



Immobilization of Pb from Contaminated Water, Soils, and Wastes by Phosphate Rock.

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REPORT SUMMARY

This research is a continuation of our previous project on Pb²⁺ immobilization by hydroxyapatite. Three manuscripts are generated as a previous effort, and they are titled "In Situ Pb Immobilization by Apatite"(Ma, et al., 1993), "Effects of NO₃⁻, Cl⁻, F⁻, SO₄²⁻, and CO₃²⁻ on Pb²⁺ Immobilization by Hydroxyapatite"(Ma, et al., 1994a), and "Effects of Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite" (Ma, et al., 1994b). We have shown that hydroxyapatite is effective in immobilizing aqueous Pb in the presence of both anions (NO₃⁻, Cl⁻, F⁻, SO₄²⁻, or CO₃²⁻) and cations (Al³⁺, Cd²⁺, Cu²⁺, Fe²⁺, Ni²⁺, or Zn²⁺) (Ma, et al., 1994a,b). In addition, we also have proven that not only hydroxyapatite but also phosphate rocks are effective in immobilizing aqueous Pb. Furthermore, we have also demonstrated that hydroxyapatite is effective in immobilizing Pb not only from aqueous solution, but also from Pb contaminated soil (Ma, et al., 1993).

The current research is a continuation of the studies aforementioned. The experiments described in this report are on natural phosphate rock and hydroxyapatite. Whereas, experiments with the former materials addressed the specific, applied objectives of this research projects, it was necessary to conduct selected experiments with the latter synthetic phosphates to gain insight into reaction mechanisms. In many instances, such information would be much more difficult to obtain in the more complex experiments which utilized the natural phosphate rocks. Nevertheless, the results of the more "idealized" hydroxyapatite experiments provide information necessary to the complete understanding of the reactions responsible for Pb attenuation and stabilization by natural rock phosphates.

Fourteen phosphate rocks obtained from five states were effective in immobilizing Pb from solutions, with percentage Pb removal ranging from 38.8 to 100%. Two phosphate rock samples from Florida (CF Chemical and Occidental Chemical) and one contaminated soil from Washington State (Burch soil) were selected in the following four column studies. Selected Florida phosphate rocks significantly reduced aqueous Pb concentrations of the Burch soil, with percentage Pb reduction ranging from 56.8 to 98.5% in the first column experiment, in which phosphate rocks were mixed with Burch soil and sequential leaching was used. In this experiment, water was leached through the same soil column at different incubation times ranging 1 to 17 days, which simulates leaching by rain. The next two column experiments were designed to test the effectiveness of phosphate rock in removing Pb after short contact time of Pb with phosphate rock. The Pb concentrations in Burch soil were reduced by 94.9 to 99.5% in the second column experiment, in which the Burch soil was packed on the top of the mixture of phosphate rocks and reagent grade Ottawa sand. Furthermore, the selected phosphate rocks reduced Pb concentrations by 70.1 to 100.0% in the third column



experiment, in which the leachate of Burch soil was passed through the mixture of phosphate rocks and reagent grade Ottawa sand. In the fourth column experiment, water was leached through different soil columns after incubating mixture of Burch soil and selected phosphate rocks from 1 day to 8 weeks, which tests the effect of incubation time on Pb immobilization by phosphate rock. The Pb reduction in this experiment ranged from 62.9% to 94.6%. The results from the above four column experiments strongly demonstrate that the selected phosphate rocks were effective in reducing Pb concentrations from Burch soil regardless of the methods used to mix Burch soil and phosphate rocks.

Additionally, hydroxyapatite was capable of removing 71.7 to 100% aqueous Pb from four contaminated soils, which were contaminated through long term application of PbHAsO_4 . In another experiment, calcite and aqueous Ca inhibited Pb immobilization, but hydroxyapatite still reduced Pb concentrations significantly, with minimum Pb reduction of 97.6 and 99.3%, respectively. In a different experiment, hydroxyapatite removed Pb from Pb-EDTA solution in the presence of excess EDTA, with 24 to 31% Pb removal. In a long term experiment, hydroxyapatite was effective in immobilizing Pb up to 16 weeks, indicating the stability of the reaction product. In another experiment, mixture of hydroxyapatite and hydroxypyromorphite were reacted with anion exchange resin. Lead concentrations in the suspension of hydroxyapatite and hydroxypyromorphite were low (<168 nmol/L) in spite of the fact that anion exchange resin extracted P from solution, which again demonstrated the stability of hydroxypyromorphite over hydroxyapatite. Additionally, the mixture of hydroxyapatite and hydroxypyromorphite was also reacted with aqueous Ca^{2+} to study the possibility of Ca^{2+} substitution for Pb^{2+} on hydroxypyromorphite. Higher Ca concentrations resulted in slightly higher Pb concentrations (<158 nmol/L), possibly as a result of hydroxyapatite precipitation and hydroxypyromorphite dissolution. Extremely high EDTA concentrations dissolved most Pb from the mixture of hydroxypyromorphite and hydroxyapatite, ranging from 85.3 to 99.8 %, indicating the limitation of this method. Hydroxyapatite was also effective in immobilizing AsO_4^{3-} in the presence of Cd^{2+} , Pb, or Zn^{2+} as well as these metals themselves.

Our results strongly demonstrated that both hydroxyapatite and phosphate rocks were effective in reducing Pb solubility through dissolution of hydroxyapatite or phosphate rocks, and precipitation of hydroxypyromorphite or carbonated fluoropyromorphite, and thus both have potential to treat Pb contaminated water, soils, and wastes cost-effectively. Furthermore, the stability of pyromorphite, in the presence of anion exchange resins (which simulates extraction of phosphate by plants) indicates that the treatment of Pb-contaminated soils with solid phosphorous sources, such as rock phosphate, should indeed result in long-term, in situ stabilization of Pb.