

## Geochemistry of anthropogenic lead stabilization by Apatite II™

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Apatite II™, from fish bones, stabilizes a wide range of metals, especially Pb, U, Cd, Zn, Cu and Al, *in situ* or *ex situ*, by chemically binding them into new phosphate minerals and other low-solubility phases that are stable over geologic time. The excellent stabilization efficiency results from the unique structure and crystal chemistry of biogenic apatite coupled with the low solubility products of the resultant metal-apatites:  $K_{sp} < 10^{-80}$  for pyromorphite. Thermodynamic stability, combined with the rapid kinetics of metal-phosphate adsorption and precipitation, ensures metal immobilization. Depending upon the metal, concentration and aqueous chemistry of the system, Apatite II™ works by four non-mutually exclusive processes: heterogeneous nucleation, pH buffering, chemisorption and biological stimulation. This mineral species has been successful with contaminated soil, groundwater, acid mine drainage and wastewater, stabilizing about 20% of its weight in metals depending upon the metal and the geochemical conditions.

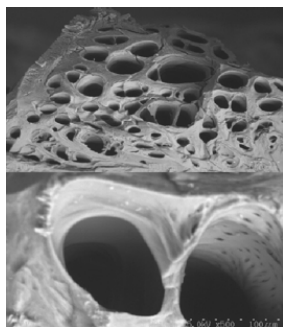


Figure 1. ApatiteII™ micro & nano-porosities

A case study is presented where Apatite II™ applied to a Pb-contaminated firing range, Camp Stanley, Boerne, TX, altered the geochemistry of the carbonate soil, reducing the average leaching of Pb from 0.373 ppm in untreated soil to 0.003 ppm in treated soil, thus eliminating potential impacts to groundwater and surface water run-off. Solids characterization shows Pb phases on the surfaces of the fish bone apatite particles. The Apatite II™ treatment also reduced Pb bioaccessibility in the soil.

## The dissolution of apatite II

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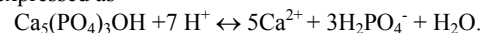
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### Introduction

Apatite II<sup>®</sup> is a hydroxylapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) obtained from fish bone. Its capacity to forming phosphate-metal compounds as dissolves makes it to be a low cost candidate to make up permeable reactive barriers, which are designed for remediation of metal contaminated soils and groundwaters. The goal is to investigate the reactivity of apatite II in the pH range between 2 to 7.5 by means of flow-through experiments, and estimate the dissolution rate-pH dependency. The sample is ground to size fraction between 250 and 500  $\mu\text{m}$ . The specific surface area is 1.75  $\text{m}^2 \text{g}^{-1}$ .

### Results and discussion

Under acidic conditions the apatite dissolution reaction can be expressed as



The apatite II dissolution is stoichiometric, i.e., the Ca/P ratio is 1.6. The dissolution rates are normalized to the initial specific surface area and obtained at undersaturation with respect to apatite II. The steady-state dissolution rates decrease as pH increases from  $-1.2 \times 10^{-9}$  at pH 2.2 to  $-5.5 \times 10^{-11}$   $\text{mol m}^{-2} \text{s}^{-1}$  at pH 7.1. Compared to the experiments of Valsamy et al. (1998) on mineral and synthetic apatite, the dissolution rate of apatite II is comparable to that of synthetic apatite in the pH range from 2 to 3 and slightly faster at near neutral pH, and is significantly slower than the rate of mineral apatite in the pH range from 4 to 5.

The overall dissolution of apatite II under acidic conditions may be governed by one reaction mechanism that consists of fast adsorption of a proton on a specific surface site followed by a slow hydrolysis step, assuming that the adsorption of the protons on this surface site is described by a simple independent Langmuir adsorption isotherm.

### References

Valsami-Jones E., Ragnarsdottir K. V., Putnis A., Bosbach D., Kemp A.J. and Gressey G. (1998) Chem. Geol. 151. 215-233.