

In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification

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Abstract

The in situ (in place) immobilization of toxic metals, using inexpensive “reactive” amendments, is considered as a simple and cost-effective approach for the treatment of soils, contaminated by the presence of heavy metals, when these soils are difficult or costly to be removed and treated ex situ. Several application studies have demonstrated that the stabilization of contaminated soils and groundwaters by the addition of apatite minerals has the potential to be a successful and widely applicable remediation strategy for the case of Pb, Cd, as well as for other toxic metals, existing in polluted soils. On the other hand, the specific immobilization mechanism(s) of these toxic metals remains rather elusive. The present work involves an interdisciplinary theoretical and experimental approach, designed to gain at the fundamental (molecular) level the understanding of respective mechanisms, considering the immobilization of Pb and Cd by the addition of apatites. The theoretical analysis of stability, regarding the apatite/Pb or apatite/Cd systems and the relevant results of sorption experiments, pointed out two different mechanisms for the immobilization of Pb or Cd by the use of apatites. The possible practical consequences of these findings for the selection/application of natural apatites for the remediation of contaminated soils by the presence of heavy metals have been also discussed.

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1. Introduction

The contamination of soils due to the presence of toxic metals, can result in serious negative consequences, such as the loss of ecosystems and of agricultural productivity, the deterioration of food chain, tainted water resources, economic damage, human and animal serious health problems etc. In several parts of the world the soil contamination represents the most severe environmental problems [1]; especially in the former Yugoslavia this issue is considered as a serious regional environmental degradation predicament [2]. Several mining and metallurgical industrial sites in this area are considered as environmental “hot spots”, because they are using rather antiquated technology, whereas the pol-

lution control devices are inadequate or even non-existing. Another permanent threat is the collapse of tailing dams, which would release large amounts of toxic/heavy metals that can reach the Danube River through its tributaries. Because the contamination of soil with heavy metals and especially with lead and cadmium is increasingly recognized as public health hazard, due to their high toxicity for humans and animals, the emergency clean up of environmental “hot spots” in Serbia and Montenegro is considered as an urgent task [2].

Currently, several technologies can be employed to clean up the soils and the mining wastes contaminated by toxic metals, including thermal, biological, and physical/chemical procedures, or their appropriate combinations. These techniques usually require the removal of contaminated soil, its subsequent treatment and either replacing it *on-site*, or disposed in specific landfills, located in most cases rather away

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from the polluted areas; therefore, creating a secondary disposal problem, due to the presence of lead and of other toxic metals. Such treatment/removal technologies are generally costly to practice and destructive to the application sites, from which the wastes are removed. In addition, these removal technologies are often partially effective for the total removal (efficient clean up) of toxic metals, or for the sufficient reduction of their mobility and bioavailability to the environment.

Recently, more attention has been focused on the development of in situ (in place) immobilization methods of metals in soils, which are generally less expensive and non-disruptive for the natural landscape, the hydrological conditions and the respective ecosystems, than the conventional excavation, treatment and disposal methods are. The in situ immobilization of metals in soils, using inexpensive amendments, such as minerals (apatite, zeolite, or clay) or waste by-products (e.g. steel shot, beringite, iron-rich biosolids) is considered as a promising alternative to the currently available remediation methods [3–6]. The main goal of in situ remediation techniques is to reduce the fraction of toxic elements or compounds, which are potentially mobile to the environment or bioavailable.

The application of these techniques is mostly relies on the fundamental understanding of natural geochemical processes, governing the speciation, migration and bioavailability of metals in the soil or groundwater environment. It is noting that these processes are also important for the detoxification of highly toxic heavy metal-loaded industrial wastes, following their treatment by stabilization using apatites [7]. The main advantage of the stabilization approach is the simple mixing of amendments with soil, using common agricultural facilities, or placing it as a liner around the contaminated location. The main disadvantage of this approach is that the final product of remediation, which contains the immobilized contaminant, although existing in inactive form, still remains in the soil.

Several application studies have demonstrated the effective immobilization of Pb, Cd and of other toxic metals by the addition of synthetic hydroxyapatite (denoted hereafter as HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) [8–11]. Therefore, indicating that the stabilization of contaminated soils and groundwaters by using apatite minerals has the potential to be a successful and widely applicable remediation strategy for the case of Pb, Cd, or of other heavy metals, when present in polluted soils. Lead especially represents the most common contaminant of soil in Serbia, as a consequence of industrial pollution (Trepca, one of the largest Pb mines in Europe is located in Kosovo) and past war activities that destroyed some oil facilities. On the other hand, the specific mechanism(s) regarding the immobilization of these toxic metals remains rather elusive. Although a mechanism has been proposed based on the adsorption of lead and cadmium on the surface of HAP, followed by cation exchange with calcium [12], most researchers have suggested that the dissolution of HAP can release phosphate anions for the subsequent precipitation of the new solid

phases, presenting lower solubility, hence increased stability [13–15].

The present work involves an interdisciplinary theoretical and experimental approach, designed to obtain a better understanding of the respective mechanisms, taking place at the fundamental (molecular) level, regarding the immobilization of lead and cadmium by the addition of HAP, as well as by natural apatites. The analysis of apatite/Pb and apatite/Cd systems was based on the calculation of ion–ion interaction potential $V(r_0)$; it was revealed that cadmium initially forms a solid solution, replacing the calcium ions from the HAP crystal lattice, whereas the immobilization of lead by HAP was based on a dissolution/precipitation mechanism, resulting in the formation of a new lead hydroxy-pyromorphite highly insoluble phase.

It has been also demonstrated that the examined natural apatites (especially the Lisina apatite, denoted hereafter as LA, whose large deposits are located in South Serbia), in contrast to the synthetic HAP, can immobilize lead due to different mechanisms: direct incorporation into the lattice, or precipitation of insoluble Pb–apatite and diffusion of Pb into the solid phase, without the destruction (dissolution) of the latter. The theoretically predicted existence of the two different mechanisms, regarding the immobilization of lead by HAP or by LA, was also experimentally confirmed. Possible advantages and disadvantages considering the application of natural apatites, especially that of LA originating from a mineral deposit in Serbia, for future clean up efforts of the environmental “hot spots” have been discussed.

2. Materials and methods

2.1. Materials (apatites)

Stoichiometric HAP was synthesized in the laboratory by a slow titration of $\text{Ca}(\text{OH})_2$ solution with H_3PO_4 at elevated temperature (95°C) in nitrogen atmosphere, following a previously described procedure [16]. Chemical analysis confirmed that the product was stoichiometric hydroxyapatite with the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, having Ca/P ratio 1.67 ± 0.02 and surface area $21 \text{ m}^2 \text{ g}^{-1}$, as determined by the application of BET method. The solid phase consists of spherical aggregates, around $10 \mu\text{m}$ in diameter. The spherical aggregates are composed of smaller particles (about $100\text{--}200 \text{ nm}$ in diameter), as it was determined from SEM micrographs.

Based on theoretical predictions the natural apatite from the phosphate ore deposit in Lisina (LA), near Bosilegrad (Serbia) was selected for sorption experiments and it was compared with HAP. This phosphate ore contains 43.3% apatite. Chemical analysis [17] showed that this sample was found to present the following composition: $\text{Ca}_{2.94}\text{Na}_{0.03}\text{K}_{0.05}\text{Al}_{1.38}\text{Fe}_{0.22}\text{Si}_6\text{P}_{1.96}\text{S}_{0.16}\text{Cl}_{0.04}\text{F}_{0.11}\text{O}_{22.28}$. The sample was ground to fine powder with particle size lower than $200 \mu\text{m}$.

Table 1
Chemical compositions of the examined apatites

Apatites	Symbol	Chemical composition	References
Hydroxyapatite	HAP	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	[16]
North Carolina Apatite	NCA	$\text{Ca}_{9.53}\text{Na}_{0.34}\text{Mg}_{0.13}\text{P}_{4.77}\text{C}_{1.23}\text{O}_{22.77}\text{F}_{2.49}$	[5]
Apatite II	Apatite II	$\text{Ca}_{9.6}\text{Na}_{0.4}\text{P}_{5.6}\text{C}_{0.4}\text{O}_{25.6}\text{H}_2$	[3]
Lisina apatite	LA	$\text{Ca}_{2.94}\text{Na}_{0.03}\text{K}_{0.05}\text{Al}_{1.38}\text{Fe}_{0.22}\text{Si}_6\text{P}_{1.96}\text{S}_{0.16}\text{Cl}_{0.04}\text{O}_{22.28}\text{F}_{0.11}$	[17]

Two more natural apatite samples, originated from USA and previously applied for soil remediation purposes (North Carolina Apatite (NCA) and Apatite II) were also evaluated for comparison reasons. The chemical compositions of the examined apatites are presented in Table 1. The different content of P in these materials has been also considered and incorporated in the applied ion–ion interaction model.

2.2. Methods

2.2.1. Sorption experiments

2.2.1.1. Kinetics of Pb removal by apatites. The kinetics of lead removal by HAP and LA apatite samples were determined in batch experiments: 0.2 g of HAP or LA were held in contact with 50 ml of a solution, containing 100 mg L^{-1} or $0.483 \text{ mmol L}^{-1}$ Pb (as nitrate salt). The suspensions were agitated using a reciprocal shaker (150 rpm) under constant temperature (at 25°C) for various time intervals (between 5 min and 5.5 h). The initial (“natural”) pH of suspension was 5.1 for HAP and 5.6 for LA and it was not further modified (controlled) during these experiments, in order to simulate the real environmental conditions existing during the remediation of contaminated soil by the application of stabilization technique, where the pH control is either not applicable, or not necessary or very difficult to be realized. For the same reason a background electrolyte was not applied. After the corresponding time interval the suspensions were sampled through direct filtration, using $0.45 \mu\text{m}$ membrane filter; the filtrates were analyzed for Pb content, using a Shimadzu AA-6501 F Atomic Absorption (flame) Spectrometer.

2.2.1.2. Sorption of Pb by apatites. The sorption properties of HAP and LA apatite samples were determined by applying standard batch experiments: 0.2 g of HAP or LA samples were mixed with 50 ml of $\text{Pb}(\text{NO}_3)_2$ solution, containing different initial concentrations in the range $0.0241\text{--}2.413 \text{ mmol L}^{-1}$ of Pb. The suspensions were thermostated at 25°C and agitated at 150 rpm for 1.5 h, i.e. for enough time to achieve equilibrium, according to the respective kinetic data (see Fig. 7), as well as according to the relevant literature data. The suspension was subsequently filtered and the concentrations of Pb and Ca content were determined as previously described.

3. Short description of the theoretical approach for the determination of stability of the studied system (additive/apatite–impurity/Pb or Cd)

The theoretical approach regarding the selection of the most suitable amendment (solid additive) in contaminated soils for the stabilization of contained toxic metals by immobilization, is based on the calculation of “ion–ion interaction potential $V(r)$ ”, which represents the main term of the cohesive energy in the respective system. This physical parameter defines: (i) the capacity of solid matrix for the incorporation of impurity, and (ii) the stability of solid matrix/impurity system. More information about the theoretical determination of $V(r)$ in the frame of the pseudo-potential theory and pseudo-atomic approximation, as well as the necessary software for the calculation of $V(r_0)$ for practical systems, was originally developed at the VINCA Institute of Nuclear Sciences and can be found in the literature [18–23].

In the following the calculation of ion–ion interaction potential $V(r)$, which used to analyze the stability of solid matrix/impurity systems, is briefly described. In the frame of pseudo-potential theory this energy component may be treated, by considering the atoms interacting in pairs, according to a central two-body potential. This two-body potential has an asymptotic form, which is independent of the precise pseudo-potential assumed and which exhibits the Friedel oscillations [20]. Considering certain suitable assumptions, which are presented and discussed in the following, an estimation of the cohesive energy can be performed, by simply assuming the energy of two-atom interactions, according to the asymptotic or Friedel potential.

Applying the real space formulation of the pseudo-potential metal theory, the cohesive energy per atom may be developed, according to the following perturbation series:

$$E = E_0 + E_1 + E_2 + \dots \quad (1)$$

whose successive terms involve perturbations at an increasing order. The 0th and the 1st order terms (i.e. the E_0, E_1) in this expansion series depend on the volume per atom (Ω), but they are independent of structure. The second order term E_2 is the first one to show the influence of structure. It can be cast in the following form:

$$E_2 = \frac{1}{2N} \sum'_{i,j} V(r_{ij}) \quad (2)$$

where N is the number of atoms, r_{ij} the distance between the i th and j th atom cores, whereas the prime on the summation symbol indicates that terms having $i=j$ will be omitted. The function $V(r_{ij})$ appearing in the summation, acts as a two-body potential in a restricted sense, i.e. it governs the change of energy in a relative displacement of atoms i and j , which leave the atomic volume, and hence the E_0 and E_1 terms constant. If the atomic volume will be fixed and the terms of higher order in the perturbation expansion will be neglected (see also [20]), then the relative cohesion energy of a given structure will be measured by E_2 .

The computation of the structure energy E_2 requires a specific expression for the effective ion–ion interaction potential $V(r)$. This potential is sensitive to specific details of the pseudo-potential used [20]. However, irrespective of the pseudo-potential, $V(r)$ has the following asymptotic form:

$$V(r) \rightarrow \frac{9\pi Z^* W(2K_F)^2 \cos(2K_F r)}{E_F(2K_F r)^3} \quad (3)$$

where Z^* is the valence number for the given metal, $K_F = (3\pi^2 Z^* / \Omega)^{1/3}$ is the Fermi wave number, Ω the atomic volume (in atomic units), $E_F = K_F^2$ the Fermi energy (in Ry, 1 Ry = 13.5 eV) and $W(2K_F)$ is the form factor of the electron–ion interaction potential (in Ry), corresponding to the wave number $2K_F$. Starting from the general model pseudo-potential [21], the term of $W(2K_F)$ can be presented in the following form:

$$W(2K_F) = \frac{\alpha_1 Z^* \sin(2\pi\alpha_2 Z^*)}{2\alpha_2} \quad (4)$$

where the coefficients α_1 and α_2 receive the following values: $\alpha_1 = -0.2500$ Ry (for short and the first half of long periods), or $\alpha_1 = -0.0625$ Ry (for the second half of long periods) and $\alpha_2 = 0.520$ or 0.048 , respectively.

It has been previously demonstrated [20] that the values of $W(2k_F)$ and $V(r)$ terms for a multi-component system can be satisfactorily determined in the frame of the pseudo-atomic approximation and in the case of solid solutions treatment, as if they were composed of identical pseudo-atoms, having average properties (Z^* , Ω , α_1 and α_2). The value of $V(r_0)$ represents the first (deep) minimum in this function and the dominant term of $V(r)$; it corresponds to the structurally dependent component of the cohesive energy. Based on this, the value of $V(r_0)$ has been proposed as a measure for the stability of multi-component systems [18,19,22].

It has to be stressed however that the proposed ion–ion interaction model predicts the stability of the solid phase as its inherent property, which does not depend on its origin, i.e. it considers the de novo precipitation or sorption by the matrix. In other words, this parameter gives certain information about which of the two or more concurrent solid phases will predominate in the final product independently on mechanisms of their generation (precipitation or sorption).

Since all phosphate minerals contain also other cations (such K, Al, Fe, Mg and Na) in addition to Ca, the effect of

these cations on the Ca–Pb and Ca–Cd interactions has been also considered in the respective calculations of the model.

4. Results and discussion

4.1. Proof of concept

The presence of metals in soils may be associated with various solid phases that can be reactive, semi-reactive or inactive. The main goal of in situ remediation techniques is to reduce the fraction of toxic elements, which is potentially mobile or bioavailable, by the transformation of reactive and semi-reactive phases to more stabilized insoluble forms. For this reason, the relevant information regarding the stability of the final product, in connection with the application of the particular remediation technique, is very important in order to estimate appropriately its efficiency.

A molecular modeling approach, which was used to predict the formation and stability of partial or total substituted chloropyromorphite minerals ($\text{Pb}_5(\text{PO}_4)\text{Cl}$), has been recently proposed [24]. In this approach, the lattice energy values were determined by the application of ab initio calculations, and used in a Born–Haber thermodynamic cycle to calculate the heat of formation of substituted chloropyromorphites. This procedure was followed by the prediction of entropy changes, based on the entropy of minerals and their elementary constituents. The respective data were used for the calculation of Gibbs free energy (ΔG_f°):

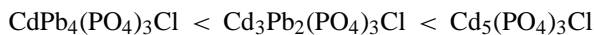
$$\Delta G_f^\circ = \Delta H_f^\circ - T \Delta S_f^\circ$$

where ΔG_f° , ΔH_f° and $T \Delta S_f^\circ$ are the standard Gibbs free energy, the heat of formation and the entropy change of crystal lattice, respectively.

The solubility product K_{sp} , which can be calculated from ΔG° according to the following equation, can determine the stability of a compound:

$$\Delta G_{\text{reaction}}^\circ = \Delta G_{\text{product}}^\circ - \Delta G_{\text{reactant}}^\circ = -2.303RT \log K_{\text{sp}}$$

The values of Gibbs free energy for the substituted by cadmium pyromorphite compounds and the corresponding values of solubility products are presented in Table 2 [24]. According to these results the following order of decreasing the (negative) Gibbs free energy values and the change (increase) of the solubility product ($\log K_{\text{sp}}$), regarding the gradual substitution of lead by cadmium in pyromorphite, was found



The order of ΔG_f° and K_{sp} values, regarding the substitution of lead by zinc in pyromorphite, was found to follow the same trend, as in the case of cadmium. It was proposed that the lattice energy and the Gibbs free energy could be determined by the application of ab initio quantum mechanics calculations as suitable parameters, which can be used for the qualitative evaluation of mineral stability [24].

Table 2

The Gibbs free energy (ΔG_f°) as determined by using the ab initio quantum mechanics approach [24], the solubility product ($\log K_{sp}$) [24] and the respective ion–ion interaction potential $V(r_0)$ of substituted pyromorphites, which is calculated in the present paper

Mineral	ΔG_f° [24] (kJ/mol)	$\log K_{sp}$ [24]	Ion–ion interaction potential, $V(r_0)$ ($\times 10^{-2}$ Ry)
Pb ₅ (PO ₄) ₃ Cl	–3716	–71	–69.69
CdPb ₄ (PO ₄) ₃ Cl	–3134	40	–49.22
Cd ₃ Pb ₂ (PO ₄) ₃ Cl	–2331	200	–11.83
Cd ₅ (PO ₄) ₃ Cl	–1544	356	–0.29
ZnPb ₄ (PO ₄) ₃ Cl	–3022	72	–48.50
Zn ₃ Pb ₂ (PO ₄) ₃ Cl	–1612	362	–11.30
Zn ₅ (PO ₄) ₃ Cl	–323	631	–0.27

It was previously proposed that the stability of the solid matrix/impurity system can be qualitatively characterized by the value of $V(r_0)$, representing the main term of the cohesive energy [18]. It is worth noting that $V(r_0)$ represents also an important component of the free energy of the system, determining the corresponding part of heat of formation [25].

In the present paper the stabilities of substituted pyromorphites, as determined by the parameters derived from the ab initio calculations [24], were compared with those based on $V(r_0)$ values, which were calculated for the same compounds, and are presented in Table 2. In Figs. 1 and 2 the solubility product ($\log K_{sp}$) is presented as a function of the number of substituted Pb atoms, of the Gibbs free energy and of the ion–ion interaction potential $V(r_0)$ for the cadmium and zinc-substituted pyromorphites, respectively. As it can be observed from these data, the change of the solubility product ($\log K_{sp}$) with the variation of Gibbs free energy and of $V(r_0)$ shows a very similar trend.

Based on the calculation of ΔG_f° values it was concluded (see also [24]): (1) the cadmium- or zinc-substitution products of minerals are highly unstable and that the stability between them was found to decrease, according to the following order:

Pb-pyromorphite \gg Cd-pyromorphite $>$ Zn-pyromorphite

and (2) both total and partial substitution of lead by cadmium or zinc seems to be unfavorable, due to the significant decrease of respective stability for the resulting system.

The results presented in Table 2 and Figs. 1 and 2 also point out the alternative use of $V(r_0)$ as a simple physical parameter, instead of ΔG_f° , which can be applied for the qualitative evaluation of mineral stability.

4.2. System hydroxyapatite–cadmium

In Fig. 3 the values of $V(r_0)$ were calculated for the HAP/Cd system. These results show a significant difference between the values of $V(r_0)$ for the case of HAP (–0.026 Ry) and for the case of Cd-substituted apatite (–0.223 Ry). The remarkable lower value of $V(r_0)$ parameter for the Cd–apatite system implies its higher stability in comparison with the pure stoichiometric HAP compound, a conclusion which is in accordance with the experimental evidence, regarding the

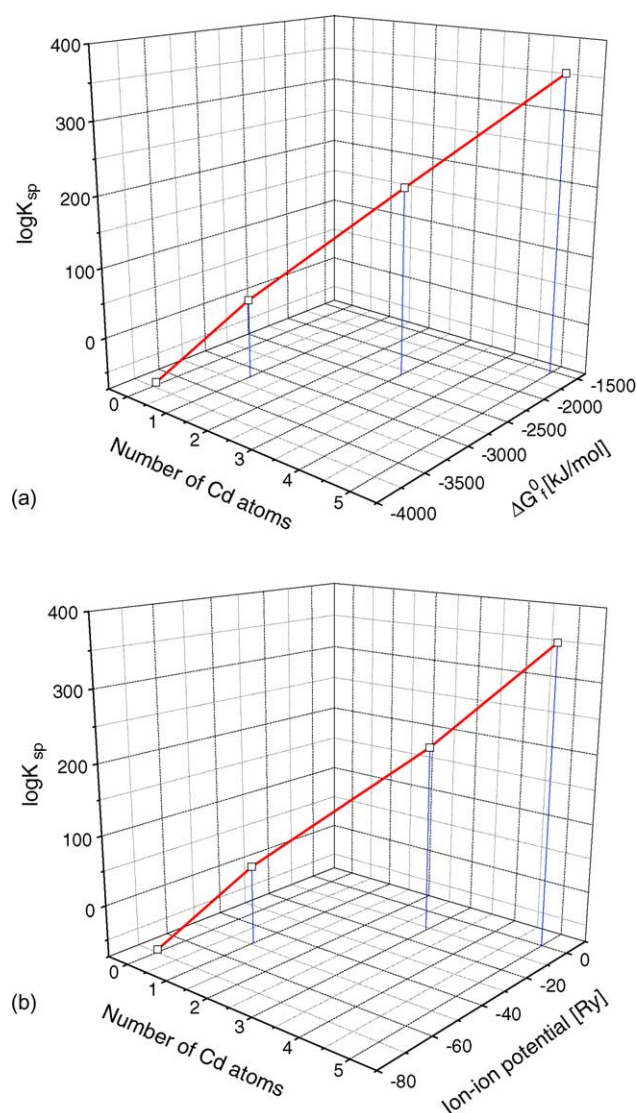


Fig. 1. Relationship between the solubility product ($\log K_{sp}$), the Gibbs free energy, the ion–ion interaction potential $V(r_0)$ and the chemical composition of Cd-substituted pyromorphites: (a) dependence of solubility product on the lattice energy and on the chemical composition, and (b) dependence of solubility product on the ion–ion interaction potential and on the chemical composition.

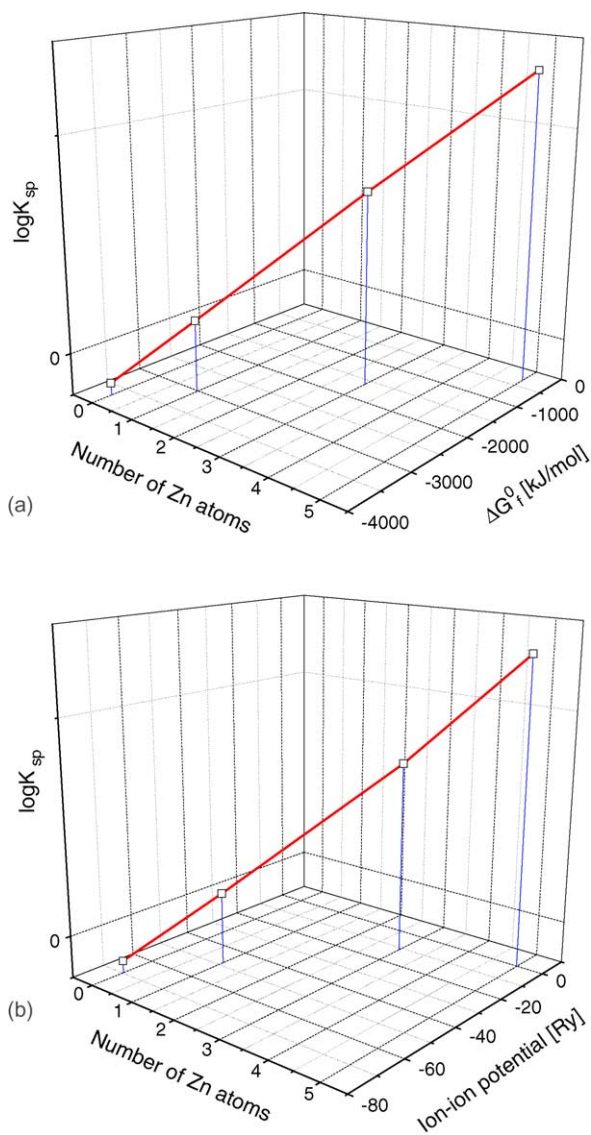


Fig. 2. Relationship between the solubility product ($\log K_{sp}$), the Gibbs free energy, the ion–ion interaction potential $V(r_0)$ and the chemical composition of Zn-substituted pyromorphites: (a) dependence of solubility product on the lattice energy and on the chemical composition, and (b) dependence of solubility product on the ion–ion interaction potential and on the chemical composition.

higher stability of Cd–apatite phase [26]. Therefore, this interesting property of Cd–apatite system may be applied for the immobilization of cadmium in polluted soil by the addition of HAP (see also [27,28]).

The results presented in Fig. 3 can also provide important information about the possible mechanism of cadmium immobilization by the addition of HAP. From these data it is obvious that the initial uptake of Cd by HAP (as represented by the left side of the diagram, Fig. 3) is followed (initially) by the increase of $V(r_0)$ and hence, by the decrease of HAP/Cd systems' stability. This result indicates that the direct incorporation of Cd ions into the HAP crystal lattice is not highly probable in this case. On the other hand, the remarkable lower

value of $V(r_0)$ for the Cd–apatite system in comparison with the case of pure HAP and the decrease of $V(r_0)$ value with the decrease of Cd content in the Cd–apatite system (as represented by the right side of the diagram, Fig. 3) point towards the two-step mechanism, regarding the immobilization of Cd by HAP. The first step can be characterized by the dissolution of HAP and the formation of new stable Cd–apatite phase on its surface. In the second step the stability of Cd–apatite phase would be further increased by the diffusion of Cd ions inside the HAP crystal lattice. Using measurements performed by a nuclear microprobe (proton induced X-ray emission and Rutherford backscattering spectrum (RBS) analysis) it was shown that cadmium was really incorporated into the bulk of apatite particles through the mechanisms of diffusion and ion exchange [9,28 and references therein]. The RBS clearly showed that accumulation of cadmium on the solid surface was not observed. On the contrary, cadmium was found to distribute throughout the whole thickness of apatite particles. These experimental results strongly support the aforementioned theoretical predictions based on the ion–ion interaction potential.

The relevant experimental results (presented in the following) demonstrate that the sorption of cadmium onto HAP would not achieve the equilibrium stage during the standard experimental time intervals [28,29], and strongly support the proposed two-step mechanism of cadmium immobilization by HAP.

The proposed mechanism can also explain other experimental findings that under different conditions the number of calcium moles released from HAP during this procedure was found to be lower, than the moles of removed cadmium (i.e. the Cd/Ca substitution ratio is around 1.5) [30]. This also implies two groups of factors determining the efficiency of cadmium immobilization by HAP. The first group encompasses certain factors, which influence the dissolution of HAP and the formation of stoichiometric Cd–apatite; these factors are predominantly determined by the properties of Cd-containing solution, such as pH value, temperature, concentration, speciation, etc. In the second group belong factors, which influence the maturation (“ageing”) of Cd–apatite phase, which are mainly determined by the properties of HAP solid phase, such as morphology, concentration of vacancies, physico-chemical properties of HAP particles, etc. The proposed two-step mechanism of cadmium immobilization by HAP is also in good agreement with recently reported experimental findings of other researchers [30,31].

4.3. System hydroxyapatite–lead

In Fig. 4 the ion–ion interaction potential $V(r_0)$ values for the HAP/Pb system are presented. The $V(r)$ values calculated for the pure (stoichiometric) HAP and for the Pb-substituted apatite (pyromorphite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$) are presented in Fig. 5. According to these data the Pb-substituted apatite (pyromorphite) is remarkably more stable ($V(r_0)_{\text{pyromorphite}} = -0.152 \text{ Ry}$) than pure HAP

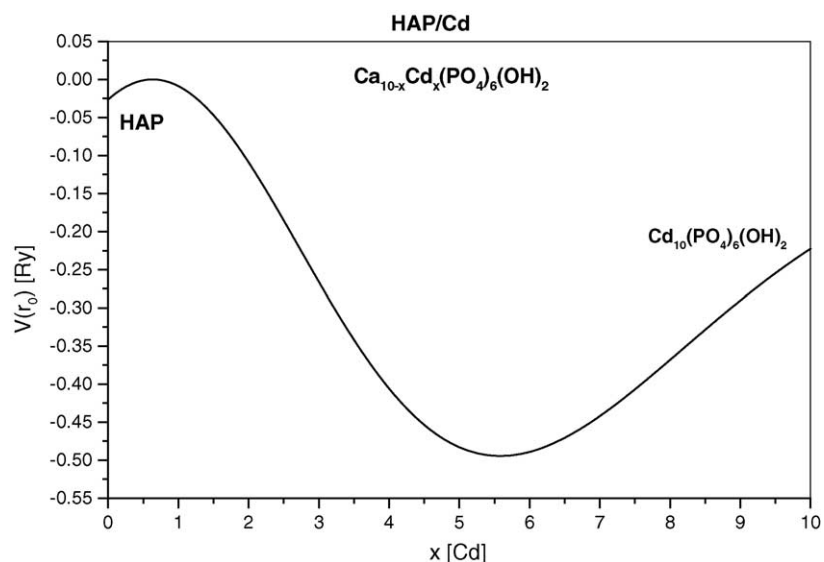


Fig. 3. The ion–ion interaction potential $V(r_0)$ for the HAP/Cd system. The number of Ca-substituted atoms by Cd in HAP is symbolized by x .

($V(r_0)_{\text{HAP}} = -0.026$ Ry). This difference of stability between HAP and pyromorphite may be applied for the use of apatite to the fixation of lead in contaminated water or soil [3,13].

The results presented in Fig. 4 point out also that the mechanism of lead immobilization by HAP is simpler, than the described mechanism of cadmium immobilization. According to these results, the direct incorporation of lead into the HAP crystal lattice by the substitution of calcium cations is not probable, because this process would result in the increase of $V(r_0)$ value and hence, in the decrease of system stability (as represented by the left side of the diagram, Fig. 4). On the other hand, the diffusion of lead from pyromorphite into HAP would be also followed by the increase of $V(r_0)$ and hence, by the decrease of the system stability (as shown in the right

side of the diagram, Fig. 4). These results indicate that the immobilization of lead by HAP is based on the formation of new, more stable pyromorphite phase, which is precipitated on the surface of HAP. This one-step mechanism of lead immobilization by HAP is in good agreement with the mechanism proposed by several researchers, suggesting that the dissolution of HAP can provide phosphate anions, available for subsequent precipitation of pyromorphite from aqueous solutions, containing lead cations [13–15], according to the following chemical reactions:

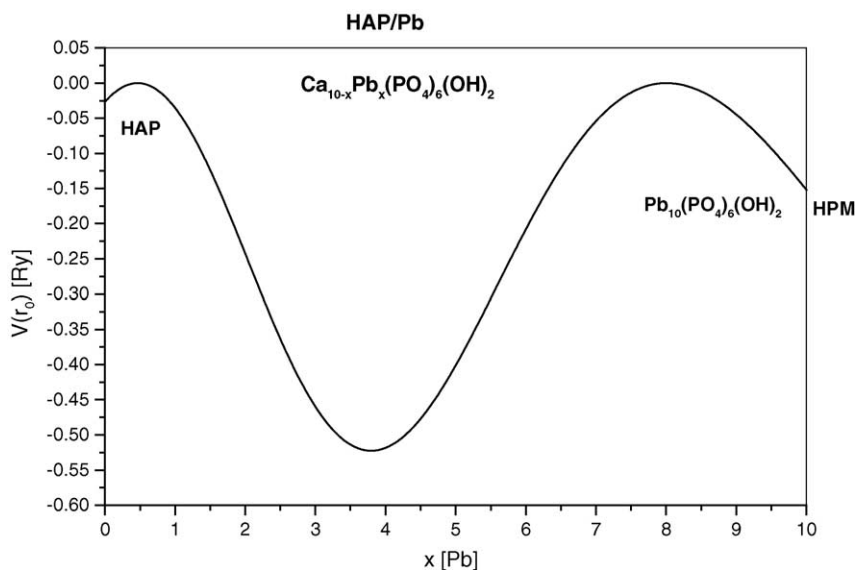
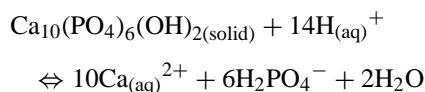


Fig. 4. The ion–ion interaction potential $V(r_0)$ for the HAP/Pb system. The number of Ca-substituted atoms by Pb in HAP is symbolized by x .

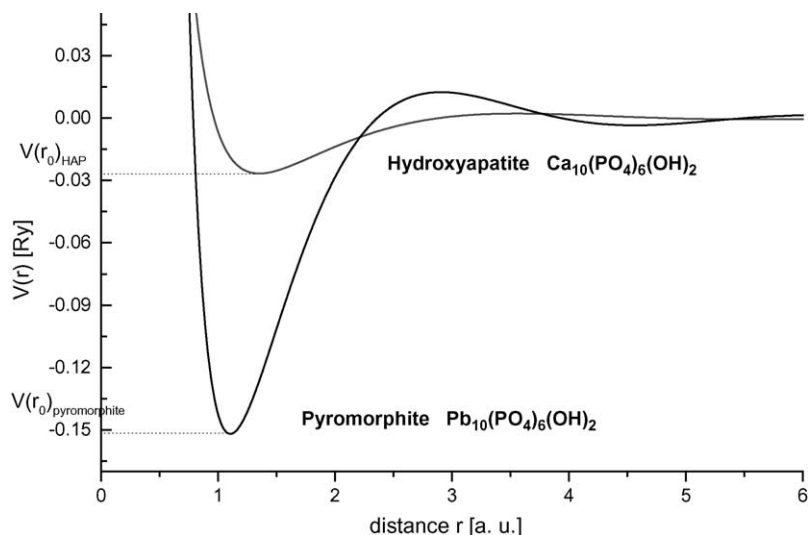
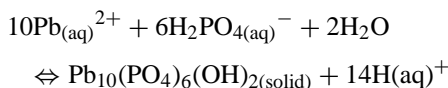


Fig. 5. The ion–ion interaction potential $V(r)$ of stoichiometric hydroxyapatite (HAP) and of Pb–apatite (pyromorphite).



It is considered of practical interest to underline certain consequences of the aforementioned mechanism on the efficiency of lead immobilization by HAP. This immobilization is the result of two co-current processes: (i) dissolution of HAP, and (ii) formation of a new solid phase (pyromorphite) and its subsequent deposition on the surface of HAP. Therefore, the process of lead immobilization will be followed by the permanent decrease of free HAP surface, which is the provider of the necessary phosphate anions for the formation of pyromorphite. After the covering of all available HAP surface by the produced pyromorphite, the process of lead removal is expected to terminate. As a consequence, the efficiency of lead removal depends on the available HAP surface, as well as on the physico-chemical parameters of metal-laden solution, which influence the dissolution of HAP and the formation of pyromorphite.

4.4. System natural apatites–lead

The available field data and the obtained research experience indicate that the in situ Pb immobilization by apatite may provide an economical alternative, when compared with the ex situ treatment methods, in order to achieve the pre-set cleanup goals and to solve the respective environmental pollution problems [3,5,6,27]. The main prerequisite for the cost-effective fixation of lead in contaminated sites and the prevention of its migration towards the groundwater resources is the availability of low-cost apatite minerals in large quantities, which present high sorption capacity for lead.

Lisina, located in Serbia, is the biggest deposit of natural apatite in the western Balkans, representing a potential

source of inexpensive material for the treatment of sites contaminated with Pb, Cd and other heavy/toxic metals. The stability and sorption properties of Lisina apatite (LA) were investigated, in order to estimate its suitability for practical application.

The results obtained with Lisina apatite (LA) were also compared with the North Carolina Apatite (NCA), as well as with Apatite II, i.e. with two other forms of natural apatites of different origin (USA), which were previously successfully used for the remediation of lead-contaminated sites, existing around mining operations in USA [3,5]. In Fig. 6 the $V(r_0)$ values are presented for the LA/Pb, NCA/Pb and Apatite II/Pb systems. Due to the low calcium content of LA (see Table 1) the respective curve of LA/Pb system was terminated at the point corresponding to the value of $x[\text{Pb}] = 3$. From these data it is obvious that the most stable form of lead-substituted apatite (presenting $V(r_0) = -0.538$ Ry) can be obtained from NCA. According to the same criterion, the stability of lead–apatite system derived from LA (showing $V(r_0) = -0.035$ Ry) and from Apatite II (with $V(r_0) = -0.076$ Ry) are expected to be similar. The shape of respective curves for the NCA/Pb and LA/Pb systems indicates the similar behavior of these apatites in terms of lead sorption (left side of the diagram in Fig. 6), in comparison with HAP (Fig. 4), or with Apatite II (Fig. 6).

Another consequence of these data is that the incorporation of lead into the crystal lattice of LA or of NCA was followed (initially) by the decrease of $V(r_0)$ values and hence, by the increase of system stability. According to the data presented in Fig. 6, LA holds another specificity; it can be noticed that in the Pb–LA system the diffusion of Pb ions into the apatite lattice is followed by the decrease of $V(r_0)$ value (right side of the diagram for LA/Pb system in Fig. 6) and hence, by the increase of system's stability. From this point of view, the Pb–LA system behaves similarly with the Cd–HAP system.

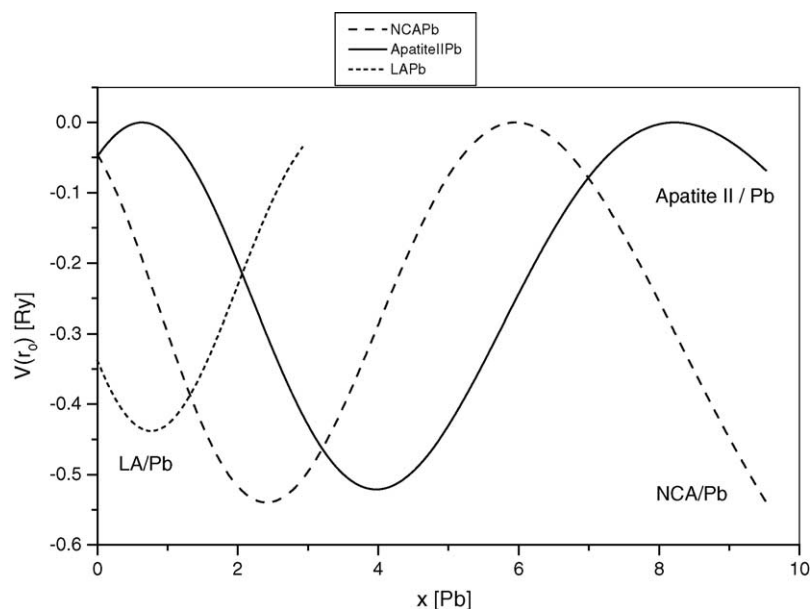


Fig. 6. The ion-ion interaction potential $V(r_0)$ of NCA/Pb, LA/Pb and Apatite II/Pb systems. The number of Ca-substituted atoms by Pb in LA, NCA and Apatite II is symbolized by x .

Based on the presented data it can be concluded that during the immobilization of lead by LA two different mechanisms are involved: the first one includes the direct incorporation of lead ions from the solution into the LA lattice. The second includes a two-step mechanism, i.e. the initial precipitation of Pb-apatite and its subsequent diffusion into the LA solid phase. It is difficult to determine which is the prevailing mechanism during the immobilization of lead by LA apatite, because this depends also on several other factors, such as the physico-chemical and morphological characteristics of applied LA, the concentration of Pb in the solution, as well as on specific environmental factors, i.e. pH, temperature, interfering substances, etc.

4.5. Sorption experiments

The presented results from the theoretical analysis point out that the natural apatite LA can be a promising material for the immobilization of lead. In order to prove this theoretical prediction, it was further experimentally tested to evaluate the sorption properties of LA.

The comparison of sorption properties between HAP and LA for the removal of lead from aqueous solutions is presented in Figs. 7 and 8. As it can be observed from these results (Fig. 7a), the process of lead removal by HAP is kinetically very fast. The concentration of lead in the solution was decreased substantially from 100 to 10 mg L⁻¹, i.e. from 0.483 to 0.04 mmol L⁻¹ during the initial 15 min. Following this period, the concentration of lead in the solution was further decreased to almost non-detecting concentrations after 90 min (i.e. below 0.00048 mmol L⁻¹). This result is in accordance with the relevant experiments of other researchers [8,13]. For example, experiments performed under similar ex-

perimental conditions but with different HAP samples from Bio-Rad Laboratories showed that the initial lead concentration of 0.486 mmol L⁻¹ was decreased drastically during the initial 2 min and falls it was below the detection within 15 min [8]. The kinetic curve in the case of LA presents a similar pattern (Fig. 7b), although the process was slower and less effective, i.e. the (residual) amount of lead in the aqueous solution was decreased from 100 to 60 mg L⁻¹ (or from 0.480 to 0.284 mmol L⁻¹) within 60 min; at that point the equilibrium was almost achieved.

Contrary to the similar trend of kinetic curves for HAP and LA (Fig. 7), the respective isotherms of these materials were found to be completely different (Fig. 8). The adsorption isotherm of LA increased almost monotonously in the whole investigated range of lead concentrations, whereas the isotherm of HAP was increased sharply in the beginning, but afterwards equilibrium (saturation) was achieved.

As the isotherm shapes are largely determined by the adsorption mechanism, they can be used to diagnose the nature of the adsorption. According to the general classification of adsorption isotherms, as proposed by Giles and Smith [32], the isotherm of Pb-LA system (Fig. 8b) is a typical C1-type isotherm ("quasi-linear"), which can be explained by the penetration of substrate (LA) micropores by the solute (Pb), whereby new adsorption sites are opened up. The respective isotherm of Pb-HAP system (Fig. 8a) is a typical L2-type isotherm, which is confined to surface ("monolayer") coverage.

This difference in the shape and trend of adsorption isotherms between HAP and LA indicates the existence of two distinct mechanisms, regarding the immobilization of lead by the application of these materials. This observation is in accordance with the results presented in Fig. 6, show-

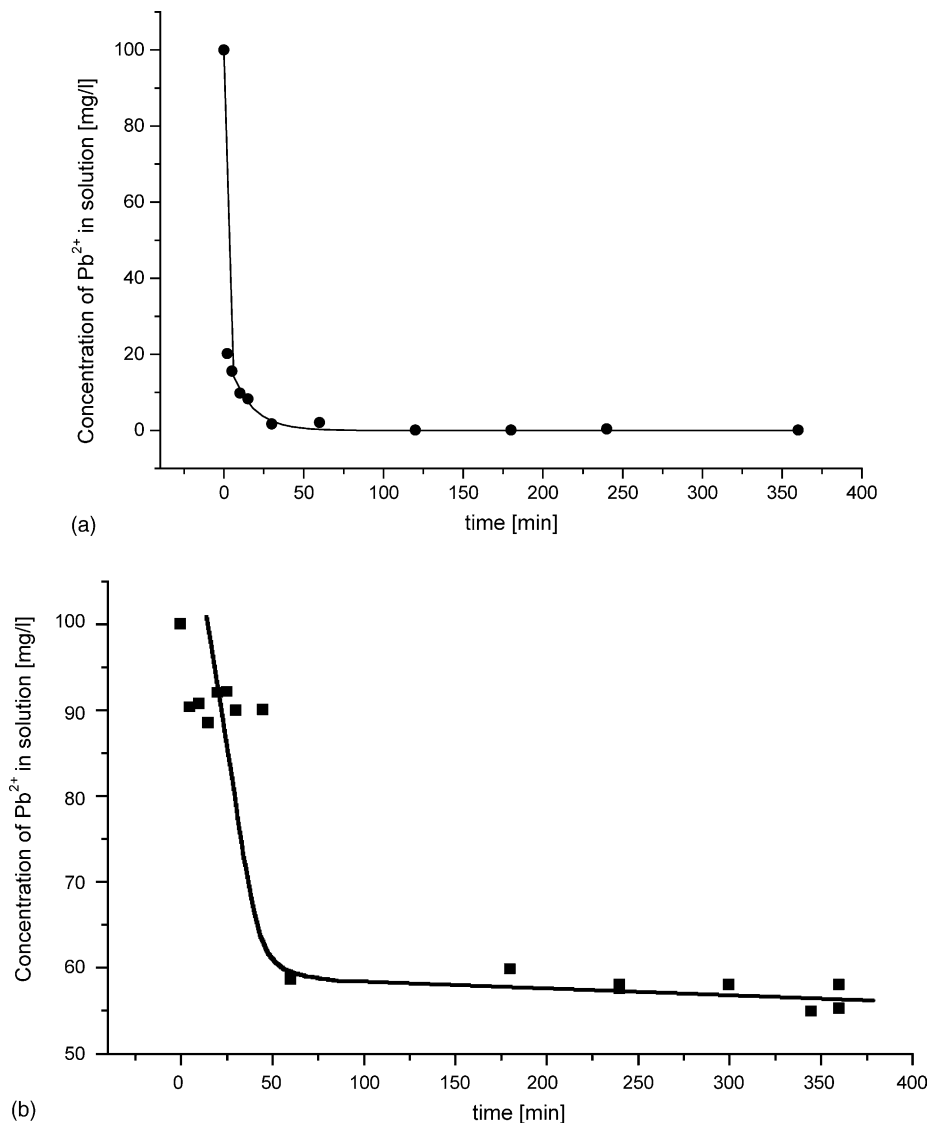


Fig. 7. Kinetics of lead removal by: (a) synthetic HAP, and (b) natural apatite (LA) at 25 °C.

ing that the mechanism of lead sorption by LA is based on its incorporation into the LA matrix. However, this process, although probably limited by diffusion processes, cannot be terminated due to the encapsulation of LA particles by the produced insoluble pyromorphite phase, which is a typical characteristic of HAP, NCA and Apatite II materials.

The principal question which can be addressed to the proposed theoretical criterion is the following: how the simple ion–ion interaction potential parameter can be used as a simple criterion for the analysis of the complex process of toxic metals immobilization by the addition of phosphates, which actually depends on several physical and chemical parameters?

In general, the factors determining the efficacy of toxic metals stabilization in polluted soils by the use of phosphates can be divided into the following two groups: (i) external physico-chemical factors, such as pH, temperature, pollutant concentration, solubility of the amendment, etc., which

are expected to influence predominantly the process kinetics, and (ii) internal factors, such as cohesive energy, lattice energy, Gibbs free energy, etc., determining mainly the stability of the final product. The ion–ion interaction potential parameter, which has been used in the present analysis belongs to the second group of factors, because it determines the stability of the final product as its inherent property.

From this point of view the proposed criterion can be considered to represent “a necessary, but not sufficient” condition for the complete estimation of efficacy of toxic metals immobilization by the addition of phosphates. In other words, when the stability of the final product obtained after the stabilization of toxic metal with a particular amendment is low, as measured by the respective value of “ion–ion interaction potential”, then the remediation process cannot be sufficiently effective, independently on the other external conditions. For this reason the ion–ion interaction potential represents an im-

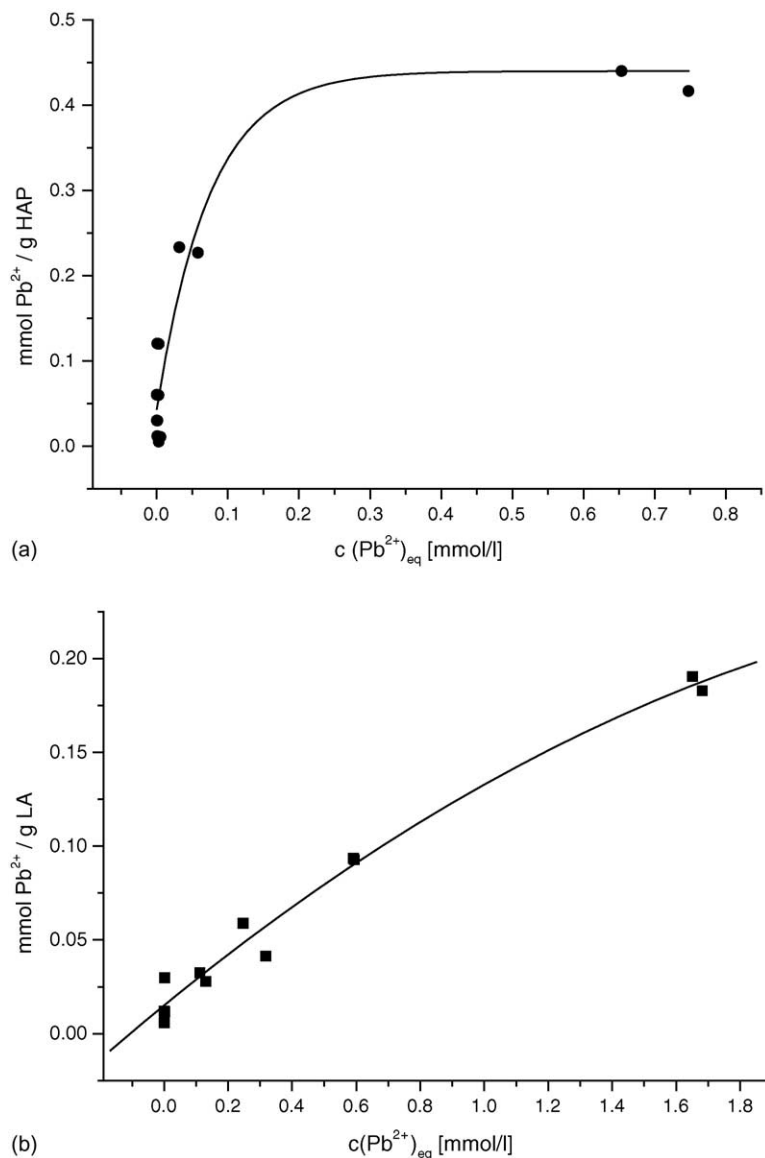


Fig. 8. Adsorption isotherm of Pb on: (a) synthetic HAP, and (b) natural apatite (LA) at 25 °C.

portant parameter, which can be applied for the pre-selection of optimal amendment candidates to be used for stabilization processes of metal-contaminated soils, during the early planning stage of a relevant project, even before the necessary experimental investigations; thereby, saving both valuable time and funding resources.

5. Concluding remarks

The main purposes of this study was: (i) to investigate the stability of apatite/Pb and apatite/Cd systems in order to compare the suitability of different apatites for the in situ immobilization of lead or cadmium, existing in contaminated soils, and (ii) to evaluate the effectiveness of natural apatite LA from a large mineral deposit in Serbia for the application

of clean up procedures of environmental “hot spots” in Serbia and Montenegro.

From the presented results it can be concluded that HAP and Apatite II samples may immobilize lead by a dissolution/precipitation mechanism, resulting in de novo formation of stable and insoluble pyromorphite. The immobilization of lead by NCA includes also the direct incorporation of lead into the apatite lattice. The stability analysis of LA/Pb system reveals that during the immobilization of lead by this natural apatite two distinct mechanisms can be involved: (i) direct incorporation of lead into the LA lattice, and (ii) precipitation of a new Pb–apatite phase and subsequent diffusion of lead into LA. The comparison of sorption isotherms between HAP/Pb and LA/Pb systems indicated the existence of different mechanisms, which are involved in the sorption of lead by the two examined apatites (HAP, LA).

In order to improve the proof of correctness of predictions based on the proposed theoretical model, we have used in this paper two sets of data: (i) data from the literature, which concern the sorption of Pb and Cd by HAP (supported by about 15 references), and (ii) experimental data obtained by the authors. The presented results from the theoretical analysis and from the sorption experiments demonstrate that the LA sample (from the Lisina deposit in Serbia) present sufficient sorption properties, qualifying that this natural apatite is a potentially useful material, which could be used for the in situ treatment of environmental “hot spots” in the area of Serbia and Montenegro, contaminated with lead and presumably with other toxic metals. According to the obtained results the main disadvantages of LA in comparison with HAP, as well as with the other evaluated natural apatites are: (i) the lower sorption capacity for lead, which possibly is a consequence of its lower calcium content, and (ii) the kinetically slower uptake of lead, which is limited by diffusion processes.

On the other hand, LA presents also certain advantages in comparison with the other examined apatites. The dissolution/precipitation mechanism of Pb immobilization by HAP, NCA and Apatite II leads to the occlusion of apatite particles within the produced stable and insoluble pyromorphite. As a consequence, the process of immobilization would be expected to terminate, when all the available apatite surfaces will be covered by pyromorphite. This problem does not exist in the case of LA application, due to its ability to incorporate lead directly into the crystal lattice and subsequently to diffuse the precipitated Pb–apatite (Fig. 6).

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