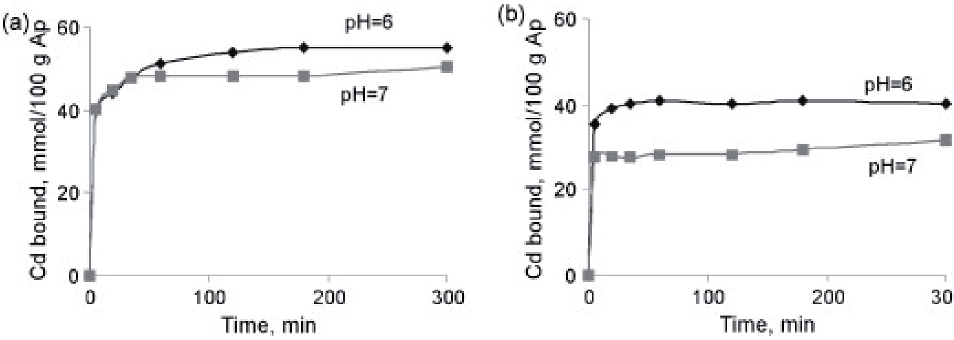

Figure 4 Kinetic curves of Cd binding with HA-ff at initial pH 6 and 7: a) in Cd and b) in Cd-EDTA complex solution

The release rate of Ca from AP (Figure 5) depends on the solution's composition and is more remarkably affected by EDTA. Almost maximum dissolution of Ca from HAP in the solution of EDTA was gained within the first five minutes and in Cd(II)EDTA in 20–30 min. In Cd solution, the reaction occurred more slowly and the equilibrium was achieved in about 5 h.

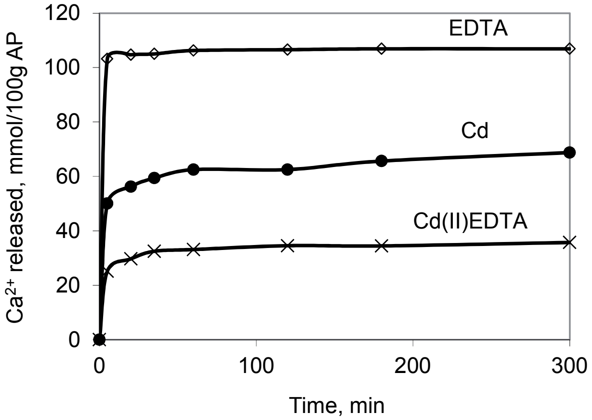

Figure 5 Kinetic curves of calcium release from apatite HA-5 in EDTA, Cd, and Cd-EDTA solutions (pH_{in}= 4)

As a result of reactions of AP with solution, the pH value changes considerably (Figure 6). Stabilisation of pH values takes place, similarly to Cd binding and Ca release, in 30–300 min, depending on the solution's composition. The greatest changes took place during the first 30 min. The shape of the curves are more complicated than that of the curves of cation concentration change in the solution, indicating that the final state is an equilibrium between several reactions occurring at different rates.

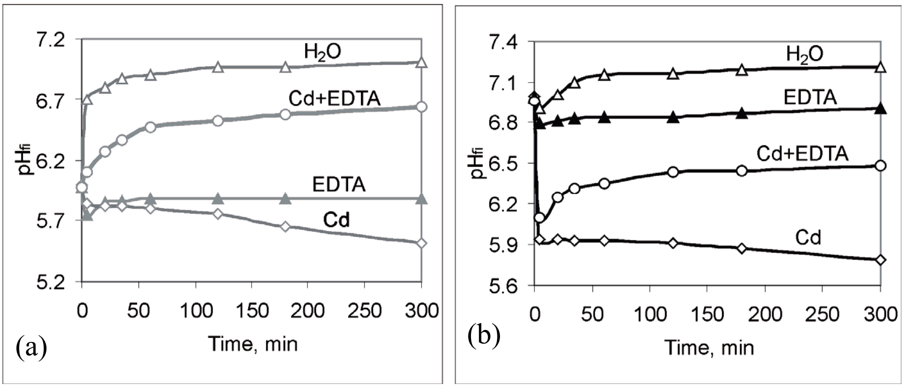

Figure 6 Change of pH with time in different solutions in the experiments with HA-5: a) pH_{in}=6; b) pH_{in}=7

Mostly, the necessary time to reach the equilibrium was about 24 h and though there was a slight increase in adsorption quantity after 24 h, that did not bring quantitatively any remarkable effect. Kinetic studies can be found where complete equilibrium was not achieved, even after some weeks or months of contact (Valsami-Jones *et al.*, 1998; Fedoroff *et al.*, 1999; Bailey *et al.*, 2005; Lee *et al.*, 2005). However, the different studies agree that cadmium and zinc immobilisation occurs through a two-step mechanism. The first phase is related to external surface sorption and sorption occurs instantaneously. The second phase is the gradual sorption stage before the metal uptake reaches equilibrium: rapid surface complexation followed by partial dissolution of apatite and ion exchange with Ca resulting in the formation of a metal-containing apatite. The presence of complexing ligands does not change the reaction kinetics observably.

4.2 pH importance and change in the metal ion sorption process on apatite

One of the most important parameters influencing sorption processes is pH, which controls not only dissociation of sorbent surface sites, but also the solution chemistry and the speciation of the metal cations.

AP exhibits large buffer capacity due to its surface amphoteric properties. Due to various processes that may occur at the solid surface/solution interface (preferential dissolution of certain constituents of crystal lattice, ionisation of surface groups, adsorption of ions or formation of complex compounds between surface groups and ions from the solution) the final pH values differ from the initial ones. It is found that for the initial pH range of 4–10, final pH values of AP suspensions are almost the same and equal/close to the pH_{PZC}. This is the pH value where the surface charge is equal to zero, namely, the pH at which the charge due to the positive surface groups is equal to negative ones (Mandjiny *et al.*, 1998; Smiciklas *et al.*, 2006; Smiciklas *et al.*, 2008).

The buffering characteristics of HAP surface are the result of acid–base reactions of the reactive surface sites in aqueous solutions (Wu *et al.*, 1991; Xu *et al.*, 1994):

$$\equiv PO^{-} + H^{+} \leftrightarrow \equiv P\text{–}OH \qquad (1)$$

$$\equiv Ca(OH)_2^{+} \leftrightarrow \equiv CaOH + H^{+} \qquad (2)$$

AP crystals begin to dissolve remarkably in pH regions lower than 4 (Harouiya *et al.*, 2007) and therefore it is not an effective sorbent material at acidic pHs. Due to this reason, present experiments mostly do not involve solutions with pHs below 4. The solubility of AP decreases with the increase of the solution pH.

Present studies comprise two kind of pH monitoring (Table 2):

1) the initial pH of sorption solution was fixed (pH_{in} = 4, 5, 6, 7) before AP addition and the pH was determined after certain time moments until the equilibrium was achieved (P I, II);

2) the initial solution composition was varied adding different amounts of H^+ or OH^- ions to get the final pH on a large scale (pH_{fin} = 4 - 11). The initial pH was not determined because it changed very quickly close to the equilibrium pH (P III, IV).

The sorption process of Cd^{2+} and Zn^{2+}, in the absence/presence of EDTA or HUM, caused the decrease of the final pH values. The most expressive results are presented in Figures 7 and 8. Without acid/base additions (H^+/OH^- added = 0, Fig. 8), the presence of Cd and/or Zn ions shifted the equilibrium pH to a lower value (Cd 5.65, Zn 5.15, Cd+Zn 4.85) compared with HAP suspension without heavy metals (7.54). A similar pH change took place in the experiments with FAP- if no acid/base was added, equilibrium pH was at 6.47 and in the presence of Cd, Zn and Cd+Zn ions was 5.18, 4.35 and 4.47, accordingly (Fig. 8a, b). The presence of EDTA and HUM does not change the equilibrium pH of HAP- and FAP-solution considerably. The main cause of pH shift is the metal sorption (Fig. 7, 8). The higher the amount of sorbed Cd and Zn, the greater the deviation of the equilibrium pH from pure apatite solution pH. A similar pH decrease is observed in previous studies (Mandjiny *et al.*, 1995; Corami *et al.*, 2007; Smiciklas *et al.*, 2008).

The drop in equilibrium pH suggests that H^+ ions are liberated from the solid surface into the aqueous phase as a result of the exchange with metal cations:

$$AP\text{–}OH + Me^{2+} \rightleftarrows AP\text{–}O\text{–}Me^{+} + H^{+} \qquad (3)$$

$$2AP\text{–}OH + Me^{2+} \rightleftarrows (AP\text{–}O)_2Me + 2H^{+} \qquad (4)$$

Therefore, decreases in final pH values suggest the formation of surface complexes (Xu et al., 1994; Smiciklas et al., 2006).

The impact of pH on apatite dissolution and metal sorption will be described in the next chapters.

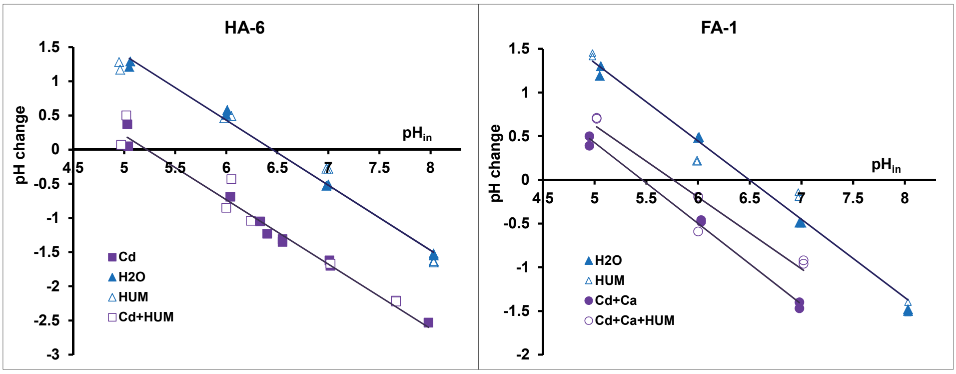

Figure 7 Change in solution pH as a result of the reaction with apatite

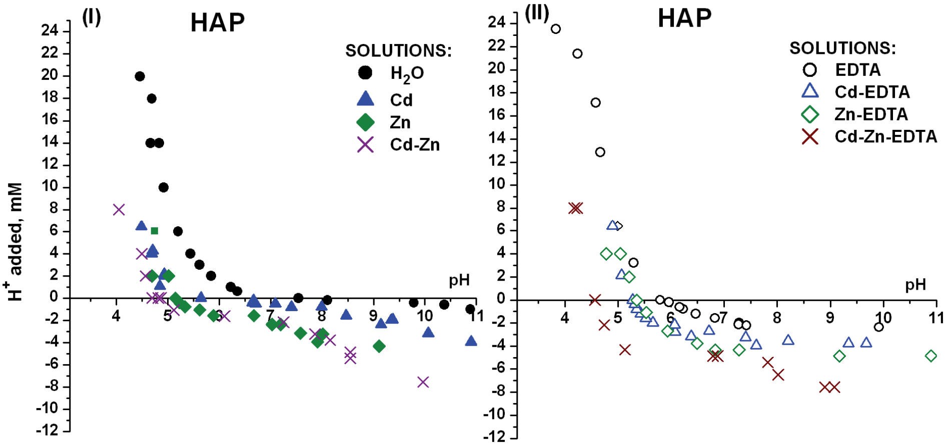

Figure 8a Dependence of equilibrium pH on the amount of H$^+$/OH$^-$ added in HAP(HA-9)- solutions in the absence (I) and presence (II) of EDTA

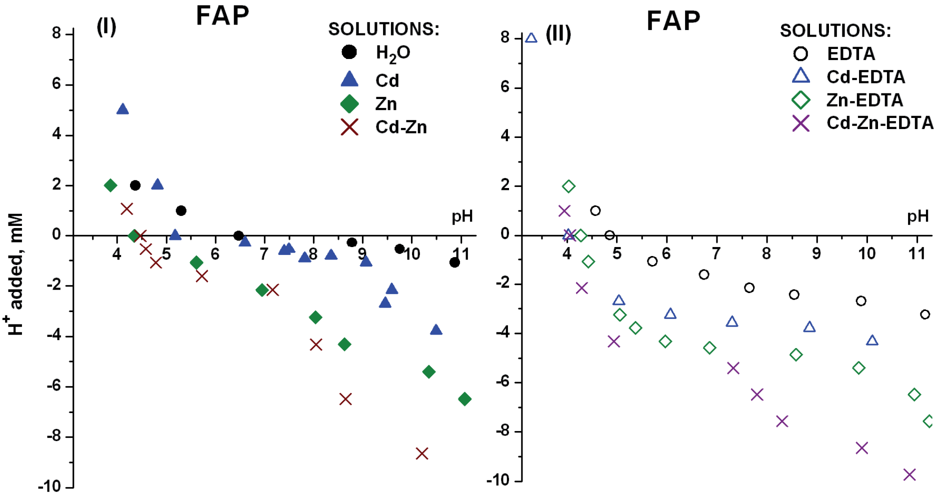

Figure 8b Dependence of equilibrium pH on the amount of H$^+$/OH$^-$ added in FAP(FA-2)- solutions in the absence (I) and presence (II) of EDTA

4.3 EDTA impact of Cd and Zn sorption on apatite

4.3.1 Cd and Zn sorption in the presence of EDTA

Initial pH adjusted (Paper I). The amounts of Cd bound with HAPs during 5 h are given in Table 3. It can be seen that binding capacity depends on the composition and characteristics of HAP. The amount of Cd bound increases a little with the increase in Ca/P ratio of apatite, but this is not a straight-forward relationship, because the SSA of the samples also affects the result. The biggest amount of Cd (66-68 mmol/100g AP) was bound with HAL-16F at pH_{in} 5–6 (Table 3). The influence of initial pH in the interval of 4–7 is not considerable because final pHs are close to each other and, therefore, the sorbed amount of Cd^{2+} is almost constant (Table 3). 70% of Cd was removed from the solution, which allows to conclude that the apatite sorption capacity was totally used.

Earlier results confirm that the most important parameter affecting the sorption capacity for Cd and Zn is the SSA (Peld *et al.*, 2004; Zhu *et al.*, 2008)– the sorption of metal ions grows with the growth of the SSA of APs. According to results in Table 3 it can be seen that the apatite composition also has a decisive effect- the amount of Cd bound is similar at HA-ff and HA-5, although the SSA-s are highly different- 37.9 and 85.5 m^2/g, accordingly. The reason for the high sorption capacity of HA-ff is Ca deficiency. At the same time, Ca excess (HAL-16F) has minor effect to the sorbed amount of Cd. The amount of bound metal in present studies is close to the amounts in other studies by APs with the same SSA (Valsami-Jones *et al.*, 1998; Smičiklas *et al.*, 2005; Zhu *et al.*, 2008; Sljivic *et al.*, 2009).

In the presence of EDTA, Cd binding with apatite decreased remarkably (Table 4). With HAL-16F it was approximately 10 % from the amount bound in Cd solution. The impact of EDTA was less remarkable for HA-5 and HA-ff. As it was expected from the Ca(II)EDTA and Cd(II)EDTA complex stability constants ($\log K_{Cd} = 16.5$, $\log K_{Ca} = 10.6$ (Kragten, 1978)), the formation of a more stable Cd(II)EDTA complex reduced the concentration of free Cd^{2+} ions and, as a consequence, Cd removal decreased. However, despite the equimolar amount of EDTA and Cd^{2+} ions in the solution, some part of Cd was bound with apatite.

Final pH adjusted (Paper III and IV). The change of total metal concentrations in solution – dissolved Ca, $[Ca^{2+}]_{sln}$) and removed Cd and Zn, $[Me^{2+}]_{sld}$) in single- and binary-metal systems with and without EDTA obtained by chemical analysis of solutions are presented in Figures 9 and 10 and Table 5.

The equilibrium pH in the interval 4–11 has a remarkable effect on the amounts of Cd bound. Results of the analysis of the solutions after equilibration show an increase in Cd sorption in the pH_{fin} range 4–11 in accordance with earlier studies (Chen *et al.*, 1997a; Smiciklas *et al.*, 2008). As pH_{fin} increased, the sorbed amount of Cd increased from 0.31 mM to 0.78 mM by HAP and from 0.18 mM to 0.69 mM by FAP. The sorbed amount of Zn was 0.54–1.44 mM by HAP and 0.65–1.08 mM by FAP (Table 5). In the pH_{fin} range 4–5, low sorption

Table 3. The amount of Ca^{2+} released and Cd^{2+} bound in water and Cd- 0.002 M solution during 5 h and the final pH of the solutions

Sample	pH_{in}	$Cd(NO_3)_2$ 0.002 M				Water	
		pH_{fin}	Released Ca^{2+} (mmol/100g AP)	Bound Cd^{2+} (mmol/100g AP)	Q_{sorb}^{*}	pH_{fin}	Released Ca^{2+} (mmol/100g AP)
HA-ff	6	5.37	47.5	55.2	1.16	7.04	2.2
	7	5.03	43.7	50.6	1.16	7.10	2.0
HA-5	4	5.62	63.7	50.2	0.79	7.00	6.1
	5	5.71	62.4	50.4	0.81	7.04	5.4
	6	5.74	56.5	48.9	0.86	7.08	5.2
	7	5.92	55.7	53.1	0.95	7.21	5.0
HAL-16F	4	5.83	87.6	51.6	0.59	6.89	7. 8
	5	×	82.8	66.1	0.80	7.07	5.6
	6	6.14	86.8	68.5	0.78	7.04	2.2
	7	5.99	86.9	61.2	0.70	7.10	2.0

Q_{sorb}^{*}: molar ratio of Cd^{2+} bound by AP to Ca^{2+} released from AP

Table 4. The amount of Ca^{2+} released and Cd^{2+} bound in EDTA and Cd(II)EDTA 0.002 M complex solution during 5 h and the final pH of the solutions

Sample	pH_{in}	Cd(II)EDTA 0.002 M				EDTA 0.002 M	
		pH_{fin}	Released Ca^{2+} (mmol/100g AP)	Bound Cd^{2+} (mmol/100g AP)	Q_{sorb}^{*}	pH_{fin}	Released Ca^{2+} (mmol/100g AP)
HA-ff	6	6.63	15.2	40.1	2.63	6.05	126.0
	7	6.71	14.1	31.9	2.27	6.97	108.0
HA-5	4	6.45	37.2	30.7	0.82	5.88	106.9
	5	6.81	21. 8	28.9	1.33	6.90	89.7
	6	6.88	20.6	28.4	1.38	6.23	130.7
	7	7.14	19.0	29.4	1.55	6.30	124.6
HAL-16F	4	7.20	28.6	10.2	0.34	6.50	123.6
	5	7.52	20.6	10.2	0.48	7.23	109.6
	6	7.64	10.7	6.3	0.55	6.05	126.0
	7	7.56	10.4	8.5	0.80	6.97	108.0

Q_{sorb}^{*}: molar ratio of Cd^{2+} bound by AP to Ca^{2+} released from AP of Cd^{2+} ions was caused by the competing effect of H^+ ions, and the increased solubility of the AP sorbent. At higher pH values the Cd and Zn concentration drops rapidly and metals are totally removed from the solution at pH 9.5. This is interpreted as the precipitation of hydroxides– the precipitation of $Zn(OH)_2$ starts at pH>7.5 and $Cd(OH)_2$ at pH>8.5 (Trussell & Wagner, 1996; Smiciklas *et al.*, 2000). Cd and Zn sorption by AP can be considered below these pH values because above these pHs the hydroxide precipitation is also responsible for metal removal from solution and, therefore, the results in the text and in Table 5 are given below these pHs.

The effect of different metal ions co-occurrence in a solution was studied by testing Cd-Zn binary solutions. The competition of metals (Cd+Zn) reduced individual sorption capacity up to 20% compared with the single component solutions (Fig. 10). The amount of Cd removed was 0.27–0.48 mM by HAP and 0.23–0.55 mM by FAP. The removed amount of Zn was 0.32–0.80 mM by HAP and 0.35–0.65 mM by FAP (Table 5).

However, the removed amount of Zn was higher than Cd in any case, but the total adsorption maximum on APs was approximately constant, irrespective of the solution's cation composition (63 mmol/100 g HAP, 60 mmol/100 g FAP). This means that the AP sorption capacity does not depend on the cation composition in solution. As already mentioned above, the maximum sorption capacity is an almost constant value per specific surface area of AP (Smičiklas *et al.*, 2005).

The presence of EDTA significantly reduced the amounts of Cd and Zn adsorbed (Figures 9, 10, Table 5) due to formation of EDTA complexes that does not adsorb on AP:

$$Me^{2+} + EDTA^{4-} + nH^{+} \leftrightharpoons Me(H)_{n}EDTA^{(2-n)-} \ (n = 0, 1) \qquad (5)$$

These complexes are very stable ($\log K_{Cd,Zn} = 16.5$, (Kragten, 1978)) and reduced the concentration of metal ions available to AP and, as a consequence, the metal removal significantly decreased. Moreover, these complexes retain metals in solution at pHs at which hydroxides could form ($Zn(OH)_2$ pH>7.5, $Cd(OH)_2$ pH>8.5), (Figures 9 and 10).

In binary metal systems the EDTA impact on the amount of metal removed was less remarkable because of the higher concentration of cations (4.1 mM of metals) in comparison with EDTA concentration (2 mM) in the solution. Accordingly, only part of the cations formed complexes with EDTA.

However, even in the presence of EDTA, the amount of Zn removed by AP stays higher compared with Cd and it can be concluded that Zn sorption was preferred.

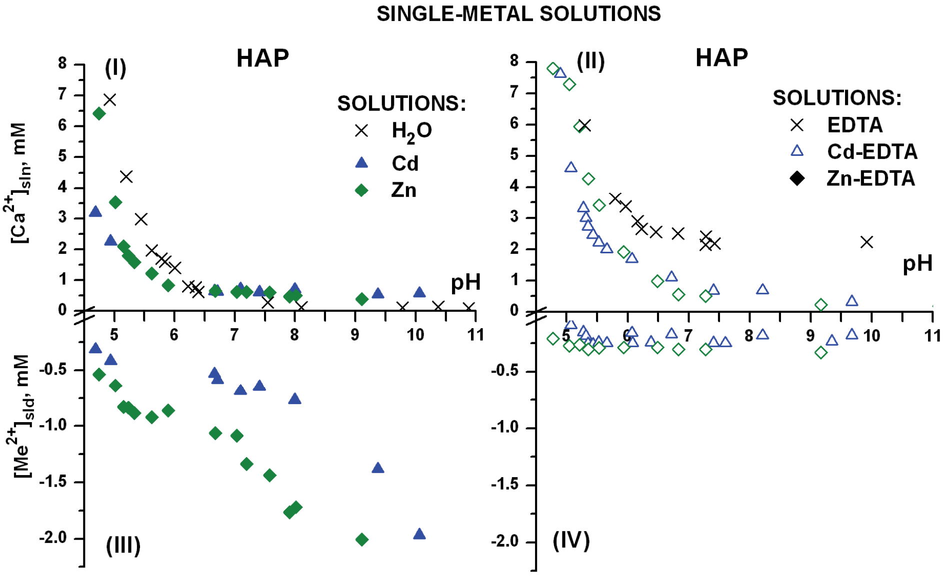

Figure 9a Dissolved Ca concentration ($[Ca^{2+}]_{sln}$) and removed Cd and Zn concentrations ($[Me^{2+}]_{sld}$) by HAP(HA-9) in the absence (I, III) and presence (II, IV) of EDTA in single metal solutions depending on equilibrium pH

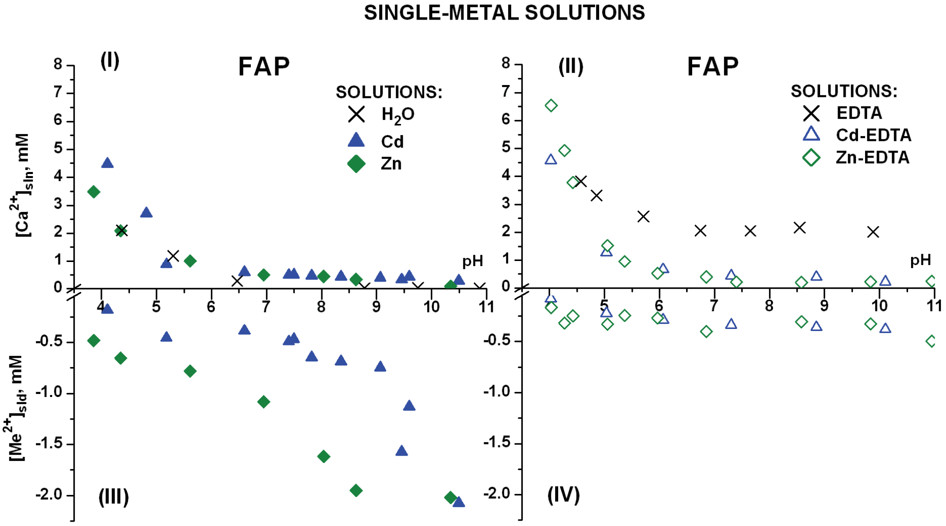

Figure 9b Dissolved Ca concentration ($[Ca^{2+}]_{sln}$) and removed Cd and Zn concentrations ($[Me^{2+}]_{sld}$) by FAP(FA-2) in the absence (I, III) and presence (II, IV) of EDTA in single metal solutions depending on equilibrium pH

**$[Me^{2+}]_{sld}$- negative sign denotes the amount of metals removed from solution that is equal to amount of metals in solid phase*

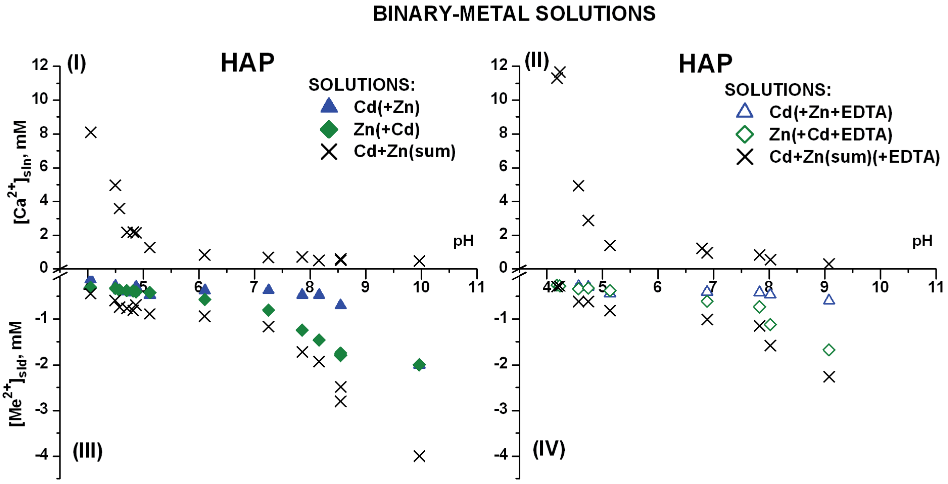

Figure 10a Dissolved Ca concentration ($[Ca^{2+}]_{sln}$) and removed Cd and Zn concentrations ($[Me^{2+}]_{sld}$) by HAP(HA-9) in the absence (I, III) and presence (II, IV) of EDTA in binary metal solutions depending on equilibrium pH

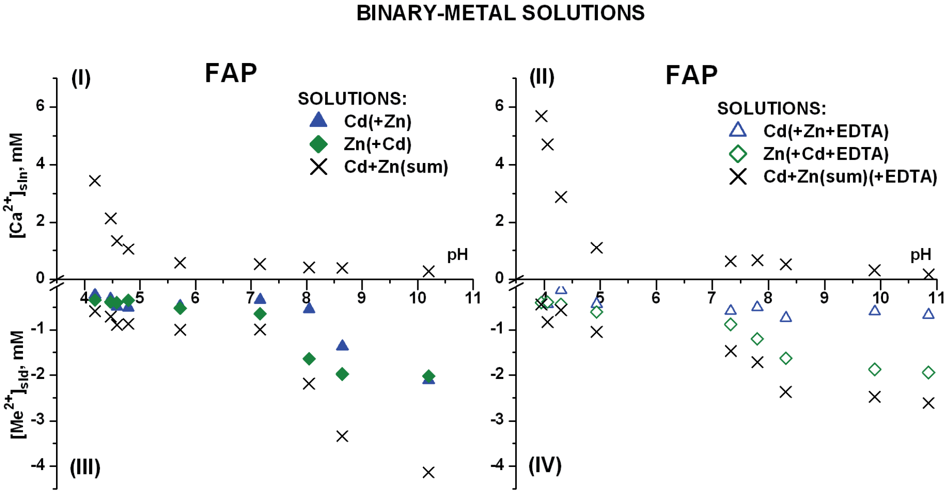

Figure 10b Dissolved Ca concentration ($[Ca^{2+}]_{sln}$) and removed Cd and Zn concentrations ($[Me^{2+}]_{sld}$) by FAP(FA-2) in the absence (I, III) and presence (II, IV) of EDTA in binary metal solutions depending on equilibrium pH

**$[Me^{2+}]_{sld}$- negative sign denotes the amount of metals removed from solution that is equal to amount of metals in solid phase*

Table 5. Lowest and highest sorbed amount of Cd and Zn in single- and binary-metal solutions in the absence/presence of EDTA in the studied pH range ($Cd(OH)_2$ and $Zn(OH)_2$ precipitation excluded)

	Solution	**HAP**			**FAP**		
		pH	mM	mmol/100g	pH	mM	mmol/100g
SINGLE METAL	Cd	4.69	0.31	16	4.11	0.18	10
		7.99	0.78	38	8.35	0.69	34
	Cd+EDTA	4.90	0.04	2	4.03	0.08	4
		8.21	0.23	9	7.30	0.34	17
	Zn	4.74	0.54	27	4.35	0.65	33
		7.58	1.44	72	6.95	1.08	54
	Zn+EDTA	4.78	0.21	10	4.28	0.32	16
		7.28	0.30	15	7.40	0.31	15
BINARY METAL	Cd(+Zn)	4.49	0.27	14	4.19	0.23	11
		8.16	0.48	23	8.05	0.55	27
	Zn(+Cd)	4.49	0.32	16	4.19	0.35	17
		7.25	0.80	40	7.16	0.65	33
	Cd(+Zn+EDTA)	4.57	0.28	13	4.30	0.13	10
		8.02	0.46	23	7.33	0.59	30
	Zn(+Cd+EDTA)	4.57	0.33	17	4.30	0.44	22
		7.83	0.73	34	7.33	0.88	44

4.3.2 Apatite dissolution in the presence of EDTA

As can be seen in Figure 11, the solution composition has a remarkable effect on Ca solubility, contrary to initial pH (Table 3, 4). Because the final pH values are similar, the dissolution rate is not affected remarkably by pH_{in}. The amount of Ca released was the highest in EDTA solutions *(Ca complexation with EDTA*), it was lower in Cd solutions (*ion exchange with Cd*), and decreased by more than two times in Cd(II)EDTA complex solution *(EDTA complex with Cd is more stable than with Ca, therefore Cd is in complex with EDTA and can not be changed with Ca)*, (Fig. 11). The pH_{in} has a bigger impact in EDTA-containing samples because of EDTA complexation with the Ca^{2+} ions from the AP surface, therefore changing the surface properties. The composition of AP has a notable effect on dissolved amount, which decreases with a decrease of Ca/P ratio (Table 3, 4).

Adjusting the final pH to a larger scale means the considerable increase in the amounts of H^+ and OH^- ion addition (Fig. 8), therefore the effect of final pH on Ca solubility is remarkable– the apatite dissolution rate (according to $[Ca^{2+}]_{sln}$) decreased in accordance to the final pH increase (Fig. 9, 10). The presence of metal ions decreased HAP solubility at pH < 6.5 (Fig. 9aI). This is explained by the formation of the new heavy-metal-containing surface phase, which has lower solubility than the initial HAP. The new Cd/Zn-containing layer isolates the surface of grains, thereby reducing solubility (Valsami-Jones *et al.*, 1998; Charlet *et al.*, 2006; Corami *et al.*, 2007). This is more noticeable for HAP because of higher solubility compared with FAP (Zhu *et al.*, 2009).

In the presence of EDTA, the dissolution of HAP as well as FAP is increased due to the high stability of Ca^{2+}-EDTA complexes (log K_{Ca} = 10.6, (Kragten, 1978)):

$$EDTA^{4-} + nH^+ \leftrightharpoons H_nEDTA^{(n-4)+} \ (n = 1, 2, 3, 4) \quad (6)$$

$$EDTA^{4-} + nH^+ + Ca^{2+} \leftrightharpoons CaH_nEDTA^{(n-2)+} \ (n = 0, 1) \quad (7)$$

The effect of EDTA on AP solubility is remarkable above pH_{fin}= 5 in the case of HAP and in the whole investigated pH range in the case of FAP (Fig. 9) in comparison with AP's solubility in water.

Phosphorus dissolved only at acidic pHs (Tables 7 and 8) and above pH 5 it was negligible.

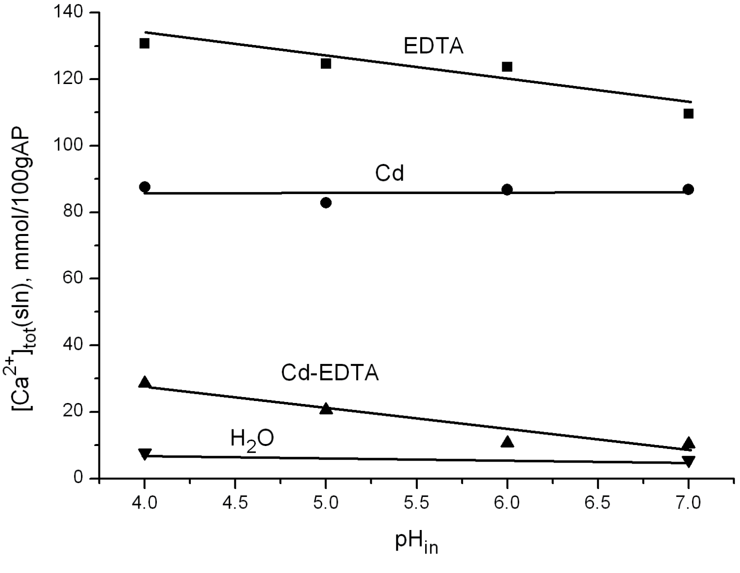

Figure 11 The impact of solution initial pH on Ca^{2+} dissolution from HAP (HAL-16F) in different solutions, experimental results (symbols) and trendlines

4.4 Humic substance impact on Cd sorption on apatite

4.4.1 Cd sorption in the presence of humic substance

The presence of HUM (Paper II) at 0.5 mg/100 mg AP (soluble form) did not affect the amount of Cd sorbed considerably in the initial pH range from 5 to 8 (Fig. 12). The remarkable difference of Cd sorption capacity is between HAP and FAP (21–27 and 15–20 mmol/100 g AP, respectively), which is explained by their different SSA values.

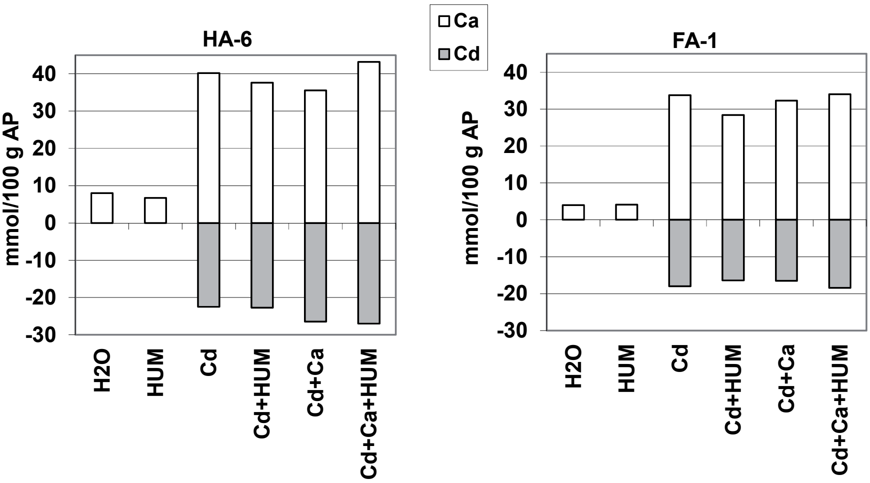

Figure 12 Changes in solution composition in the Cd sorption experiments with and without soluble HUM

The results of thermal analysis (p.81 in P II) of solid residues after sorption experiments revealed that HUM adsorbs on apatites. The amount of HUM adsorbed on AP in water and Cd-containing solution was almost the same and was equal to the amount of HUM in the solution. The amounts of HUM precipitated on AP were higher after desorption experiments carried out in HUM-containing solutions. These results indicated that HUM were readily adsorbed on AP, as found previously (Vermeer *et al.*, 1999; Borghetti *et al.*, 2003).

The layer of HUM on the crystal surface alters the chemical and physical characteristics of the solid phase. It was found that humic acids are able to block the crystal growth by inhibiting any further precipitation of apatite onto the crystal surface. In reality apatite can be completely or partially covered by humic acid molecules (Borghetti *et al.*, 2003) and this can change the Cd sorption mechanism with apatite.

The impact of soluble HUM on the AP Cd-binding was not observed in the binding experiments in the pH range studied despite the humic acid's ability to remove metals from solutions at an acidic pH (Coles & Yong, 2006).

4.4.2 Ca dissolution in the presence of humic substance

Apatite (Ca) dissolved slightly in H_2O and HUM solutions (Fig. 12). Cd sorption increased the amount of dissolved Ca owing to the ion exchange with apatite. The adsorption of humic matter on an AP surface, which hinders the dissolution process, explains the lower dissolution of Ca^{2+} in HUM-containing solutions (Fig. 12).

4.5 Sorption mechanism

To ascertain the predominant sorption mechanism the following approaches were used:

- the analysis of molar ratio (Q_{sorb}) of cations bound by AP to Ca^{2+} released from AP and equilibrium pH,
- the analysis of structural changes caused by metal sorption (XRD),
- the analysis of surface composition (XPS), and
- thermodynamic modelling.

4.5.1 Molar ratio of cations bound to Ca^{2+} released

Taking into account that the mole ratio of metal ions bound by AP to Ca^{2+} ions released from AP (Q_{sorb}) can characterise the main mechanism of the sorption process, some conclusions can be made (Peld *et al.*, 2004). When $Q = 1$, the quantities of the cations bound and released are equal, which represents the ion exchange of cations between the AP and solution. However, the dissolution–precipitation can also take place with the same proportion of cations. $Q > 1$ indicates that nonstoichiometric sorption (surface complexation or filling of cationic vacancies in crystal lattice) dominates. When $Q < 1$, dissolution of solid phase and precipitation of a new phosphate phase with a lower cation to phosphate molar ratio occurs. These processes may also occur simultaneously, which complicates the estimation of the sorption mechanism.

Q_{sorb} values of the experiments with APs of different Ca/P ratios, given in Table 3 and Table 4, indicate that the sorption mechanism depends on the composition of AP and solution composition. For HA-ff (Ca/P=1.44) Q_{sorb} is slightly over 1 in Cd solution (Table 3), which is expected in the case of ion exchange and of filling cationic vacancies in AP structure. For HA-5 (Ca/P=1.66) $Q_{\mathrm{sorb}} \leq 1$ in Cd solution, that corresponds to an ion exchange type process. Taking into account increased Ca release, the formation of new phosphate phase, having lower cation to phosphate molar ratio, is also possible. In the case of Ca excess in HAL-16F (Ca/P=1.94) Q_{sorb} is the lowest, which could be explained by higher and faster Ca solubility from the impurity phases like $CaCO_3$ or $Ca(OH)_2$ as compared to that from apatite. With the samples HA-ff and HA-5, Q_{sorb} increases in the Cd(II)EDTA complex solution (Table 4), which evidently indicates Cd binding due to adsorption. The ion exchange and dissolution of AP and precipitation of a new Cd-bearing solid phase can be presumed to be dominant sorption mechanisms also in the presence of HUM, where more cations were released in respect to the amount of cations sorbed ($Q_{\mathrm{sorb}} \leq 1$), (Fig. 12).

As already mentioned, the main interactions responsible for the surface properties of AP in aqueous solutions are surface reactions (1) and (2). According to this, the positively charged $\equiv CaOH_2^+$ and neutral $\equiv POH^0$, $\equiv PO_xH_2$ and $\equiv PO_xH$ sites must prevail on the AP surface in acidic solutions (Jarlbring *et al.*, 2006), making surface charge in this pH region positive and at higher pH values negative. Cadmium exists in such a solution only in the form of Cd^{2+} ions, since no hydrolysis takes place at pH values lower than 8.5 (Smiciklas *et al.*, 2000). Consequently, Cd^{2+} could be bound, more or less, by ion exchange in accordance with the Q_{sorb} value.

According to the batch experiments, HAP solubility is lowered in the presence of heavy metals at more acidic pHs (pH>6.5). At the same time, at near to neutral and alkaline pHs, $[Ca^{2+}]_{\mathrm{sln}}$ values are higher than in the metals-excluded AP system (Fig. 9, 10). This observation also reflects the replacement of Ca from AP due to ion exchange reactions:

$$AP–Ca^{2+} + Me^{2+} = AP–Me^{2+} + Ca^{2+} \qquad (8)$$

However, the Q_{sorb} is only an evaluative parameter and does not afford more information about the mechanism. The sorption mechanism in the absence/presence of EDTA is explained in detail with the help of XPS-analysis and modelling (following paragraphs).

4.5.2 Apatite crystal morphology and structure analyses

SEM images reveal preservation of the morphology and size of AP crystals in the Cd sorption process (Fig. 12) similar to the earlier results (Jeanjean *et al.*, 1996; Chen *et al.*, 1997b; Yasukawa *et al.*, 2007).

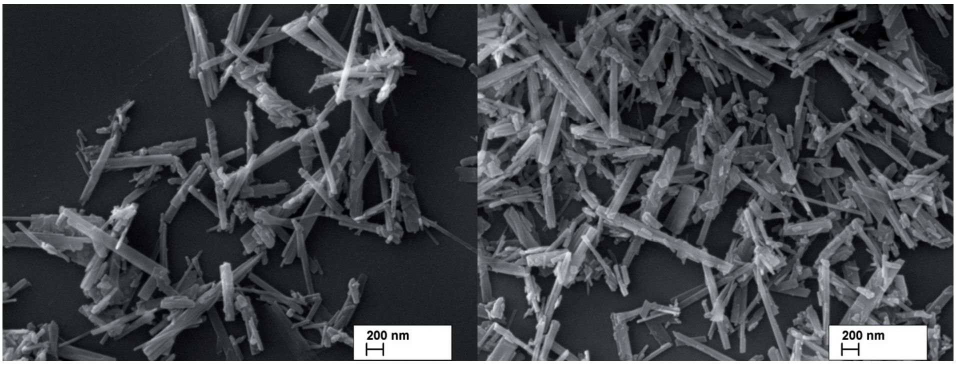

Figure 13 SEM images before (left) and after (right) Cd sorption on HA-6 at pH 6.8

The concentration of sorbed cations in the solid phase (atomic ratio of metal/Ca ≈ 0.05) is often too small to induce significant changes of cell parameters of apatite. Therefore XRD, particularly in the case of a multi-component solution, does not reveal recognisable changes in the solid phase.

In accordance with the fit of the Cd atom into the AP structure (ion radius of Cd^{2+} (0.97 Å) slightly differs from that of Ca^{2+} (0.99 Å) (King, 2005)), the substitution causes very little change of the unit cell parameters. Table 6 presents the unite cell parameters calculated from XRD patterns of the original HA-6 powder and Cd^{2+}-loaded samples. Small structural changes of HAP were detected in the solid residue obtained after interaction with 2 mM Cd^{2+} solution.

The unit cell parameters of the starting HAP were a=b=9.442 Å and c=6.874 Å, while values of a=b=9.434/9.433 Å and c=6.871/6.896 Å were calculated for the Cd-exchanged sample. The presence of EDTA did not change these values remarkably. The slight decrease in unit cell parameters is in agreement with the lower ionic radii of the Cd^{2+} ion. These data support the ion-exchange mechanism for Cd^{2+} sorption by HAP (Smiciklas *et al.*, 2006; Zhu *et al.*, 2008; Terra *et al.*, 2010).

Table 6. Apatite unit cell parameters before and after Cd sorption on HA-6

Sample	Parameters		Cell volume	Cd_{sld}/Ca_{sld}
	a [Å]	*c* [Å]	Å^3	
HA-6	9.442	6.874	530.67	–
HA-6+Cd (pH_{fin}=6.86)	9.434	6.871	529.64	0.022
HA-6+Cd (pH_{fin}=7.88)	9.433	6.896	531.40	0.045
HA-6+Cd+EDTA (pH_{fin}=6.91)	9.434	6.869	529.44	0.006

4.5.3 Apatite surface X-ray photoelectron spectroscopy analysis

To elucidate heavy metal sorption mechanisms on AP, more information is obtained by X-ray photoelectron spectroscopy (XPS), which shows exact surface composition before and after reaction with Cd and Zn (Marchat *et al.*, 2006; Yasukawa *et al.*, 2007; Zhang *et al.*, 2009). Results based on XPS-analysis can be found in Papers III and IV. The XPS spectra are included in Appendix A.

The results of AP XPS analyses before and after sorption experiments are given in Figure 14 and in Tables 7 and 8. The mole ratios in bulk solid are calculated according to solution analyses. XPS data demonstrated significant changes of AP surface composition and the difference from bulk composition (in terms of atomic ratios of Ca/P, Cd/Ca, and Zn/Ca) after equilibration in sorption solutions.

In metal solutions, the amount of metals at the surface of the AP particles increased with pH increase (Cd/Ca = 0.27–0.75, Zn/Ca = 0.16–1.03, (Cd+Zn)/Ca = 0.35–1.89). In the same time, Ca/P atomic ratio decreased due to heavy metal sorption (HAP: 1.24 → 1.03–1.09 by Cd, 1.11–1.12 by Zn, 1.02–1.07 by Cd+Zn; FAP: 1.29 → 1.01–1.12 by Cd, 1.11–1.16 by Zn, 1.00–1.09 by Cd+Zn) and remained practically constant at all pH-s (Table 7, 8). The corresponding mean atomic ratio (Ca+Cd+Zn)/P (1.4 ± 0.1) (Fig. 14) at the surface was higher than the AP initial Ca/P ratio (1.24/1.29) and did not change remarkably up to pH 7.5. Further prominent increases in Cd and Zn surface concentration at the highest pHs was related to the disappearance of metal ions from the solution caused by $Cd(OH)_2$ and $Zn(OH)_2$ precipitation.

The amount of Cd at the surface was noticeably lower in the presence of EDTA (Cd/Ca = 0.14–0.22, Zn/Ca = 0.02–0.04, Table 7, 8). However, the atomic ratio (Ca+Cd)/P remained almost the same (1.4 ± 0.1), (Fig. 14).

According to XPS results, the impact of EDTA to the (Cd+Zn)/Ca ratio in binary-metal solution was less remarkable because of the higher concentration of cations (4.1 mM of metals) in comparison with EDTA concentration (2 mM) in the solution. Accordingly, only part of the cations formed complexes with EDTA.

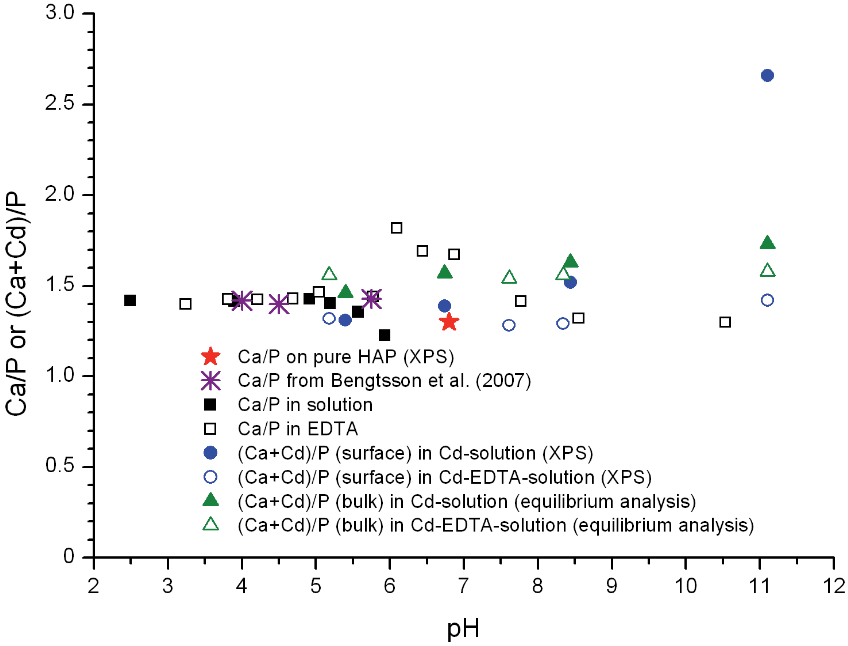

Figure 14 The Ca/P ratio in solution and (Ca+Cd)/P on HA-6 according to equilibrium and XPS analysis

The difference of total Ca/P and (Cd+Zn)/Ca ratios of solids according to chemical analysis and on the surface (XPS) indicates that the AP surface differs from whole bulk and that metals are concentrated on apatite surface in accordance with earlier results, where it is found that the sorption of metal ions occurs only on the surface phase of apatite particles (Badillo-Almaraz *et al.*, 2003; Marchat *et al.*, 2006; Yasukawa *et al.*, 2007; Zhang *et al.*, 2009). The changes of atomic ratios on the surface indicate that the heavy metal removal mechanism differs depending on pH (ion exchange and new surface formation *vs* hydroxide precipitation), (Table 7, 8).

However, it is important to notice that the total cations ratio to phosphorus increases when metal ions are sorbed (1.24/1.29 → 1.4 ± 0.1) and remains practically constant (irrespective of solution composition), except for the highest pH values studied (Fig. 14), indicating the ion exchange $Ca^{2+} \leftrightarrow Me^{2+}$ and a formation of new surface solid-solution phase.

It should also be mentioned that the depth of XPS analysis at apatite's surface is approximately 6 nm, and the atomic ratios discussed above represent average values within this surface layer.

Table 7. The composition of solution, bulk solid and surface of HAP (HA-9)

SOLUTION					**BULK SOLID**		**SURFACE (XPS)**				
pH	Ca, mM	P, mM	Cd, mM	Zn, mM	(Ca+Cd+Zn)/P	(Cd+Zn)/Ca	Ca/P	Cd,at%	Zn,at%	(Ca+Cd+Zn)/P	(Cd+Zn)/Ca
HAP											
7.54	0.29	0	–	–	1.59	–	1.24	–	–	–	–
HAP + 2.1 mM Cd											
4.94	2.26	0.85	1.70	–	1.56	0.025	1.03	3.26	–	1.31	0.27
6.71	0.63	0	1.53	–	1.61	0.032	1.09	4.68	–	1.44	0.33
9.37	0.54	0	0.73	–	1.68	0.075	1.05	7.49	–	1.84	0.75
HAP + 2.1 mM Cd + 2 mM EDTA											
5.07	4.60	2.73	2.02	–	1.59	0.007	1.13	2.19	–	1.29	0.14
6.72	1.10	0	1.94	–	1.54	0.010	1.11	2.41	–	1.30	0.17
9.35	0.15	0	1.87	–	1.62	0.012	1.22	2.54	–	1.44	0.18
HAP + 2 mM Zn											
4.70	3.47	1.69	–	1.31	1.59	0.045	1.12	–	2.97	1.34	0.20
6.68	0.65	0	–	0.96	1.65	0.058	1.11	–	5.08	1.51	0.36
9.11	0.40	0	–	0.02	1.75	0.108	1.12	–	11.1	2.28	1.03
HAP + 2 mM Zn + 2 mM EDTA											
4.78	7.80	4.37	–	1.81	1.54	0.018	1.25	–	0.34	1.28	0.02
6.83	0.55	0.35	–	1.72	1.65	0.017	1.28	–	0.36	1.31	0.02
9.17	0.23	0	–	1.69	1.62	0.017	1.30	–	0.63	1.35	0.04
HAP + 2.1 mM Cd + 2 mM Zn											
4.87	2.16	0.71	1.84	1.60	1.58	0.040	1.02	2.99	1.49	1.38	0.35
6.10	0.82	0	1.76	1.43	1.62	0.051	1.04	3.12	2.33	1.46	0.40
8.55	0.50	0	1.43	0.24	1.78	0.134	1.07	3.83	11.0	3.09	1.89
HAP + 2.1 mM Cd + 2 mM Zn + 2mM EDTA											
4.23	11.9	5.97	2.13	1.73	1.31	0.036	1.08	1.90	0.87	1.30	0.21
6.79	1.21	0	1.70	1.31	1.61	0.063	1.00	2.76	2.28	1.46	0.46
8.90	0.24	0	1.54	0.35	1.78	0.120	1.08	3.49	6.97	2.36	1.18

Table 8. The composition of solution, bulk solid and surface of FAP (FA-2)

SOLUTION					BULK SOLID		SURFACE (XPS)				
pH	Ca, mM	P, mM	Cd, mM	Zn, mM	(Ca+Cd+Zn)/P	(Cd+Zn)/Ca	Ca/P	Cd, at%	Zn, at%	(Ca+Cd+Zn)/P	(Cd+Zn)/Ca
FAP											
6.47	0.28	0	–	–	1.66	–	1.29	–	–	1.29	0
FAP + 2.1 mM Cd											
5.16	0.88	0	1.67	–	1.64	0.025	1.01	3.94	–	1.31	0.30
7.49	0.52	0	1.64		1.68	0.025	1.12	3.93	–	1.43	0.28
FAP + 2.1 mM Cd+ 2 mM EDTA											
5.10	1.29	0.42	1.85	–	1.83	0.012	1.21	2.29	–	1.41	0.16
7.33	0.47	0	1.78	–	1.67	0.018	1.15	2.96	–	1.40	0.22
FAP + 2 mM Zn											
4.34	2.22	1.70	–	1.33	1.78	0.038	1.16	0.06	2.35	1.35	0.16
6.97	0.49	0.28	–	0.92	1.75	0.058	1.11	0.06	6.16	1.59	0.43
FAP + 2mM Zn+ 2mM EDTA											
5.05	1.53	0.84	–	1.68	1.70	0.019	1.26	–	0.55	1.30	0.03
8.58	0.19	0	–	1.71	1.69	0.016	1.26	–	0.29	1.29	0.02
FAP + 2.1 mM Cd + 2.1 mM Zn											
4.83	1.11	0.49	1.60	1.70	1.75	0.048	1.00	3.39	1.44	1.36	0.35
8.05	0.42	0.00	1.55	0.37	1.83	0.116	1.09	2.95	8.95	2.50	1.30
FAP + 2.1 mM Cd + 2 mM Zn + 2mM EDTA											
4.95	1.1	0.63	1.63	1.37	1.78	0.058	1.12	3.21	0.65	1.45	0.29
7.81	0.66	0.00	0.08	0.82	1.77	0.092	1.11	2.92	4.28	1.84	0.66

4.5.4 Modelling

Surface complexation modelling, in conjunction with X-ray photoelectron spectroscopy (XPS), provides valuable insights into the mechanism of enhancement for the Cd(II)–Zn(II)–EDTA–AP system (P III, IV).

The information from the chemical analyses and XPS data was used to design an equilibrium model that takes into account dissolution, solution and surface complexation, as well as possible phase transformations. The total concentration of calcium, phosphate, EDTA, and cadmium in solution were used in the equilibrium calculations. The model used in the present work are developed assuming a constant capacitance for the electrical double layer at the surface. In the calculations the computer code WinSGW (Karlsson & Lindgren, 2006), which is based on the SOLGASWATER algorithm (Eriksson, 1979), was used. The details of model construction are presented in Paper III (Chapter 3, "Modelling").

Based on a Ca/P atomic ratio of 1.4 (Fig. 14, HA-6) the composition of the surface is assumed to be $Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ (Bengtsson *et al.*, 2009). It has been suggested that the HAP surface undergoes a change when it comes into contact with an aqueous solution, and creates vacancies on Ca and OH sites and protonation of phosphate groups (Brown & Martin, 1999; Garcia Rodenas *et al.*, 2005; Rey *et al.*, 2007).

Experimental $[Ca^{2+}]_{tot}$(sln) and $[HPO_4^{2-}]_{tot}$(sln) were used to calculate the dissolution constant of HAP:

$$\log K_s(Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s) + 4.8H^+ \leftrightharpoons \\ 8.4Ca^{2+} + 6HPO_4^{2-} + 0.4H_2O) = -19.34 \pm 0.05.$$

As can be seen from Fig. 15 and 16, this constant gives a good explanation to experimental solubility data.

Modelling results also showed that the solubility of HAP with respect to $[HPO_4^{2-}]_{tot}$(sln) decreases with increasing additions of Cd at all pH-values (Fig. 16). This is also the case with respect to $[Ca^{2+}]_{tot}$(sln) and pH≤ 6.5 (Fig. 15). At higher pH values the $[Ca^{2+}]_{tot}$(sln) values are higher than in the pure HAP-system with 2 mM Cd solution. This observation reflects the replacement of Ca from HAP due to ion exchange reactions like (9) or (10):

$$\equiv CaOH + nH^+ + Cd^{2+} \leftrightharpoons \equiv CdOH_{n+1}^{n+} + Ca^{2+} \ (n = 0, 1) \qquad (9)$$

$$Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s) + xCd^{2+} \leftrightharpoons$$

$$Ca_{8.4-x}Cd_x(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s) + xCa^{2+} \qquad (10)$$

The formation of a solid solution acc. (10) had found to be more likely than the formation of a surface complex acc. (9). This is because of the high adsorption capacity of HAP in relation to the low surface site concentration of ≡CaOH sites (0.57 mM).

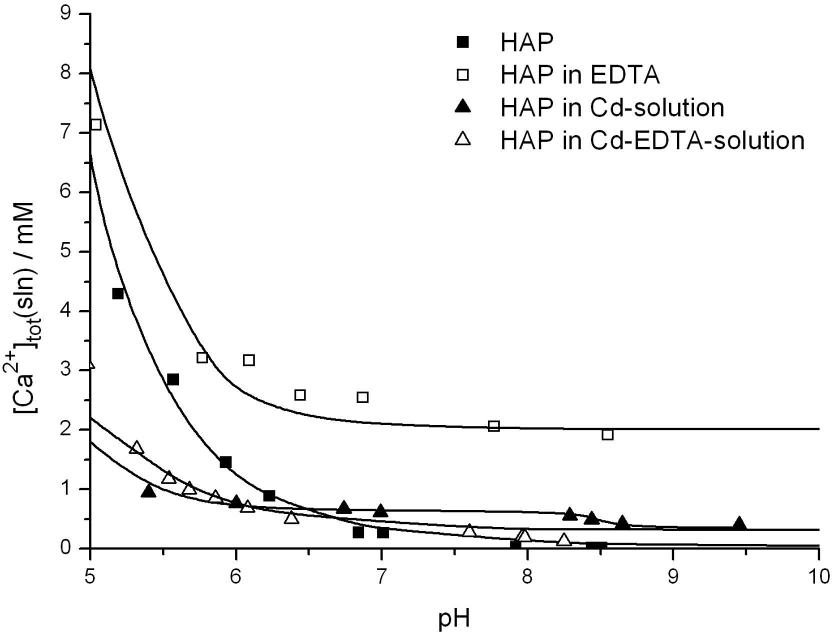

Figure 15 The impact of solution final pH to Ca^{2+} dissolution from AP HA-6 in different solutions, experimental (symbols) and calculated results (lines)

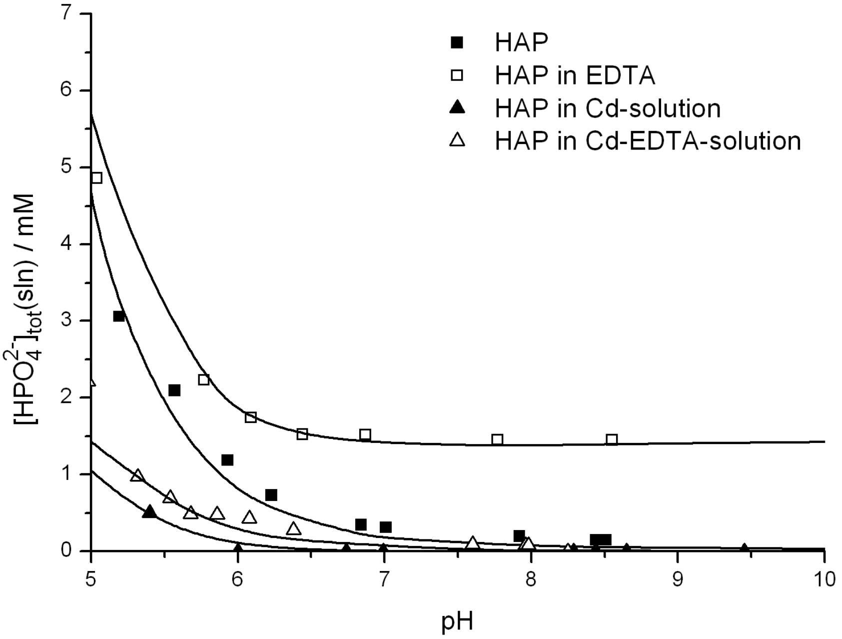

Figure 16 The impact of solution final pH to HPO_4^{2-} dissolution from AP HA-6 in different solutions, experimental (symbols) and calculated results (lines)

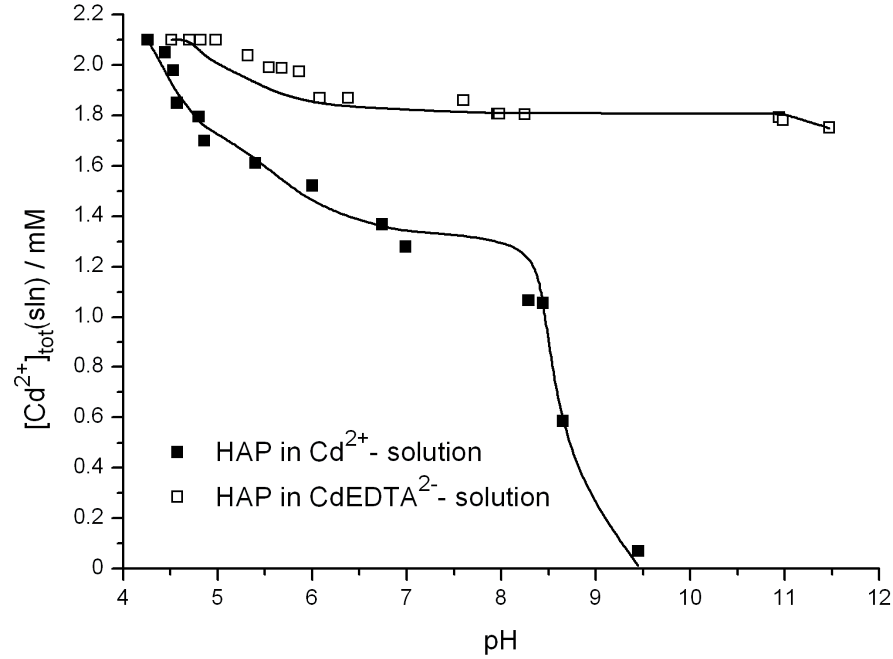

Figure 17 Experimental (symbols) and calculated (lines) results of Cd^{2+} *sorption on HAP in Cd- and Cd-EDTA-solution*

HAP and $CdEDTA^{2-}$. Based on equilibrium solution analysis results, a calculation of the composition of Cd-containing HAP phase (assuming a homogeneous distribution) results in a Cd/Ca ratio of 0.004–0.009 (Table 3 in Paper III). However, results from the XPS analysis show a much higher ratio (0.15-0.18). This implies that the reacted Cd is present within a surface layer of the HAP particles. By assuming the solid solution composition and by considering the different XPS results in terms of Cd/Ca ratios an approximate composition can be calculated. A series of calculations were performed with intervals of Cd/Ca of 0.1 to 0.2 and the "best" fit for Cd-EDTA solution was obtained for Cd/Ca = 0.1 giving

$$\log K_s(Ca_{7.6}Cd_{0.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s) + 4.8H^+ \leftrightharpoons$$

$$7.6Ca^{2+} + 0.8Cd^{2+} + 6HPO_4^{2-} + 0.4H_2O) = -28.03 \pm 0.07.$$

In these calculations the total concentrations of Ca and HPO_4^{2-} of the Cd-containing surface layer have to be given as input values. As can be seen from Figures 15, 16 and 17 the fit of the model to experimental $[Ca^{2+}]_{tot}(sln)$, $[HPO_4^{2-}]_{tot}(sln)$ and $[Cd^{2+}]_{tot}(sln)$, data is good. A distribution diagram showing the Cd-speciation (Cd^{2+}, $CdEDTA^{2-}$, $Ca_{7.6}Cd_{0.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$) is shown in Fig. 18.

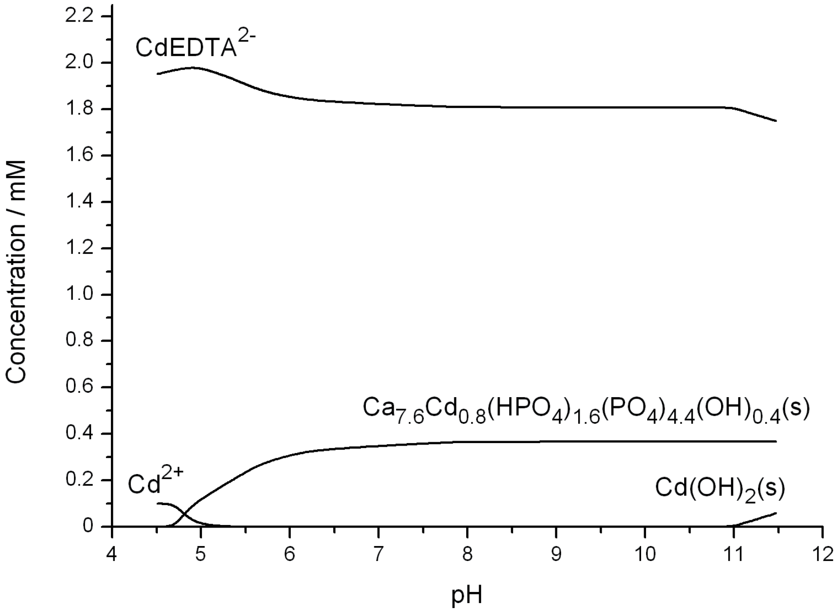

Figure 18 The speciation of Cd in Cd-EDTA-solution

HAP and Cd^{2+}. The interaction between Cd^{2+} in solution and HAP particles starts at pH ≈ 4.4 and increases with increasing pH (Fig. 17). Again, the XPS analysis shows a HAP surface enriched in Cd with a Cd/Ca ratio increasing from 0.29 to 1.7 with increasing pH (Table 3 in Paper III). The value at pH 11.1 indicates the formation of a $Cd(OH)_2$ precipitate (which also is postulated from the equilibrium analysis). In Cd solution the Ca/Ca ratio calculation interval was 0.2-0.3 and the best fit obtained for composition with $\log K_s(Ca_{5.6}Cd_{2.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}) = -27.39 \pm 0.06$. Figures 15–17 show a good agreement between experimental data, ($[Ca^{2+}]_{tot}$(sln), $[HPO_4^{2-}]_{tot}$(sln) and $[Cd^{2+}]_{tot}$(sln)) and the corresponding calculated values. The equilibrium analysis also showed the formation of $Cd(OH)_2(s)$ with $pH \geq 8$. The different phase distributions with pH are shown in Fig. 19. Both of the Cd-containing HAP phases are formed at this high Cd concentration. It seems likely that there is a Cd-gradient from the surface with the Cd-rich phase being formed in the topmost layer. However, data showing this is not available at present. Cd near-surface depth profile can be reconstructed using angle-resolved XPS. Unfortunately, such data are possible to acquire only with monocrystal surfaces, which is not the case for powder samples.

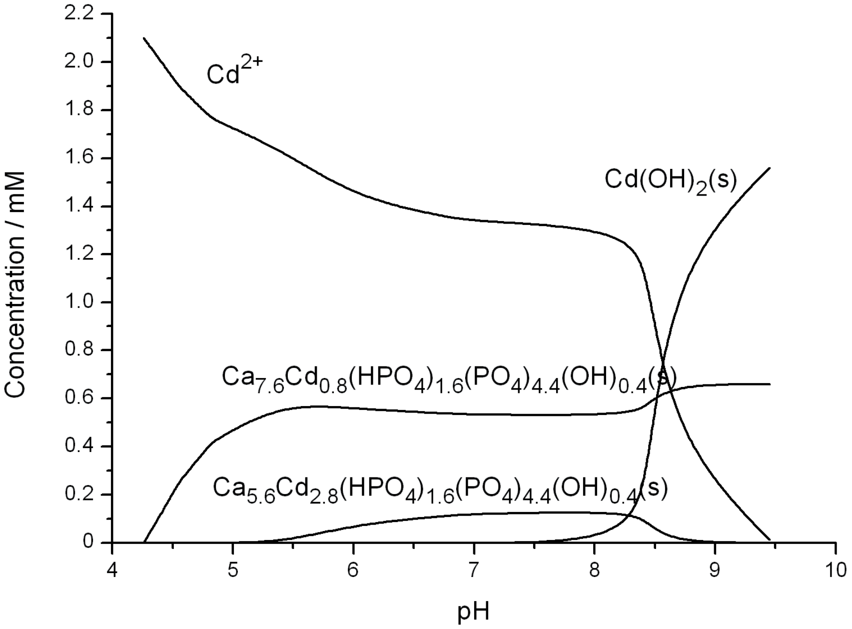

Figure 19 The speciation of Cd in Cd-solution

4.6 Desorption

In order to evaluate the reversibility of cadmium sorption onto HAP, desorption characteristics in water, Ca, Ca(II)EDTA, HUM, and Ca-HUM-solutions were determined. The desorption of Cd ions from HAP was investigated with samples obtained in sorption experiments in the absence/presence of EDTA (Paper I) and HUM (Paper II).

Cadmium desorption from synthetic HAP depends on the composition and pH of the extracting solution. The amount of desorbed cadmium was higher at pH 6 than at pH 7. This is in accordance with increased HAP stability at a higher pH. Ca^{2+}, as a native cation of HAP, is a strong competing cation, which makes application of synthetic HAP for Cd^{2+} removal less effective in hard waters (Smiciklas *et al.*, 2006).

The amount of Cd^{2+} ions released in water was negligible, but it is about 10 times higher for the samples obtained in the presence of EDTA. The release of Cd is remarkably higher in Ca solution and reaches 16 % from the amount of Cd bound. In Ca(II)EDTA complex solution, the release of Cd is in the range of 83–96%. The desorption extent is even higher in the case when Cd sorption was carried out with the solution containing EDTA (Table 4 in Paper I).

Simultaneous with Cd release, rebinding of Ca^{2+} ions takes place. Generally, the bigger the amount of Cd released, the bigger the amount of Ca bound. Ca binding is also dependent on AP pretreatment conditions.

In Ca solution, Ca^{2+} goes mainly into AP lattice as a native ion. As Cd(II)EDTA complex is more stable compared to Ca(II)EDTA, more Cd is released from AP to form Cd(II)EDTA complex. Thereby, equivalent amounts of free Ca^{2+} ions are liberated from the complex, partly replacing Cd^{2+} ions in AP.

In the desorption experiments by HUM (Figure 20), more Cd was released from FAP (FA-1), which is less reactive than HAP (HA-6) (Elliot, 1994) and has a lower SSA (Table 1). Slight dissolution of Cd as well as Ca up to 1.5 rel. % was detected in water and HUM solution. The additional adsorption of HUM on apatite was observed by TA and that might explain the differences of pH of suspensions with and without HUM. Noticeable desorption of Cd up to 6.8 and 33 rel. % from HAP and FAP, respectively, was caused by Ca ions in a solution. Stability of the Cd-HAP bond was slightly higher if Cd was bound without HUM, which indicates the different bonding mechanisms, despite the amount of Cd bound, was almost equal (Figure 20). With FAP this effect was not observed.

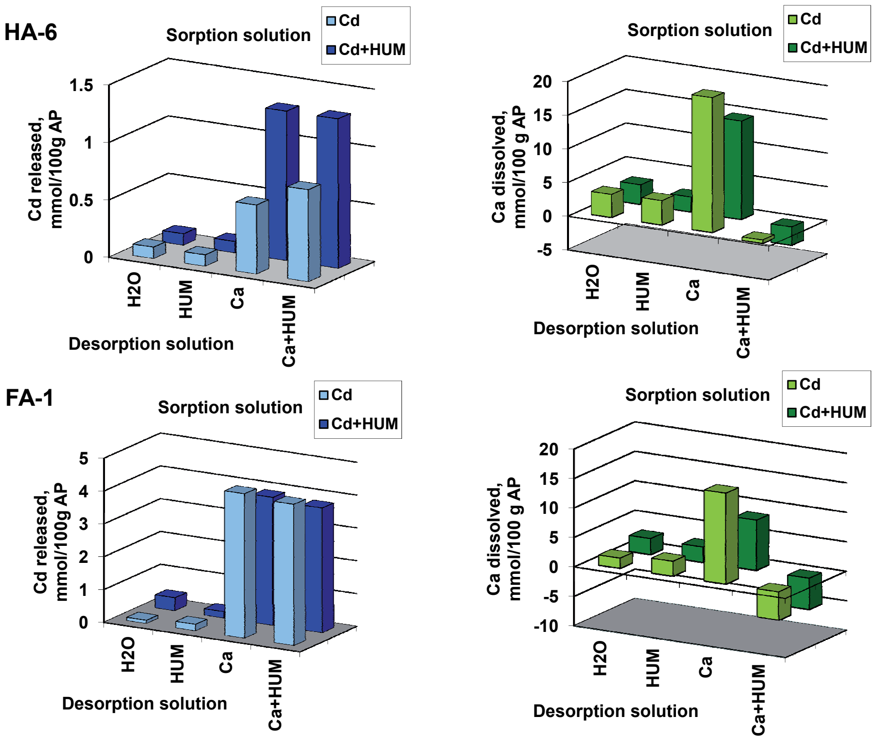

Figure 20. Changes in the solution composition in desorption experiments with and without soluble HUM.

Soluble HUM in a Ca-containing desorption solution did not affect the desorption level of Cd but had an impact on AP (Ca) solubility. During the desorption process, the pH decreased by up to 4.3 and the amount of Ca increased in the solution without HUM, which is explained by the increase in AP solubility. However, in the HUM-containing solution, additional HUM and Ca adsorption on the solid phase were observed. Vermeer *et al.*(Vermeer *et al.*, 1998) found that humic acid adsorption increases with decreasing pH because the carboxylate groups on the macromolecular humate structure bind calcium ions from the solution and these calcium ions, in turn, promote the precipitation of humic acid (Weng *et al.*, 2002; Alvarez *et al.*, 2004). This explains the higher sorption of Ca from desorption solutions.

In conclusion, the desorption of Cd^{2+} depends on the leaching solution composition. A remarkable desorption of Cd^{2+} of up to 96% took place in a solution that contained Ca^{2+} and EDTA, whereas in water and the HUM solution, it was up to 6%. Ca is quite readily rebound by AP, increasing Cd desorption. Cd sorbed in the presence of EDTA and HUM is more easily removed from AP.

CONCLUSIONS

Apatite, which is 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 Cd(II) and Zn(II) 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 Cd(II) and Zn(II) ions 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 Cd(II) and Zn(II) 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 Zn(II) ions adsorbed is slightly higher than that of Cd(II) ions in single- as well as in binary- cation solutions.
- The amount of Cd 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 Cd(II) and Zn(II) 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.
- Cd sorbed in the presence of EDTA and humic compounds is more easily removed from apatite at desorption. The strength of Cd 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 Cd 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.

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ABSTRACT

Because of their ability to bind toxic metal ions from solutions into their structure, apatites (AP) are suitable sorbents in contaminated soil and water systems. As real systems often contain different complexing ligands, it is important to examine how these ligands affect metal ions sorption processes by apatite. The aim of the present thesis was to study the sorption processes of Cd(II) and Zn(II) ions (Me) on hydroxy- and fluorapatite in the absence/presence of EDTA or a humic substance (HUM).

Sorption experiments were performed with and without complexing ligands in the pH range from 4 to 11 at room temperature with hydroxy- and fluorapatites having different compositions. In a solution analysis atomic absorption spectroscopy and spectrophotometric methods were used. The surface composition of the solid phases was analysed by X-ray photoelectron spectroscopy (XPS). To design an equilibrium model, the computer code WinSGW, which is based on the SOLGASWATER algorithm, was used.

The sorption of Cd(II) and Zn(II) ions shifted the equilibrium pH of solutions to lower values. The higher the amount of sorbed metal ions, the greater the deviation of the equilibrium pH from pure AP suspension pH. The amount of metal ions sorbed increased with pH, and reached 100% due to precipitation of hydroxides at pH 9.5 for Cd(II) and pH 8.5 for Zn(II). 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 zinc in single- and binary-metal solutions was higher than that of cadmium.

The presence of EDTA increased the dissolution of apatite and decreased the amounts of Me ions sorbed because of the formation of Ca/Cd/ZnEDTA^{2-} complexes. It was found that the EDTA and Cd/ZnEDTA^{2-} complexes do not adsorb on AP to 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 Cd bound to apatite was not affected by HUM.

Comparison of the solutions' chemical analysis results and XPS analysis results indicated that the apatite surface layer differs from the bulk. The XPS analysis revealed a Me/P ratio (Ca+Cd+Zn)/P= 1.4 ± 0.1 which was the same in the absence as well as in the presence of Cd(II) and/or Zn(II) ions. This observation implies that the sorption of Cd(II) and Zn(II) ions on AP occurs mainly by ion exchange reactions with Ca(II) 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 Cd^{2+} and CdEDTA^{2-}. The model obtained describes well experimental results and reveals that metal ions are sorbed by formation of a new, less soluble metal-substituted surface layer with the composition $Ca_{8.4-x}Me_x(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$.

In the desorption process it was found that Cd(II) ions sorbed in the presence of EDTA and HUM are more easily removed from apatite in comparison with Cd(II) ions that are sorbed in the absence of ligands. HUM impact on Cd(II) ions bonding with apatite emerges in the different Cd(II) ions desorption levels, depending on the presence or absence of HUM. The desorption level of bound Cd(II) ions depends on the composition of the leaching solution. For instance, Ca(II) ions are quite readily readsorbed by apatite, increasing Cd(II) ions desorption. The presence of EDTA may cause complete Cd(II) ions desorption from apatite.

It was established that sorption of Cd(II) and Zn(II) ions on apatite depends not only on the specific surface area of the apatite particles, but also on solution pH, solution cationic composition, Ca/P mole ratio in apatite, as well as on the presence of chelating compounds. The addition of apatite into soil will decrease the mobility of toxic metal ions by binding them to the apatite surface. 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. Considering apatites as possible sorbents for heavy metals in environment, it is necessary to take into account the presence of chelating compounds that can notably change the character of the binding process and stability of the compounds formed.

KOKKUVÕTE

Apatiidid on sobiv sidumismaterjal saastatud pinnase ja vete puhastamisel, kuna suudavad siduda toksilisi metalli-ioone lahusest oma struktuuri. Reaalsetes süsteemides esineb alati ka kompleksimoodustajaid, mis üldjuhul mõjutavad metalli-ioonide sidumisprotsesse. Käesoleva doktoritöö eesmärgiks oli selgitada Cd(II)- ja Zn(II)-ioonide (Me) sidumisprotsesside seaduspärasused hüdroksü- ja fluorapatiidiga EDTA ning humiinaine juuresolekul.

Eksperimentaalne töö viidi läbi tahke-vedel mudelsüsteemis nii kompleksimoodustajate juuresolekul kui ka ilma pH vahemikus 4 kuni 11 toatemperatuuril, kasutades erineva koostisega hüdroksü- ja fluorapatiite. Vedelfaasi analüüsimisel kasutati aatomabsorptsioonspektroskoopiat ja spektrofotomeetrilist analüüsi. Tahkete faaside pinna koostist analüüsiti röntgenfotoelektronspektroskoopiaga (XPS). Termodünaamilise mudeli koostamiseks kasutati arvutikeelt WinSGW, mis põhineb algoritmil SOLGASWATER.

Kompleksimoodustajateta võrdlussüsteemi uurimisel näidati, et Cd(II)- ja Zn(II)-ioonide sidumine apatiidiga nihutas lahuste tasakaalulise pH happelisemaks. Mida suurem oli seotud metalli-ioonide kogus, seda suurem oli pH kõrvalekalle puhta apatiidi suspensiooni pH-st. Seotud metalli-ioonide kogus suurenes koos pH tõusuga ning saavutas ~100 % pH 9,5 juures Cd puhul ja pH 8,5 juures Zn puhul. Kahte metalli-iooni samaaegselt võrdselt sisaldanud lahuses vähendas metalli-ioonide konkurents individuaalset seotavat kogust kuni 20 % võrreldes ühekomponentse lahusega. Samal ajal jäi apatiidi summaarne sidumismahtuvus konstantseks. Seotud Zn kogus oli suurem võrreldes Cd-ga nii ühe- kui kahekomponentses lahuses. EDTA juuresolek suurendas apatiidi lahustumist ja vähendas märgatavalt apatiidiga seotud metalli-ioonide kogust $Ca/Cd/ZnEDTA^{2-}$ komplekside moodustumise tõttu. Leiti, et EDTA ja $Cd/ZnEDTA^{2-}$ kompleksid ei adsorbeeru apatiidil mõõdetavas koguses. Seetõttu sõltub apatiidiga seotud ioonide hulk EDTA kontsentratsioonist lahuses. Vastupidiselt EDTA-le, seostus lahustunud humiinaine apatiidiga. Seotud Cd(II) kogust humiinaine juuresolek ei mõjutanud.

Lahuste keemilise ja XPS-analüüsi tulemuste võrdlus näitas, et apatiidi pinna koostis erineb kogumassi omast. Vastavalt XPS-analüüsile on metallide ja fosfori moolsuhe pinnal sama [(Ca+Cd+Zn)/P= 1.4 ± 0.1] nii metallide juuresolekul kui ka ilma. Sellest tulemusest järeldati, et Cd(II)- ja Zn(II)-ioonide sidumine toimub peamiselt ioonvahetusreaktsiooni tulemusel Ca-ioonidega. Koostati mudel, mis kirjeldab apatiidi lahustumist EDTA juuresolekul ning apatiidi pinna koostise muutumist Cd^{2+} ja $CdEDTA^{2-}$ juuresolekul tasakaaluolukorras. Saadud mudel kirjeldab hästi eksperimentaalseid tulemusi ja näitab, et metalli-ioonide sidumisprotsessi käigus moodustub uus vähemlahustuv pinnafaas koostisega $Ca_{8.4-x}Me_x(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$.

Cd(II), mis oli seotud EDTA ja humiinaine juuresolekul, eraldus apatiidist kergemini. Humiinaine mõju sidumisprotsessile avaldus tagasilahustunud Cd(II)-ioonide koguste erinevuses sõltuvalt sellest, kas sidumine viidi läbi humiinaine juuresolekul või ilma. Seotud metalli eraldamine sõltub tagasilahustamise lahuse koostisest. Ca(II)-ioonid seotakse hõlpsalt uuesti apatiidiga suurendades seeläbi Cd(II)-ioonide tagasilahustumist. EDTA juuresolek võib põhjustada täieliku seotud Cd(II) eraldumise.

Saadud tulemused kinnitasid, et Cd(II)- ja Zn(II)-ioonide sidumine apatiidiga ei sõltu ainult apatiidi osakeste eripinnast vaid ka lahuse pH-st, lahuse katioonsest koostisest, apatiidi Ca/P moolsuhtest ja kompleksimoodustajate juuresolekust. Apatiitide lisamine pinnasesse vähendab toksiliste metallide liikuvust apatiidi pinnale sidumisega. Hüdroksü- ja fluorapatiit on sarnaste sidumisomadustega, mis kinnitab, et ka looduslikke apatiite, mis on enamasti fluorapatiidid, saab edukalt kasutada pinnase ja vete raskmetallidest puhastamisel. Kasutades apatiite raskmetallide eraldamiseks keskkonnast, tuleb arvesse võtta kompleksimoodustajate juuresolekut, mis võib muuta sidumisprotsessi olemust ja moodustunud ühendite stabiilsust.

APPENDIX A: X-RAY PHOTOELECTRON SPECTROSCOPY SPECTRA AND DATA

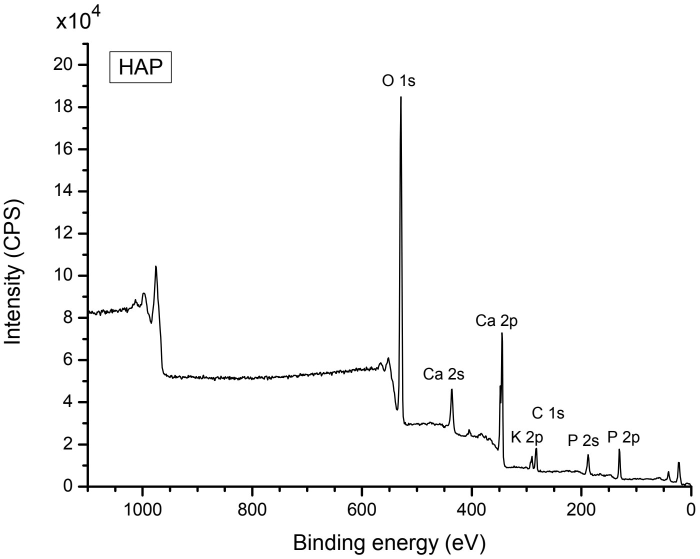

Figure I. Survey XPS spectrum of initial HAP (HA-6)

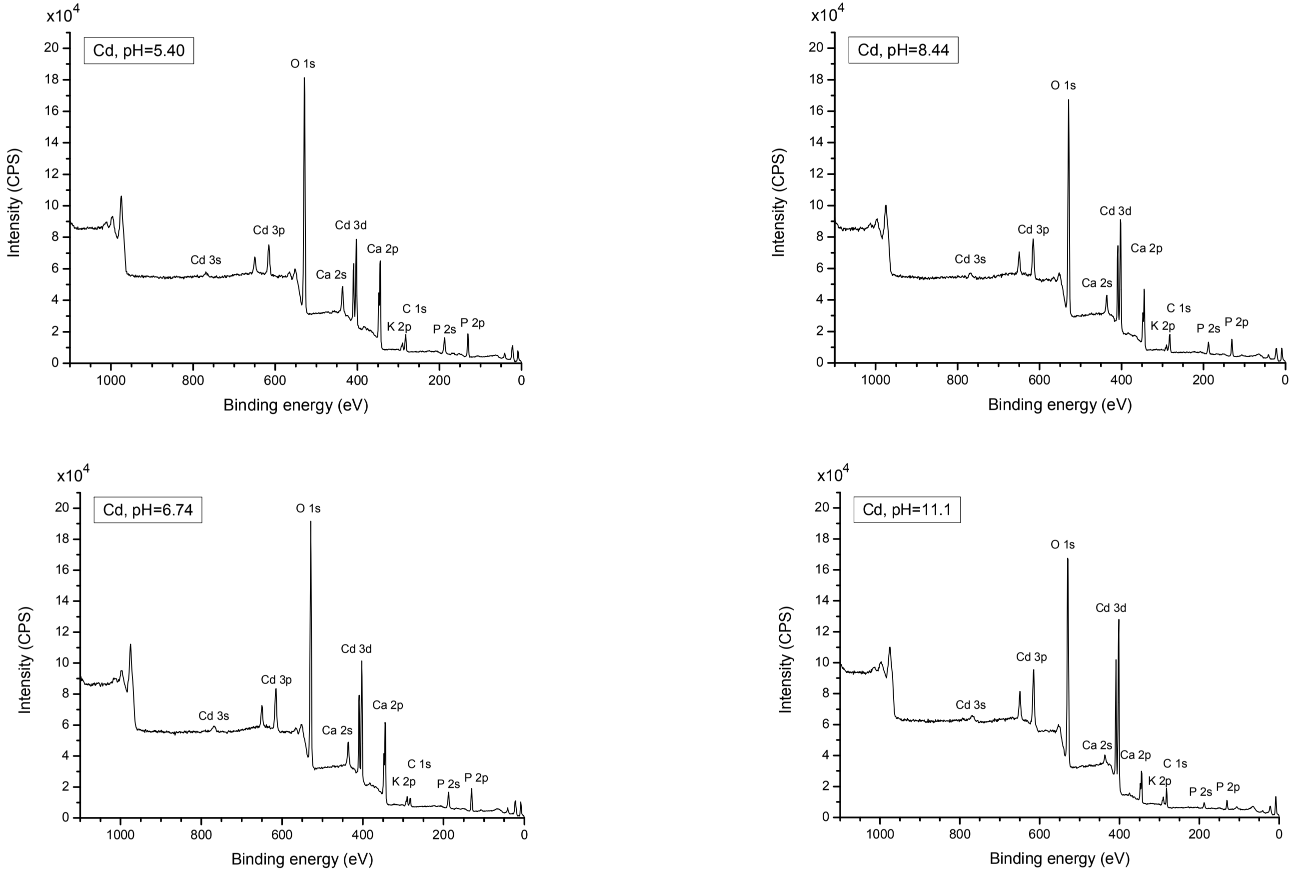

Figure II. Survey XPS spectra of HA-6 in the presence of Cd^{2+}

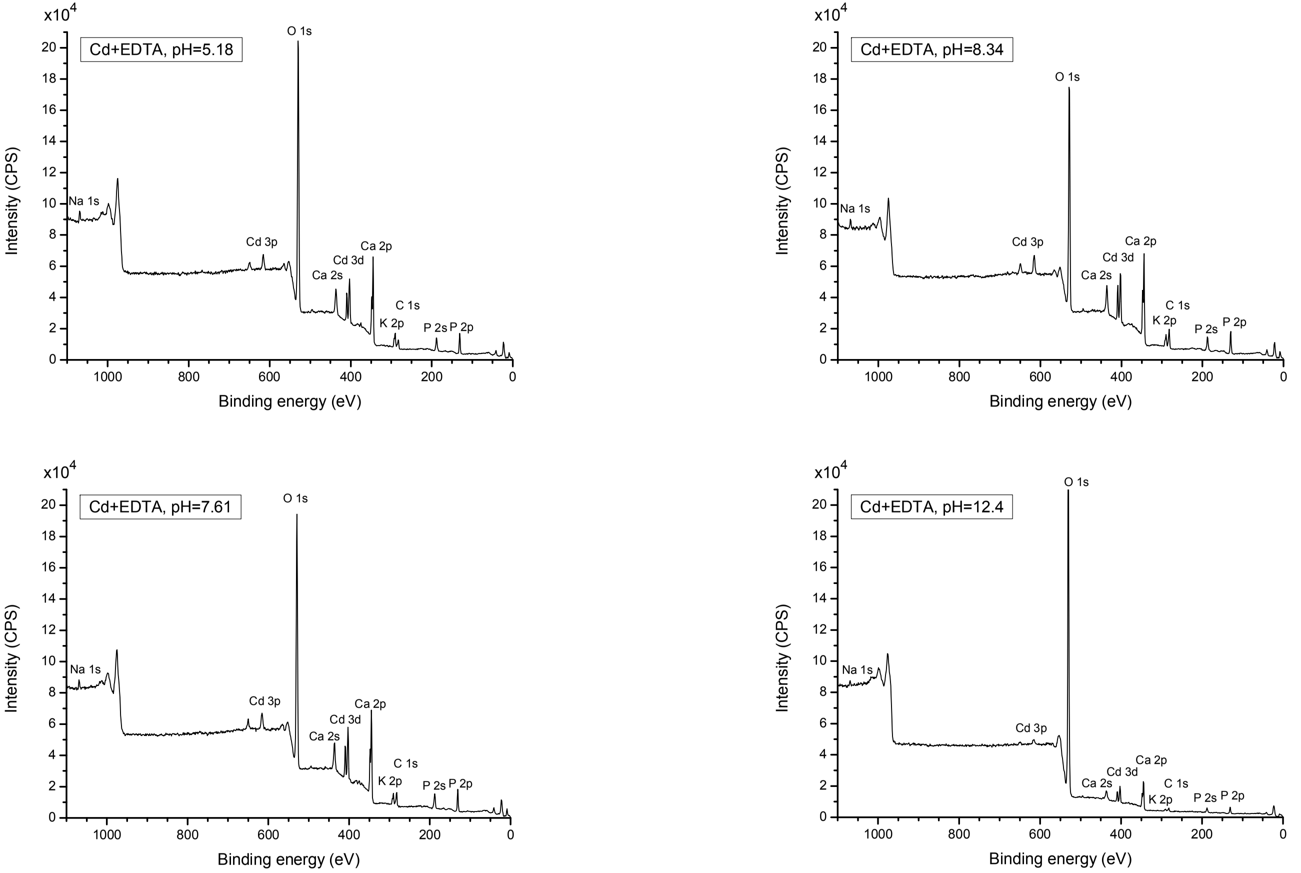

Figure III. Survey XPS spectra of HA-6 in the presence of $CdEDTA^{2-}$

Table Ia. XPS data (binding energies (BE), full width on half maximum (FWHM) and atomic concentrations (AC)) for HA-6 samples in the absence and presence of Cd^{2+}

Line	HAP			HAP+Cd pH=5.40			HAP+Cd pH=6.74			HAP+Cd pH=8.44			HAP+Cd pH=11.1		
	BE, eV	FWHM, eV	AC, at.%	BE, eV	FWHM, eV	AC, at.%	BE, eV	FWHM, eV	AC, at.%	BE, eV	FWHM, eV	AC, at.%	BE, eV	FWHM, eV	AC, at.%
C 1s	285.0	1.45	9.87	285.0	1.4	9.69	285.0	1.5	4.69	285.0	1.5	11.57	285.0	1.25	11.79
	286.7	1.75	3.96	286.6	1.5	3.34	286.7	1.6	2.36	286.9	1.65	3.9	286.5	1.3	1.16
	288.5	1.85	0.61	288.0	1.35	0.89	288.3	1.15	0.43				287.6	2	0.7
				289.0	1.35	0.85	289.5	1.1	0.19	289.2	1.8	1	289.7	1.3	1.55
O 1s	531.3	1.65	34.05	531.3	1.6	36.97	531.2	1.55	37.23	531.3	1.55	31.84	531.5	1.5	25.28
	533.1	1.7	22.49	532.9	1.65	15.42	532.9	1.7	19.47	532.9	1.65	21.94	533.2	1.7	33.18
	534.3	1.75	2.64	534.1	1.5	2.68	534.1	1.75	2.66	533.9	1.55	3.76	534.5	2	3.41
Ca 2p 3/2	347.4	1.5	13.25	347.4	1.5	11.9	347.4	1.45	11.49	347.4	1.5	8.89	347.6	1.4	4.93
P 2p 3/2	133.2	1.55	10.53	133.2	1.55	11.74	133.1	1.5	11.79	133.2	1.5	9.12	133.4	1.45	4.82
Cd 3d 5/2		-		405.5	1.6	3.44	405.4	1.45	4.9	405.4	1.55	4.97	405.3	1.45	7.87
K 2p 3/2	293.0	1.4	1.52	293.0	1.35	1.26	292.9	1.35	1.46	293.0	1.35	1	293.2	1.35	1.86
N 1s	407.4	1.5	1.1	407.3	1.45	2.23	406.9	1.4	3.32	407.1	1.45	2.01	407.1	1.4	3.45
Na 1s															
Ca/P		1.26			1.01			0.97			0.97			1.02	
Cd/Ca		-			0.29			0.43			0.56			1.70	
(Cd+Ca)/P		-			1.31			1.39			1.52			2.66	
K/NO3		1.38			0.57			0.44			0.5			0.54	

Table Ib. XPS data (binding energies (BE), full width on half maximum (FWHM) and atomic concentrations (AC)) for HA-6 samples in the presence of $CdEDTA^{2-}$

Line	HAP+Cd+EDTA pH=5.18			HAP+Cd+EDTA pH=7.61			HAP+Cd+EDTA pH=8.34			HAP+Cd+EDTA pH=12.4		
	BE, eV	FWHM, eV	AC, at.%	BE, eV	FWHM, eV	AC, at.%	BE, eV	FWHM, eV	AC, at.%	BE, eV	FWHM, eV	AC, at.%
C 1s	285.0	1.3	4.39	285.0	1.35	6.92	285.0	1.4	10.13	285.0	1.5	2.03
	286.5	1.55	2.44	286.6	1.55	3.09	286.5	1.4	3.69	286.7	1.7	0.7
	288.8	1.8	1.73	288.0	1.2	0.48	287.7	1.35	1.08	288.6	1	0.21
				289.0	1.45	1.26	288.9	1.3	1.07	289.7	1.3	0.39
O 1s	531.6	1.6	29.98	531.5	1.6	33.19	531.3	1.55	34.24	531.2	1.35	9.9
	533.3	1.8	31.52	533.2	1.7	24.06	532.8	1.65	16.21	533.2	1.6	73.51
	534.8	1.5	1.73	534.6	1.55	2.52	534.0	1.5	3.38	534.8	1.45	3.26
Ca 2p 3/2	347.7	1.45	10.39	347.6	1.45	11.2	347.4	1.5	11.89	347.5	1.6	4.57
P 2p 3/2	133.5	1.5	9.04	133.4	1.5	10.32	133.2	1.55	10.86	133.3	1.55	3.75
Cd 3d 5/2	405.7	1.5	1.56	405.7	1.55	1.96	405.5	1.65	2.08	405.7	1.65	0.74
K 2p 3/2	293.2	1.35	2.45	293.2	1.45	1.95	293.0	1.4	2.17	293.3	1.6	0.42
N 1s	400.3	1.5	0.72	400.3	1.4	0.8	400.3	1.55	0.79			
Na 1s	1071.7	1.65	0.54	1071.6	1.55	0.37	1071.6	1.8	0.51	1071.9	1.9	0.18
Ca/P		1.15			1.09			1.09			1.22	
Cd/Ca		0.15			0.18			0.18			0.16	
(Cd+Ca)/P		1.32			1.28			1.29			1.4	
K/NO3		0.7			1.02			1.14			1.27	

APPENDIX B: PUBLICATIONS

PAPER I

K. Tõnsuaadu, *K. Viipsi*, A. Trikkel

EDTA impact on Cd^{2+} migration in apatite – water system

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EDTA impact on Cd^{2+} migration in apatite–water system

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Abstract

The impact factors on Cd sorption and desorption in aqueous solution on apatite were studied. Batch experiments were carried out using synthetic hydroxyapatite with Ca/P 1.44, 1.66 and 1.94 in $Cd(NO_3)_2$ and $Cd(NO_3)_2$–EDTA equimolar complex solutions in the pH range from 4 to 7. It was established that Cd sorption on apatite depends not only on apatite specific surface area but also on Ca/P mole ratio in apatite as well as on the presence of chelating compounds. Presence of EDTA in the solution decreases the amount of Cd bound. $[CdEDTA]^{2-}$ prevents chemical sorption of Cd^{2+} ions on apatite. EDTA considerably decreases the sorption capacity of apatite with Ca excess. Impact of EDTA is smaller for the stoichiometric apatite and for the apatite with calcium deficiency. Cd bound due to adsorption is more easily removed from apatite. Ca^{2+} ions increase and presence of EDTA in a solution cause total Cd desorption from apatite.

Keywords: Hydroxyapatite; Cadmium; Sorption; Desorption; EDTA; pH

1. Introduction

Mining, manufacture and disposal of metals and metal-containing materials inevitably cause soil and water contamination. Cadmium is one of the major heavy toxic elements, which is found in surface and ground waters [1,2].

An effective and cheap method proposed for soil remediation is in situ stabilization of metals by immobilizing them in order to reduce the risks of groundwater contamination, plant uptake, and hazard to other living organisms [3,4]. It has been shown that apatites are able to bind cadmium and other heavy metal ions from aqueous solutions [5–9]. The first positive results of in situ experiments in nature have been published [10].

The main mechanisms of binding metal ions with apatites are ion-exchange, surface adsorption and co-precipitation [5,6,9,11]. The extent of metal sorption depends on apatite characteristics as well as on the metal ion. Sorption conditions such as solution properties (pH, anionic composition, presence of chelating compounds and ions of other metals), temperature, contact time, etc. are also important. Among these factors less attention has been paid to the effect of chelating agents found in soil.

Heavy metal bonding with minerals and plant uptake is affected by natural (humic compounds) and synthetic chelating agents [12–15]. It was found that if apatite amendment to Pb, Zn, Cd, and Cu contaminated soil reduced bioavailability, then addition of ethylene diamine tetraacetic acid (EDTA) enhanced heavy metal uptake by plants [13,14]. In batch experiments the effect of EDTA's concentration on Co and Pb sorption characteristics on apatite was clarified [14,15]. The amount of metal ion removed from solution decreased significantly with the increase in the concentration of chelating ligands due to formation of complexes with lower sorption affinities.

EDTA is a chelating compound that forms very stable negatively charged complexes $[Me(II)EDTA^{2-}]$ with two-valent cations in solution [16] that can prevent adsorption and cation exchange processes on apatite surface. The amount of synthetic EDTA increases continuously in the environment [17]. In agricultural practice EDTA is introduced into soil as a common ingredient of fertilizers or for increasing heavy metal ions bioavailability in phytoextraction.

The aim of the present study was to investigate EDTA's impact on sorption and desorption of Cd^{2+} ions in aqueous

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Table 1
Chemical composition of the apatite samples

Apatite	CaO (%)	P_2O_5 (%)	CO_2 (%)
HA(1.94)	55.9	36.6	1.3
HA(1.66)	52.4	40.0	0.2
HA(1.44)	48.5	42.8	0.6

solutions containing apatite at different pH of the solution and with varying stoichiometry of apatite.

2. Material and methods

2.1. Materials

In the experiments three synthetic hydroxyapatites (HAp) with different stoichiometry were used. Apatite sample HA(1.94)[1] has a slight Ca excess (Ca/P = 1.94 that is above the stoichiometric value 1.67) and it contains 1.3% of CO_2. Sample HA(1.66) synthesized by Tõnsuaadu et al. [19] is a stoichiometric apatite. HA(1.44) is an apatite with Ca deficiency (Fluka, fast flow) (Ca/P < 1.67). Their specific surface area (SSA) is 82.5, 85.5, and 37.9 m^2/g, respectively. IR analysis revealed some carbonate content in the structure of HA(1.94) and HPO_4 groups in HA(1.44). Chemical composition of the apatites used is given in Table 1.

2.2. Sorption and desorption experiments

Sorption experiments of Cd^{2+} with apatites were performed by batch method at room temperature with initial pH of a solution 4–7. The initial pH of the solutions was adjusted by adding nitric acid or ammonia. Apatite and solution were mixed at a solid to solution ratio 1:500. Solutions with concentration 0.002 and 0.003 M were prepared from analytical grade $Cd(NO_3)_2$ and Na_2EDTA. Cd(II)EDTA complex solution was obtained by mixing equal amounts of $Cd(NO_3)_2$ and Na_2EDTA solutions with the same concentration (0.004 M). Cd concentration in the solution used was determined before every experiment. The suspensions formed were shaken in closed flasks at 188 rpm. To obtain time-dependencies, varying experiment durations were used: 5, 20 and 35 min; 1, 2, 3, 5, and 24 h. The sorption experiments as well as chemical analysis were performed minimum in duplicates.

Desorption experiments were performed with the apatites obtained in sorption experiments – with apatite HA(1.66) subjected to sorption in 0.003 M $Cd(NO_3)_2$ solution with initial pH 6 or 7 [samples CdAp(6) and CdAp(7)], and in Cd(II)EDTA complex solutions at the same pH values [samples CdAp(E6) and CdAp(E7)]. The amount of Cd bound with these samples was 54.1, 52.1, 36.4, and 38.4 mmol/100 g Ap, respectively.

To follow the release of bound metal ions from apatite, calcium salt solutions, which are supposed to exchange Ca^{2+} ions with bound and exchangeable metal ions in the solid apatite phase [20], were used. Desorption experiments were carried out similar to sorption experiments, shaking the samples in pure water, 0.003 M $Ca(NO_3)_2$ solution or 0.003 M Ca(II)EDTA complex solution with pH 6 and 7 during 5 h.

Solubility of apatites in water was determined at the same pH values. The suspensions were centrifuged and after that pH value and Ca, Cd and P concentration in the solutions were determined. Chemical composition of solid phase was calculated from the results of these analyses.

2.3. Analytical methods

The concentration of Ca^{2+} and Cd^{2+} ions in the solutions were measured by atomic absorption spectrometry (VARIAN Spectra AA 55B) and that of PO_4^{3-} by spectrophotometer (SPEKOL 11, Carl Zeiss Jena) as phosphomolybdate yellow complex. The concentration of Ca^{2+} in apatite was determined titrimetrically, titrating with EDTA in NH_4OH-NH_4Cl buffer at pH 10–12. pH was measured with CyberScan pH/Ion 510 Electrode connected to a Bench pH/Ion/mV Meter.

The SSA measurements were performed by BET-method (adsorptive gas N_2, carrier gas He, heating temperature 150 °C) using sorptometer EMS-53 and KELVIN 1040/1042 software (Costech International).

3. Results and discussion

Experiment results of Cd sorption on apatite depend on many factors, whereby, for studying a new factor the background experiments must also be repeated with the apatite used in the experiment. For that reason also solubility of apatites in water and EDTA was studied in addition to the Cd binding experiments in $Ca(NO_3)_2$ and Cd(II)EDTA complex solution.

3.1. Sorption experiments

The interval of pH values for the first series was chosen taking into consideration that apatite's solubility increases remarkably at pH values under 4 and Cd^{2+} ions hydrolyze at pH > 7 [21].

3.1.1. Cd uptake

The results of kinetic studies with apatite HA(1.44) at pH_{in} 6–7 (Fig. 1) confirmed that a major part of Cd^{2+} was bound within the first five minutes. After that Cd content in apatite increased slowly and within 5 h reached to equilibrium. Addition of EDTA into the solution did not affect Cd sorption kinetics considerably. The same tendencies were followed also with apatites HA(1.66) and HA(1.94).

The amounts of Cd bound with apatites during 5 h are given in Tables 2 and 3. It can be seen that binding capacity depends on the composition of apatite and is decreased by EDTA. The influence of pH in the interval of 4–7 is not considerable. In the parallel experiments with 0.002 and 0.003 M $Cd(NO_3)_2$ solution 70 and 30% of Cd was removed from the solution, respectively. Hereby, the binding capacity of apatite should be utilized entirely.

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[1] Prepared at the Institute of Inorganic Chemistry, Riga Technical University [18].

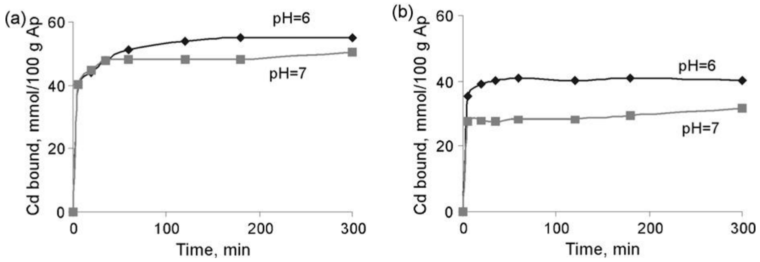

Fig. 1. Kinetic curves of Cd binding with HA(1.44): a) in $Cd(NO_3)_2$ and b) in Cd(II)EDTA complex solution.

Table 2
The amount of Ca^{2+} released and Cd^{2+} bound in water and $Cd(NO_3)_2$ 0.002 M solution during 5 h and the final pH of the solutions

Sample	pH_{in}	$Cd(NO_3)_2$ 0.002 M				Water	
		pH_{fin}	Released Ca^{2+} (mmol/100 g Ap)	Bound Cd^{2+} (mmol/100 g Ap)	Q_{sorb}[a]	pH_{fin}	Released Ca^{2+} (mmol/100 g Ap)
HA(1.44)	6	5.37	47.5	55.2	1.16	7.04	2.2
	7	5.03	43.7	50.6	1.16	7.10	2.0
HA(1.66)	4	5.62	63.7	50.2	0.79	7.00	6.1
	5	5.71	62.4	50.4	0.81	7.04	5.4
	6	5.74	56.5	48.9	0.86	7.08	5.2
	7	5.92	55.7	53.1	0.95	7.21	5.0
HA(1.94)	4	5.83	87.6	51.6	0.59	6.89	7. 8
	5	×	82.8	66.1	0.80	7.07	5.6
	6	6.14	86.8	68.5	0.78	7.04	2.2
	7	5.99	86.9	61.2	0.70	7.10	2.0

[a] Q_{sorb}: molar ratio of Cd^{2+} bound by apatite to Ca^{2+} released from apatite.

The amount of Cd bound from *$Cd(NO_3)_2$ solution* (Table 2) increases a little with the increase in Ca/P ratio of apatite, but this is not straight-forward relationship, because SSA of the sample can also affect the result [8]. The biggest amount of Cd (66–68 mmol/100 gAp) was bound with HA(1.94) at pH 5–6.

In the presence of EDTA Cd binding with apatite decreased remarkably. With HA(1.94) it was approximately 10% from the amount bound in $Cd(NO_3)_2$ solution. The impact of EDTA was less remarkable for HA(1.66) and HA(1.44). As it was expected from the Ca(II)EDTA and Cd(II)EDTA complexes stability constants ($\log K_{Cd} = 16.5$, $\log K_{Ca} = 10.6$ [16]), the formation of more stable Cd(II)EDTA complex reduced the concentration of free Cd^{2+} ions and, as a consequence, Cd removal decreased. However, despite the equimolar amount of EDTA and Cd^{2+} ions in the solution, some part of Cd was bound with apatite.

3.1.2. Ca release

The release rate of Ca from apatite depends on solution's composition and is strongly affected by EDTA. Almost maximum dissolution of Ca from HAp in the solution of EDTA was gained within first five minutes and in Cd(II)EDTA in

Table 3
The amount of Ca^{2+} released and Cd^{2+} bound in EDTA and Cd(II)EDTA 0.002 M complex solution during 5 h and the final pH of the solutions

Sample	pH_{in}	Cd(II)EDTA 0.002 M				EDTA 0.002 M	
		pH_{fin}	Released Ca^{2+} (mmol/100 g Ap)	Bound Cd^{2+} (mmol/100 g Ap)	Q_{sorb}	pH_{fin}	Released Ca^{2+} (mmol/100 g Ap)
HA(1.44)	6	6.63	15.2	40.1	2.63	6.05	126.0
	7	6.71	14.1	31.9	2.27	6.97	108.0
HA(1.66)	4	6.45	37.2	30.7	0.82	5.88	106.9
	5	6.81	21. 8	28.9	1.33	6.90	89.7
	6	6.88	20.6	28.4	1.38	6.23	130.7
	7	7.14	19.0	29.4	1.55	6.30	124.6
HA(1.94)	4	7.20	28.6	10.2	0.34	6.50	123.6
	5	7.52	20.6	10.2	0.48	7.23	109.6
	6	7.64	10.7	6.3	0.55	6.05	126.0
	7	7.56	10.4	8.5	0.80	6.97	108.0

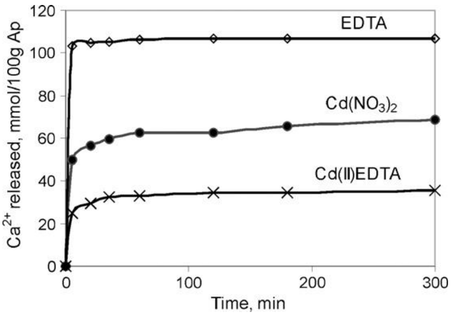

Fig. 2. Kinetic curves of calcium release from apatite HA(1.66) in EDTA, $Cd(NO_3)_2$, and Cd(II)EDTA complex solutions at $pH_{in} = 4$.

20–30 min (Fig. 2). In $Cd(NO_3)_2$ solution, the reaction occurred more slowly and the equilibrium was achieved in about 5 h.

The amount of Ca released was the biggest in EDTA solutions, it was lower in $Cd(NO_3)_2$ solutions, and decreased more than twice in Cd(II)EDTA complex solution (Tables 2 and 3). The amount of Ca released in Cd(II)EDTA solution depends more on solution's pH_{in} and less on apatite stoichiometry. Ca release in water at pH 4–7 is fractional in comparison with the other solutions (Table 2). As it was expected, the amount of Ca dissolved in water decreases with the increase in pH_{in} of water.

Differences in kinetics and amounts of Ca released at Cd binding with or without EDTA refer to different character of these processes. In the solution of EDTA solubility of Ca is enhanced by EDTA. Different release rates of Ca from the studied apatites can be caused by different stoichiometry and SSA of the samples.

3.1.3. P release

There was practically no dissolution of phosphorus from apatite in water and in $Cd(NO_3)_2$ solution, except from the apatite with Ca deficiency. Remarkable dissolution of phosphorus takes place in EDTA. It decreased with the increase in pH_{in} and in accordance with the decrease in Ca release. The structure of apatite is destroyed as a result of Ca(II)EDTA complex formation and phosphorus remains in the solution. In $Cd(NO_3)_2$ solution, low levels of phosphorus dissolution were noticed in the case of HA(1.44), in Cd(II)EDTA solution no dissolution was fixed.

3.1.4. pH of solution

As a result of reactions of apatite with solution, the pH value changes considerably. Stabilization of pH value takes place, similarly to Cd binding and Ca release, in 30–300 min depending on the solution's composition (Fig. 3). The biggest changes take place during the first 30 min. Shape of the curves is more complicated than that of the curves of cation concentration change in the solution, indicating that the final state is an equilibrium between several reactions occurring at different rates.

The electrochemical properties of apatites have been found to be a complex function of Ca/P mole ratio, ionic composition of solution etc. [22,23]. pH of water–apatite suspensions stabilizes at 6.9–7.2, independently on the value of pH_{in} due to amphoteric properties of apatite surface [23,24]. In $Cd(NO_3)_2$, EDTA and Cd(II)EDTA complex solutions, the equilibrium pH value depends on pH_{in} and Ca/P ratio of the apatite (Tables 2 and 3) and is the lowest (5.0–6.1) in $Cd(NO_3)_2$-containing solution. The drop in equilibrium pH in the solutions containing metal cations has been explained by liberation of H^+ ions from the apatite surface during surface sorption of cations [15,25]. In our experiments the amount of Ca^{2+} ions released was also high in $Cd(NO_3)_2$.

3.1.5. Cd binding mechanism

Taking into account that the mole ratio of metal ions bound by apatite to Ca^{2+} ions released from apatite (Q_{sorb}) can characterize the main mechanism of sorption process [26], some conclusions can be made.

When $Q = 1$, the quantities of the cations bound and released are equal that stands for the ion-exchange of cations between the apatite and solution. However, the dissolution–precipitation can also take place with the same proportion of cations. $Q > 1$ indicates that nonstoichiometric sorption (surface complexation or filling of cationic vacancies in crystal lattice) dominates. When $Q < 1$ dissolution of solid phase and precipitation of a new phosphate phase having lower cation to phosphate molar ratio occurs. These processes may also occur simultaneously that complicates the estimation of the sorption mechanism.

Q_{sorb} values given in Tables 2 and 3 depend on the composition of apatite and solution indicating to different mechanisms of Cd sorption.

For HA(1.44) Q_{sorb} is slightly over 1 in $Cd(NO_3)_2$ solution (Table 2) that is expected in the case of ion exchange and of filling cationic vacancies in apatite structure. Q_{sorb} doubles in

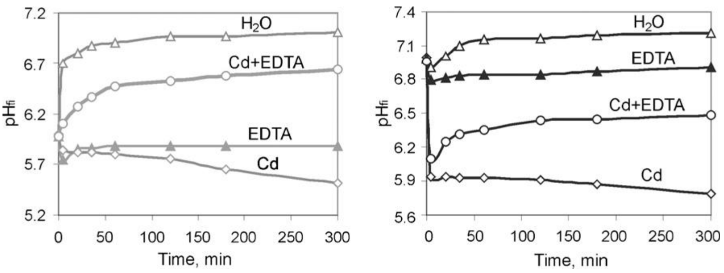

Fig. 3. Change of pH with time in different solutions in the experiments with HA(1.66). a) Initial pH = 6; b) Initial pH = 7.

the Cd(II)EDTA complex solution that evidently refers to Cd binding due to adsorption.

For HA(1.66) $Q_{sorb} \leq 1$ in $Cd(NO_3)_2$ solution that corresponds to an ion exchange type process and taking into account increased Ca release also to formation of a new phase having lower cation to phosphate molar ratio. Q_{sorb} value increases in the solution containing EDTA, noticeably, at pH_{in} 7 when the amount of Ca released decreases. Therefore, we can also suppose adsorption of Cd-EDTA complex on apatite.

For HA(1.94) with Ca excess Q_{sorb} is the lowest, that could be explained by higher and faster Ca solubility from the impurity phases like $CaCO_3$ or $Ca(OH)_2$ as compared to that from apatite. The low Q_{sorb} value in EDTA solutions can also be a result of blocking of the apatite surface active sites by EDTA complex.

According to Wu et al. [27] the main interactions responsible for the surface properties of HAp in aqueous solutions are:

$$\equiv PO^- + H^+ \leftrightarrow \equiv POH^0$$

$$\equiv CaOH_2{}^+ \leftrightarrow \equiv CaOH^0 + H^+.$$

The positively charged $\equiv CaOH_2{}^+$ and neutral $\equiv POH^0$, $\equiv PO_xH_2$ and $\equiv PO_xH$ sites must prevail on Ap surface in acidic solutions [28,29], making surface charge in this pH region positive and at higher pH values negative.

Cadmium exists in such a solution only in the form of Cd^{2+} ions, since no hydrolysis takes place at pH values lower than 6 [30]. Consequently, in acidic solutions where apatite surface is positively charged, Cd^{2+} could be bound due to ion exchange in accordance with the Q_{sorb} value that affirms the previous results [26,31]. In Cd^{2+}–EDTA equimolar solution the negatively charged EDTA complexes may be bound to apatite surface by adsorption, similarly to Co^{2+} sorption on hydroxyapatite in the EDTA containing solution [15]. This is in accordance with the decrease in the amount of Cd bound and Ca released, being even more noticeable at higher pH_{in} values. In the case when pH_{fin} is above 7, attraction of $Cd(II)EDTA^{2-}$ ions to apatite surface is repulsed. In both solutions, Q_{sorb} is more likely affected by changes in Ca release which can be related to apatite structure than by changes in Cd binding.

3.2. Desorption

For dersorption experiments the same samples obtained in Cd^{2+} sorption experiments with HA(1.66) at pH 6 and 7 were used. They were washed with distilled water and dried at 105 °C. The amounts of Cd^{2+} released and Ca^{2+} bound from different solutions and pH_{fin} of the solutions are presented in Table 4.

The amount of Cd^{2+} ions released in water does not depend on its pH neither on the pH_{in} of the solution were preceding sorption was carried out, but it is about 10 times higher for the samples obtained in the presence of EDTA. In the last case about 6% from the Cd bound was released. The release of Cd is remarkably higher in $Ca(NO_3)_2$ solution and reaches to 16% from the amount of Cd bound. In Ca(II)EDTA complex solution, the release of Cd is in the range of 83–96%. The desorption extent is even higher in the case

Table 4
The amount of Cd^{2+} released and Ca^{2+} bound in desorption experiments during 5 h and the final pH of the solutions

Solution	Sample	pH_{in}	pH_{fin}	Cd^{2+} released		Ca^{2+} bound (mmol/100 g Ap)	Q_{des}[a]	Ca_{rel}/Ca_{bound}
				%	mmol/100 g Ap			
H_2O	CdAp(6)	6	6.46	0.5	0.3	–	–	
		7	6.86	0.3	0.2	–	–	
	CdAp(7)	6	6.56	0.5	0.2	–	–	
		7	6.90	0.3	0.2	–	–	
	CdAp(E6)	6	6.60	6.4	2.3	–	–	
		7	6.81	6.1	2.2	–	–	
	CdAp(E7)	6	6.66	6.4	2.4	–	–	
		7	6.89	6.4	2.5	–	–	
$Ca(NO_3)_2$	CdAp(6)	6	5.86	15.1	8.1	45.9	5.66	1.35
		7	6.06	14.4	7.8	44.5	5.72	1.39
	CdAp(7)	6	6.03	16.1	8.4	43.5	5.18	1.44
		7	6.12	15.9	8.2	47.6	5.79	1.32
	CdAp(E6)	6	6.22	15.0	5.4	33.2	6.10	1.09
		7	6.34	14.7	5.3	32.6	6.11	1.11
	CdAp(E7)	6	6.36	15.1	5.8	–	–	–
		7	6.40	12.2	4.7	41.2	8.81	0.95
Ca(II)EDTA	CdAp(6)	6	7.32	86.3	46.5	102.4	2.20	0.60
		7	7.48	83.4	44.9	99.1	2.20	0.63
	CdAp(7)	6	7.36	89.3	46.4	102.4	2.20	0.61
		7	7.53	87.1	45.3	103.0	2.28	0.61
	CdAp(E6)	6	7.23	95.4	34.6	79.4	2.29	0.46
		7	7.38	96.1	34.9	81.0	2.32	0.45
	CdAp(E7)	6	7.26	93.0	35.5	77.8	2.19	0.50
		7	7.43	91.6	35.0	80.5	2.30	0.48

[a] Q_{des}: mole ration of Ca^{2+} bound to Cd^{2+}.

when Cd sorption was carried out with the solution containing EDTA.

Simultaneously with Cd release *rebinding of Ca^{2+} ions* takes place. Generally, the bigger the amount of Cd released the bigger the amount of Ca bound. Ca binding is also dependent on apatite pretreatment conditions. Presence of EDTA in solutions used for Cd sorption decreases the amount of Ca bound during desorption by 20–30%, however, also less Cd was bound. The amount of Ca bound during desorption in $Ca(NO_3)_2$ solution is equal or lower than the amount of Ca released during Cd sorption ($Ca_{rel}/Ca_{bound} \sim 1–1.4$) and higher in Ca(II)EDTA complex solution ($Ca_{rel}/Ca_{bound} \sim 0.45–0.6$) as shown in Table 4. The higher sorption of calcium in Ca(II)EDTA complex solution could be explained by higher desorption extent that can create more active sites for Ca binding.

This supports once more the conclusion that Cd bound in the presence of EDTA was possibly bound by a different mechanism – partly by adsorption of Cd(II)EDTA complexes, so, it was more easily removed during desorption in water. In $Ca(NO_3)_2$ solution Ca^{2+} goes mainly into apatite lattice as a native ion, but in Ca(II)EDTA solution also Ca^{2+}–EDTA complexes could be bound by apatite to some extent.

The mole ratio of Ca^{2+} ions bound to Cd^{2+} ions released (Q_{des}) is in the range of 5.2–8.8 in $Ca(NO_3)_2$ solution and 2.2–2.3 in Ca(II)EDTA complex solution. As Cd(II)EDTA complex is more stable as compared to Ca(II)EDTA, more Cd is released from apatite to form Cd(II)EDTA complex diminishing Q_{des} value. Thereby, equivalent amount of free Ca^{2+} ions are liberated from complex, partly replacing Cd^{2+} ions in apatite.

No significant impact of Cd sorption conditions (pH_{in}) on Q_{des} value can be noticed. Q_{des} values are much higher than Q_{sorb} that indicate on changes in apatite surface characteristics as a result of first sorption reaction.

So, it should be taken into consideration that in Ca-rich environment Ca^{2+} is quite readily rebound by apatite, even in the presence of chelating compounds.

4. Conclusions

Impact of EDTA on Cd sorption and desorption in apatite–water systems was studied. In batch experiments, it was established that Cd sorption with apatite depends not only on the specific surface area of apatite but also on Ca/P mole ratio in apatite as well as on the presence of chelating compounds. Presence of EDTA in the solution decreases considerably the amount of Cd bound, especially, for the apatite with Ca excess. Impact of EDTA is less significant for the stoichiometric apatite and for the apatite with calcium deficiency. Sorption mechanism of Cd(II)EDTA complex differ from the Cd^{2+} cation sorption on apatite.

Cd sorbed in the presence of EDTA is more easily removed from apatite. Ca is quite readily rebound by apatite increasing Cd desorption, the presence of EDTA may cause complete Cd desorption from apatite.

Considering apatites as possible sorbents for heavy metals in environment, it is necessary to take into account the presence of chelating compounds that change the character of binding process and stability of the compounds formed.

Acknowledgements

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Paper II

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Impact of soluble humic substance on Cd^{2+} sorption on apatite in aqueous solutions

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Impact of soluble humic substance on Cd^{2+} sorption on apatite in aqueous solutions

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The effect of soluble humic substances (HUM) on Cd sorption and desorption on apatite in aqueous solutions is studied. Batch experiments were carried out using synthetic hydroxyapatite (HAp) and fluorapatite (FAp). Parallel experiments in distilled water, Cd^{2+}, Ca^{2+}, HUM, Cd^{2+} + HUM, $Cd^{2+} + Ca^{2+}$ and Ca^{2+} + HUM solutions showed that the solubility of apatite did not increase in the initial pH range from 5 to 8 in the presence of dissolved HUM. Dissolved HUM were bound on apatite in suspensions. The pH of suspensions stabilised at 6.4–6.5 in water. The presence of soluble HUM did not change this. Cd uptake resulted in a reduction in pH. The amount of Cd bound on apatite was not changed by HUM, but HUM affected the desorption level of sorbed Cd^{2+}.

Keywords: humic substance; apatite; cadmium; sorption; desorption

1. Introduction

The stabilisation of heavy metal ions in soil can be achieved by soil amendments that can adsorb and bind trace elements or co-precipitate with them. Among the different amendments, apatite $[Ca_{10}(PO_4)_6(OH,F)_2]$ (Ap) has been recommended as a metal ion binding material [1,2].

Cadmium is regarded as one of the most toxic metals commonly present in contaminated soils and is relatively soluble and bioavailable in comparison with other trace metals. The main sources of cadmium in natural waters are industrial waste and phosphate fertilisers [1,3,4]. The binding process on apatite is controlled by a number of factors, including pH, contact time, surrounding ionic strength, type of metal ions in solution and the physico-chemical of apatite properties. The fixation of metal ions onto an apatite surface can take place via one or more simultaneous mechanisms: ion exchange, surface complexation, the dissolution of apatite with the formation of new metal phosphates or the substitution of Ca^{2+} in apatite by other metal ions during recrystallisation [5–7]. In soils and natural waters, metal ion complexation by organic ligands and competing sorbates must also be considered [8–10]. Humic substances (HUM) belong to the most important complexing agents. Humic acid has a variety of sites for metal adsorption of which the phenolic (−OH) and carboxylic (−COOH) groups are the most active. For Cd, direct bonding to carbon-bonded sulphur may also be important, especially at low Cd concentrations

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[11]. Dissolution of HUM at pH values of 3.7–8.4 found in soils [11–13] makes possible the formation of soluble metal–humic complexes, retaining metal in solution even at a pH at which a hydroxide can form [14]. At the same time, organic ligands can enhance metal sorption to mineral surfaces through the formation of ternary complexes [15]. General findings about HUM adsorption–desorption indicate that retention of HUM by solid surfaces decreases as pH increases. This is the combined effect of decreased specific interactions between the functional groups of HUM and the solid surface, and increased electrostatic repulsion between HUM molecules and the solid surface, and among HUM molecules themselves [16]. Calcium ions can promote the coagulation and precipitation of humic acids [17]. The aim of this study was to specify the impact of soluble HUM on cadmium ions binding with hydroxyapatite (HAp) or fluorapatite (FAp) in aqueous solutions.

2. Materials and methods

2.1. *Solid materials*

Humic substances (Flucka, Switzerland, Tech.) with an 18% ash content and 49.8% C content were used. The water-soluble Ca content was 0.19%, and was determined in an experiment in which 200 mg of HUM was mixed with 100 mL of water at pH 6.5. Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] (HAp6) and fluorapatite [$Ca_{10}(PO_4)_6F_2$] (FAp1) were synthesised by precipitation, as described in Tõnsuaadu et al. [18]. The characteristics of apatite are given in Table 1. The apatitic structure of the obtained materials was confirmed by X-ray diffraction (XRD) and Fourier transform-infrared (FT-IR) analyses.

2.2. *Solutions*

Solutions with a concentration of 2 mM Ca, Cd and Ca + Cd (2 + 2 mM) were prepared from nitrate salts (analytical grade) in distilled water. Because of the low solubility of HUM in the studied pH region (5–8) and sensitivity to salinity [19], a concentration $10\,\mathrm{mg \cdot L^{-1}}$ was used (0.5 mg HUM per 100 mg of Ap). Even at this low HUM content, 2 mM Cd in solution at pH 8 caused coagulation of the HUM. This may be explained by the formation of cadmium hydroxide nanostrands [$Cd_{6n}(OH)_{11n}(H_2O)_n]^{n+}$ [20] and the adsorption of HUM on them.

The initial pH of the solution was adjusted to the desired value (5, 6, 7 or 8) using KOH or HNO_3, and was measured using a CyberScan pH/Ion 510 electrode connected to a Bench pH/Ion/mV meter.

2.3. *Batch experiments*

Solubility, sorption and desorption experiments were carried out by mixing the suspensions on a magnetic stirrer for 24 h at room temperature 23 ± 1 °C. The solid/solution ratio was 100 mg Ap/50 mL. The solid phase was separated by filtration through Whatman paper filter Grade 52 for the retention of particles $> 7\,\mu m$ and was washed repeatedly with distilled water.

Table 1. The chemical composition and specific surface area (SSA) of apatites.

Sample	SSA ($m^2 \cdot g^{-1}$)	CaO (%)	P_2O_5 (%)	F (%)	H_2O (%)	Ca/P
FAp1	26.5	54.2	41.3	3.4	1.2	1.66
HAp6	37.5	51.1	41.3	0	5.0	1.57

Experiments were carried out at least in duplicate. For desorption experiments, solid materials obtained in the sorption experiments of Cd with and without HUM were used, washed with distilled water and dried at 105 °C.

2.4. *Methods of analyses*

Ca^{2+} and Cd^{2+} concentrations before and after the experiments in the solutions with apatite and/or HUM were determined by AAS analysis (VARIAN Spectra AA 55B). Before AAS analysis, HUM molecules present in the solution were decomposed using H_2O_2 or hydrochloric acid. The amount of Cd sorbed/desorbed by the solid phase was calculated as the difference between the amount in the solution before and after the batch experiment. The accuracy of the Ca and Cd analyses was ± 0.1 mmol/100 g Ap (relative error 5%).

Specific surface area (SSA) measurements were performed using the BET method (adsorptive gas N_2, carrier gas He, heating temperature 150 °C) with a sorptometer EMS-53 and KELVIN 1040/1042 software (Costech International). For thermal analysis (TA), a Setaram LabSys 2000 instrument was used. Differential thermal analysis (DTA) analysis was carried out at a heating rate of $10\,°C \cdot min^{-1}$ in an air flow of $50\,mL \cdot min^{-1}$ in open Pt crucibles, sample mass ~20 mg.

3. Results and discussion

Several processes took place simultaneously in the studied system. Cd binding with the solid phase may be a result of Cd ion sorption on apatite or Cd–humate complex sorption on apatite. At the same time, the dissolution of apatite, HUM complexation with the released Ca ions and sorption of HUM and their complexes on apatite should also be considered.

3.1. *Sorption experiments*

3.1.1. *pH changes*

Because of the various processes that could occur at the solid surface/solution interface (preferential dissolution of certain constituents of the crystal lattice, ionisation of surface groups, physical adsorption of ions or formation of complex compounds between surface groups and ions from the solution), the final pH values after the reaction with apatite differ from the initial pH of the solution (Figure 1).

The buffering properties of synthetic HAp powders are well known, i.e. the addition of HAp increases the pH of acidic solutions and decreases the pH of alkaline solutions to the point of zero

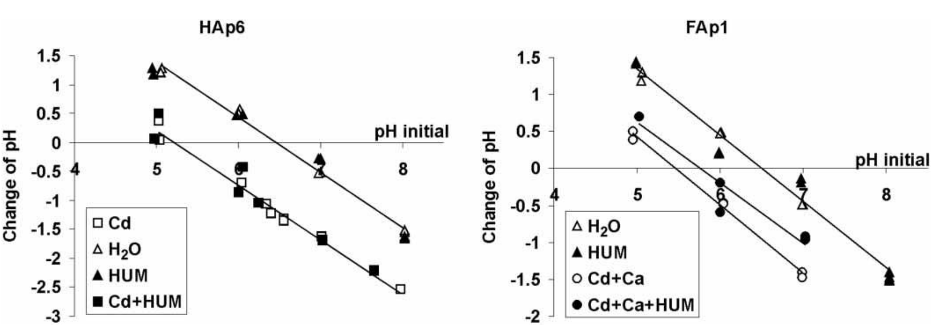

Figure 1. Change in solution pH as a result of the reaction with apatite.

charge (pH_{PZC}), which is the constant final value achieved as a result of sorption of either H^+ or OH^- ions from the solution by surface active sites [21,22]. In our experiments, pH stabilised at 6.4 for HAp6 and 6.5 for FAp1 in water. The presence of soluble HUM did not change this level.

Cd uptake resulted in a reduction in pH, both in the presence and absence of HUM. The final pH values were in the range 5.1–5.6 independent of the initial pH of the solution. In the case of FAp, a small shift in the final pH to a higher value in the presence of HUM in Cd-containing solutions was observed.

Wu et al. [23] showed that the significant surface species at $pH < pH_{PZC}$ are $\equiv$POH, whereas at pH values close to and higher than pH_{PZC} the dominant surface species are $\equiv PO-$ and $\equiv Ca(OH)^{2+}$, respectively. Therefore, the observed pH decrease is explained by proton leaching from $\equiv$POH sites of HAp as well as of FAp, because of the surface complexation of Cd^{2+} [22–25].

3.1.2. *Cd uptake*

The initial pH range from 5 to 8 did not considerably affect the amounts of sorbed Cd and dissolved Ca because the equilibrium pH values did not differ sizably. The mean values are presented in Figure 2. Apatite (Ca) dissolved slightly in H_2O and HUM solutions. Cd sorption increased the amount of dissolved Ca owing to ion exchange with apatite. The pH decrease during Cd sorption caused additional apatite dissolution and, therefore, the amount of Ca dissolved was higher than the amount of Cd bound. The presence of HUM at 0.5 mg/100 mg Ap (soluble form) did not affect the amount of Cd adsorbed. The biggest difference was found between HAp and FAp Cd sorption capacity (21–27 and 15–20 mmol/100 g Ap, respectively), which is explained by their different SSA values [25,26]. Because of the low Cd sorption capability of the apatites used in comparison with Smičiklas et al. [6], the impact of Ca^{2+} on Cd sorption was not established.

3.1.3. *HUM adsorption on apatite*

The adsorption of HUM on apatite was quantified with the help of TA of the solid residues after the sorption and desorption experiments. The oxidation of HUM on heating caused an exothermal

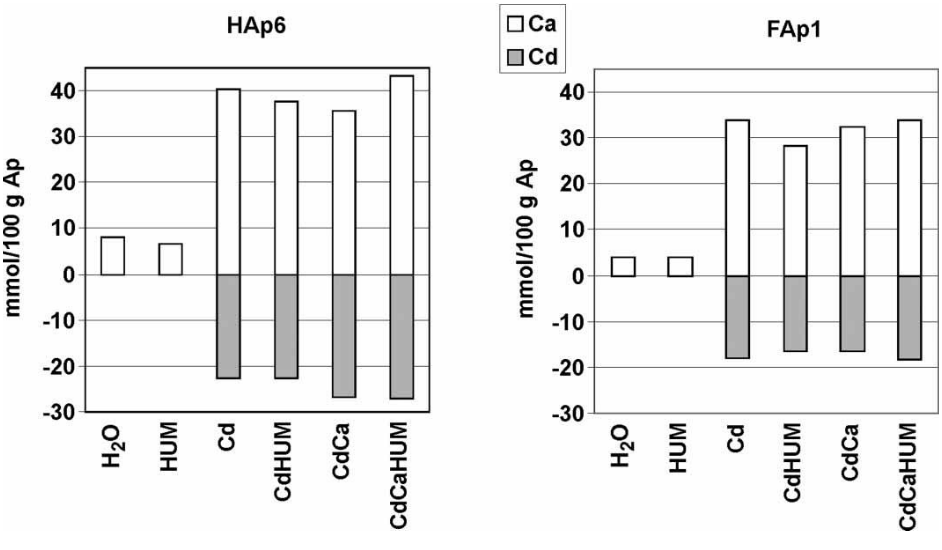

Figure 2. Changes in solution composition in the Cd sorption experiments with and without soluble HUM.

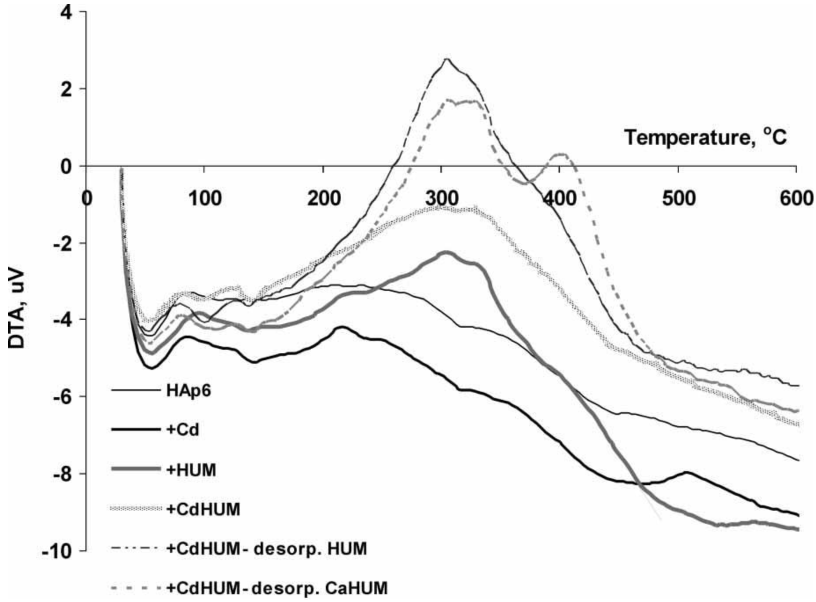

Figure 3. Differential TA curves of HAp6 and the solid residues after sorption and desorption experiments.

Table 2. Peak area (ΔP) values of the exothermic effect of apatites and the solid products of sorption and desorption experiments at temperatures of 150–500 °C.

HAp6			FAp1		
Sorption solution	Desorption solution	ΔP ($\pm 10\,\mu V\,s \cdot g^{-1}$)	Sorption solution	Desorption solution	ΔP ($\pm 10\,\mu V\,s \cdot g^{-1}$)
		−60			−70
Cd		−60	Cd		−120
HUM		−170	HUM		−150
Cd + HUM		−140	CdCa + HUM		−190
Cd + HUM	HUM	−250	Cd	HUM	−190
Cd + HUM	Ca + HUM	−300	Cd + HUM	Ca + HUM	−290
			0.5 mg HUM[a]		−140

Note: [a] 0.5 mg of solid HUM were added to 100 mg of FAp1.

effect in the temperature interval from 150 to 450–500 °C with a peak at 300–330 °C (Figure 3). An additional peak was remarkable at 400 °C in the case of higher HUM contents. The exothermic peak area was comparative to the heat of the combustion of organic matter [27]. Unfortunately, the thermal effects caused by the structural changes in precipitated apatite also took place at the same temperature interval [28] and this may have affected the exact value of the thermal effect of the oxidation of HUM. However, despite this indefiniteness, the main outline could be followed using the model mixture of FAp1 + HUM. The values of the peak area (ΔP) of the exothermic effects are given in Table 2.

The results show that the amount of HUM adsorbed on apatite in water and Cd-containing solution was almost the same and was equal to the amount of HUM in the solution. The amounts of HUM precipitated on apatite were higher after desorption experiments carried out in HUM-containing solutions. These results indicated that HUM were readily adsorbed on apatite, as found previously [22,29]. The adsorption of humic matter on an apatite surface, which hinders the dissolution process, explains the lower dissolution of Ca^{2+} in HUM-containing solutions.

3.2. *Desorption of Cd*

The results of desorption experiments in solutions with an initial pH of 6.3 are presented in Figure 4 and Table 3. A slight dissolution of Cd as well as Ca up to 1.5 rel.% was detected in the water and HUM solution. The impact of HUM adsorbed on apatite during sorption experiments was not clear. The pH of the suspension decreased more in pure water than in HUM solution (Table 3). The additional adsorption of HUM on apatite, which was observed by TA (Figure 3), might explain the differences in the final pH of the solutions with and without HUM.

The noticeable desorption of Cd up to 6.8 and 33 rel.% from HAp and FAp, respectively, was caused by the Ca ions in solution. The stability of the Cd–HAp bond was slightly higher if Cd was bound without HUM, indicating that the different bonding mechanisms were almost equal despite the amount of Cd bound (Figure 2). This effect was not observed with FAp.

Soluble HUM in a Ca-containing desorption solution did not affect the desorption level of Cd but did have an impact on apatite (Ca) solubility. During the desorption process, the pH decreased by up to 4.3 and the amount of Ca increased in the solution without HUM, which is explained by the

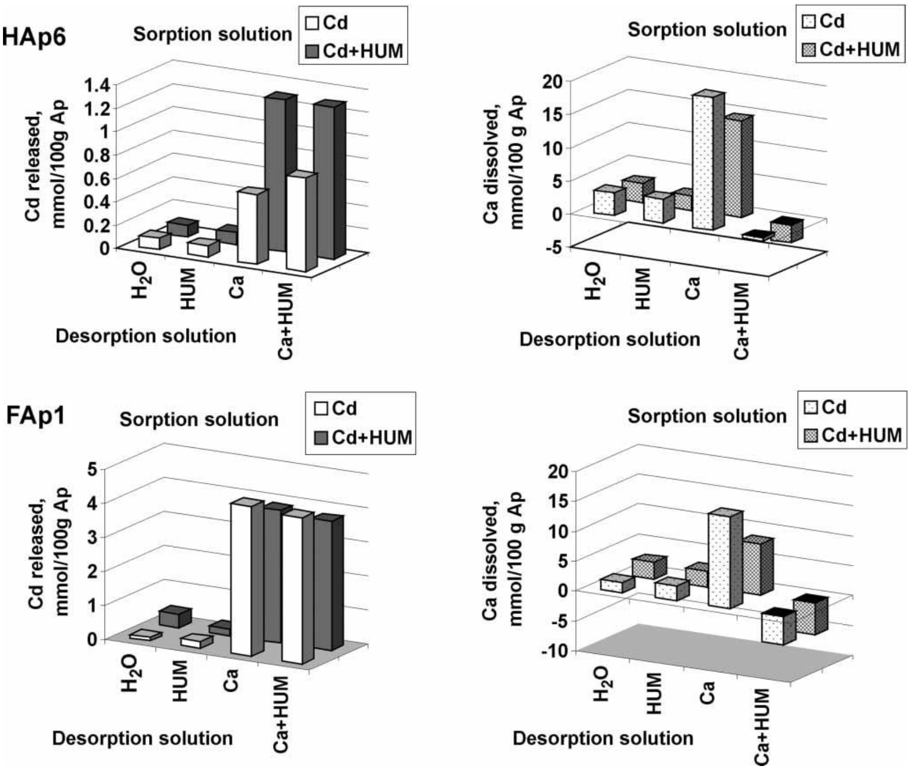

Figure 4. Changes in the solution composition in desorption experiments with and without soluble HUM.

Table 3. Equilibrium pH in desorption experiments.

	Equilibrium pH			
Desorption solution	HAp6 + Cd	HAp6 + CdHUM	FAp1 + Cd	FAp1 + CdHUM
Water	5.3	5.4	5.0	5.0
HUM 10 mg · L^{-1}	5.8	5.6	5.4	5.5
$Ca(NO_3)_2$ 2 mM	4.3	4.3	4.3	4.3
$Ca(NO_3)_2$ 2 mM + HUM 10 mg · L^{-1}	4.4	4.3	4.3	4.4

increase in apatite solubility. However, in the HUM-containing solution, additional HUM and Ca adsorption on the solid phase were observed (Figure 3). Vermeer et al. [19] found that humic acid adsorption increases with decreasing pH because the carboxylate groups on the macromolecular humate structure bind calcium ions from the solution and these calcium ions, in turn, promote the precipitation of humic acid [17,30]. This explains the higher sorption of Ca from desorption solutions.

3.3. *Cd uptake mechanism*

The immobilisation of Cd by HAp was found following the two-step mechanism. 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 the Cd–apatite phase was further increased by the diffusion of Cd ions inside the HAp crystal lattice [31]. Marchat et al. [32] showed that a part of cadmium was quickly adsorbed at the grain surface in the form of hydrated complexes $[Cd(OH_2)_n]^{2+}$. Another part of Cd was slowly incorporated into a solid solution $Ca_{10-x}Cd_x(PO_4)_6(OH)_2$. Raicevic et al. [31] showed that Cd–Ca apatite had higher stability than pure stoichiometric apatite compounds, being highest at ∼5.5 Ca-substituted atoms by Cd. This interesting property of the Cd–apatite system might be the impulsive force for Cd sorption.

At a solution pH of 5.1–5.6, the molar ratios of Cd-bound/Ca-released for all investigated solutions were <1, suggesting that, because of enhanced apatite dissolution, more cations were released in respect to the amount of cations sorbed. Ion exchange and the dissolution of apatite and precipitation of the Cd-bearing solid phase can be presumed to be dominant mechanisms.

In the desorption experiments, more Cd was released from FAp, which is less reactive than HAp [33] and has lower SSA. We assume that during desorption the hydrated part of Cd is removed and the part of Cd introduced into the Ap structure is bound more strongly.

The layer of HUM on the crystal surface alters the chemical and physical characteristics of the solid phase. Humic acids were able to block crystal growth by inhibiting any further precipitation of apatite onto the crystal surface. In reality, apatite can be completely or partially covered by humic acid molecules [22], and this can change the mechanism of Cd sorption with apatite. The impact of soluble HUM on the apatite Cd-binding capacity was not observed in the binding experiments in the pH range studied despite the humic acid's ability to remove metals from solutions at an acidic pH [34]. The desorption experiments showed that Cd bound with HAp in the presence of HUM was more easily removed than without HUM because of the different binding mechanisms.

4. Conclusions

Parallel experiments in distilled water, Cd^{2+}, Ca^{2+}, HUM, Cd^{2+} + HUM, Cd^{2+} + Ca^{2+} and Ca^{2+} + HUM solutions showed that dissolved HUM do not increase the solubility of apatite in the initial pH range from 5 to 8. The dissolved HUM were bound to apatite in suspensions. The amount of Cd bound to apatite was not changed by HUM. HUM molecules impact Cd bonding with apatite that emerges in the different Cd desorption levels depending on the presence or absence of the humic substance. Cd^{2+} were more strongly bound on HAp than on FAp. The desorption of sorbed Cd^{2+} depends on the leaching solution composition. A remarkable desorption of Cd^{2+} up to 30% took place in a solution that contained Ca^{2+}, whereas in water and the HUM solution it was ∼1%.

The addition of apatite into soil will decrease the mobility of Cd ions by binding them to the apatite structure. This process decreases the pH of the system, which then decreases the solubility of HUM and, in turn, the mobility of Cd.

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Paper III

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Surface phase transformations, surface complexation and solubilities of hydroxyapatite in the absence/presence of Cd(II) and EDTA

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Surface phase transformations, surface complexation and solubilities of hydroxyapatite in the absence/presence of Cd(II) and EDTA

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ABSTRACT

The removal of Cd from aqueous solutions by hydroxyapatite (HAP) was investigated with and without EDTA being present. Batch experiments were carried out using synthetic hydroxyapatite with Ca/P 1.57 and a specific surface area of 37.5 m^2/g in the pH range 4–9 (25 °C; 0.1 M KNO_3). The surface composition of the solid phases were analysed by X-ray Photoelectron Spectroscopy (XPS). The surface layer of HAP was found to undergo a phase transformation with a (Ca + Cd)/P atomic ratio of 1.4 and the involvement of an ion exchange process ($Ca^{2+} \leftrightarrow Cd^{2+}$). The amount of Cd removed from the solution increased with increasing pH, reaching ≈100% at pH 9. In the presence of EDTA Cd removal was reduced due to the formation of $[CdEDTA]^{2-}$ in solution. The solubility of HAP increases in the presence of EDTA at pH values above 5, mainly due to the formation of $[CaEDTA]^{2-}$. In contrast to this, the solubility was found to decrease in the presence of Cd^{2+} and $CdEDTA^{2-}$. Using XPS the formation of a Cd-enriched HAP surface was found, which was interpreted as the formation of a solid solution of the general composition: $Ca_{8.4-x}Cd_x(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$.

The information from the chemical analyses and XPS data was used to design an equilibrium model that takes into account dissolution, solution and surface complexation, as well as possible phase transformations. The total concentration of Ca, phosphate, EDTA, and Cd in solution were used in the equilibrium analysis. In the calculations the computer code WinSGW, which is based on the SOLGASWATER algorithm, was used. The following equilibria and compositions of the solid solutions were found to give the best fit to experimental data: $\log K_s(Ca_{7.6}Cd_{0.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s) + 4.8H^+ \leftrightharpoons 7.6Ca^{2+} + 0.8Cd^{2+} + 6HPO_4^{2-} + 0.4H_2O) = -28.03 \pm 0.07$. The corresponding value for the composition $Ca_{5.6}Cd_{2.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s)$ is -27.39 ± 0.06.

The proposed model can be used to predict HAP dissolution and surface phase transformations in the presence of Cd and EDTA.

1. Introduction

Contaminated soil and water presents an unacceptable risk to human and ecological health and must be remediated. Among different amendments hydroxyapatite (HAP–$Ca_{10}(PO_4)_6(OH)_2$) has been recommended as an effective metal ion binding material (Conca and Wright, 2006; Zhu et al., 2008).

Cadmium is regarded as one of the most toxic metals commonly present in contaminated soils and is relatively soluble and bioavailable in comparison to other trace metals. Chronic intoxication by Cd can have serious consequences on the kidneys, the lungs and the bones (osteoporosis, Itai–Itai disease). The main sources of Cd in natural waters are industrial wastes and phosphate fertilizers (Bal Ram Singh, 1999; Cobb, 2007; Zhu et al., 2008).

The binding process of metal ions on HAP is controlled by a number of factors including pH, contact time, type of metal ions in solution, HAP physico-chemical properties, etc. The fixation of metal ions on the HAP surface may take place through one or more simultaneous mechanisms like ion exchange, surface complexation, phase transformation of HAP to form new metal phosphates, and substitution of Ca^{2+} ions in HAP by other metal ions during recrystallization (Xu et al., 1994; Valsami-Jones et al., 1998; Smiciklas et al., 2008; Dybowska et al., 2009). In soils and natural waters metal complexation by organic ligands and competing sorbates must be considered as well (Malandrino et al., 2006; Smiciklas et al., 2006; Tõnsuaadu et al., 2008).

In agricultural practices ethylene diamine tetraacetic acid (EDTA) is applied to the soil as a common ingredient of fertilizers to improve micronutrient availability. Recent studies have shown that EDTA strongly alters soil metal bioavailability and affects the efficiency of phytoremediation (Smiciklas et al., 2006). The metal

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complexation with EDTA can interfere the use of HAP as a metal remediation agent (Wang et al., 2009).

Studies of trace metal binding mechanisms on apatite by XRD are complicated because the concentrations of bound cations are too small to induce significant modifications of cell parameters. Several possible processes could take place simultaneously. In this case modelling the equilibrium state of multicomponent/multiphase systems may lead to a better understanding of the immobilisation mechanism. Computer aided thermodynamic modelling is a valuable tool in the interpretation of experimental data and the prediction of surface properties at the molecular level, which are not accessible to experimental investigation (Perrone et al., 2001; Charlet et al., 2006; Bengtsson et al., 2009).

The main objective of the present study was to design an equilibrium model that is based upon experimental solubility data (total Ca and phosphate) in the presence of Cd and/or EDTA. Surface analysis utilizing X-ray Photoelectron Spectroscopy (XPS) was used to obtain information on changes in the surface chemical composition during the different processes occurring at the HAP–aqueous solution interface.

2. Materials and methods

Hydroxyapatite [HAP–$Ca_{10}(PO_4)_6(OH)_2$] was synthesized by precipitation as described in Tõnsuaadu et al. (1995). The HAP characteristics are given in Table 1. Furthermore, the apatite structure of the obtained materials was proved by XRD and FTIR analyses.

2.1. Solutions

The HAP dissolution and Cd sorption experiments were performed by a batch method at room temperature (23 ± 2 °C) within the pH range 3-11. Solutions of 2.1 mM Cd, 2 mM EDTA and 2.1 mM Cd + 2 mM of EDTA were prepared from analytical grade $Cd(NO_3)_2$ and Na_2EDTA. An ionic medium of 0.1 M KNO_3 was used.

2.2. Batch experiments

The solubility and adsorption experiments were carried out by mixing the suspensions on a rotating stirrer for a minimum of 3 days at room temperature (23 ± 2 °C). The solid/solution ratio was 2 g/L. The solid phase was separated by centrifugation (7000 rpm, 15 min) and filtration. All experiments were performed in duplicate.

2.3. Analytical methods

The pH was measured with a Mettler Toledo electrode DG-112 Pro calibrated with Mettler Toledo pH Buffer Solutions (4.01; 7.00; 9.21) and connected to an automatic titrator T90 under N_2 flow. The soluble concentrations of Ca^{2+} and Cd^{2+} were determined by atomic absorption spectrometry (VARIAN Spectra AA 55B) and the concentration of PO_4^{3-} was determined spectrophotometrically (SpectroDirect) as the phosphomolybdate yellow complex (Horwitz, 1965).

The surface area of the HAP particles was measured by the BET-method (adsorptive gas N_2, carrier gas He, heating temperature 150 °C) using sorptometer EMS-53 and KELVIN 1040/1042 software (Costech International).

The centrifuged (4000 rpm, 15 min) wet pastes of HAP suspensions were used for cryogenic XPS measurements. The fast-freezing procedure applied to wet pastes is described in detail elsewhere (Shchukarev and Sjöberg, 2005; Shchukarev, 2006).

The XPS spectra were recorded with a Kratos Axis Ultra DLD electron spectrometer using a monochromated Al Kα source operated at 150 W, a hybrid lens system with magnetic lens providing an analysis area of $0.3 \times 0.7\ mm^2$, and a charge neutralizer. The binding energy (BE) scale was referenced to the C 1s line of aliphatic C contamination, set at 285.0 eV. Processing of the spectra was accomplished with Kratos software.

Table 1
The chemical composition and specific surface area of HAP.

Sample	SSA (m^2/g)	CaO (%)	P_2O_5 (%)	H_2O (%)	CO_2 (%)	Ca/P (bulk)
HAP6	37.5	51.1	41.3	5.0	0.9	1.57

3. Modelling

The equilibrium analysis in the present work closely follows the approach outlined by Bengtsson et al. (2009). Here justification for the chosen surface complexation model is given and also the necessity for using a combination of wet chemical analysis and data from surface sensitive spectroscopic techniques to obtain equilibrium models as reliable as possible.

3.1. Proton promoted dissolution of HAP

The dissolution of HAP (1) is strongly pH dependent and involves both protonation/deprotonation (2), (3) and complexation (4) reactions.

$$Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s) + 4.8H^+ \leftrightharpoons 8.4Ca^{2+} + 6HPO_4^{2-} + 0.4H_2O \qquad (1)$$

$$PO_4^{3-} + nH^+ \leftrightharpoons H_nPO_4^{(3-n)-}; \quad (n = 1, 2, 3) \qquad (2)$$

$$Ca^{2+} + H_2O \leftrightharpoons CaOH^+ + H^+ \qquad (3)$$

$$Ca^{2+} + PO_4^{3-} + nH^+ \leftrightharpoons CaH_nPO_4^{(n-1)+}; \quad (n = 0, 1, 2) \qquad (4)$$

Surface reactions such as adsorption and desorption of H^+ as well as the re-adsorption of phosphate species according to reactions (5)–(8) have been shown to be important (Bengtsson et al., 2009).

$$\equiv CaOH + H^+ \leftrightharpoons \equiv CaOH_2^+ \qquad (5)$$

$$\equiv OPO_3H_2 \leftrightharpoons \equiv OPO_3H^- + H^+ \qquad (6)$$

$$\equiv CaOH_2^+ + HPO_4^{2-} \leftrightharpoons \equiv CaOPO_3H^- + H_2O \qquad (7)$$

$$\equiv OPO_3H_2 + K^+ \leftrightharpoons \equiv OPO_3K^- + 2H^+ \qquad (8)$$

3.2. Dissolution of HAP in the presence of EDTA

Due to the high stability of Ca^{2+}–EDTA complexes the dissolution of HAP is increased in the presence of EDTA (Arbel et al., 1991). These effects are considered in the modelling by including the reactions:

$$EDTA^{4-} + nH^+ \leftrightharpoons H_nEDTA^{(n-4)+}(n = 1, 2, 3, 4) \qquad (9)$$

$$EDTA^{4-} + nH^+ + Ca^{2+} \leftrightharpoons Ca\ H_nEDTA^{(n-2)+}(n = 0, 1) \qquad (10)$$

The adsorption of EDTA on HAP was found to be negligible with all EDTA being found in solution. This was also confirmed from the XPS-analysis.

3.3. Dissolution of HAP in the presence of Cd^{2+} and Cd^{2+} - EDTA complexes

The possibility that Cd^{2+} ions will take part in ion exchange/surface reactions (11) and (12) as well as forming solid solutions (13) and precipitating as $Cd(OH)_2$ (14) has been considered:

$$\equiv \mathrm{CaOH} + n\mathrm{H}^+ + \mathrm{Cd}^{2+} \leftrightharpoons\ \equiv \mathrm{CdOH}_{n+1}^{n+} + \mathrm{Ca}^{2+} (n = 0, 1) \tag{11}$$

$$\equiv \mathrm{OPO_3H_2} + \mathrm{Cd}^{2+} \leftrightharpoons\ \equiv \mathrm{OPO_3Cd} + 2\mathrm{H}^+ \tag{12}$$

$$\begin{aligned}&\mathrm{Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s)} + x\mathrm{Cd}^{2+}\\ &\leftrightharpoons \mathrm{Ca}_{8.4-x}\mathrm{Cd}_x\mathrm{(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s)} + x\mathrm{Ca}^{2+}\end{aligned} \tag{13}$$

$$\mathrm{Cd}^{2+} + 2\mathrm{H_2O} \leftrightharpoons \mathrm{Cd(OH)_2(s)} + 2\mathrm{H}^+ \tag{14}$$

In addition to these reactions complexation between Cd^{2+} and EDTA (15) and phosphate anions (16) has to be accounted for:

$$\mathrm{Cd}^{2+} + \mathrm{EDTA}^{4-} + n\mathrm{H}^+ \leftrightharpoons \mathrm{Cd(H)}_n\mathrm{EDTA}^{(2-n)-} (n = 0, 1) \tag{15}$$

$$\mathrm{Cd}^{2+} + \mathrm{PO}_4^{3-} + n\mathrm{H}^+ \leftrightharpoons \mathrm{Cd(H)}_n\mathrm{PO}_4^{(3+n)-} (n = 1, 2) \tag{16}$$

The possible formation of binary $Cd^{2+} - PO_4^{3-}$ precipitates such as $Cd_3(PO_4)_2$ are ruled out. Matusik et al. (2008) showed solubility minima between pH 6.75 and 9, which in the presence of HAP is a range were phosphate concentration is too low to allow their precipitation. Their formation is also contradicted by the strong experimental evidence showing Cd removal from solution by an ion exchange process involving Ca^{2+}.

The formation of a number of charged surface species results in a charge accumulation at the HAP surface. Therefore, the different surface equilibrium constants must be corrected for the coulombic energy of the charged surface.

The conditional constant, β_{11}^{s} (cond.) defining a protonation reaction of a generic surface site ≡SOH:

$$\equiv \mathrm{SOH} + \mathrm{H}^+ \leftrightharpoons\ \equiv \mathrm{SOH}_2^+ \tag{17}$$

is related to the intrinsic constant β_{11}^{s} (intr.) according to the equation:

$$\beta_{11}^{s}(\mathrm{intr.}) = \beta_{11}^{s}(\mathrm{cond.})\mathrm{e}^{\mathrm{F}\Psi/\mathrm{RT}} \tag{18}$$

where Ψ is the acting surface potential calculated according to (19).

Table 2

Thermodynamic data (I = 0.1 M; 25 °C) used in the model calculations. Site densities N_s = 3.0 and 4.3 sites/nm^2 for total phosphate and Ca concentrations, respectively. These values correspond to $[\equiv CaOH]_{tot}$ = 0.57 mM and $[\equiv PO_4H_2]_{tot}$ = 0.37 mM. The capacitance value used in the calculations is C = 1.29 (CV^{-1}/m^2) (Bengtsson et al., 2009).

Species	Log β	H^+	Ca^{2+}	HPO_4^{2-}	≡CaOH	$\equiv OPO_3H_2$	K^+	Cd^{2+}	$EDTA^{4-}$	Phase
H^+	0	1	0	0	0	0	0	0	0	Soluble
Ca^{2+}	0	0	1	0	0	0	0	0	0	Soluble
HPO_4^{2-}	0	0	0	1	0	0	0	0	0	Soluble
≡CaOH	0	0	0	0	1	0	0	0	0	Surf. comp
$\equiv OPO_3H_2$	0	0	0	0	0	1	0	0	0	Surface
K^+	0	0	0	0	0	0	1	0	0	Soluble
Cd^{2+}	0	0	0	0	0	0	0	1	0	Soluble
$EDTA^{4-}$	0	0	0	0	0	0	0	0	1	Soluble
OH^-	−13.78	−1	0	0	0	0	0	0	0	Soluble
PO_4^{3-}	−11.65	−1	0	1	0	0	0	0	0	Soluble
$H_2PO_4^-$	6.74	1	0	1	0	0	0	0	0	Soluble
H_3PO_4	8.65	2	0	1	0	0	0	0	0	Soluble
$Ca(OH)^+$	−12.9	−1	1	0	0	0	0	0	0	Soluble
$Ca(PO_4)^-$	−6.45	−1	1	1	0	0	0	0	0	Soluble
$Ca(HPO_4)$	1.73	0	1	1	0	0	0	0	0	Soluble
$Ca(H_2PO_4)^+$	7.32	1	1	1	0	0	0	0	0	Soluble
$\equiv CaOPO_3H^-$	11.63	1	0	1	1	0	0	0	0	Surface
$\equiv OPO_3H^-$	−1.11	−1	0	0	0	1	0	0	0	Surface
$\equiv CaOH_2^+$	8.41	1	0	0	1	0	0	0	0	Surface
$\equiv OPO_3K^-$	−11.08	−2	0	0	0	1	1	0	0	Surface
$CdEDTA^{2-}$	16.46	0	0	0	0	0	0	1	1	Soluble
$CdHEDTA^-$	19.36	1	0	0	0	0	0	1	1	Soluble
$CdOH^+$	−10.08	−1	0	0	0	0	0	1	0	Soluble
$Cd(OH)_2$	−20.4	−2	0	0	0	0	0	1	0	Soluble
HEDTA	10.24	1	0	0	0	0	0	0	1	Soluble
H_2EDTA	16.4	2	0	0	0	0	0	0	1	Soluble
H_3EDTA	19.06	3	0	0	0	0	0	0	1	Soluble
H_4EDTA	21.06	4	0	0	0	0	0	0	1	Soluble
$CaEDTA^{2-}$	10.69	0	1	0	0	0	0	0	1	Soluble
$CaHEDTA^-$	13.87	1	1	0	0	0	0	0	1	Soluble
$CdH_2PO_4^+$	7.04	1	0	1	0	0	0	1	0	Soluble
$CdHPO_4$	2.85	0	0	1	0	0	0	1	0	Soluble
HAP[a]	19.34	−4.8	8.4	6	0	0	0	0	0	Solid
Ca7.6Cd0.8[b]	28.03	−4.8	7.6	6	0	0	0	0.8	0	Solid
Ca5.6Cd2.8[c]	27.39	−4.8	5.6	6	0	0	0	2.8	0	Solid
$Cd(OH)_2(s)$	−13.89	−2	0	0	0	0	0	1	0	Solid
$Ca(OH)_2(s)$	−22.8	−2	1	0	0	0	0	0	0	Solid

The solid phases included are the composition of the surface layer of HAP and new solid-solutions of HAP. This is supported by the result from XPS measurements which are presented below. All constants, except those for the surface complexation model, were taken from Smith and Martell (1978) and NIST Standard Reference Database 46 (Motekaitis, 2004).

[a] $Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ – solid phase in solution in the absence of Cd.

[b] $Ca_{7.6}Cd_{0.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ – solid phase postulated in Cd–EDTA-solution.

[c] $Ca_{5.6}Cd_{2.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ – solid phase postulated in Cd-solution.

The models used in the present work were developed assuming a constant capacitance for the electrical double layer at the charge surface (Schindler and Gamsjäger, 1972):

$$\Psi = T_\sigma \cdot F/(s \cdot A \cdot C) \tag{19}$$

where Ψ is the surface potential (V), C is a constant with the dimensions of specific capacitance (CV^{-1}/m^2), T_σ is the molarity of total surface charge (mol/dm^3), s is the specific surface area (m^2/g), and A is the solid concentration (g/dm^3).

The activity coefficients of the different species in solution are controlled by an ionic medium of constant ionic strength ($I = 0.1$ M). In addition, the activity coefficients of the surface species were assumed to be constant. When necessary, the individual activity coefficients γ_i of an ionic species were recalculated to an ionic strength (I) of 0.1 utilizing the Davis equation (Davis, 1962) where z_i denotes the ionic charge number.

$$\log\gamma_i = -0.509z_i^2(I^{1/2}/(1+I^{1/2}) - 0.3I) \tag{20}$$

In the different calculations the computer code WinSGW (Karlsson et al., 2006), which is based on the SOLGASWATER algorithm (Eriksson, 1979), was used. The thermodynamic data used for the calculations are listed in Table 2.

The equilibrium model shown in Table 2 is defined by the eight components: $H^+, Ca^{2+}, Cd^{2+}, HPO_4^{2-}, EDTA^{4-}, K^+, \equiv CaOH$ and $\equiv OPO_3H_2$. A general equilibrium reaction can be written as:

$$\begin{aligned} &pH^+ + qCa^{2+} + rCd^{2+} + sHPO_4^{2-} + tEDTA^{4-} + uK^+ + v \equiv CaOH + x \\ &\equiv PO_4H_2 \leftrightharpoons (H^+)_p(Ca^{2+})_q(Cd^{2+})_r(HPO_4^{2-})_s(EDTA^{4-})_t(K^+)_u \\ &(\equiv CaOH)_v(\equiv PO_4H_2)_x \end{aligned} \tag{21}$$

This equation defines the formation constant $\beta_{pqrstuvx}$.

The total concentration of Ca^{2+}, Cd^{2+} and phosphate in solution is known from chemical analysis. These experimental values can also be compared with model dependent calculated values, which can be derived from Table 2.

$$\begin{aligned} [Ca^{2+}]_{tot}(sln) = {} & [Ca^{2+}] + [CaOH^+] + [CaPO_4^-] + [CaHPO_4] \\ & + [CaH_2PO_4^+] + [CaEDTA^{2-}] + [CaHEDTA^-] \end{aligned} \tag{22}$$

$$\begin{aligned} [HPO_4^{2-}]_{tot}(sln) = {} & [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] \\ & + [CaPO_4^-] + [CaHPO_4] + [CaH_2PO_4^+] \end{aligned} \tag{23}$$

$$\begin{aligned} [Cd^{2+}]_{tot}(sln) = {} & [Cd^{2+}] + [Cd(OH)^+] + [Cd(OH)_2(aq)] \\ & + [Cd(HPO_4)(aq)] + [Cd(H_2PO_4)^+] \\ & + [CdHEDTA^-] + [CdEDTA^{2-}] \end{aligned} \tag{24}$$

In the different model calculations error squares of sums (U):

$$U(Ca) = \sum \left(\left[Ca^{2+}\right]_{tot}(sln)^{calc} - \left[Ca^{2+}\right]_{tot}(sln)^{exp}\right)^2 \tag{25}$$

$$U(P) = \sum \left(\left[HPO_4^{2-}\right]_{tot}(sln)^{calc} - \left[HPO_4^{2-}\right]_{tot}(sln)^{exp}\right)^2 \tag{26}$$

$$U(Cd) = \sum \left([Cd]_{tot}(sln)^{calc} - [Cd]_{tot}(sln)^{exp}\right)^2 \tag{27}$$

were used in fitting a model to experimental proton, $[Ca^{2+}]_{tot}(sln)$, $[HPO_4^{2-}]_{tot}(sln)$ and $[Cd]_{tot}$ (sln) data. The ultimate goal of the equilibrium analysis is to design a model that gives a good fit to U(Ca) + U(P) + U(Cd). It is assumed that literature data describing complexation in solution is known, and no attempts are made to refine any of the corresponding complexation constants. It is also assumed that the surface complexation constants are the same as in the HAP system studied by Bengtsson et al. (2009).

4. Results and discussion

4.1. HAP solubility in the absence/presence of EDTA

The dissolution of apatite is a complex process that depends on many parameters e.g. pH, Ca/P of apatite, salinity and composition of the solution (Dorozhkin, 1997, 2002; Valsami-Jones et al., 1998). The dissolution reaction of HAP (1) shows that the solubility will increase by adding protons or by lowering the "free" Ca^{2+} and/or HPO_4^{2-} concentrations. In the presence of EDTA it is thus expected that the total soluble concentrations of Ca^{2+} and phosphate will increase due to EDTA complexation with Ca^{2+} (Eq. (10)). This is clearly seen in Fig. 1. From Fig. 2 one can also observe a corresponding increase in the total soluble concentration of HPO_4^{2-} with EDTA in solution.

Based upon XPS measurements (see Fig. 3) and analysis of total soluble concentrations of Ca and P, the surface of pure HAP has a Ca/P or (Ca + Cd)/P atomic ratio of 1.4 obtained in the absence as well as in the presence of Cd(II) and EDTA. The composition of the surface, therefore, is assumed to be $Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ (Bengtsson et al., 2009). It has been suggested that the HAP surface undergoes a change when it is in contact with an

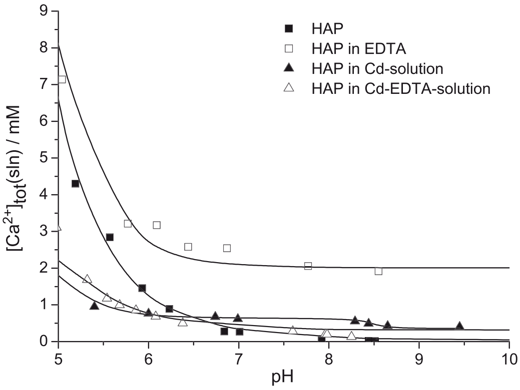

Fig. 1. Experimental (symbols) and calculated (lines) results of Ca^{2+} dissolution. Solid concentration 2 g/L; $I = 0.1$ M KNO_3; $T = 23 \pm 1$ °C.

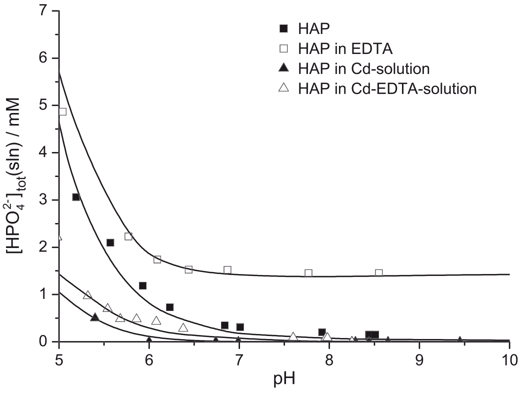

Fig. 2. Experimental (symbols) and calculated (lines) results of HPO_4^{2-} dissolution. Solid concentration 2 g/L; $I = 0.1$ M KNO_3; $T = 23 \pm 1$ °C.

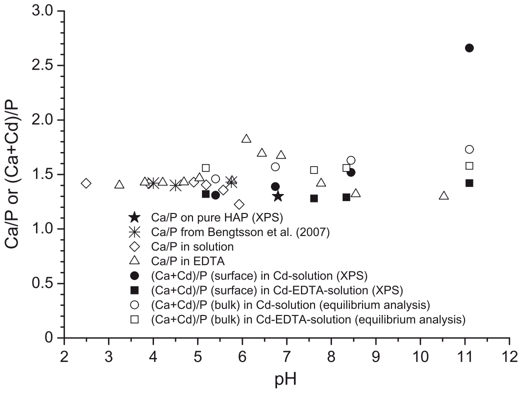

Fig. 3. The Ca/P ratio in solution and (Ca + Cd)/P on HAP according to equilibrium and XPS analysis.

aqueous solution, and creates vacancies in Ca and OH sites and protonation of phosphate groups (Brown and Martin, 1999; Garcia Rodenas et al., 2005; Rey et al., 2007).

Experimental $[\mathrm{Ca}^{2+}]_{\mathrm{tot}}(\mathrm{sln})$ and $[\mathrm{HPO}_4^{2-}]_{\mathrm{tot}}(\mathrm{sln})$ were used to calculate the dissolution constant defined according to Eq. (1) giving:

$$\log K_s(\mathrm{Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s)} + 4.8\mathrm{H}^+ \leftrightharpoons 8.4\mathrm{Ca}^{2+} + 6\mathrm{HPO}_4^{2-} + 0.4\mathrm{H_2O}) = -19.34 \pm 0.05.$$

As can be seen from Figs. 1 and 2 this constant gives a good explanation for experimental solubility data. A distribution diagram showing the solubility characteristics in the presence of EDTA is given in Fig. 4.

4.2. HAP reactions in the presence of Cd^{2+} and CdEDTA^{2-}

4.2.1. XPS analysis

Cryogenic XPS data presented in Table 3 demonstrate significant changes of HAP surface composition (in terms of atomic ratios Ca/P, and Cd/Ca) after equilibration in Cd and Cd–EDTA solutions (original XPS spectras and data are presented in Supplementary data). However, it is important to note that the ratio (Ca + Cd)/P remains practically constant except for the highest pH values studied.

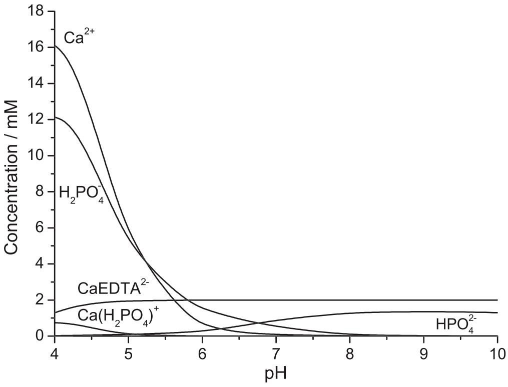

Fig. 4. Distribution diagram in the presence of EDTA.

Table 3
Results from batch experiments and XPS analysis.

Solution				Bulk solid		Surface (XPS)		
$\mathrm{pH_{fin}}$	Cd (mM)	Ca (mM)	P (mM)	(Cd + Ca)/P	Cd/Ca	Ca/P	(Cd + Ca)/P	Cd/Ca
Initial solution: Cd 2.1 mM								
5.40	1.58	1.07	0.14	1.46	0.03	1.01	1.31	0.29
6.74	1.37	0.80	0	1.57	0.04	0.97	1.39	0.43
8.44	1.08	0.44	0	1.63	0.06	0.97	1.52	0.56
11.1	0	0.23	0	1.73	0.11	1.02	2.66	1.70
Initial solution: Cd 2.1 mM + EDTA 2 mM								
5.18	2.03	2.18	1.32	1.56	0.004	1.15	1.32	0.15
7.61	1.97	0.88	0.14	1.54	0.008	1.09	1.28	0.18
8.34	1.94	0.38	0	1.56	0.009	1.09	1.29	0.18
12.4	1.94	0.10	0	1.58	0.009	1.22	1.42	0.16

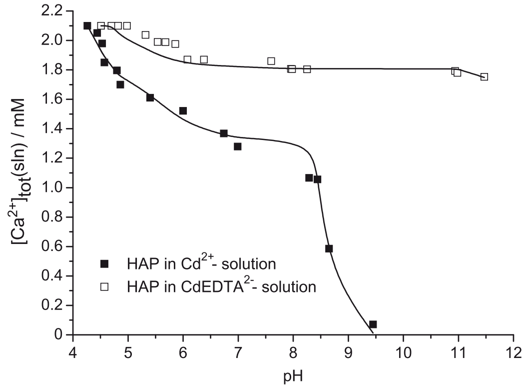

Fig. 5. Experimental (symbols) and calculated (lines) results of Cd sorption on HAP in Cd- and Cd–EDTA-solution.

In Cd solutions, the amount of Cd at the surface of the HAP particles increases with pH (Cd/Ca = 0.29–1.70), while Ca/P atomic ratio decreases (1.4 → 0.97–1.02) due to Cd sorption and remains practically constant at all pHs (Table 3). The corresponding atomic ratio (Ca + Cd)/P (1.4 ± 0.1) at the surface does not change remarkably in the pH range 5.4–8.4 (Fig. 3) indicating ion exchange $\mathrm{Ca}^{2+} \leftrightarrow \mathrm{Cd}^{2+}$ and the formation of a new surface solid-solution phase with the composition $\mathrm{Ca_{8.4}Cd_{8.4-\mathit{x}}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}}$. Further prominent increase in Cd surface concentration at highest pH 11.1 is related to the disappearance of Cd ions from solution caused by $\mathrm{Cd(OH)_2}$ precipitation, the process seems to start at pH > 8.4 (Fig. 5). The possible formation of $\mathrm{Cd_3(PO_4)_2}$ is also ruled out as it would yield Cd/P ratios (Ca/P $*$ Cd/Ca) around 1.5. The values obtained from XPS measurements are within the range 0.3–0.5 (Table 3, pH 5.40–8.44). A calculation including this solid phase also showed its non existence.

The amount of Cd at the surface was noticeable lower in the presence of EDTA (Cd/Ca = 0.15–0.18, Table 3). However, the atomic ratio (Ca + Cd)/P remains almost the same indicating that the HAP surface phase has a similar composition as in pure Cd solutions (Fig. 3). It should also be emphasized that the depth of analysis in XPS for HAP is approximately 6 nm, and the atomic ratios discussed above represent average values within this surface layer.

4.2.2. Batch experiments

The results of the analysis of the solutions after equilibration show increases in Cd sorption in the pH range 4.5–8 (Fig. 5) in accordance with earlier studies (Chen et al., 1997; Smiciklas et al., 2008). At higher pH values the Cd concentration drops rapidly and Cd is totally removed from the solution at pH 9.5. This is interpreted as the precipitation of $Cd(OH)_2$ (Figs. 5 and 7, Eq. (14)), which also was supported by the equilibrium analysis (see below).

The presence of EDTA reduces the amount of Cd removed by HAP (Fig. 5) due to the formation of $[CdEDTA]^{2-}$ in solution (Eq. (15)). In Cd–EDTA solutions the extent of cation exchange $Ca^{2+} \leftrightarrow Cd^{2+}$ on HAP is less extensive due to Cd complexation with EDTA and therefore the Ca^{2+} concentration in solution is minor (Fig. 1).

4.2.3. Modelling

Questions to be answered when Cd is added as Cd^{2+} or $CdEDTA^{2-}$ are: (i) Is the solubility of HAP affected? (ii) How is Cd reacting with the HAP-particles? Are we dealing with surface complexation reactions like (11), (12) or the formation of a new Cd-containing HAP phase according to (13)? (iii) Is this new phase to be regarded as a Cd-containing HAP phase with a homogeneous distribution of Cd or does it represent a surface layer? (iv) Does the high stability of the $CdEDTA^{2-}$ complex prevent Cd to react with HAP?

To find the answers to these questions solubility experiments were performed in a 2.1 mM Cd^{2+} solution as well as in a 2 mM $CdEDTA^{2}$-solution with an excess Cd^{2+} amounting to 0.1 mM. In this way the possible formation of the solid solution can be studied at two different Cd^{2+} concentrations (0.1 and 2.0 mM) and also it may be possible to find the answer to iv).

From Fig. 2 it can clearly be seen that the solubility of HAP with respect to $[HPO_4^{2-}]_{tot}(sln)$ decreases with increasing additions of Cd at all pH-values. This is also the case with respect to $[Ca^{2+}]_{tot}(sln)$ and pH $\leqslant$ 6.5 and is caused by lower solubility of the new surface layer that is forming in Cd-containing solution. Additionally, the new Cd-containing layer isolates the surface of grains thereby reducing solubility (Valsami-Jones et al., 1998; Corami et al., 2007). At higher pH-values $[Ca^{2+}]_{tot}(sln)$ values are found which are higher than in the pure HAP-system with 2 mM Cd-solution. This observation reflects the replacement of Ca from HAP due to ion exchange reactions like (11), (13). The formation of a solid solution as in (13) is found to be more likely than the formation of a surface complex as in (11). This is because of the high adsorption capacity of HAP in relation to the low surface site concentration of $\equiv CaOH$ sites (0.57 mM).

4.3. HAP and $CdEDTA^{2-}$

Experimental $[Cd^{2+}]_{tot}(sln)$ data with EDTA shows a slight (0-0.4 mM) decrease with increasing pH (pH $\geqslant$ 5). This implies that not only does the Cd-excess react with the HAP-particles but a fraction of Cd from the EDTA complex also reacts. From Table 3, a calculation of the composition of the Cd-containing HAP phase (assuming a homogeneous distribution) results in a Cd/Ca ratio of 0.004–0.009. However, results from the XPS analysis show a much higher ratio (0.15–0.18; Table 3). This implies that the reacted Cd is present within a surface layer of the HAP-particles. By assuming the solid solution composition as defined in (13) and by considering the different XPS results in terms of Cd/Ca ratios an approximate composition can be calculated. Including uncertainties (0.16 ± 0.02) in this ratio gives an interval in Cd/Ca of 0.1–0.2, which corresponds to the following compositions $Ca_{7.6}Cd_{0.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ with Cd/Ca = 0.1 and $Ca_{7.0}Cd_{1.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ with Cd/Ca = 0.2.

A series of calculations were performed and the "best" fit was obtained with Cd/Ca = 0.1 with $\log K_s(Ca_{7.6}Cd_{0.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s) + 4.8H^+ \leftrightharpoons 7.6Ca^{2+} + 0.8Cd^{2+} + 6HPO_4^{2-} + 0.4H_2O) = -28.03 \pm 0.07$. In these calculations the total concentrations of Ca and HPO_4^{2-} of the Cd-containing surface layer have to be given as input values. These were obtained by an interpolation of experimental $[Ca^{2+}]_{tot}(sln)$ and $[HPO_4^{2-}]_{tot}(sln)$ data to get the corresponding values at the onset of the surface precipitation (pH = 4.6). The values so obtained were 3.1 and 2.2 mM, respectively. As can be seen from Figs. 1, 2 and 5, the fit of the model to experimental $[Ca^{2+}]_{tot}(sln)$, $[HPO_4^{2-}]_{tot}(sln)$ and $[Cd^{2+}]_{tot}(sln)$, data is good. A distribution diagram showing the Cd-speciation (Cd^{2+}, $CdEDTA^{2-}$, $Ca_{7.6}Cd_{0.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$) is shown in Fig. 6.

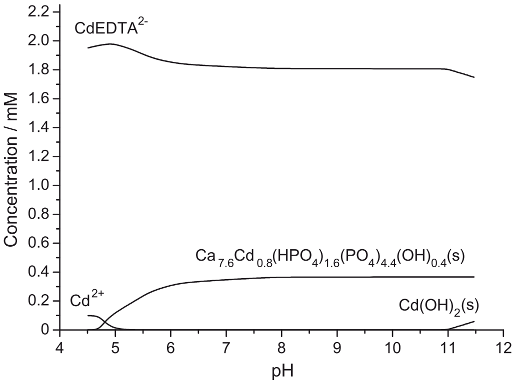

Fig. 6. The speciation of Cd in Cd–EDTA-solution.

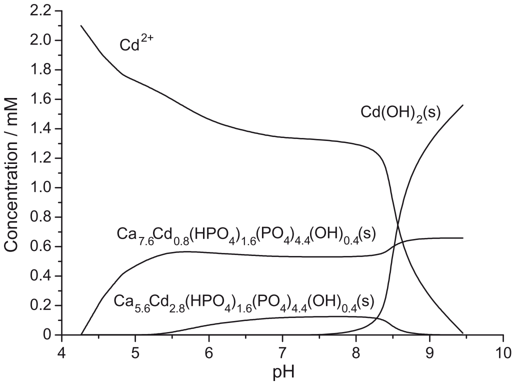

Fig. 7. The speciation of Cd in Cd-solution.

4.4. HAP and Cd^{2+}

The interaction between Cd^{2+} in solution and HAP-particles starts at pH ≈ 4.4 and increases with increasing pH (see Fig. 7). Again, the XPS analysis (see Table 3) show a HAP surface enriched in Cd with a Cd/Ca ratio increasing from 0.29 to 1.7 with increasing pH. The value at pH 11.1 indicates the formation of a $Cd(OH)_2$ precipitate (which is also postulated from the equilibrium analysis (see above). Cadmium/Ca ratios between 0.29 and 0.56 (Table 3) indicate the possible composition of the surface layer varying between $Ca_{6.5}Cd_{1.9}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ and $Ca_{5.4}Cd_{3.0}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$. The equilibrium analysis showed the "best" fit to be obtained for a surface phase with the composition $Ca_{5.6}Cd_{2.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ and a $\log K_s$ value of -27.39 ± 0.06. Input values for the total concentrations of Ca^{2+} and HPO_4^{2-} (5.4 and

3.9 mM, respectively) of the surface layer were interpolated as described above. Figs. 1, 2 and 7 show a good agreement between experimental data ($[Cd^{2+}]_{tot}(sln)$, $[Ca^{2+}]_{tot}(sln)$ and $[HPO_4^{2-}]_{tot}(sln)$) and the corresponding calculated values. The equilibrium analysis also showed the formation of $Cd(OH)_2(s)$ at $pH \geqslant 8$. The different phase distributions with pH are shown in Fig. 7. Both of the Cd-containing HAP-phases are formed at this high Cd-concentration. It seems likely that there is a Cd-gradient from the surface with the Cd-rich phase being formed in the topmost layer. However, data showing this is not available at present.

Cadmium near-surface depth profile can be reconstructed using angle-resolved XPS. Unfortunately, it is possible to acquire such data only with a monocrystal surface which is not the case for powder samples.

5. Summary

Hydroxyapatite dissolution and surface phase transformations in the absence and presence of EDTA, Cd^{2+} and $CdEDTA^{2-}$ were studied over a wide pH range. The different samples were characterised utilizing the surface sensitive XPS technique and by measuring the total sorption of Cd^{2+} as well as Ca^{2+} and HPO_4^{2-} ions dissolved from HAP.

The solution pH affects the dissolution of HAP and the amounts of sorbed Cd in the equilibrium pH range 4.5–9. The batch experiments and XPS analysis indicate that the apatite surface layer differs from the bulk. The dissolution and Cd sorption mechanisms on HAP are complex and involve the combination of several simultaneous aqueous and surface reactions.

The proposed model was used in the present study to quantify proton and ligand (EDTA) promoted dissolution of HAP and surface phase transformations in the presence of Cd^{2+} and $CdEDTA^{2-}$. It was observed that the complex $CdEDTA^{2-}$ does not adsorb on HAP. Cadmium sorption on HAP occurs mainly by ion exchange reactions by formation of new more insoluble surface phases with a composition $Ca_{7.6}Cd_{0.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ in case of low “free” Cd^{2+} concentration in solution and additionally $Ca_{5.6}Cd_{2.8}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ in the presence of higher concentration of Cd^{2+}. It seems that additional compositions within the solid solution series are likely to form. However, as the strategy of the equilibrium analysis has been to present as simple a model as possible, no attempts were made to include more parameters.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apgeochem.2011.08.010.

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Paper IV

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Hydroxy- and fluorapatite as sorbents in Cd- Zn- multicomponent solution in the presence of EDTA.

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Hydroxy- and fluorapatite as sorbents in Cd(II) - Zn(II) multicomponent solution in the presence of EDTA

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Abstract

The removal of cadmium and zinc from aqueous solutions by hydroxyapatite (HAP) and fluorapatite (FAP) is investigated by batch experiments with and without EDTA being present in the pH range 4 to 11 (25 °C; 0.1 M KNO_3). The surface composition of the solid phases is analysed by X-ray photoelectron spectroscopy (XPS).

The surface layer of apatites (AP), according to (Ca+Cd+Zn)/P atomic ratio, is found to change from 1.2 to 1.4±0.1 due to ion exchange process ($Ca^{2+} \leftrightarrow Cd^{2+}/Zn^{2+}$) in solution. The amount of Cd^{2+} and Zn^{2+} removed from the solution increases with increasing pH, reaching ≈ 100 % at pH 9. The removal capacity of Zn is higher (72 mmol/100 g HAP, 54 mmol/100 g FAP) compared with Cd (38 mmol/100 g HAP, 34 mmol/100 g FAP). In the Cd-Zn binary system, competitive metal sorption reduces the individual removal capacity (40 mmol Zn/100 g HAP, 33 mmol Zn/100 g FAP, 23 mmol Cd/100 g HAP, 27 mmol Cd/100 g FAP) but the total adsorption maximum is approximately constant.

In the presence of EDTA, the Cd and Zn removal is reduced remarkably due to the formation of $[CdEDTA]^{2-}$ and $[ZnEDTA]^{2-}$ in solution. The solubility of AP increases in the presence of EDTA at pH values above 5. Contrary to this, the HAP solubility is found to decrease in the presence of Cd^{2+} and Zn^{2+}.

XPS reveales an enrichment of AP surface by Cd and Zn, which is interpreted as the formation of new surface solid-solution phase.

1. Introduction

Calcium phosphates with apatite structure [$Ca_{10}(PO_4)_6(OH/F)_2$] possess an ability to bind metal ions from solutions and are, therefore, considered to be prospective materials for reducing heavy metal toxicity by decreasing their mobility and bioavailability from polluted soils, sediments, and waters.

Different investigations indicate that divalent metal sorption range on apatite, as well as the sorption mechanisms, strongly depend on: type of divalent metal, AP physico chemical properties and other factors such as metal concentration, solution pH, contact time, presence of other ionic species and complexing ligands etc. (Monteil-Rivera & Fedoroff, 2002; Smiciklas *et al.*, 2008). It is found that apatite sorption capacity depends mainly on its specific surface area (SSA), ranging from 16 to 78 and from 11 to 79 mmol/100g of AP for Cd and Zn, respectively (Peld *et al.*, 2004).

Depending on metal ion and apatite characteristics, sorption can proceed via different mechanisms. Sorbed metal ions can be bound at the surface (adsorption), or introduced into the apatite structure, followed by the filling of cationic vacancies in a nonstoichiometric apatite (absorption), or exchanged with apatite lattice cations (ion-exchange). Dissolution of calcium apatite and the formation of new metal phosphate phases is also possible (dissolution-precipitation method) (Xu *et al.*, 1994; Mandjiny *et al.*, 1995; Charlet *et al.*, 2006). However, because of the limited knowledge about the relative importance of each process in metal removing, it seems that all four mechanisms could be involved.

Several investigations show that the main mechanism of Cd removal is the ion exchange with Ca^{2+} (Mandjiny *et al.*, 1995; Jeanjean *et al.*, 1996; da Rocha N. C. C., 2007) and partial dissolution of apatite with subsequent precipitation of a Cd-containing hydroxyapatite with the formula $Cd_xCa_{10-x}(PO_4)_6(OH)_2$ (Raicevic *et al.*, 2005; Marchat *et al.*, 2007; Corami *et al.*, 2008).

Different investigations have increasingly insisted that the sorption is determined by apatite surface. They show that Cd sorption on HAP occurs by forming the new less soluble surface layer and not through the bulk (Marchat *et al.*, 2006; Yasukawa *et al.*, 2007; Zhang *et al.*, 2009).

The mechanism of Zn sorption on apatites is less clear. To explain Zn immobilisation on apatite, many concurrent processes mentioned above are also proposed (Xu *et al.*, 1994; Sheha, 2007; Smiciklas *et al.*, 2008). According to Corami et al (Corami *et al.*, 2007), Zn immobilisation takes place through a two-step mechanism: the first step is the surface complexation on specific sites of HAP surface; the second step is ion exchange with Ca^{2+} and the formation of a heavy metal-containing hydroxyapatite.

Since industrial effluents may contain more than one metal, several studies have been examined such systems and have shown that apatite also effectively sorbs heavy metals from multi-metal solutions, but the individual sorbed amount decreases in the presence of competing cations (Kandah, 2004; Corami *et al.*, 2007; 2008; Smiciklas *et al.*, 2008).

Crystal structure investigations show that there are minor modifications of the crystallite morphology after cadmium (Jeanjean *et al.*, 1996; Yasukawa *et al.*, 2007) and zinc fixation (Chen *et al.*, 1997b). The concentrations of sorbed cations in solid phase (atomic ratio of heavy metal/Ca $\approx$ 0.05) are too small to induce significant changes of cell parameters and therefore the XRD and FTIR analyses, particularly in the case of multi-component solution, do not reveal changes in solid phase. More information is obtained by X-ray photoelectron spectroscopy (XPS) that shows exact surface composition before and after reaction with Cd and Zn (Marchat *et al.*, 2006; Yasukawa *et al.*, 2007; Zhang *et al.*, 2009).

Heavy metal bonding with minerals and plant uptake in environmental conditions is affected by natural (humic compounds) and synthetic chelating agents (Grcman *et al.*, 2001; Kos & Lestan, 2004; Smiciklas *et al.*, 2006). The amount of synthetic ethylene diamine tetraacetic acid (EDTA), a strong chelating compound, increases continuously in the environment (Grundler *et al.*, 2005). In agricultural practice EDTA is introduced into soil as a common ingredient of fertilisers or for increasing heavy metal ion bioavailability in phytoextraction. It is found that if apatite amendment to Pb, Zn, Cd, and Cu-contaminated soil reduces their bioavailability, then addition of EDTA enhances heavy metal uptake by plants (Grcman *et al.*, 2001; Kos & Lestan, 2004). In batch experiments the effect of EDTA concentration on Cd, Co and Pb sorption characteristics on apatite is clarified (Kos & Lestan, 2004; Smiciklas *et al.*, 2006; Tõnsuaadu *et al.*, 2008). The amount of metal ion removed from solution decreases significantly with the increase in the concentration of chelating ligands.

Zn and Cd are studied as typical heavy metals, of wide presence in surface and ground waters, soils and sediments caused by 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 cadmium 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 are atmospheric pollution, farm manures, sewage sludge, fertilisers, agro chemicals, limes and industrial wastes (Mirsal, 2008).

It is evident that the mechanism of metal interaction with apatites varies depending on system conditions, particularly on the environmental pH, the properties and composition of the metal ions and the presence of complexing ligands in solution**.** Relatively few studies have concerned the sorption mechanism of heavy metals in the presence of chelating compounds.

The aim of this study is to evaluate and compare hydroxy- and fluorapatite capabilities for Cd and Zn simultaneous sorption in the presence of EDTA and to specify the adsorption mechanisms in a wide pH interval.

2. Materials and methods

Apatites (HA-9 and FA-2) were prepared by precipitation from aqueous solution. Two solutions, one containing $Ca(NO_3)_2$, the other containing $(NH_4)_2HPO_4$ or NH_4F, were added simultaneously to NH_4OH-NH_4NO_3 solution under N_2 flow. The pH of the solution was adjusted and maintained at 9.0 throughout the reaction by adding a concentrated ammonia solution. The suspension was stirred for 3 hours at the room temperature in order to improve the homogenity and crystallinity of the precipitate, and then kept at room temperature for 24 hours. The precipitates were filtered, washed thoroughly with distilled water and dried at 110°C. The apatite characteristics are given in Table 1. The synthesized materials were identified by X- ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses.

Table 1 The characteristics of apatites used

Sample	SSA, m^2/g	CaO, %	P_2O_5, %	F, %	Ca/P (bulk)
HAP (HA-9)	40.2	52.9	41.9	0	1.60
FAP (FA-2)	39.0	54.0	40.7	3.1	1.68

2.1. Solutions

The HAP/FAP dissolution and Cd/Zn sorption experiments were performed in batch experiments at room temperature within the final pH range 4–11. Sorption solutions with different components contained of 2.1 mM Cd, 2 mM Zn, 2 mM EDTA and were prepared from analytical grade $Cd(NO_3)_2$, metallic Zn (dissolved in HNO_3) and Na_2EDTA.

Solution combinations used: Cd^{2+}; Cd^{2+}+EDTA; Zn^{2+}; Zn^{2+}+EDTA; Cd^{2+}+Zn^{2+}; Cd^{2+}+Zn^{2+}+EDTA. The final pH of solutions was adjusted adding different amounts of KOH or HNO_3. An ionic medium of 0.1 M KNO_3 was used.

2.2. Batch experiments

The solubility and adsorption experiments were carried out by mixing the suspensions on a rotating stirrer for 7 days at room temperature (23 ± 2 °C). The solid/solution ratio was 2 g/L. The solid phase was separated by filtration. All experiments were performed in duplicate.

2.3. Analytical methods

pH was measured with Mettler Toledo electrode DG-112 Pro calibrated with Mettler Toledo pH buffer solutions (4.01; 7.00; 9.21) and connected to an automatic titrator T90 under N_2 flow. The concentrations of Ca^{2+} and Cd^{2+} in solution were determined by atomic absorption spectrometry (VARIAN Spectra AA 55B) and the concentration of PO_4^{3-} was determined spectrophotometrically (SpectroDirect) as the phosphomolybdate yellow complex.

The surface area of the AP particles was measured by the BET-method (adsorptive gas N_2, carrier gas He, heating temperature 150°C) using sorptometer EMS-53 and KELVIN 1040/1042 software (Costech International).

The centrifuged (4000 rpm, 15 min) wet pastes of AP suspensions were used for cryogenic XPS measurements. The fast-freezing procedure applied to wet pastes is described in detail elsewhere (Shchukarev & Sjöberg, 2005; Shchukarev, 2006).

The XPS spectra were recorded with a Kratos Axis Ultra DLD electron spectrometer using a monochtomated Al K_α source operated at 150 W, a hybrid lens system with magnetic lens providing an analysis area of 0.3 x 0.7 mm^2, and a charge neutraliser. The binding energy (BE) scale was referenced to the C 1s line of aliphatic carbon contamination, set at 285.0 eV. Processing of the spectra was accomplished with Kratos software.

3. Results

3.1. Final pH of solutions

The amounts of acid or base added to the solution to achieve the final pH after reaction with HAP in the pH interval from 4 to 11 are presented in Figure 1. The shape of the curves is complicated and indicates occurrence of different reactions. 3–5 regions depending on the solution composition could be differentiated. The amounts of proton added to get the acidic solutions with pH < 6 were remarkable. In the pH range 6–10 the final pH was achieved with a very small acid/base addition in solutions without cations. More OH^- was needed to achieve the same pH value in the solutions containing Cd and Zn and once more in the presence of EDTA (Fig. 1b). These results indicate use of protons or binding of OH^- ions in cation sorption reactions.

Without acid/base additions (H^+/OH^- added = 0) the presence of Cd and/or Zn ions shifted the equilibrium pH to a lower value (Cd 5.65, Zn 5.15, Cd+Zn 4.85) compared with HAP suspension without heavy metals (7.54) (Fig 1a). Similar pH change took place in the experiments with FAP (Figure I in Appendix)- if no acid/base was added, equilibrium pH was at 6.47 and in the presence of Cd, Zn and Cd+Zn ions was 5.18, 4.35 and 4.47, accordingly.

The remarkably higher OH^- consumption is caused by precipitation of $Cd(OH)_2$ (pH>8.5) and $Zn(OH)_2$ (pH>7.5) (Trussell & Wagner, 1996; Smiciklas *et al.*, 2000).

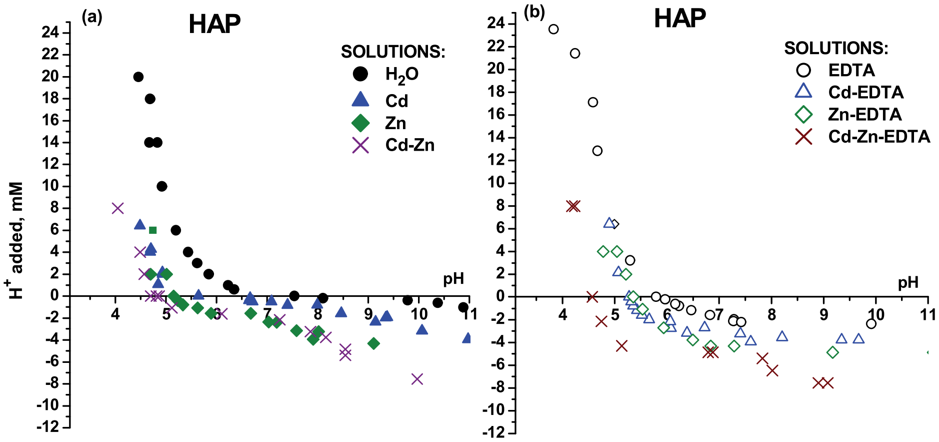

Figure 1. The amount of H^+/OH^- added and the resultant equilibrium pH of HAP solutions without (a) and with (b) EDTA

3.2. Apatite dissolution

The change of total metal concentrations in solution (dissolved Ca, $[Ca^{2+}]_{sln}$) and in solid phase (removed Cd and Zn, $[Me^{2+}]_{sld}$) in single- and binary-metal systems obtained by chemical analysis of solutions by HAP are presented in Figure 2 and 3, respectively.

It is well known that HAP is much more soluble than FAP (Figure II in Appendix) (Zhu *et al.*, 2009). The dissolution of Ca in sorption experiments depends on the solution composition as well as on the pH. Apatite dissolution rate (according to $[Ca^{2+}]_{sln}$) decreased in accordance to the final pH increase. The presence of metal ions decreased hydroxyapatite solubility at pH < 6.5 and there was no remarkable difference in AP's solubility in single Cd- and Zn- solutions (Fig. 2a). In the case of FAP the impact of heavy metals on Ca dissolution was minor. Ca solubility increased remarkably in EDTA-solution above pH 5 (Figure II in Appendix).

Phosphorus dissolved only at acidic pH-s (Table 3, 4) and above pH 5 it was negligible.

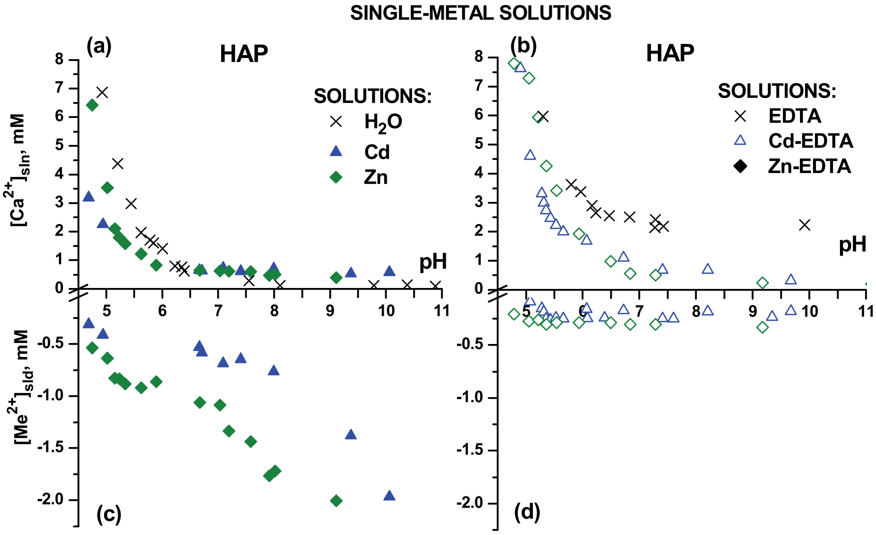

Figure 2. Dissolved Ca concentration ($[Ca^{2+}]_{sln}$) and removed Cd and Zn concentrations ($[Me^{2+}]_{sld}$) by HAP in single-metal solutions without (a, c) and with EDTA (b, d) depending on equilibrium pH.

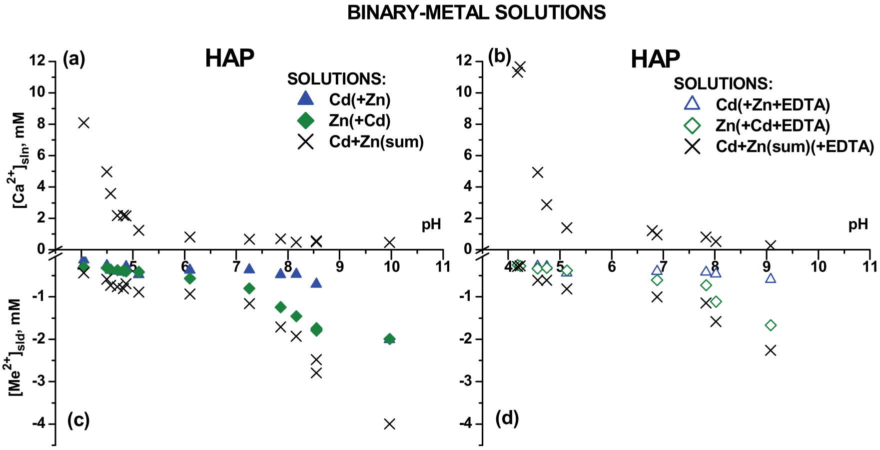

Figure 3. Dissolved Ca concentration ($[Ca^{2+}]_{sln}$) and removed Cd and Zn concentrations ($[Me^{2+}]_{sld}$) by HAP in binary-metal solutions without (a, c) and with EDTA (b, d) depending on equilibrium pH.

Table 2. Lowest and highest sorbed amount of Cd and Zn in single- and binary-metal solutions in the absence/presence of EDTA in the studied pH range ($Cd(OH)_2$ and $Zn(OH)_2$ precipitation excluded)

	Solution	**HAP**			**FAP**		
		pH	mM	mmol/100g	pH	mM	mmol/100g
SINGLE METAL	Cd	4.69	0.31	16	4.11	0.18	10
		7.99	0.78	38	8.35	0.69	34
	Cd+EDTA	4.90	0.04	2	4.03	0.08	4
		8.21	0.23	9	7.30	0.34	17
	Zn	4.74	0.54	27	4.35	0.65	33
		7.58	1.44	72	6.95	1.08	54
	Zn+EDTA	4.78	0.21	10	4.28	0.32	16
		7.28	0.30	15	7.40	0.31	15
BINARY METAL	Cd(+Zn)	4.49	0.27	14	4.19	0.23	11
		8.16	0.48	23	8.05	0.55	27
	Zn(+Cd)	4.49	0.32	16	4.19	0.35	17
		7.25	0.80	40	7.16	0.65	33
	Cd(+Zn+EDTA)	4.57	0.28	13	4.30	0.13	10
		8.02	0.46	23	7.33	0.59	30
	Zn(+Cd+EDTA)	4.57	0.33	17	4.30	0.44	22
		7.83	0.73	34	7.33	0.88	44

3.3. Metal sorption

In Figures 2(c, d) and 3(c, d) four regions with different cation sorption rates could be followed. Up to pH values 4.5–5 Cd and Zn sorption continuously increased with the decrease in AP dissolution. In the next region up to pH-s 7 and 8 for Zn and Cd, respectively, in single solutions, the sorption rate was almost constant. Above these pHs the amount of cations removed from solution increased rapidly with pH increase and achieved a new constant value at 8–8.5 and 10 for Zn and Cd, respectively. In binary cation solution these stages were wider and smoother and, in the presence of EDTA, almost not noticeable.

The precipitation of $Zn(OH)_2$ starts at pH>7.5 and $Cd(OH)_2$ at pH>8.5 (Trussell & Wagner, 1996; Smiciklas *et al.*, 2000). Consequently, at pH region above 7.5-8.5 we cannot interpret the decrease of metal content in solution as only the metal sorption on apatites. Therefore, talking about sorbed metal amounts (Table 2), below are considered the amounts removed up to the pH values at which precipitation of hydroxides starts.

As pH increased, the sorbed amount of Cd increased from 0.31 mM to 0.78 mM (16–38 mmol/100 g) by HAP and from 0.18 mM to 0.69 mM (10–34 mmol/100 g) by FAP. The sorbed amount of Zn was 0.54–1.44 mM (27–72 mmol/100 g) by HAP and 0.65–1.08 mM (33–54 mmol/100 g) by FAP (Table 2).

In the Cd-Zn binary system (Figure 3), the amount of Cd removed was 0.27–0.48 mM (14–23 mmol/100 g) by HAP and 0.23–0.55 mM (11–27 mmol/100 g) by FAP. The removed amount of Zn was 0.32–0.80 mM (16–40 mmol/100 g) by HAP and 0.35–0.65 mM (17–33 mmol/100 g) by FAP (Table 2).

Competitive metal sorption reduced the individual removal capacity of HAP by 6–14% and 10–14% for Cd and Zn, respectively, compared to the single-metal system. The Cd sorption was not affected remarkably in the presence of Zn on FAP. In the same time, the sorbed amount of Zn on FAP reduced up to 20 %. The total adsorption maximum on apatite was approximately constant, irrespective of solution's cation composition.

The presence of EDTA significantly reduced the amounts of Cd and Zn adsorbed. The removed amount of Cd was 0.04–0.23 mM (2–9 mmol/100 g) by HAP and 0.08–0.34 mM (4–17 mmol/100 g) by FAP. In the case of Zn, the values were 0.21–0.30 mM (10–15 mmol/100 g) by HAP and 0.32 mM (0.16 mmol/100 g) by FAP (Table 2). However, the removed amount of Zn was higher than Cd in any case, even in the presence of EDTA.

In binary metal systems EDTA impact on the amount of metal removed was less remarkable because of the higher concentration of cations (4.1 mM of metals, Table 3, 4) in comparison with EDTA concentration (2 mM) in the solution. Accordingly, only part of the cations formed complexes with EDTA. The sorbed amount of Cd was 0.28–0.46 mM (13–23 mmol/100 g) by HAP and 0.13–0.59 mM (10–30 mmol/100 g) by FAP. The removed amount of Zn was 0.33–0.73 mM (17–34 mmol/100 g) by HAP and 0.44–0.88 mM (22–44 mmol/100 g) by FAP (Table 2).

3.4. XPS analysis of solid samples

The results of cryogenic XPS-analysis are presented in Table 3 (HAP) and Table 4 (FAP). The mole ratios in bulk solid are calculated according to solution analyses. XPS data demonstrate significant changes of AP surface composition and the difference from bulk composition (in terms of atomic ratios of Ca/P, Cd/Ca, and Zn/Ca) after equilibration in sorption solutions.

In metal solutions, the amount of metals at the surface of the AP particles increased with pH [Cd/Ca = 0.27–0.75, Zn/Ca = 0.16–1.03, (Cd+Zn)/Ca = 0.35–1.89], while Ca/P atomic ratio decreased (HAP: 1.24 → 1.03–1.09 by Cd, 1.11–1.12 by Zn, 1.02–1.07 by Cd+Zn; FAP: 1.29 → 1.01–1.12 by Cd, 1.16–1.11 by Zn, 1.00–1.09 by Cd+Zn) due to heavy metal sorption and remained practically constant at all pHs (Table 3, 4). Corresponding atomic ratio (Ca+Cd+Zn)/P (1.4 ± 0.1) at the surface was higher than AP initial Ca/P ratio (1.24/1.29) and did not change remarkably up to pH 7.5. Further prominent increase in Cd and Zn surface concentration at highest pHs was related to disappearance of metal ions from solution caused by $Cd(OH)_2$ and $Zn(OH)_2$ precipitation.

The amount of Cd at the surface was noticeably lower in the presence of EDTA (Cd/Ca = 0.14–0.22, Zn/Ca = 0.02–0.04, Table 3, 4). However, the atomic ratio (Ca+Cd)/P remained almost the same (1.4 ± 0.1).

In a multicomponent solution (Cd+Zn and Cd+Zn+EDTA), according to solution analysis, more Zn was sorbed than Cd. At the same time, according to XPS results, the Cd concentration was higher than Zn concentration on the surface (Table 3, 4). This contradiction emerged at pH 4.87 and 6.10 in the HAP+Cd+Zn system, at pH 4.23 and 6.79 in the HAP+Cd+Zn+EDTA system and at pH 4.95 in the FAP+Cd+Zn+EDTA system.

According to XPS results, the presence of EDTA in multi-metal solution did not impact the (Cd+Zn)/Ca ratio remarkably compared with the same solutions in the absence of EDTA.

It should also be mentioned that the depth of XPS analysis at apatite's surface is approximately 6 nm, and the atomic ratios discussed above represent average values within this surface layer.

Table 3. The composition of solution, bulk solid and surface of HAP (HA-9)

SOLUTION					**BULK SOLID**		**SURFACE (XPS)**				
pH	Ca, mM	P, mM	Cd, mM	Zn, mM	(Ca+Cd+Zn)/P	(Cd+Zn)/Ca	Ca/P	Cd,at%	Zn,at%	(Ca+Cd+Zn)/P	(Cd+Zn)/Ca
HAP											
7.54	0.29	0	–	–	1.59	–	1.24	–	–	–	–
HAP + 2.1 mM Cd											
4.94	2.26	0.85	1.70	–	1.56	0.025	1.03	3.26	–	1.31	0.27
6.71	0.63	0	1.53	–	1.61	0.032	1.09	4.68	–	1.44	0.33
9.37	0.54	0	0.73	–	1.68	0.075	1.05	7.49	–	1.84	0.75
HAP + 2.1 mM Cd + 2 mM EDTA											
5.07	4.60	2.73	2.02	–	1.59	0.007	1.13	2.19	–	1.29	0.14
6.72	1.10	0	1.94	–	1.54	0.010	1.11	2.41	–	1.30	0.17
9.35	0.15	0	1.87	–	1.62	0.012	1.22	2.54	–	1.44	0.18
HAP + 2 mM Zn											
4.70	3.47	1.69	–	1.31	1.59	0.045	1.12	–	2.97	1.34	0.20
6.68	0.65	0	–	0.96	1.65	0.058	1.11	–	5.08	1.51	0.36
9.11	0.40	0	–	0.02	1.75	0.108	1.12	–	11.1	2.28	1.03
HAP + 2 mM Zn + 2 mM EDTA											
4.78	7.80	4.37	–	1.81	1.54	0.018	1.25	–	0.34	1.28	0.02
6.83	0.55	0.35	–	1.72	1.65	0.017	1.28	–	0.36	1.31	0.02
9.17	0.23	0	–	1.69	1.62	0.017	1.30	–	0.63	1.35	0.04
HAP + 2.1 mM Cd + 2 mM Zn											
4.87	2.16	0.71	1.84	1.60	1.58	0.040	1.02	2.99	1.49	1.38	0.35
6.10	0.82	0	1.76	1.43	1.62	0.051	1.04	3.12	2.33	1.46	0.40
8.55	0.50	0	1.43	0.24	1.78	0.134	1.07	3.83	11.0	3.09	1.89
HAP + 2.1 mM Cd + 2 mM Zn + 2mM EDTA											
4.23	11.9	5.97	2.13	1.73	1.31	0.036	1.08	1.90	0.87	1.30	0.21
6.79	1.21	0	1.70	1.31	1.61	0.063	1.00	2.76	2.28	1.46	0.46
8.90	0.24	0	1.54	0.35	1.78	0.120	1.08	3.49	6.97	2.36	1.18

Table 4. The composition of solution, bulk solid and surface of FAP (FA-2)

SOLUTION					BULK SOLID		SURFACE (XPS)				
pH	Ca, mM	P, mM	Cd, mM	Zn, mM	(Ca+Cd+Zn)/P	(Cd+Zn)/Ca	Ca/P	Cd, at%	Zn, at%	(Ca+Cd+Zn)/P	(Cd+Zn)/Ca
FAP											
6.47	0.28	0	–	–	1.66	–	1.29	–	–	1.29	0
FAP + 2.1 mM Cd											
5.16	0.88	0	1.67	–	1.64	0.025	1.01	3.94	–	1.31	0.30
7.49	0.52	0	1.64		1.68	0.025	1.12	3.93	–	1.43	0.28
FAP + 2.1 mM Cd+ 2 mM EDTA											
5.10	1.29	0.42	1.85	–	1.83	0.012	1.21	2.29	–	1.41	0.16
7.33	0.47	0	1.78	–	1.67	0.018	1.15	2.96	–	1.40	0.22
FAP + 2 mM Zn											
4.34	2.22	1.70	–	1.33	1.78	0.038	1.16	0.06	2.35	1.35	0.16
6.97	0.49	0.28	–	0.92	1.75	0.058	1.11	0.06	6.16	1.59	0.43
FAP + 2mM Zn+ 2mM EDTA											
5.05	1.53	0.84	–	1.68	1.70	0.019	1.26	–	0.55	1.30	0.03
8.58	0.19	0	–	1.71	1.69	0.016	1.26	–	0.29	1.29	0.02
FAP + 2.1 mM Cd + 2.1 mM Zn											
4.83	1.11	0.49	1.60	1.70	1.75	0.048	1.00	3.39	1.44	1.36	0.35
8.05	0.42	0.00	1.55	0.37	1.83	0.116	1.09	2.95	8.95	2.50	1.30
FAP + 2.1 mM Cd + 2 mM Zn + 2mM EDTA											
4.95	1.1	0.63	1.63	1.37	1.78	0.058	1.12	3.21	0.65	1.45	0.29
7.81	0.66	0.00	0.08	0.82	1.77	0.092	1.11	2.92	4.28	1.84	0.66

4. Discussion

4.1. *Effect of pH*

pH is probably the most significant parameter controlling the heavy metal removal process. Since AP particles exhibit pH-dependent surface charge, and the presence of heavy metal hydrolytic species depend on pH, this parameter significantly influences the sorption process.

AP exhibits large buffer capacity due to its amphoteric surface. Due to various processes that may occur at the solid surface/solution interface (preferential dissolution of certain constituents of crystal lattice, ionisation of surface groups, adsorption of ions or formation of complex compounds between surface groups and ions from the solution) the final pH values differ from the initial ones. It is found that for initial pH range 4–10 final pH values of apatite suspensions are the same and equal to pH_{PZC} - pH value where the surface charge is equal to zero, namely, the pH at which the charge due to the positive surface groups is equal to that due to the negative ones (Mandjiny *et al.*, 1995; Smiciklas *et al.*, 2008). Therefore, we monitored only final pH in equilibrium state.

The high consumption of protons at pH < 6 (Fig. 1) is related to apatite dissolution reaction (1):

$$Ca_{8.4}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}(s) + 4.8H^+ \leftrightharpoons$$

$$8.4Ca^{2+} + 6HPO_4^{2-} + 0.4H_2O \qquad (1)$$

The amount of protons in solution is also affected by protonation/deprotonation (2, 3) and complexation (4) reactions:

$$PO_4^{3-} + nH^+ \leftrightharpoons H_nPO_4^{(3-n)-} \; (n = 1, 2, 3) \qquad (2)$$

$$Ca^{2+} + H_2O \leftrightharpoons CaOH^+ + H^+ \qquad (3)$$

$$Ca^{2+} + PO_4^{3-} + nH^+ \leftrightharpoons CaH_nPO_4^{(n-1)+} \; (n = 0, 1, 2) \qquad (4)$$

Surface reactions such as adsorption and desorption of H^+ as well as the re-adsorption of PO_4-species according to reactions (5) – (8) have been shown to be important (Bengtsson *et al.*, 2009).

$$\equiv CaOH + H^+ \leftrightharpoons \equiv CaOH_2^+ \qquad (5)$$

$$\equiv OPO_3H_2 \leftrightharpoons \equiv OPO_3H^- + H^+ \qquad (6)$$

$$\equiv CaOH_2^+ + HPO_4^{2-} \leftrightharpoons \equiv CaOPO_3H^- + H_2O \qquad (7)$$

$$\equiv OPO_3H_2 + K^+ \leftrightharpoons \equiv OPO_3K^- + 2H^+ \qquad (8)$$

The equilibrium pH in apatite solutions in the absence of metals is 7.54 and 6.41 with HAP and FAP, respectively. In our experiments the sorption of Cd and Zn shifts the pH to lower values (Fig. 1, 2). The higher the sorbed amount is, the greater the deviation of the equilibrium pH from pure apatite solution pH. A similar pH decrease is observed in previous studies (Mandjiny *et al.*, 1995; Corami *et al.*, 2007; Smiciklas *et al.*, 2008; Viipsi *et al.*, 2010) and attributed to the release of H^+ ions of AP surface groups during the metal sorption.

The low adsorption of both Cd^{2+} and Zn^{2+} at acidic pH may be due to the positively-charged sorbent and sorbate species, which leads to an electrostatic repulsion interaction. As pH increases, the concentration of H^+ decreases and the concentrations of Cd^{2+} and Zn^{2+} in the solid phase increases.

According to the equilibrium $[Ca^{2+}]_{tot}$(sln) concentrations (Fig. 3, 4), the solubility of APs itself decreases with final pH increase. In the case of HAP, below pH 6.5, the total amounts of released Ca^{2+} are lower in divalent metal solutions where sorption takes place, than in the inert electrolyte (Fig. 3). This is explained by formation of the new heavy-metal-containing surface phase which has lower solubility than initial HAP. The new Cd/Zn-containing layer isolates the surface of grains, thereby reducing solubility (Valsami-Jones *et al.*, 1998; Charlet *et al.*, 2006; Corami *et al.*, 2007). This is more noticeable for HAP because of higher solubility compared with FAP.

The amounts of divalent cations removed from the solution increase with pH until ≈100% of metals are in a solid phase (Fig. 3, 4, Table 3, 4). However, regarding sorption on AP, we can talk only at below pHs where hydroxides start to precipitate. $Cd(OH)_2$ precipitates at pH>8.5 and $Zn(OH)_2$ pH>7.5 and above these pHs the hydroxide precipitation is also responsible for metal removal from solution. The remarkably higher values of (Ca+Cd+Zn)/P and (Cd+Zn)/P according to XPS analysis at highest pHs also confirm $Cd(OH)_2$ and $Zn(OH)_2$ precipitation (Table 3, 4).

4.2. *Effect of competing cations*

In binary solution (Cd+Zn) the competition of metals reduces individual sorption capacity up to 20% compared with the single component solutions, but the total adsorption maximum is approximately constant (63 mmol/100 g HAP, 60 mmol/100 g FAP). This means that the apatite sorption capacity does not depend on the cation composition in solution.

The maximum sorption capacity is an almost constant value per specific surface area of apatite (Peld *et al.*, 2004).

Earlier results have also shown that although in the multi-metal system, competitive sorption of aqueous metal ions affects individual sorbed amount, AP still selectively and efficiently removes them from solutions (Mandjiny *et al.*, 1995; Chen *et al.*, 1997a; Kandah, 2004; Corami *et al.*, 2007; 2008; Smiciklas *et al.*, 2008).

It is found that HAP most selectively sorbs metal cations with high electronegativity and ionic radii in the range 0.90-1.30 Å (the ionic radius of Ca^{2+} is 0.99Å) (Charlet *et al.*, 2006; Smiciklas *et al.*, 2008). Therefore Cd ions of proper radii (0.97Å) and higher electronegativity (1.69) should be preferred to Zn ions with ionic radii of 0.74 Å and electronegativity 1.65 (Manku, 1980).

The contradiction of sorbed amount of metals obtained from solution and surface analysis (Table 3, 4) seems to be related to non-uniform distribution of Zn- and Cd- containing precipitates into the depth of the samples. It looks like the surface is enriched with Cd. It is possible, that because of the smaller size of Zn atom, it penetrates deeper and thereby Cd is concentrated more on the surface. The general composition of new surface phase on AP does not change remarkably in comparison with single metal solutions and the (Ca+Cd+Zn)/P ratio remains equal to 1.4 ± 0.1.

The higher amount of adsorbed zinc in single- and binary- metal solutions in comparison with cadmium, also found by Kandah (Kandah, 2004), could be therefore explained by the smaller size of the zinc atom compared with that of cadmium.

4.3. *Effect of EDTA*

Similar to previous results (Tõnsuaadu *et al.*, 2008), the dissolution of HAP is increased in the presence of EDTA due to the high stability of Ca^{2+}-EDTA complexes:

$$EDTA^{4-} + nH^{+} \leftrightharpoons H_nEDTA^{(n-4)+} \ (n = 1, 2, 3, 4) \qquad (9)$$

$$EDTA^{4-} + nH^{+} + Ca^{2+} \leftrightharpoons CaH_nEDTA^{(n-2)+} \ (n = 0, 1) \qquad (10)$$

The effect of EDTA on apatite solubility is remarkable above pH 5 in the case of HAP and in whole investigated pH range in case of FAP (Fig. 3) in comparison with apatite's solubility in water.

In the presence of EDTA, which is a strong chelator, the amount of Cd and Zn removed by AP (Fig. 3, 4) is reduced because of the formation of $[Cd/ZnEDTA]^{2-}$ in solution:

$Me^{2+} + EDTA^{4-} + nH^{+} \leftrightharpoons Me(H)_{n}EDTA^{(2-n)-}$ ($n = 0, 1$) (11)

Therefore, in Cd-EDTA and Zn-EDTA solutions, the cation exchange $Ca^{2+} \leftrightarrow Cd^{2+}/Zn^{2+}$ on AP is less extensive due to heavy metal complexation with EDTA, the bound amount is lower and therefore the Ca^{2+} concentration in solution is minor.

XPS data are in agreement with the results obtained by solution analyses. The amount of Cd and Zn at the surface is noticeably lower [(Cd+Zn)/Ca ratios in Table 3, 4] in EDTA-containing solutions. However, the (Ca+Cd+Zn)/P remains almost the same, indicating that the AP surface phase has a similar composition as without EDTA present.

In a Cd-Zn-EDTA solution, the concentration of EDTA (2 mM) is lower than the cation concentration (4.1 mM) and therefore the total amount of cations sorbed is not affected by EDTA. The amount of Zn sorbed is higher than Cd, despite equality of the complex stabilities (logK of $[CdEDTA]^{2-}$ and $[ZnEDTA]^{2-}$ is 16.5) (Motekaitis, 2004).

Values of Zn (at%) on the surface in binary solution at pH 8.90 (Table 3) and 7.81 (Table 4) confirm precipitation of $Zn(OH)_2$ in the presence of EDTA. However, the smaller values compared with results where EDTA is excluded, show that EDTA impedes $Zn(OH)_2$ precipitation in a binary system. $Cd(OH)_2$ precipitation is not affected remarkably in binary solution with EDTA.

4.4. Sorption mechanism

The difference of total (Cd+Zn)/Ca ratios of solids according to chemical analysis and on the surface (XPS) indicates that metals are concentrated on apatite surfaces in accordance with earlier results, where it is found that the sorption of metal ions occurs only on the surface phase of apatite particles (Badillo-Almaraz *et al.*, 2003; Marchat *et al.*, 2006; Yasukawa *et al.*, 2007; Zhang *et al.*, 2009). The changes of atomic ratios on the surface indicate that the heavy metal removal mechanism differs depending on pH (Table 3, 4).

According to the batch experiments, HAP solubility is lowered in the presence of heavy metals at more acidic pHs (pH>6.5). At the same time, at near to neutral and alkaline pHs, we find $[Ca^{2+}]_{sln}$ values higher than in the metals excluded AP-system. This observation reflects the replacement of Ca from HAP due to ion exchange reactions:

$AP–Ca^{2+} + Me^{2+} = AP–Me^{2+} + Ca^{2+}$ (12)

However, similarly with our previous study (Viipsi *et al.*, 2011), it is important to notice that the total cations ratio to phosphorus increases when metal ions are sorbed (1.24/1.29 → 1.4 ± 0.1) and remains practically constant (irrespective of solution composition), except for the highest pH values studied, indicating the ion exchange $Ca^{2+} \leftrightarrow Me^{2+}$ and a formation of new surface solid-solution phase with the composition $Ca_{8.4}Me_{8.4-x}(HPO_4)_{1.6}(PO_4)_{4.4}(OH)_{0.4}$ (Viipsi *et al.*, 2011). The decrease of solution pH during metal sorption indicates that among surface reactions the ion exchange $H^+ \leftrightarrow Me^{2+}$ is also involved.

Our observations discussed above confirm that similar mechanisms take place in Cd- and Zn- containing solutions with and without EDTA.

The high values of (Ca+Cd+Zn)/P ratio at the highest pH values used is caused by precipitation of Cd- and Zn-hydroxydes.

5. Conclusions

Apatites are suitable sorbent materials for contaminated soil and water remediation because of their low solubility and ability to bind toxic metals from solutions into their structure. Whereas in real systems different complexing ligands are present, it was important to examine how these ligands affect apatite metal sorption process.

Hydroxy- and fluorapatite as sorbents in Cd- and Zn-binary solutions in the presence of EDTA, which is strong chelating agent, were investigated. It is revealed that Cd and Zn ions sorption process on HAP and FAP is strongly affected by solution pH, the presence of EDTA, and solution cationic composition. The sorption of Cd and Zn shifted the equilibrium pH of solutions to lower values. The higher the sorbed amount of metal was the greater was the deviation of the equilibrium pH from pure apatite suspension pH. The sorbed amount of heavy metals increased with pH, but we can consider sorption on AP only below pHs at which heavy metal hydroxides started to precipitate. Above this pH, the hydroxide precipitation was also responsible for metal removal from solution. In binary cation solution (Cd+Zn), the competition of metals reduced individual amounts bound up to 20% compared with the single component solutions. At the same time the total adsorption maximum was approximately constant. The amount of adsorbed zinc in single- and binary- metal solutions was higher than that of cadmium.

The XPS analysis revealed non-uniform distribution of Zn- and Cd-containing precipitates on the AP surface, but the composition of the surface phase, expressed as Me/P ratio, did not change remarkably [(Ca+Cd+Zn)/P= 1.4 ± 0.1] in comparison with single metal solutions.

Ion exchange as a main mechanism of Cd and Zn sorption on AP surface in the pH range of about 5-7 with formation of a new less soluble surface phase was shown. The sorption mechanism in the presence of EDTA was also ion exchange, but the amount of sorbed metals was reduced because of heavy metal complexation with EDTA. Consequently, the sorbed amount on apatites depended on the content of “free” metal ions in solution, not the total metal content.

Hydroxy- and fluorapatites have similar sorption properties and therefore the natural apatites, which are mostly fluorapatites, could be used as well for heavy metal sorption in remediation.

The reduced efficiency of HAP and FAP in relation to specific cations in binary-systems and in the presence of EDTA should be carefully considered in processing of soil or wastewater contaminated by heavy metals with apatites.

Acknowledgements

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APPENDIX: FAP figures

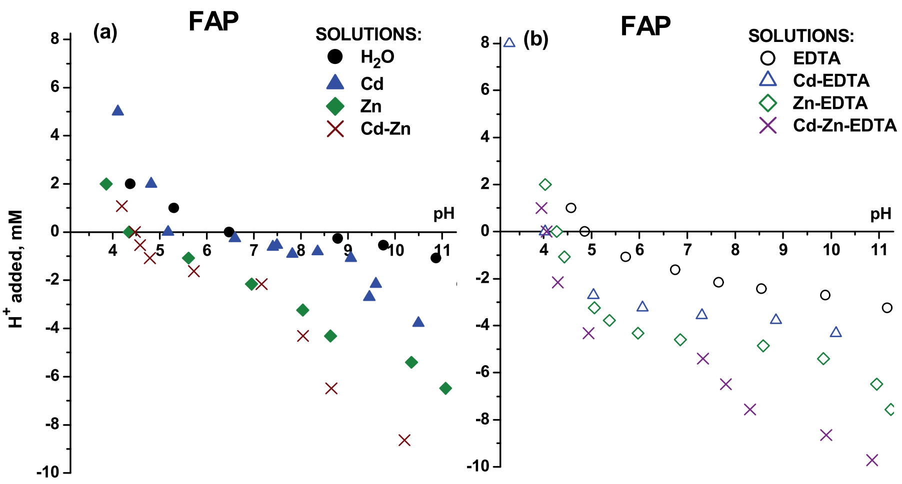

Figure I. The amount of H^+/OH^- added and the resultant equilibrium pH of FAP solutions without (a) and with (b) EDTA

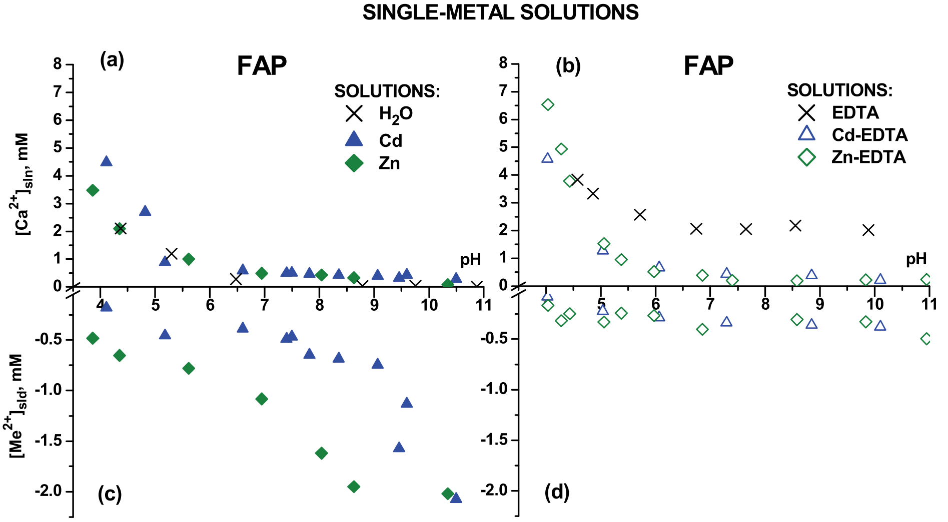

Figure II. Dissolved Ca concentration ($[Ca^{2+}]_{sln}$) and removed Cd and Zn concentrations ($[Me^{2+}]_{sld}$) by FAP in single-metal solutions without (a, c) and with EDTA (b, d) depending on equilibrium pH.

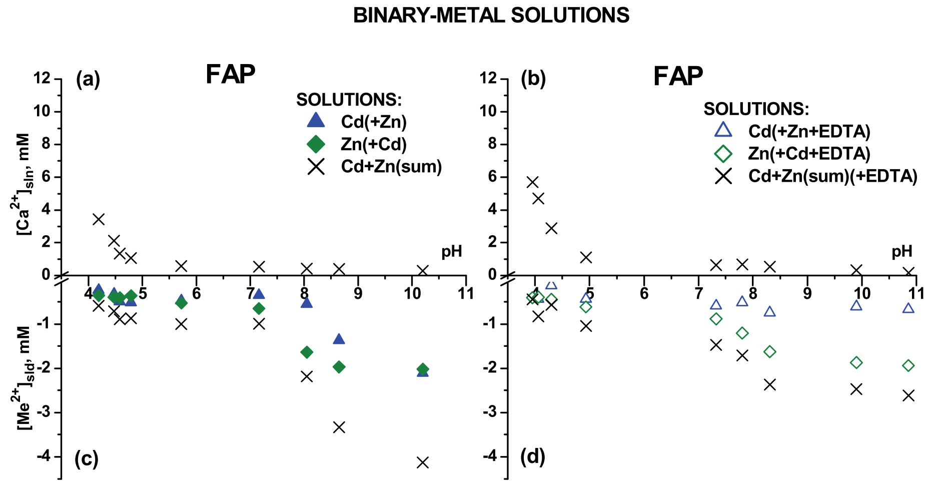

Figure III. Dissolved Ca concentration ($[Ca^{2+}]_{sln}$) and removed Cd and Zn concentrations ($[Me^{2+}]_{sld}$) by FAP in binary-metal solutions without (a, c) and with EDTA (b, d) depending on equilibrium pH

APPENDIX C: CURRICULUM VITAE

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonnanimi	Karin Viipsi
Sünniaeg ja -koht	11.12.1982 Haapsalu
Kodakondsus	Eesti

2. Kontaktandmed

Aadress	Ehitajate tee 49-42, 12612 Tallinn
Telefon	+372 5168748
E-posti aadress	karin.viipsi@ttu.ee

3. Hariduskäik

Õppeasutus (nimetus lõpetamise ajal)	Lõpetamise aeg	Haridus (eriala/kraad)
Tallinna Tehnikaülikool	2006-…	Keemia- ja materjalitehnoloogia, doktoriõpe
Haapsalu Kutsehariduskeskus	2009	Loodusturismi korraldus, kutseharidus
Tallinna Tehnikaülikool	2006	Keemia- ja keskkonnakaitsetehnoloogia, loodusteaduste magistrikraad
Tallinna Tehnikaülikool	2005	Keemia- ja keskkonnakaitsetehnoloogia, loodusteaduste bakalaureusekraad
Türi Majandusgümnaasium	2001	Keskharidus

4. Keelteoskus

Keel	Tase
eesti keel	emakeel
inglise keel	kõrgtase
saksa keel	algtase
vene keel	algtase

5. Täiendõpe

Õppimise aeg	Täiendusõppe läbiviija nimetus
2011	Tallinna Tehnikaülikool, tööalane inglise keel, 32 ak. tundi
2011	Tallinna Tehnikaülikool, sotsiaalse tarkvara õpituba- tabelarvutus (Excel 2010), 26 tundi
2009-2010	Umeå Ülikool, modelleerimisalane täiendõpe, 2 kuud
2009-…	Doktorikool “Funktsionaalsed materjalid ja tehnoloogiad” (Tartu

	Ülikool ja Tallinna Tehnikaülikool)
2007-2009	Doktorikool “Uued tootmistehnoloogiad ja protsessid” (Tartu Ülikool ja Tallinna Tehnikaülikool)
2009	Technical University of Denmark, Advanced course on Thermodynamic Models: Fundamentals & Computational Aspects
2006	Tallinna Tehnikaülikool, vene keel, 60 ak. tundi
2005-2006	Tallinna Tehnikaülikool, inglise keel keemikutele
2005	Tallinna Tehnikaülikool, inglise keel, 40 ak. tundi

6. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
2005-…	Tallinna Tehnikaülikool, Anorgaaniliste materjalide teaduslaboratoorium	insener
02.2006-11.2006	Intertec Eurolab OÜ, kütuselabor	keemik
2004-2006	AS Tallinna Vesi, veelabor	keemik
2003-2004	AS Tallinna Vesi, mikrobioloogia labor	laborant
05.2002-08.2002	AS Tallinna Vesi, veelabor	laborant

7. Kaitstud lõputööd

Magistritöö: EDTA mõju Cd^{2+} ioonide liikuvusele süsteemis apatiit-vesi. Tallinna Tehnikaülikool, Anorgaaniliste materjalide teaduslaboratoorium, 2006. Juhendaja: K. Tõnsuaadu

Bakalaureusetöö: Triloon-B mõju hüdroksüülapatiidi Cd^{2+} sidumisvõimele vesilahustes, Tallinna Tehnikaülikool, Anorgaaniliste materjalide teaduslaboratoorium, 2005. Juhendaja: K. Tõnsuaadu

8. Teadustöö põhisuunad

Sorptsiooniprotsessid apatiidil

9. Teised uurimisprojektid

SF0140082s08 Karbonaat- ja fosfaatpõhiste anorgaaniliste süsteemide keemia ja rakendused (2008 – 2013)

SF0142518s03 Anorgaaniliste mitmekomponentsete süsteemide keemia ja rakendused (2003 – 2007)

ETF7159 Biomineraalide omadused: teke, diagenees ja süntees (2007 – 2010)

ETF8207 Katalüsaatorid hüdroksüülapatiidil baseeruvatest hübriidmaterjalidest (2010 – 2013)

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Name	Karin Viipsi
Date and place of birth	11.12.1982 Haapsalu

2. Contact information

Address	Ehitajate tee 49-42, 12612 Tallinn
Phone	+372 5168748
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3. Education

Educational institution	Graduation year	Education (field of study/degree)
Tallinn University of Technology	2006-…	Chemical and Materials Technology, doctoral studies
Haapsalu Vocational School	2009	Ecotourism organisation
Tallinn University of Technology	2006	M. Sc. in Natural sciences
Tallinn University of Technology	2005	B. Sc. in Natural sciences
Türi High School of Economics	2001	High school education

4. Language competence/skills

Language	Level
Estonian	Fluent
English	Average
German	Basic skills
Russian	Basic skills

5. Special Courses

Period	Educational or other organisation
2011	Tallinn University of Technology, English, 32 h
2011	Tallinn University of Technology, Excel 2010, 26 h
2009-2010	Umeå University, modelling, 2 months
2009-…	Graduate school “Functional Materials and Processes” (University of Tartu and Tallinn University of Technology)
2007-2009	Graduate school “New Production Technologies and Processes” (University of Tartu and Tallinn University of Technology)

2009	Technical University of Denmark, Advanced course on Thermodynamic Models: Fundamentals & Computational Aspects
2006	Tallinn University of Technology, Russian, 60 h
2005-2006	Tallinn University of Technology, English for chemists
2005	Tallinn University of Technology, English, 40 h

6. Professional Employment

Period	Organisation	Position
2005-…	Tallinn University of Technology, Laboratory of Inorganic Materials (Estonia)	Engineer
02.2006-11.2006	Intertec Eurolab OÜ, Lab of Fuels	Chemist
2004-2006	AS Tallinna Vesi, Water Lab	Chemist
2003-2004	AS Tallinna Vesi, Microbiology Lab	Lab assistant
05.2002-08.2002	AS Tallinna Vesi, Water Lab	Lab assistant

7. Defended theses

M. Sc. thesis: EDTA impact on Cd^{2+} migration in apatite-water system. Tallinn University of Technology , Faculty of Chemical and Materials Technology, Laboratory of Inorganic Materials, 2006. Supervisor: K. Tõnsuaadu

B. Sc. thesis: Triloon-B mõju hüdroksüülapatiidi Cd^{2+} sidumisvõimele vesilahustes, Tallinn University of Technology , Faculty of Chemical and Materials Technology, Laboratory of Inorganic Materials, 2005. Supervisor: K. Tõnsuaadu

8. Main areas of scientific work

Sorption processes on apatite

9. Other research projects

SF0140082s08 Chemistry and applications of carbonate-phosphate-based inorganic systems (2008 – 2013)

SF0142518s03 Chemistry and applications of inorganic multicomponent systems (2003 – 2007)

ETF7159 Properties of biominerals: genesis, diagenetic alteration and synthesis (2007 – 2010)

ETF8207 Hydroxyapatite based hybrid materials for catalysts (2010 – 2013)

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *NATURAL AND EXACT SCIENCES*

1. **Olav Kongas**. Nonlinear Dynamics in Modeling Cardiac Arrhytmias. 1998.

2. **Kalju Vanatalu**. Optimization of Processes of Microbial Biosynthesis of Isotopically Labeled Biomolecules and Their Complexes. 1999.

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