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.
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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.

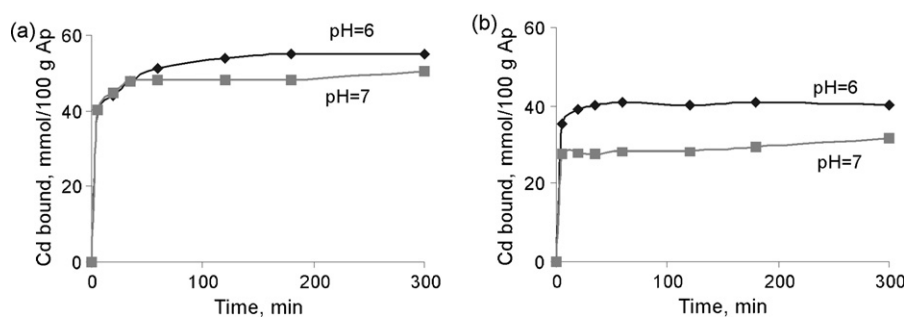[1] Prepared at the Institute of Inorganic Chemistry, Riga Technical University [18].

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

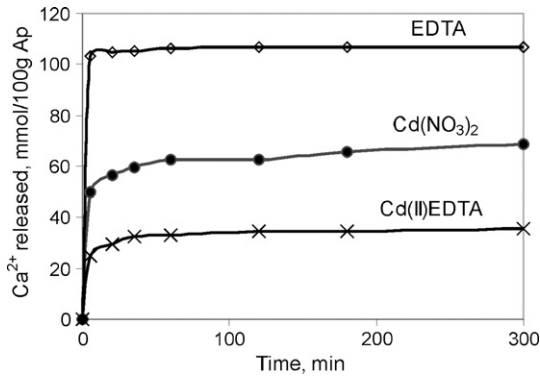| Sample	pH_{in}	Cd(II)EDTA 0.002 M				EDTA 0.002 M	
		pH_{fin}	Released Ca^{2+} (mmol/100 g Ap)	Bound Cd^{2+} (mmol/100 g Ap)	Q_{sorb}	pH_{fin}	Released Ca^{2+} (mmol/100 g Ap)
HA(1.44)	6	6.63	15.2	40.1	2.63	6.05	126.0
	7	6.71	14.1	31.9	2.27	6.97	108.0
HA(1.66)	4	6.45	37.2	30.7	0.82	5.88	106.9
	5	6.81	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
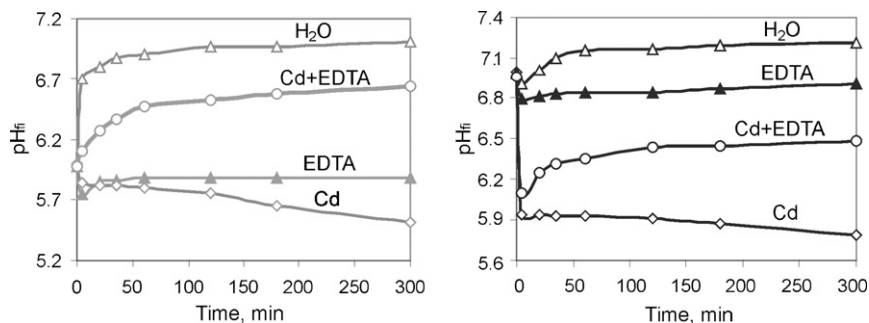

Fig. 3. Change of pH with time in different solutions in the experiments with HA(1.66). a) Initial pH = 6; b) Initial pH = 7.

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:

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

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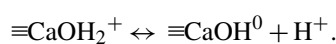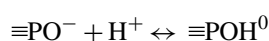
The positively charged $\equiv CaOH_2^+$ and neutral $\equiv POH^0$, $\equiv PO_xH_2$ and $\equiv PO_xH$ sites must prevail on Ap surface in acidic solutions [28,29], making surface charge in this pH region positive and at higher pH values negative.

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$_2$O	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$_{bound}$ ∼ 1–1.4) and higher in Ca(II)EDTA complex solution (Ca$_{rel}$/Ca$_{bound}$ ∼ 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 char-

acter of binding process and stability of the compounds formed.

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