T. KALUĐEROVIĆ RADOIČIĆ[1]
S. RAIČEVIĆ[2]

[1]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia
[2]Vinča Institute for Nuclear Sciences, Box 522, Belgrade, Serbia

SHORT COMMUNICATION

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IN SITU LEAD STABILIZATION USING NATURAL AND SYNTHETIC APATITE

In this work, mineral apatite was investigated for the remediation of lead contamination. Two different apatite minerals were used: synthetic apatite, $Ca_{10}(PO_4)_6(OH)_2$ (hereafter denoted as HAP) and natural apatite from Lisina, near Bosilegrad, Serbia (hereafter denoted as LA). Phosphate ore from Lisina deposit consists of 43.3 % apatite in the form of fluorapatite, $Ca_{10}(PO_4)_6(F)_2$. Sorption properties of HAP and LA were investigated. The results show that both of these minerals are effective in lead removal from the water solution. Sorption capacity of HAP obtained in this experiment is 0.216 mmol Pb/g HAP, while the value for LA is 0.162 mmol Pb/g LA. Modeling of these systems was conducted using Visual Minteq computer program. The values obtained from the computer simulation were compared to experimental values.

Key words: hydroxyapatite; natural apatite; soil remediation; stabilization; lead.

One of the most wide-spread groups of contaminants in environment, especially in ground water and soil are heavy metals. Heavy metals are natural substances which have always been present in the Earth's crust. Due to different industrial and mining activities, a distribution and form in which heavy metals are present in the environment have been changed. Heavy metals were transformed from geochemically stable solid phases to more reactive and bioavailable forms. Heavy metals primarily accumulate in soil. Leaching of heavy metals from the soil contaminates surface and ground waters, as well as drinking water.

The resent research [1] has shown that the total heavy metal concentration is not the true measure of its bioavailability. The toxicity of a heavy metal is controlled by a physical and chemical form in which it is present in the environment. Based on this fact, in situ methods were developed, which are also called natural remediation processes. The aim of these processes is the use of abundant, rather inexpensive natural substances or industrial by-products for heavy metal stabilization. This approach can be used for Pb contamination as, in most cases, Pb is present in the environment in the form of highly soluble minerals such as PbO, $Pb(CO_3)_2$ and $PbSO_4$ [2]. For the remediation of Pb contamination, phosphate minerals, zeolite and clay were suggested [3,4]. The most promising of these processes is a treatment of lead contaminated waters and soil by apatites: synthetic hydroxyapatite (HAP) [$Ca_{10}(PO_4)_6(OH)_2$] [5] and natural apatites [6-8]. Naturally occurring apatite minerals (phosphate rock) could be used as a low cost alternative to synthetic HAP.

The present investigation has been undertaken to examine the possibility of utilization of the inexpensive apatite mineral from the phosphate ore deposit Lisina near Bosilegrad, Serbia, for the application of Pb contamination stabilization. Sorption properties of LA were investigated and compared to sorption properties of synthetic HAP. The systems were modeled using Visual Minteq computer program [9].

MATERIALS AND METHODS

Materials

Two sorbents were used in this study: stoichiometric hydroxyapatite (HAP) and natural apatite from phosphate ore deposits in Lisina (LA), near Bosilegrad (Serbia).

Stoichiometric HAP with formula $Ca_{10}(PO_4)_6(OH)_2$, was synthesized in the laboratory by a slow titration of $Ca(OH)_2$ solution with H_3PO_4 at elevated temperature (95 °C) in nitrogen atmosphere, following a previously described procedure [10]. Ca/P ratio of synthetic HAP was 1.67±0.02 and surface area 21.0 $m^2.g^{-1}$, as determined by the application of BET method.

Natural apatite from the phosphate ore deposits in Lisina (LA) contains 43.3 % apatite. Chemical analysis showed that this sample has the following composition:

$Ca_{2.94}Na_{0.03}K_{0.05}Al_{1.38}Fe_{0.22}Si_6P_{1.96}S_{0.16}Cl_{0.04}F_{0.11}O_{22.28}$
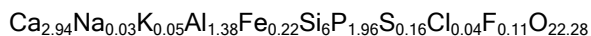
The surface area of 4.49 m^2 g^{-1} was determined using BET method. The sample was ground to fine powder with particle size lower than 200 μm and was used without further modifications.

Methods

Batch sorption experiments were carried out: 2 g of HAP or LA samples were mixed with 100 mL of $Pb(NO_3)_2$ solution, containing 4.826 mmol L^{-1} of Pb. The suspensions were thermostated at 25 °C and agitated at 150 rpm for 5.5 h, *i.e.* enough time for achieving equilibrium, according to the respective kinetic data from our previous work [11]. The suspensions were sampled through direct filtration, using 0.45 μm membrane filter. pH values of the filtrates were measured. The filtrates were analyzed for Pb and Ca content using Shimadzu AA-6501 F atomic absorption (flame) spectrometer. The batch experiments were conducted in duplicate and mean values were calculated.

Equilibrium modeling was conducted using a thermodynamic program, Visual Minteq ver. 2.50 [9]. Modeling was performed at 25 °C, and the results were compared with the experimental results of this work and our previous investigations [11].

RESULTS AND DISCUSSION

Sorption experiments

The results of the sorption experiments are shown in Table 1. The initial concentration of 4.826 mmol L^{-1} Pb^{2+} was reduced to 0.506 mmol L^{-1} after sorption with HAP, and to 1.578 mmol L^{-1} after sorption with LA. The sorption capacities for Pb obtained in this experiment are 0.216 mmol Pb/g HAP, and 0.162 mmol Pb/g LA. These results show that both HAP and LA could be efficiently used for Pb^{2+} removal from aqueous solutions. During the process of Pb sorption, Ca^{2+} is re-

Table 1. Results of Pb^{2+} sorption by HAP and LA

Time, h	c(Pb^{2+}) mmol L^{-1}	Amount of sorbed Pb, mmol Pb/g apatite	c(Ca^{2+}) mmol L^{-1}
		HAP	
0	4.826	-	0.0
5.5	0.506	0.216	1.5
		LA	
0	4.826	-	0.0
5.5	1.578	0.162	0.2

leased into the solution, indicating that possible mechanisms for Pb attenuation could include: a) dissolution of apatite and precipitation of new Pb phosphate, b) ion exchange processes and c) substitution of Ca in apatite by Pb. As the Ca/Pb molar ratio is not equal to one in our experiment, the surface complexity can not be excluded.

Visual Minteq computer program simulation

Visual Minteq is a thermodynamic program used for equilibrium modeling. It is used for the calculation of concentrations of ions present in the solution in a given system, adsorbed amounts of different ions, as well as types and amounts of precipitated minerals at equilibrium. The program also calculates the pH value of the solution. In this work the following input values for Visual Minteq were used:

c(Pb^{2+})$_{initial}$ = 0.4826×10^{-3} mol L^{-1}
m(HAP)$_{initial}$ = 0.2 g

The values of pH and Pb and Ca concentrations at equilibrium obtained in the experiment and the values from Visual Minteq computer program simulations for Pb/HAP system are presented in Table 2.

Table 2. Comparison of Visual Minteq calculations and experimental results in Pb/HAP system at 25 °C

Result	pH	c(Ca^{2+}) mol L^{-1}	c(Pb^{2+}) / mol L^{-1} Dissolved	Adsorbed	Precipitated	Removed %
Calculated	7.54	4.83·10^{-4}	1.54·10^{-7}	4.95·10^{-6}	4.8·10^{-4}	99.97
Experimental	6.16	3.33·10^{-4}	19.0·10^{-7}	-	-	99.60

The comparison between calculated and experimental values shows that the amount of Pb in the newly precipitated solid phase (4.8·10^{-4} mol L^{-1}) is two orders of magnitude greater than the amount of adsorbed Pb (4.95·10^{-6} mol L^{-1}). It can be concluded that according to Visual Minteq program the main mechanism of Pb removal from the solution is dissolution of synthetic hydroxyapatite and the precipitation of the new solid phase, hydroxypyromorphite. The process can be described with the following equation:

$$Ca_{10}(PO_4)_6(OH)_2 + 10Pb^{2+} \rightleftharpoons$$
$$\rightleftharpoons Pb_{10}(PO_4)_6(OH)_2 + 5Ca^{2+}$$
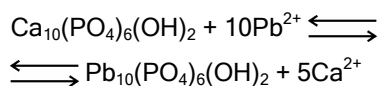
The percentage of Pb^{2+} removed from the solution calculated by Visual Minteq is 99.97 %, while our experimental value is 99.60 %. This agreement between the two values also supports the theory of dissolution-precipitation mechanism. The difference between experimental and calculated pH values of the solution is $\approx$ 1.4 units at 25 °C.

Sorption capacity of HAP and LA

Visual Minteq program was also used to calculate HAP and LA sorption capacity for Pb^{2+}. The sorption capacity in Visual Minteq calculations was defined as the amount of HAP/LA needed to eliminate 99.9 % of different initial concentrations of Pb^{2+}. These calculated values are shown in Figure 1, together with experimental ones. The slope of the lines in Figure 1

dissolution-precipitation mechanism suggested in the Pb/HAP system. The sorption capacities calculated on the assumption of dissolution-precipitation mechanism are much larger than the values found in the experiments indicating that some form of apatite inactivation occurs during the reaction. The mechanism of Pb remediation using HAP and LA needs further investigation.
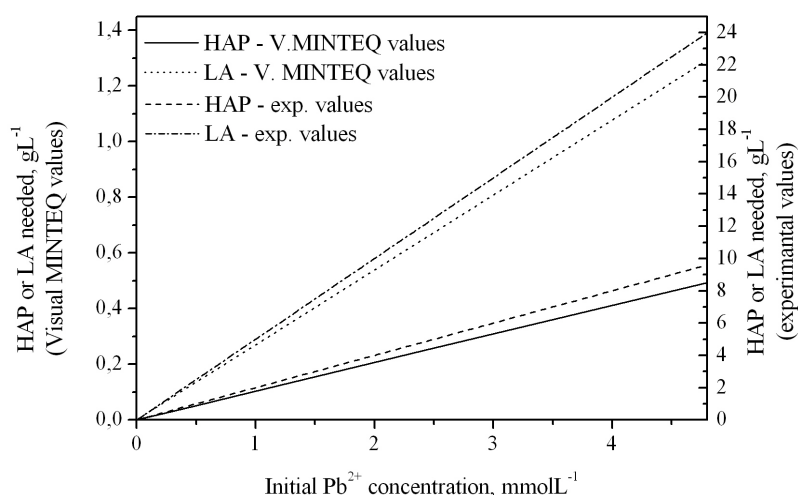

Figure 1. Comparison of experimental and Visual Minteq calculated values of sorption capacities.

represent sorption capacities for Pb^{2+}. The Visual Minteq calculated values of sorption capacities are 9.7 mmol Pb/g HAP and 3.71 mmol Pb/g LA. They are close to theoretical values based on asumption that 1 mole of HAP or LA provides PO_4^{3-} ions for precipitation of 5 moles of Pb^{2+}. The value of this theoretical sorption capacity is 9.9 mmol Pb/g HAP.

The difference between experimental (Table 1) and calculated values of sorption capacities is great. Even the largest values reported in literature are much smaller than Visual Minteq values. From this large difference it can be concluded that some form of inactivation occurs during the process of Pb stabilization using HAP or LA. This means that the whole amount of apatite present in the system can not be effectively used for remediation of Pb contamination.

CONCLUSIONS

The results of this study show that both HAP and LA can be used for Pb immobilization. Synthetic hydroxyapatite is more effective than Lisina apatite in the process of Pb contamination remediation. However, the lower cost of natural phosphate mineral supports the use of Lisina apatite as a cost-effective remediation material. Visual Minteq results support the

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