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REVIEW PAPER

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## REMEDICATION OF ENVIRONMENT CONTAMINATED BY LEAD USING SYNTHETIC AND NATURAL APATITES

*Lead contamination is an environmental concern due to its effect on human health. One of the ways of remediating lead contamination is the in situ stabilization of this heavy metal. This can be achieved by converting different types of lead species into Pb-phosphates (pyromorphites), which are among the least soluble Pb-bearing solids. Synthetic hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) and natural apatite can be used for this purpose. Both hydroxyapatite and some natural apatites are effective in reducing the aqueous Pb concentration to below  $15 \mu\text{g l}^{-1}$  (EPA drinking water limit). The main mechanism in the case of hydroxyapatite is its dissolution and subsequent precipitation of pyromorphites. The mechanism and the effectiveness of natural apatites depend on the type of apatite, its composition, crystallinity and presence of impurities. Apatites are also effective in reducing the Pb concentration in leachets from contaminated soils in the pH range from 6 to 10. The percentage of Pb concentration reduction is from 60 to 99.9% depending on the type of contamination and type of apatite amendment applied. These data suggest that apatites have potential to provide cost-effective in situ Pb immobilization.*

Human activity has altered the distribution and form of various elements, including lead. Lead has been converted from non-reactive, geochemically stable solids into forms that are more soluble and bioavailable, increasing its toxicity. One of the possible approaches of lead contamination remediation is reversing this process, transforming reactive forms to less liable species. This does not remove lead from the environment, but prevents it from accumulating in the biosphere. Materials under consideration for this purpose are synthetic and natural apatite. These materials induce the formation of Pb-phosphates (pyromorphites), which have very low solubility, and according by low bioavailability.

### LEAD CONTAMINATION

Lead is a naturally occurring metal. It has always been present in soils, surface waters and ground waters. The natural lead concentration in soils ranges from 2 to 200 mg/kg [1]. As a result of human activities, the distribution and forms of lead in the environment have been altered and local soil concentrations significantly increased. Due to this reason lead has become one of the most serious environmental and health hazards. Sources of lead contamination can be classified in three categories:

1. Industrial activities (mining and smelting)
2. Urban activities (use of lead petrol and paint)
3. Agricultural activities (use of insecticides that contain Pb)

Due to these activities environmental systems have become repositories for this metal. This is especially true for soils which behave as lead reservoirs continuously contaminating surface and ground waters.

Lead is hazardous to children, and high Pb blood levels have been shown to reduce the IQ and learning ability of young children [2]. Lead from soils contaminated by paint, automotive emissions and smelting have been found to increase Pb blood levels in children when the soil concentration exceeds 500–1000 mg/kg [3, 4]. In some other cases little or no increases in Pb blood levels were observed even in the case of soils containing more than 5000 mgPb/kg [5]. These investigations suggested that the total soil concentration was not a good measure of Pb bioavailability or chemical lability and a subsequent danger for children's health. In fact, the toxicity of a substance, including lead is controlled by its chemical and physical state, or speciation.

There has been much research on the remediation of Pb-contamination by employing chemical, physical or biological treatments [6, 7, 8]. At first the emphasis of this research was on removing lead from contaminated soils. The methods that are now available for this purpose are electro kinetic remediation, phytoremediation and soil flushing. All of these technologies can significantly reduce the soil lead concentration, but they are very expensive and are used mainly on small contaminated areas with a very high contaminant concentration.

Recently, the understanding of lead exposure and factors which effect its bioavailability have allowed the development of less costly *in situ* stabilization methods [6, 9]. The fact that Pb-phosphates (pyromorphites) are some of the most insoluble Pb(II) minerals (Table 1), lead to investigations concerning the possibility of converting the Pb in contaminated sites into Pb-phosphates. At standard state Pb-phosphates are at least 44 orders of magnitude less soluble than anglesite ( $\text{PbSO}_4$ ), cerussite ( $\text{PbCO}_3$ ) and litharge ( $\text{PbO}$ ), which are solids common in soils contaminated by lead paint and smelting [7, 10]. Among all Pb-phosphate minerals chloropyromorphite has the lowest solubility. Several types of phosphate sources were investigated and apatites proved to be the most useful for this purpose.

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Table 1. Solubility products of some Pb minerals [11]

Mineral	Formula	Log K <sub>sp</sub>
Litharge	PbO	12.9
Anglesite	PbSO <sub>4</sub>	-7.7
Cerussite	PbCO <sub>3</sub>	-12.8
Chloropyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	-84.4
Hydroxypyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)	-76.8
Fluoropyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	-71.6
Bromopyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Br	-78.1
Corkite	PbFe <sub>3</sub> (PO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>	-112.6
Hindsalite	PbAl <sub>3</sub> (PO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>	-99.1
Plumbogummite	PbAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> · H <sub>2</sub> O	-99.3

## APATITES

Apatites are minerals with the formula Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>X where X is OH in hydroxyapatite (HAP), Cl in chloroapatite and F in fluoroapatite. They form hexagonal crystals with two different sites for the Ca<sup>2+</sup> ion. The Ca<sup>2+</sup>(1) site is coordinated to nine oxygens, while the Ca<sup>2+</sup>(2) site is comprised of CaO<sub>5</sub>X octahedron (Figure 1).

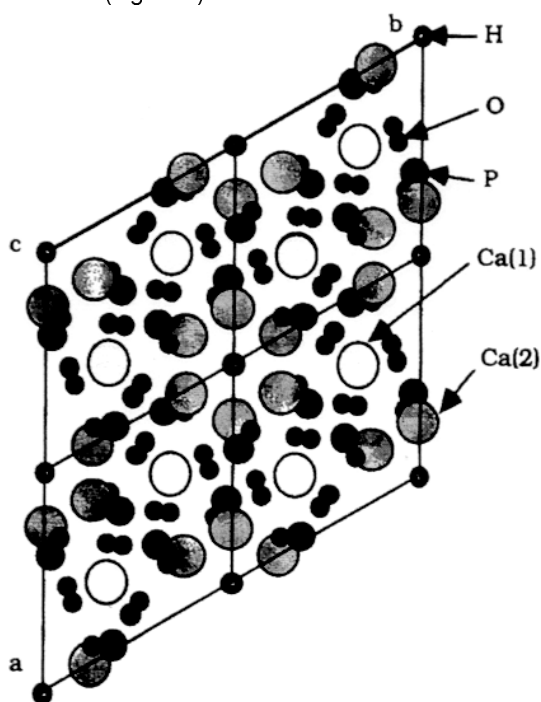


Figure 1. Projection of the hydroxyapatite down the c axis with the two cation sites in hydroxyapatite [14]

Pure stoichiometric apatites can be synthesized in the laboratory [12–14]. Apatites of geologic origin are dominated by fluoroapatites, exhibiting an inhomogeneous solid solution with Cl<sup>-</sup>, OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. Natural apatites (NA) exhibit the substitution of Ca with K, Na, Mn, Cu, Co, Zn, Sr, Ba and other elements in both Ca<sup>2+</sup> sites.

Table 2. Solubility products of apatites [15]

Mineral	logK
Ca <sub>p</sub> (PO <sub>4</sub> ) <sub>3</sub> OH ⇌ 5Ca <sup>2+</sup> + 3PO <sub>4</sub> <sup>3-</sup> + OH <sup>-</sup>	-58.5
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F ⇌ 5Ca <sup>2+</sup> + 3PO <sub>4</sub> <sup>3-</sup> + F <sup>-</sup>	-60.6
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl ⇌ 5Ca <sup>2+</sup> + 3PO <sub>4</sub> <sup>3-</sup> + Cl <sup>-</sup>	-57.8

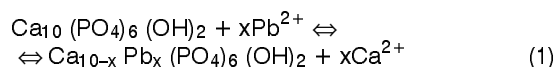
The solubility products of some apatites are shown in Table 2. The solubility of apatites does not show a great temperature dependency. On the other hand, pH has a great influence on the solubility of hydroxyapatite. During the dissolution of hydroxyapatite, OH<sup>-</sup> ions are released into the solution. When the pH is low, H<sup>+</sup> ions will combine with OH<sup>-</sup> to form water, increasing hydroxyapatite solubility. In cases of high pH, the high concentration of OH<sup>-</sup> ions will suppress dissolution, diminishing the solubility of hydroxyapatite.

Both synthetic and natural apatites were have been for the remediation of lead contamination.

## REACTIONS OF DISSOLVED Pb WITH SYNTHETIC AND NATURAL APATITES

### Mechanism of Pb removal by hydroxyapatite

Hydroxyapatite has been shown to provide an effective means for removing dissolved Pb and other heavy metals from aqueous solutions [16–32]. In their works Suzuki et al. [24, 25] showed that synthetic hydroxyapatite has a very high capacity for removing divalent heavy metal ions from water. The authors concluded that the main mechanism for the removal of heavy metals was the ion-exchange reaction. The order of the ions according to the amount exchanged was: Pb<sup>2+</sup> > Cu<sup>2+</sup> > Mn<sup>2+</sup> ≈ Co<sup>2+</sup>. The maximum value for the removal of the Pb<sup>2+</sup> ion was 230 mg/g of hydroxyapatite. Suzuki et al. described this process by the following reaction:



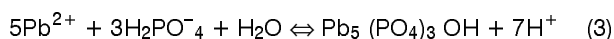
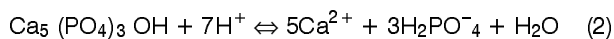
A number of authors [15, 26–30] argued that this reaction could not explain the changes in pH during the process, and also the fact that a lower pH resulted in greater Pb<sup>2+</sup> attenuation. The reaction takes place faster in a pH range where HAP is more soluble and, therefore, the release of phosphate is faster. Xu and Schwartz [15] argued that the ionic radius of Pb<sup>2+</sup> (1.26 Å) is much larger than that of Ca<sup>2+</sup> (1.08 Å) and that the crystal lattice parameters of hydroxypyromorphite (HPM) are significantly different from that of hydroxyapatite (Table 3). The phase transformation of HAP to HPM results in the increases of both dimensions a and c, and the volume of the unit cell from 529 to 633 Å<sup>3</sup>. This expansion of approximately 20 % is very difficult to achieve without breaking up the crystal surface. Valsami-Jones et al. [27] argued that the low diffusion

Table 3. Lattice parameters of apatites and pyromorphites

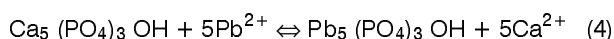
Mineral	Formula	a (Å)	c (Å)	a/c	V <sub>c</sub> (Å <sup>3</sup> )*
Chloroapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	9.634[15]	6.778	1.421	544.8 [15]
Hydroxyapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	9.418[15]	6.884	1.368	528.8 [15]
Chloropyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	9.987 [15]	7.330	1.362	633.1 [15]
Hydroxypyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	9.877 [15]	7.427	1.330	627.5 [15]

\*V<sub>c</sub> – the volume of the unit cell was calculated assuming a hexagonal crystal system

coefficients reported in the literature for Pb [33] indicate that the process is too slow to consume aqueous Pb<sup>2+</sup> at the rates they observed in their experiments. The major evidence Suzuki et al. gave to support their theory of the ion-exchange reaction is that the molar ratio of Pb removed / Ca released was approximately 1 in their experiments. Alternatively, it was suggested [15, 26, 27, 31] that the main mechanism for Pb<sup>2+</sup> removal from the solution was HAP dissolution and hydroxypyromorphite (HPM) precipitation according to the following reactions:

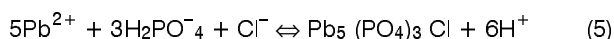


The overall reaction



is exothermal with a standard state Gibbs energy change of -137.08 kJmol<sup>-1</sup>.

The above reactions occur if there are no Cl<sup>-</sup> ions in the system. If, however, Cl<sup>-</sup> ions are present, chloropyromorphite (CPM) would form as a more stable phase [15, 32] (Table 1):

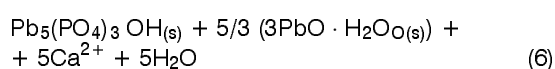
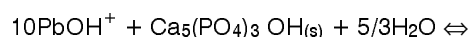


It is suggested that these reactions take place at pH < 7 [15, 27, 31], as the dissolution rate of HAP at these pH is sufficient to provide enough phosphate for HPM or CPM precipitation. These reactions could also explain the fact that the molar ratio of Pb removed / Ca released was approximately 1 in the experiments [6, 15, 26, 27]. The solubility product constant, logK<sub>sp</sub> of HAP is ≈ 26 and ≈ 18 orders of magnitude higher than those of chloropyromorphite (CPM) and HPM, respectively, and can act as a driving force for this process. This difference shows that the dissolution of HAP and the precipitation of CPM or HPM in lead aqueous solutions is thermodynamically preferable. All of these facts support the conclusion that aqueous lead is dominantly removed by the HAP dissolution and CPM or HPM precipitation process. The dissolution of HAP releases phosphate, which combines immediately with aqueous lead to form the less soluble HPM or CPM. By removing one of the products of the reaction of HAP dissolution, the process continues until complete consumption of the mineral. The experiments of Valsami-Jones [27] also showed that the aqueous phosphate concentration remains below the detection limit throughout,

suggesting that this ion has an insignificant residence time in solution before it reprecipitates as HPM.

Lusvardi et al. [31], however, concluded that two mechanisms (the adsorption of Pb<sup>2+</sup> on the HAP surface and the dissolution/precipitation mechanism) had an effect on Pb<sup>2+</sup> removal from aqueous solutions. They concluded that at initial molar Pb/Ca ratios > 0.01, the dissolution/precipitation mechanism was dominant and that adsorption, if present at all, could be neglected. At very low Pb<sup>2+</sup> concentrations, the Pb/Ca molar ratio < 0.01, the adsorption reaction should be taken into account.

Lusvardi et al. [31] suggested that at pH values higher than 6, another reaction takes place, as the Pb in the solution is mainly in the form of the PbOH<sup>+</sup> ion:



Discrete products of Pb reactions with hydroxyapatite are detectable by powder x-ray diffraction (XRD) and by scanning electron microscopy (SEM) in aqueous systems when the initial Pb<sup>2+</sup> concentrations are > 5 mg l<sup>-1</sup> and the initial pH ranges from 3 to 7 [26]. The primary reaction product in these experiments was HPM, which did not contain Ca. SEM micrographs showed separate rod-shaped HPM crystals that formed near the HAP particles.

Xu and Schwartz [15] found that the main difference between CPM and HPM precipitation was the fact that CPM crystals were formed as a coating on the existent HAP surfaces, significantly reducing the solubility of hydroxyapatite and its ability to remove Pb<sup>2+</sup> ions from the solution, while HPM formed as a separate phase in the system.

Lower et al. [34] studied HPM nucleation and growth in detail. They concluded that the nucleation of HPM occurred primarily homogeneously in solution. As HAP is the only source of phosphate, HPM nuclei would likely form near the HAP surface, where there was increased probability of successful collisions of Pb with phosphate. HPM formed needle-shaped crystals which had homogeneous size distribution. This suggested that once crystals nucleated, further Pb loss from solution was due to the growth of these crystals, rather than the continued nucleation of additional crystals.

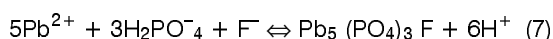
### Kinetics of lead removal by hydroxyapatite

Different authors have concluded that the immobilization process is fast. Ma et al. [26] concluded that the process was near completion in about 30 min. Hydroxyapatite reduced initially dissolved  $Pb^{2+}$  concentrations of 5–500 mg/l to below 5  $\mu\text{g/l}$ . In all the cases reported the aqueous  $Pb^{2+}$  concentration was reduced to below the U.S. Environmental Protection Agency (EPA) level of 15  $\mu\text{g/l}$  for drinking water after 1 h [35]. In their paper Xu and Schwartz [15] reported a reduction in the  $Pb^{2+}$  concentration from 100 mg/l to below the detection limit of 0.5  $\mu\text{g/l}$  within several minutes of reaction.

Lusvardi et al. [31] also investigated the influence of the initial Pb/Ca molar ratio on the kinetics of the process of lead removal from aqueous solution. They concluded that the kinetics of the reaction were faster at low initial Pb/Ca molar ratios (0.01–0.2). In one experiment with the Pb/Ca molar ratio=0.1, 2000 mg/l initial  $Pb^{2+}$  concentration was reduced to 1.38 mg/l after 7 h of contact. For large Pb/Ca molar ratios (0.6–1.0), the reaction took several months to complete. Temperature does not have a significant effect on the kinetics of this reaction [10].

### Influence of different anions and cations on Pb removal by hydroxyapatite

Ma et al. also investigated the influence of other anions and cations that could be present in the environmental system of  $Pb^{2+}$  immobilization by HAP [32, 36]. In their study [32] HAP was reacted with  $Pb^{2+}$  in the presence of  $NO_3^-$ ,  $Cl^-$ ,  $F^-$ ,  $SO_4^{2-}$  or  $CO_3^{2-}$ . The authors concluded that  $NO_3^-$  anion did not have any effect on  $Pb^{2+}$  immobilization by HAP and that reaction (3) takes place in this case. However, in the presence of the  $Cl^-$  ion, CPM precipitates according to reaction (5). In the presence of  $F^-$  ions the following reaction takes place:



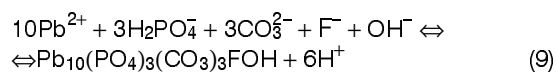
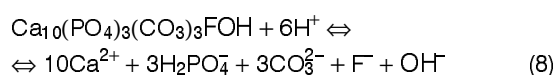
These reaction products were identified by XRD and SEM. The function of HAP is to provide P for the precipitation of either of the pyromorphite minerals. The dissolved  $Pb^{2+}$  concentrations were below 15  $\mu\text{g/l}$  after HAP reacted with  $Pb^{2+}$  in the presence of  $Cl^-$  or  $F^-$  ions. The fact that CPM and FPM were formed does not alter the effectiveness of HAP. Pb was also removed from solution in the presence of  $SO_4^{2-}$  or  $CO_3^{2-}$  ions.  $SO_4^{2-}$  ion did not have any effect on HAP effectiveness, while large concentrations of  $CO_3^{2-}$  resulted in somewhat poorer  $Pb^{2+}$  removal. This can be due to the higher pH of the solution in the presence of  $CO_3^{2-}$  ion, resulting in the lower solubility of HAP.

Competition with other metal ions also influences the reactions of aqueous Pb with apatites [36]. Nickel had little effect on Pb immobilization by HAP. However, Al, Cd and Zn caused decreases in Pb immobilization by

HAP, but only at the highest initial Pb concentration (100 mg/l) and M/Pb ratios greater than 1. The maximum inhibitions were approximately 64, 22 and 6 %, respectively. Copper and Fe(II) exhibited the greatest inhibition on Pb immobilization. This occurred to all of the concentrations except the lowest Pb concentration (5 mg/l) and at most M/Pb ratios greater than 1. The maximum inhibitions by Cu and Fe(II) were 63 and 37 %, respectively. The presence of cations in molar ratios M/Pb less than 1 had little or no effect on HAP effectiveness in reducing the Pb concentration. In fact, HAP also reduced the concentrations of competing metal cations. All metal concentrations decreased after reaction with HAP and the reduction varied from metal to metal and with the initial metal ion concentrations. The nature of this inhibition is not known, but it is possible that these metal ions passivate the surfaces of the apatite, through the formation of sorbed or surface-precipitated species.

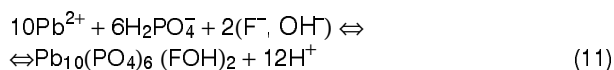
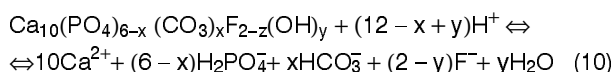
### Reaction of aqueous $Pb^{2+}$ with natural apatites

Some research has been devoted to the interactions of natural apatites (NA) with aqueous  $Pb^{2+}$  [1, 10, 28, 37]. Ma et al. investigated the interactions of dissolved Pb with natural fluoroapatites and carbonated fluoroapatites. These solids varied in their capacity to remove aqueous  $Pb^{2+}$ . The effectiveness of natural apatites was increased significantly by increasing the amount of phosphate rock added at the same initial Pb concentrations. A smaller increase in Pb removal was obtained by increasing the reaction time from 2 to 6h. However, the Pb removing efficiency improved greatly when the reaction time was increased to 1 day. They proposed that the mechanism of Pb removal was natural apatite dissolution followed by the precipitation of a carbonated fluoropyromorphite-like mineral:

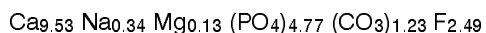


According to the above hypothesis, the higher the solubility of apatites, the more effective they are in reducing the aqueous Pb concentration. As hydroxyapatite is much more soluble than natural apatites, it is expected to be more efficient in removing  $Pb^{2+}$  ions. The Pb-removal capacity of HAP is 0.125 g of Pb / g of HAP [26], and for the most efficient natural apatite investigated 0.02 g of Pb / g of NA [1]. The lower Pb removal efficiency can be attributed to the lower solubility and purity of natural apatites than hydroxyapatite.

Chen et al. [28] supported the dissolution/precipitation mechanism at pH range 3 to 6, but argued (on the basis of XRD analysis) that the  $CO_3^{2-}$  ion was not incorporated in the reaction product. They described the mechanism by the following reactions:



They used natural apatite with the composition:



and obtained Pb-removal capacity of 0.151 g of Pb / g of NA. This value is even higher than that obtained for HAP [26]. They think that the reason for this is the difference in the surface area and reactivities of different types of apatite powders, as well as the difference in the initial Pb concentrations applied.

### REACTION OF APATITES WITH Pb-CONTAMINATED SOILS

As pyromorphites are much less soluble than the other Pb-solids commonly present in the environment, it is expected that if sufficient soluble P is present, pyromorphites will form at the expense of other Pb-solids.

Although numerous data exist about Pb removal by HAP from aqueous solutions, the literature concerning Pb removal from contaminated soils is less abundant [26, 30]. Ma et al. [26] studied contaminated soil material with an initial Pb concentration of 2273 µg/l. This concentration was reduced to 36 µg/l after the reaction of 6 g contaminated soil with 2 g of HAP in 30 ml of deionized water. XRD analysis detected hydroxypyromorphite as the reaction product. Laperche et al. [30] studied the chemical and mineralogical characteristics of Pb-contaminated soil and its reaction with synthetic hydroxyapatite. They selected a Pb-enriched fraction of contaminated soil and reacted it with HAP at ambient temperature. The Pb-concentration in the suspension decreased from 0.82 mg/l to 0.22 mg/l after reaction with HAP at pH 5. However, at pH 7.7 it decreased from 0.82 mg/l to 0.71 mg/l at other reaction conditions the same. HPM was identified by XRD patterns only in a system with pH 5. They concluded that HPM formation was limited by kinetic, not thermodynamic factors. Given enough time, at pH < 8 they anticipated that HPM would have formed in all the samples.

A number of authors investigated the leaching of Pb from contaminated soil with the addition of natural apatite [1, 10, 28, 37]. Ma et al. [1] reported that natural apatite reduced the concentration of leached Pb from 56.8 % to 98.5 %, compared to untreated soil. Chen et al. [28] found 62.3 % to 99.9 % reduction of Pb the leachates concentration after mixing the contaminated soil with 2 % of NA. They used the leaching agents in the pH range from 3 to 12. The greatest reduction of Pb leaching was found at pH values 6 – 10. The values of Pb concentrations in the leachets in this pH range were below the EPA drinking water limit of 15 µg/l<sup>-1</sup>. The mechanisms of these reactions are still unknown, as no

pyromorphite-like minerals have been detected by XRD analysis. This could be due to small concentrations of pyromorphites in the soil material, but further investigations are necessary.

### CONCLUSIONS

The results of different authors strongly demonstrate that both hydroxyapatite and natural apatites are effective in reducing the aqueous Pb concentration to below 15 µg/l<sup>-1</sup> (EPA drinking water limit). The main mechanism in the case of hydroxyapatite is the dissolution of HAP and the subsequent precipitation of pyromorphites. The type of pyromorphite precipitated (hydroxypyromorphite, chloropyromorphite or fluoropyromorphite) depends on the initial solution composition, but this fact does not alter the effectiveness of Pb removal. The overall process is kinetically very fast, and the reaction products are stable over a wide range of temperatures and pH. The effectiveness of natural apatites depends on their composition, crystallinity and presence of impurities. That is why the choice of the natural apatite to be used as an amendment is a critical step. In the case of natural apatites the mechanism is not quite clear. Some data support the dissolution/precipitation mechanism, but further investigations are necessary.

HAP and NA are also effective in reducing the Pb concentration in leachets from contaminated soils in the pH range from 6 to 10. The percentage of Pb concentration reduction is from 60 to 99.9 % depending on the type of contamination and type of apatite amendment applied.

The effective and rapid Pb<sup>2+</sup> immobilization from solution and contaminated soils by hydroxyapatite and some natural apatites, the limited effect of other cations and anions on the process, the stability of the reaction products and the low cost and abundance of natural apatites suggest that this approach may have great potential for the cost-effective *in situ* immobilization of Pb contaminated water, soil and wastes.

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## IZVOD

### STABILIZACIJA ZAGAĐENJA OLOVOM KORIŠĆENJEM SINTETIČKIH I PRIRODNIH APATITA

(Pregledni rad)

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Ljudske aktivnosti su dovele do promene distribucije i oblika u kojem se nalaze različiti elementi, uključujući olovo. Olovo je pretvoreno iz nereaktivnog, geohemijski stabilnog oblika u rastvorljiva jedinjenja te je tako postalo dostupno za biosferu. Jedan od mogućih pristupa saniranju zagađenja olovom je promena smera ovog procesa, odnosno transformacija reaktivnih i rastvornih jedinjenja ovog metala u stabilnije oblike. Ovim procesom se olovo ne uklanja iz životne sredine, ali se sprečava njeno akumulacija u biosferi. Jedan od materijala koji se ispituju za korišćenje u ovu svrhu je sintetički hidroksiapatit ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) i prirodni apatit. Ovi materijali omogućavaju formiranje Pb-fosfata (piromorfita) koji su veoma slabo rastvorljivi i u skladu sa tim, slabo dostupni biosferi.

Korišćenje obe ove vrste apatita omogućava snižavanje koncentracije olova u vodenim rastvorima ispod  $15 \mu\text{g}^{-1}$ , što je gornja granica za pijaću vodu Američke agencije za zaštitu životne sredine (EPA). U slučaju hidroksiapatita osnovni mehanizam ovog procesa je njegovo rastvaranje i taloženje piromorfita. Efikasnost prirodnog apatita mnogo zavisi od sastava minerala, stepena kristalčnosti i količine prisutnih nečistoća. Mehanizam stabilizacije olova prirodnim apatitom nije u potpunosti utvrđen. Postoje dokazi koji potvrđuju mehanizam rastvaranja apatita i taloženja piromorfita, ali potrebna su dalja istraživanja u ovoj oblasti.

Apatiti su takođe efikasni u smanjivanju koncentracije rastvorljivog olova u zagađenom zemljištu u opsegu pH od 6 do 10. Ovo smanjenje se kreće od 60 do 99.9 % u zavisnosti od vrste zagađenja i primenjenog apatita. Ovi podaci ukazuju da apatiti mogu biti korišćeni za *in situ* stabilizaciju olova.

Ključne reči: Zagađenje okoline • Olovo • Hidroksiapatit • Prirodni apatit •

Key words: Environmental protection • Lead • Hydroxyapatite • Natural apatite • Contamination remediation •

