

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 $200 \mu\text{m}$.

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