ABSTRACT

During the past years as a consequence of war and some accidents in neighboring countries large areas in Serbia were contaminated by toxic heavy metals, including lead, cadmium and uranium. For example, the concentrations of Pb, Cd, Cu and Cr have been doubled above the allowed maximum value in the Romanian part of the Danube while sediments near the border in Bulgaria have higher concentrations of Pb 3 times, Cu 1400 times and Cd 30 times more than the average long-standing levels. Furthermore, an estimated 10 tons of depleted uranium (DU) was spread mainly throughout the territory of Kosovo. This contamination is a potential source of different chronic diseases including malignant diseases and represents a long-term threat for the population living in the affected areas. For this reason, remediation of contaminated sites represents an urgent need and priority. The standard remediation procedure which includes soil removal, treatment (washing, chalating), conditioning etc. is costly, disruptive and not sustainable. This study was carried out to evaluate apatite from the Lisina deposit as soil amendment for in situ stabilization of toxic heavy metals. Preliminary theoretical and experimentally results presented here point out this natural apatite as an ecological, nontoxic material which can be used for efficient and cost-effective remediation of large areas contaminated with Pb, Cd and U.

Key words: soil contamination, remediation, lead, cadmium, uranium, apatite

INTRODUCTION

Contamination of water and soil resources with toxic heavy metals such as lead (Pb) and cadmium (Cd) represents one of the most pressing and potentially costly threats to the environment worldwide. In Yugoslavia it is even more compelling after years of mis-
treatment, a decade of economic sanctions and NATO bombing in 1999 which released a significant amount of toxic heavy metals, among other pollutants, into the environment. As a consequence of this pollution the concentrations of Pb, Cd, Cu and Cr have considerably increased in water and aquifer sediments above the average long-standing levels. The recent ecological accident in Baia Mare, Romania discharged a significant quantity of Pb, Zn, Fe, Mn, Cd and Cu together with cyanide to rivers and surrounding soil. Furthermore, an estimated 10 tons of depleted uranium (DU) was spread mainly throughout the territory of Kosovo. There is an urgent need for remediation of this pollution because it will represent a serious and long-term health problem for the population in the entire region encompassing parts of Romania, Hungary, Yugoslavia and Bulgaria.

The United States Environmental Protection Agency (USEPA) established the treatment standard for lead waste and particularly for lead contaminated soils and solid wastes. According to this regulation (effective Nov. 8, 1990) any solid waste containing leachable lead levels in excess of 5 mg/l, measured by TCLP (Toxicity Characteristic Leaching Procedure), is considered characteristically toxic and hence hazardous, and as such is restricted from land disposal. Such waste must be treated with at least one of the Best Demonstrated Available Technologies (BDAT) before land-filling is permitted. The cost of disposing lead toxic hazardous waste materials is extensive including the cost of treatment, plus the cost of transporting the hazardous material to landfills for hazardous waste, which do not exist in every state in the USA. In Yugoslavia a repository for the disposal of hazardous waste does not exist at all.

Currently, many technologies are employed to clean up contaminated soils and wastes including thermal, biological and physical/chemical treatments. These techniques generally require removing the contaminated soil, treating it, and either replacing it on-site or disposing of it away from the area of contamination. Such removal technologies are costly to practice, and destructive to the sites from which wastes are removed. Furthermore, because of the bulk of wastes that must be removed it presents a disposal problem when the removed materials are disposed of away from the site of contamination. In addition, these removal technologies are often ineffective in fully removing heavy metals or reducing their bioavailability.

**IN SITU STABILIZATION**

For a large area of contaminated soil and aquifer sediments in situ stabilization of metals is appealing since it is much less disruptive to the ecosystem and hydrology, reduces the risk of worker exposure during remediation and is typically less expensive. In situ remediation involves minimizing the mobility of contaminants by transferring them to stable, nonlabile phases via chemically induced transformation.

In situ metal stabilization involve addition to the soil of additives with usually multi-pathway activity which includes: providing of ions to the solution that can combine with metal in solution to form new metal-containing solids that can precipitate, buffering of the pH to a degree that makes leaching of metals less likely or induces the precipitation of metals into a new solid, inducing adsorption of the metal onto an existing solid surface, and adsorption of metals onto its own surface. All of these possible actions depend upon the chemistry and conditions in the specific location and depend upon the additive used. Many additives have been proposed for in situ metal stabilization: calcium phosphate materials, iron filings, zeolites, clay, or organics of different types. Among calcium phosphate containing materials, synthetic hydroxyapatite was considered, but readily available and inexpensive solids like naturally occurring apatite, dibasic calcium phosphate or phosphate rock are preferable. Geochemists have long known that metal phosphate materials...
compounds are generally less soluble and more stable than other metal compounds. Because of this stability, as well as the broad reactivity with many metals and radionuclides, apatite and apatite-like minerals represent favorite materials for in situ metal stabilization.8-12

STABILITY OF METAL-PHOSPHATE PHASES

The basic problem in the approach of the in situ remediation is the stability of the final product under various environmental conditions.13 One of the unique and scientifically most challenging aspect of this problem is extrapolation of short-term laboratory data (hours to years) to a long time periods (10^3 - 10^4 years). Even though, this issue has been investigated extensively in literature, a satisfactory general approach for long-term estimation of stability of the solid matrix-impurity system has not been established. Recently it was demonstrated that the ion-ion interaction potential V(r_0), representing the main term of the cohesive energy of the solid system, strongly correlates with its stability.14 In this study we have calculated the V(r_0) values for different mineral phases in order to compare their stability. Results of this analysis are presented in Table I.

Table I Stability of some lead and uranium mineral phases

<table>
<thead>
<tr>
<th>Mineral phases</th>
<th>Formula</th>
<th>V(r_0) 10^-2 [Ry]</th>
<th>log K_sp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerussite</td>
<td>PbCO_3</td>
<td>-9.1</td>
<td>-12.8</td>
</tr>
<tr>
<td>Pyromorphite</td>
<td>Pb_{10}(PO_4)_{6}Cl_2</td>
<td>-69.7</td>
<td>-84.4</td>
</tr>
<tr>
<td>Autunite</td>
<td>Ca(UO_2)<em>{2}(PO_4)</em>{2}</td>
<td>-41.5</td>
<td>-49.0</td>
</tr>
</tbody>
</table>

From the presented results it can be concluded that relative stability increase in order S_{Pb_{10}(PO_4)Cl_2} > S_{Ca(UO_2)_{2}(PO_4)_{2}} > S_{PbCO_3}, where S is stability represented by V(r_0). It is interesting to compare this finding with the order of relative stability based on the solubility product (K_sp) for the analyzed mineral phases, which are also given in Table I. It can be seen that order of increase of stability of analyzed phases obtained according to this parameter (K_{Pb_{10}(PO_4)Cl_2} > K_{Ca(UO_2)_{2}(PO_4)_{2}} > K_{PbCO_3}) is the same as order based on V(r_0). Most stable phase is Pb-apatite (pyromorphite) which is final product of Pb immobilization by apatite followed by U-phosphate (autunite) which is final product of U immobilization by apatite. These metal phosphates are twenty to seventy orders of magnitude more insoluble than quartz.

Therefore, apatite is particularly effective for non-redox-sensitive metals such as Pb, Cd and Zn and for U and Pu with their complex redox behavior.

SORPTION PROPERTIES OF APATITE

Based on the above results it can be concluded that natural apatite represent promising materials for in situ remediation of sites contaminated with Pb. We further compared sorption capacity of natural apatite from Lisina deposit (Yu) with the sorption capacity of two other apatites, which are in practical use. The sorption capacity of apatite from Lisina deposit is determined in batch experiments at 25 °C and sorption kinetics and other properties of this apatite are given in reference.15 Results of this comparison are given in Table II. According to the presented results sorption capacity of the Lisina apatite is approximately four times lower than Apatite II and two times greater then for (CF) apatite.
Table II Sorption capacity of some mineral apatites

<table>
<thead>
<tr>
<th>Phosphate phase</th>
<th>Sorption capacity [mmol Pb/g]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Carolina - Apatite II</td>
<td>151</td>
<td>9</td>
</tr>
<tr>
<td>Florida phosphate rock (CF)</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Natural apatite from Lisina (NA)</td>
<td>41</td>
<td>this work</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Taking into account the presented results, as well as possible significantly lower price of NA Lisina in comparison with Apatite II (500 $/t), and availability of this mineral in a large quantity at Lisina deposit, it can been concluded that this domestic natural mineral represents a suitable material for in situ remediation of large sites contaminated with Pb and other toxic heavy metals.

REFERENCES