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# Feasibility of using natural fishbone apatite as a substitute for hydroxyapatite in remediating aqueous heavy metals

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## Abstract

Fishbone, a natural, apatite rich substance, was examined for suitability as a substitute for hydroxyapatite in the sequestering of aqueous divalent heavy metal ions. The fishbone exhibited lower metal removal capacity than pure hydroxyapatite, due primarily to its purity (~ 70% apatite equivalent). In other ways the fishbone behaves in a similar manner as pure hydroxyapatite in the sequestration process. It was observed that it can remove all  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  to below detectable levels as measured by inductively coupled plasma atomic absorption, and the rate of reaction with either  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , or  $\text{Pb}^{2+}$  was also found to be similar to hydroxyapatite. Also, a two level, three variable full factorial design was performed for the Pb/apatite reaction and both apatites performed similarly. The main difference, besides capacity, was on exposure to high (2.4 mM) Pb concentrations. The fishbone removed less of the  $\text{Pb}^{2+}$  than capacity correction predicted. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Apatite; Heavy metals; Remediation; Fishbone; Sequestration

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## 1. Introduction

Contamination of groundwater and surface water by heavy metals from previously abandoned disposal sites and some currently operating sites has been a concern for some time. It has been determined that heavy metals are toxic to mammals. The presence of

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even low levels of heavy metals in waters is a concern primarily because the metals tend to bioaccumulate in the food chain. Therefore, considerable effort has been spent in treating metal-containing wastes at their source. Considerable progress has been made in methods such as coagulative precipitation, adsorption onto chelating resins, ion exchange, and reverse osmosis [1,2]. Of particular concern in Idaho, as well as in many other areas of the USA and the world, is lead contamination. Although various methods of treatment, such as mentioned above, have been used to remove heavy metals from soils and waste water, solubility data suggest that an effective way to remove lead, and other heavy metals, would be by precipitation in an apatite mineral solid [3]. Much research has been focused on the reactions of lead with hydroxyapatite.

Nriagu [3] looked at the precipitation of lead phosphates at controlled pH in the presence of either phosphoric acid or potassium hydroxide. He found that  $\text{Pb}_4\text{O}(\text{PO}_4)_2$ ,  $\text{Pb}_3(\text{PO}_4)_2$  and hydroxypyromorphite ( $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) were the stable precipitates formed between pH 4.2 and 9.5. He then investigated the stability of chloropyromorphite ( $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ ) [4]. Here he found that chloropyromorphite was the stable solid over a pH range of 2.7–7.1. Based on the solubility data obtained in these equilibrium studies, Nriagu [5] then calculated that, in oxidizing environments, pyromorphites ( $\text{Pb}_{10}(\text{PO}_4)_6\text{X}_2$ , where X is  $\text{Cl}^-$ ,  $\text{F}^-$ , or  $\text{OH}^-$ ) and plumbgummite ( $\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ ) were the dominate precipitates.

There were several studies into the reaction of aqueous cations with synthetic hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ). Suzuki et al. [6] reacted synthetic hydroxyapatite with either aqueous  $\text{Ba}^{2+}$ , Cd aqueous  $^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ , or  $\text{Zn}^{2+}$  as nitrates. The reactions were conducted both in batch vessels and by passing the aqueous ions through a column containing the hydroxyapatite. The ranking of molar capacities of the metals ions was:  $\text{Cd} > \text{Zn} > \text{Ni} > \text{Ba} > \text{Mg}$ . Suzuki et al. [7] further tested the hydroxyapatite–metal ion interaction, looking at  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Pb}^{2+}$  as nitrates. Using similar methods to the previous study, the selectivity for these ions was found to be:  $\text{Pb} > \text{Cu} > \text{Mn} \sim \text{Co}$ . Takeuchi et al. [1] contacted synthetic hydroxyapatite with either  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , or  $\text{Cd}^{2+}$  as nitrates in a well stirred batch reactor at a constant pH of 3.0, 4.0, or 5.0. They found the order of molar capacity was:  $\text{Cu} > \text{Pb} \sim \text{Cd}$  at pH 4 or 5, but the apatite dissolved at pH 3, so no metals were removed from solution. Ma et al. [8] and Xu and Schwartz [9] both found that synthetic hydroxyapatite could reduce aqueous lead from up to 1000 mg/l to less than 1 mg/l.

Investigators have attempted to determine the mechanism of reaction between  $\text{Pb}^{2+}$  and hydroxyapatite. Suzuki et al. [7] postulated that the reaction was cation exchange based on structure, ionic radius, and stoichiometric ion replacement. Ma et al. [8], using similar observational evidence with the addition of formation of pyromorphite crystals on ion-exchange media that had been saturated with  $\text{Pb}^{2+}$  and placed in a vessel containing water and hydroxyapatite, concluded that the reaction was a dissolution of hydroxyapatite followed by precipitation of pyromorphite.

Competition with lead ions by other cations in the hydroxyapatite reaction has also been explored. Takeuchi and Arai [2] looked at the reaction of two and three metal ion mixtures ( $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  and/or  $\text{Cd}^{2+}$ ) with synthetic hydroxyapatite in a well stirred tank reactor with constant pH of 4.0 or 5.0. The presence of other cations slowed the attainment of equilibrium, but did not reduce the capacity. Suzuki et al. [10] found that

Mn in the presence of Pb reduced the Mn removal but had little effect on Pb removal by synthetic hydroxyapatite. Ma et al. [11] did find inhibition by other cations in the synthetic hydroxyapatite– $\text{Pb}^{2+}$  reaction. These effects were measured at both high and low  $\text{Pb}^{2+}$  concentrations. At high  $\text{Pb}^{2+}$  concentrations the inhibition by single cations was:  $\text{Al} > \text{Cu} > \text{Fe(II)} > \text{Cd} > \text{Zn} > \text{Ni}$  and at low  $\text{Pb}^{2+}$  concentrations:  $\text{Cu} > \text{Fe(II)} > \text{Cd} > \text{Zn} > \text{Al} > \text{Ni}$ .

The effects of aqueous anions with  $\text{Pb}^{2+}$  were significant for the synthetic hydroxyapatite reaction. Suzuki et al. [10] investigated  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{NO}_3^-$  at constant pH of 3.0, 4.0, or 5.0. It was found that the lower the pH, the more  $\text{Pb}^{2+}$  was removed. In order of final  $\text{Pb}^{2+}$  concentration, the anion effect was  $\text{Cl}^- > \text{NO}_3^- > \text{F}^-$ . Takeuchi and Arai [2] tested  $\text{Cl}^-$  and  $\text{NO}_3^-$  and found  $\text{Cl}^- > \text{NO}_3^-$  in terms of final  $\text{Pb}^{2+}$  aqueous concentration, similar to Suzuki. Ma et al. [12] looked at  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  effects on the  $\text{Pb}^{2+}$ –hydroxyapatite reaction at an initial pH of 6.0. It was found that  $\text{Cl}^-$  and  $\text{F}^-$  were incorporated into the pyromorphite structure;  $\text{SO}_4^{2-}$  was precipitated as lead sulfate and neither  $\text{CO}_3^{2-}$  nor  $\text{NO}_3^-$  participated in the reaction. In this case, the anion effect in descending order of final  $\text{Pb}^{2+}$  concentration was:  $\text{CO}_3^{2-} > \text{F}^- > \text{Cl}^- > \text{NO}_3^- \sim \text{SO}_4^{2-}$ .

The rate of the removal of aqueous  $\text{Pb}^{2+}$  by synthetic hydroxyapatite has also received some attention. Takeuchi et al. [1,2] found that the  $\text{Pb}(\text{NO}_3)_2$ –hydroxyapatite reaction in a well stirred tank reactor was complete in  $\sim 10$  min. Substitution of  $\text{Cl}$  for  $\text{NO}_3$  cut the reaction rate about in half. Addition of competing cations ( $\text{Cu}$  or  $\text{Cd}$ ) caused a ten-fold rate reduction. Xu and Schwartz [9] found  $\text{Pb}(\text{NO}_3)_2$ –hydroxyapatite reaction in a stirred tank reactor to be complete in about 10 min, and that substitution of  $\text{Cl}^-$  for  $\text{NO}_3^-$  doubled the time for completion, also. The initial  $\text{Pb}$  concentration was  $5 \times 10^{-4}$  M, final concentration was  $< 10^{-9}$  M. Ma et al. [8] found the reaction of  $\text{Pb}(\text{NO}_3)_2$ –hydroxyapatite took  $\sim 24$  h to complete in a shaken reaction vessel.

Reactions involving natural apatites (phosphate ores) have also been explored. Phosphate ores occur as  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ , where X is either OH, Cl, or F. Ma et al. [8,13] screened several phosphate ores for their ability to attenuate aqueous lead. All apatites tested had some ability to reduce aqueous lead ( $\text{Pb}(\text{NO}_3)_2$ ) concentrations. Two of the better performing phosphates were added directly to Pb-contaminated soil and both reduced the deionized water leachable lead by 57 to 100%. Ruby et al. [14] evaluated a site contaminated with both galena ( $\text{PbS}$ ) and mono sodium phosphate. Using a combination of field samples and geochemical modeling, it was determined that 40% of the  $\text{PbS}$  had been altered to lead phosphates in 13 years. Natural apatite has also been tested for Acid Mine Waste treatment. Choi and West [15] used pebbles of natural apatite (3/8"-30 mesh) to precipitate Al and Fe(III) while converting Fe(III) to Fe(II) by aerobic oxidation in a fixed bed column. It was found that  $\text{SO}_4^{2-}$ , Al, and Fe(III) could be removed by the phosphate pebbles. Chen et al. [16] investigated the pH effect on metal sorption to mineral apatite and found that Pb sorption was not pH dependent whereas Zn and Cd sorption were.

It is also well known that organic phosphates have high affinities for adsorption to mineral surfaces, therefore, fish bones generated as waste from fish processing could be used as a phosphate source to remediate soils or waste water contaminated by heavy metals [17]. Laperche et al. [18] found that  $\text{PbO}$  and  $\text{PbCO}_3$  in a contaminated soil was

converted to lead pyromorphite when exposed to hydroxyapatite. Laperche et al. [19] looked at bioavailability of apatite-amended Pb by measuring plant Pb uptake. It was found that both synthetic and mineral apatite amendments could lower the bioavailability of soil Pb.

The objective of this research is to assess the potential for using natural fishbone apatite, which contains reactive phosphate material, in the remediation of soils or sludge contaminated with heavy metals such as lead, cadmium, chromium, nickel, and zinc. Fishbone is a cheaper source of apatite than synthetic hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ). The primary difference between natural and hydroxyapatite is substitution. Natural apatite contains some fluoride or chloride in place of the hydroxide and some divalent metals in place of calcium. Fishbone also compares favorably to apatite ores because it has more apatite and typically is lower in heavy metals content.

## 2. Materials and methods

Fishbones were obtained from fish caught in the Gulf of Alaska. The bones were cleaned of organics and dried. For this investigation, they were ground to 1/8th in. diameter.

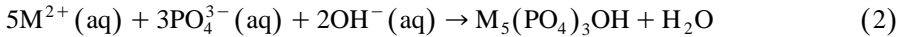
Metal analysis was performed using inductively coupled plasma atomic absorption (ICP-AA). Certified aqueous standards were obtained from Aldrich Chemical. Samples were diluted in a nitric acid matrix. Equilibrium metal binding experiments were conducted by placing a given mass of fishbone in a 250 ml polypropylene flask and introducing 200 ml of metal nitrate solution. The flasks were then covered with parafilm (Fisher), and placed in a temperature controlled shaker (New Brunswick) for 48 h. Metal solutions were prepared by dissolving the target amount of reagent grade solid metal nitrate in class II deionized water. Samples were removed from the flasks with a plastic syringe equipped with a 0.7-mm borosilicate glass fiber filter (Fisher).

For the kinetics experiments, 200 ml of aqueous metal solution were added to 250 ml polypropylene beakers and covered with polystyrene plates at time zero. The solutions were agitated by teflon-coated stir bars. The solutions were agitated at zero, low, or high stir rates. Zero was no agitation; low meant the solution was stirred as fast as possible without forming a vortex; and high meant the solution stir rate was high enough to form a vortex just reaching the stir bar. The samples were taken using a 3-ml polypropylene syringe equipped with a 7- $\mu\text{m}$  borosilicate glass filter (Fisher). The sampling time was every 2 min for the first 6 min, then the interval between samples was doubled after each sample. Collected samples were acidified, diluted and analyzed by ICP-AA.

Direct comparison of hydroxyapatite and fishbone apatite was performed using a three-factor two level full factorial design. Apatite (30 or 60 mg) was added to 100 ml deionized water and gently agitated overnight in a shaker. The pH was then adjusted to 5 or 7 using nitric acid. Sufficient concentration of lead nitrate solution was added to each flask to result in a final volume of 200 ml and a lead concentration of 0.483 or 2.41 mM, respectively. The experiment was performed for both fishbone and synthetic apatite. The synthetic apatite was obtained from Aldrich Chemical and was used as received.

### 3. Results

The exact mechanism of metal ion removal by apatite is not known, although recent evidence supports a dissolution–precipitation mechanism [8,9]:



Where  $\text{M}^{2+}$  is a divalent metal.

This mechanism was assumed to dominate for the purpose of this study. Equilibrium metal concentrations were predicted using MINTEQA2/PRODEFA2 [20]. This is a geochemical equilibrium speciation modeling program. It can be used to compute equilibria among sorbed, solid, gas and aqueous phases. The model uses equilibrium constants to partition all of the components based on their aqueous activities. The user inputs the initial conditions, e.g. the amount of hydroxyapatite, the amount of metal nitrate, the partial pressure of  $\text{CO}_2$ , etc. and the model iterates around the most out of balance components until equilibria is achieved. For this investigation no sorption models were employed, only solubility data from the MINTEQA2 thermodynamic data were used.

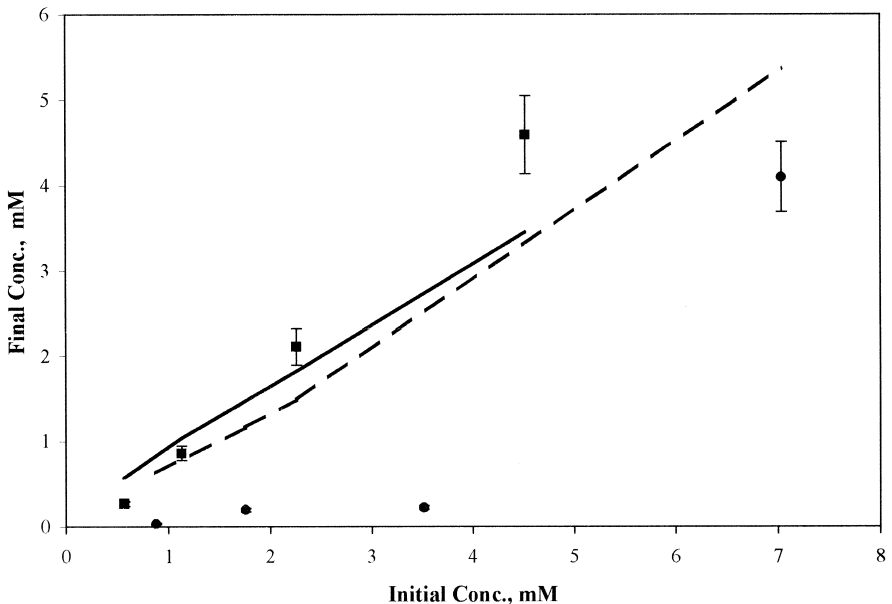


Fig. 1. Predicted and observed aqueous metal ion concentrations using MINTEQA2/PRODEFA2. - - Predicted final Ni concentration, (■) observed final Ni concentration, ——— predicted final Zn concentration, (●) observed final Zn concentration.

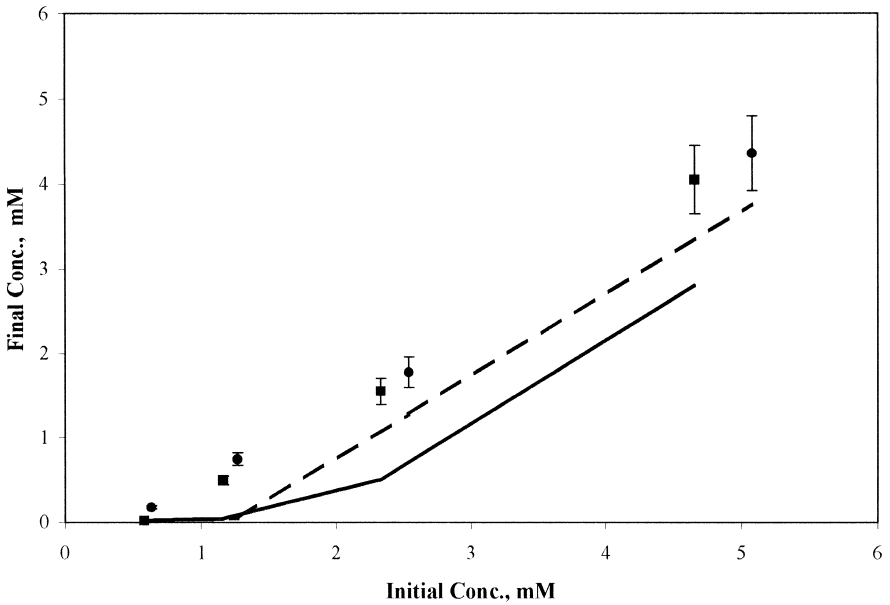


Fig. 2. Predicted and observed aqueous metal ion concentrations using MINETEQA2/PRODEFA2. ——— Predicted final Cu concentration, (■) observed final Cu concentration, - - predicted final Cd concentration, (●) observed final Cd concentration.

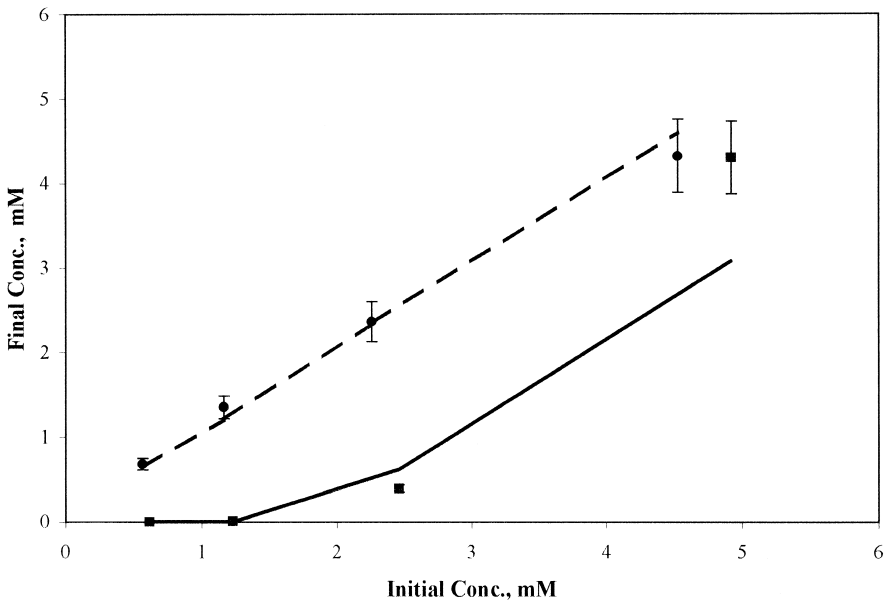


Fig. 3. Predicted and observed aqueous metal ion concentrations using MINETEQA2/PRODEFA2. ——— Predicted final Pb concentration, (■) observed final Pb concentration, - - predicted final Mg concentration, (●) observed final Mg concentration.

Table 1

Typical composition of dry fishbone apatite used in this investigation

Element	Ca	P	Mg	Zn	Cu	Pb	Cd	Ni
$\mu\text{mol/g}$	4466	2990	187.6	2.22	0.22	0.11	0.012	0.115

Several metals were contacted with fishbone apatite to see if the performance of this natural apatite was comparable to hydroxyapatite. The metals used were  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ni}^{2+}$ . All metals were in the +2 oxidation state with nitrate as the anion. Nitrate was chosen because, in studies with hydroxyapatite, it was shown to not interact with the apatite structure [12]. The fishbones removed some or most of the tested cations, with the exception of  $\text{Mg}^{2+}$  (Figs. 1–3). In fact the aqueous concentration of  $\text{Mg}^{2+}$  increased after exposure to fishbone apatite, which was explained by the residual  $\text{Mg}^{2+}$  in the fishbones (Table 1). The order of selectivity for the cations was  $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$ .

The aqueous metal ion concentrations in Figs. 1–3 are compared to values predicted by MINTEQA2/PRODEFA2 [18] using metal removal by precipitation only. The predictions were based on the fishbone apatite analysis in Table 1, using the Ca analysis as the basis for hydroxyapatite input to the model. The predicted values agree reasonably well for all the metals with the exceptions of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ .  $\text{Zn}^{2+}$  appears to be sorbed to the surface of the apatite in addition to precipitating.  $\text{Cu}^{2+}$  concentrations agree at the lowest tested value, but are increasingly below the predicted value with increasing initial concentration. This trend can also be seen in  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$ . A possible explanation for this is metal phosphate precipitate coating the apatite surface, preventing its dissolution/precipitation.

A preliminary investigation of the reaction kinetics was performed as well. A simple experiment using beakers with teflon coated stir bars was employed. Three different

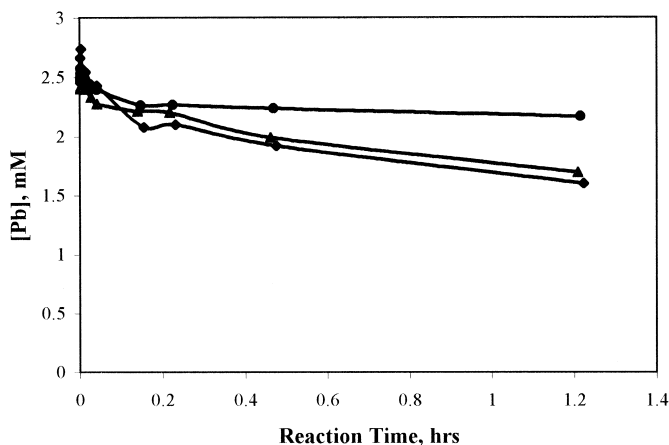


Fig. 4. Rate of reaction between Pb and fishbone apatite, high initial Pb concentration. ◆ — No stirring. ● — Low stir rate. ▲ — High stir rate.

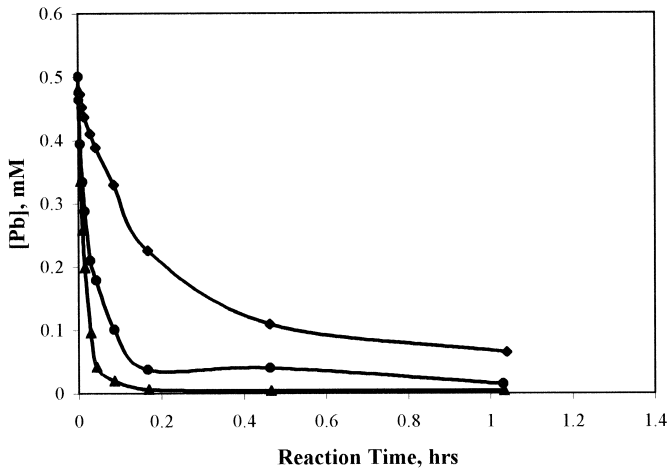


Fig. 5. Rate of reaction between Pb and fishbone apatite, low initial Pb concentration. ◆ — No stirring. ● — Low stir rate. ▲ — High stir rate.

agitation rates and two different initial concentrations of  $\text{Pb}^{2+}$  were used.  $\text{Pb}^{2+}$  removal as a function of agitation and initial  $\text{Pb}^{2+}$  concentration is shown in Figs. 4 and 5. From this it is apparent that the reaction is diffusion limited at lower concentrations and, at high initial Pb concentration, the reaction is essentially complete after 15 min. The rates of reaction of fishbone apatite with high initial  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  concentrations acted similarly to the high  $\text{Pb}^{2+}$  (Fig. 6). These fast reaction rates support the use of fishbone apatite in either a column or in a barrier form for heavy metal containment or sequestration.

A final test of fishbone apatite was to compare it to synthetic hydroxyapatite in the lab. For this experiment a three factor, two level full factorial design was used (Table 2). The design was executed for both hydroxyapatite and for fishbone apatite. The two apatites respond in a similar manner to pH and Pb, the main difference being a greater capacity for hydroxyapatite to remove the lead (Table 2). These results imply that

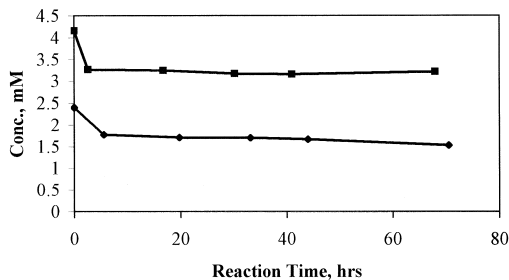


Fig. 6. Rate of reaction of fishbone apatite with Zn and with Ni, high initial metal concentration. ◆ — Zn concentration. ■ — Ni concentration.



Table 2

Full three factor two level factorial design and results. For apatite, + is 60 mg and – is 30 mg per 200 ml metal solution. For initial pH, + is 7 and – is 4. For [Pb] + is 2.41 mM (500 ppm) and – is 0.483 mM (100 ppm)

Apatite	pH	Pb	Fishbone		Hydroxyapatite	
			Pb, mM	pH	Pb, mM	pH
+	+	+	1.82	5.22	0.11	3.49
+	+	+	1.81	5.12	0.12	3.46
+	+	–	0.01	6.84	0.00	5.84
+	+	–	0.00	6.61	0.00	5.90
+	–	+	1.11	3.35	0.80	2.70
+	–	+	1.04	3.34	0.76	2.74
+	–	–	0.00	5.77	0.03	3.36
+	–	–	0.01	6.25	0.05	3.24
–	+	+	2.11	5.29	1.03	3.22
–	+	+	2.18	5.06	1.05	3.22
–	+	–	0.03	5.93	0.00	5.53
–	+	–	0.05	6.02	0.00	5.43
–	–	+	1.70	3.39	1.34	2.81
–	–	+	1.69	3.34	1.26	2.79
–	–	–	0.05	4.50	0.06	3.28
–	–	–	0.05	4.74	0.07	3.28

fishbone apatite is a reasonable substitute for hydroxyapatite in a barrier, column, or other aqueous divalent metal removal application.

#### 4. Conclusion

A natural apatite, composed of fishbones, was compared to synthetic apatite for: removal of various aqueous metal ions; removal of Pb at different pH's; and for reaction kinetics with  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ . All these comparisons found that fishbone apatite was comparable to hydroxyapatite on a Ca content basis. Fishbone apatite is cheaper than synthetic hydroxyapatite and also compares favorably to apatite ores because of its purity and lower substitution of undesirable metals. Based on this investigation, fishbone apatite would be an effective alternative to synthetic hydroxyapatite for removal of divalent heavy metal ions from aqueous solutions.

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