REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
May 1995

3. REPORT TYPE AND DATES COVERED
Technical report, May 1995

4. TITLE AND SUBTITLE
Adsorption Isotherms: North Carolina Apatite Induced Precipitation of Lead, Zinc, Manganese, and Cadmium from the Bunker Hill 4000 Soil

5. FUNDING NUMBERS
N/A

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Bechtel Hanford, Inc.
Richland, Washington
Pacific Northwest Laboratory

8. PERFORMING ORGANIZATION REPORT NUMBER
BHI-00197 Rev.00

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
SERDP
901 North Stuart St. Suite 303
Arlington, VA 22203

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
N/A

11. SUPPLEMENTARY NOTES
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12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release: distribution is unlimited

12b. DISTRIBUTION CODE
A

13. ABSTRACT *(Maximum 200 Words)*

Adsorption isotherm experiments using varying amounts of different apatites and a 10:1 water-to-soil ratio were used in combination with a thermodynamic model to determine the amount of apatite necessary to treat a given soil. These experiments suggest that soils may be remediated by extrapolating from the isotherm experiments. Given that a ton of soil has a mass of 9.07×10^2 kg, and that, from this study, most metal precipitation occurs at 1% or less added NC apatite, remediation of a ton of contaminated soil would require 10 kg of NC apatite. Considering the shipping and material cost of the NC apatite, this remediation would be $5.49 per treated ton of soil. By comparison, grouting techniques can required as much as 30% to 50% by weight, depending on the porosity of the soil.

14. SUBJECT TERMS
adsorption isotherm, apatite, SERDP, remediation

15. NUMBER OF PAGES
25

16. PRICE CODE
N/A

17. SECURITY CLASSIFICATION OF REPORT
unclass

18. SECURITY CLASSIFICATION OF THIS PAGE
unclass

19. SECURITY CLASSIFICATION OF ABSTRACT
unclass

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

179 - 1995

BHI-00197
Rev. 00

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Date Published
May 1995

19980806 120

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Bechtel Hanford, Inc.
Richland, Washington

BHI-00197
REV: 00
OU: N/A
TSD: N/A
ERA: N/A

APPROVAL PAGE

Title of Document: ADSORPTION ISOTHERMS: NORTH CAROLINA APATITE INDUCED PRECIPITATION OF LEAD, ZINC, MANGANESE, AND CADMIUM FROM THE BUNKER HILL 4000 SOIL

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5/1/95
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BHI-DIS 5-1-95

TOTAL PAGES:____

EXECUTIVE SUMMARY

The objective of this study is to demonstrate that the incorporation of North Carolina apatite (NC apatite) into contaminated soils stabilizes lead, zinc, manganese, and cadmium into metal-phosphate minerals, thus preventing leaching into the groundwater. The reactive phosphate compounds responsible for causing the precipitation of metals into insoluble minerals are constituents in geologic compounds referred to as hydroxyapatites (HA), and have the general chemical formula $Ca_{10}(PO_4)_6(OH)_2$*. An almost identical chemical formula is found in minerals called apatites. Geologists recognize more than 300 minerals classified as apatites, with the primary constituents being the calcium and phosphate ions, with a molar ratio similar to HA. These minerals form naturally and are widely disseminated in the geologic and soil environment. The reactivity of the apatite (dissolution in water) is a primary function of the other components such as fluoride, carbonate, and substitution of metals for calcium. Lanthanides, actinides, and heavy metals are all known to form insoluble, stable precipitates in the presence of apatites. In fact, these minerals are so stable in rock formations that their relative abundance has been used to calculate the ages of strata in the ocean floor (Wright et al. 1987). For the objective of this study, NC apatite, with the general formula* $Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}$*, will be used to demonstrate metal stabilization utility. The NC apatite is supplied from the Texasgulf Mining Company of North Carolina. The results of this study demonstrate that stabilization of contaminated soils and groundwater by NC apatite has the potential to be an extremely successful and widely applicable remediation strategy for heavy metals and radionuclides.*

Adsorption isotherm experiments using varying amounts of different apatites and a 10:1 water-to-soil ratio were used in combination with a thermodynamic model to determine the amount of apatite necessary to treat a given soil. These experiments suggest that soils may be remediated by extrapolating from the isotherm experiments. Given that a ton of soil has a mass of 9.07×10^2 *kg, and that, from this study, most metal precipitation occurs at 1% or less added NC apatite, remediation of a ton of contaminated soil would require 10 kg of NC apatite. Considering the shipping and material cost of the NC apatite, this remediation would be $5.49 per treated ton of soil. By comparison, grouting techniques can require as much as 30% to 50% by weight, depending on the porosity of the soil.*

Some specific highlights of the study include the following:

- *The NC apatite adsorption isotherms indicate that soluble lead, zinc, manganese, and cadmium are precipitated from solution at 1% added NC apatite.*
- *Using the MINTEQ-A2 geochemical model, thermodynamic predictions for the formations of pyromorphytes* ($Pb_5(PO_4)_3\ (OH, Cl)$)*, hopeite* ($Zn_3(PO_4)_2\ 4H_2O$)*, and rhodochrosite* ($MnHPO_4$) *at less than 1% addition of NC apatite confirms the precipitation of lead, zinc, and manganese at less than 1% apatite in the adsorption isotherms. The thermodynamic prediction for the formation of pyromorphytes* ($Pb_5(PO_4)_3\ (OH, Cl)$) *at less than 1% addition of NC apatite also confirms the molar ratio calculation scenario of* $Pb{:}PO_4$ *for pyromorphytes.*
- *The kinetics of formation for lead, zinc, and cadmium phosphate complexes are 24 hours or less; the kinetics of formation for manganese phosphate complexes appears to be at 48 hours.*

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1.0 INTRODUCTION

The objective of this study is to develop and demonstrate that phosphatic granules, solutions, and slurries will react with lead (Pb), zinc (Zn), manganese (Mn), and cadmium (Cd) in contaminated soils, causing the precipitation of metal-substituted apatite minerals. Metals sequestered in apatites have great durability and leach resistance that significantly exceeds other chemically stabilized waste forms because the metal-apatite mineral structure is very stable over a wide range of environmental conditions for geologically long time periods (Wright et al. 1978; Wright 1990). This constitutes applied research that will lead to advanced technology development that can be implemented to remediate metal and radiologically contaminated soils and groundwater at U.S. Department of Energy (DOE) sites and industrial sites where metal contamination of soils and groundwater is a pervasive problem.

The leachability of metals sequestered in apatite is insensitive to pH changes over the range of 2 to 12, and the bioavailability of ingested metals is also limited (Davis et al. 1992; Ruby et al. 1992). The reaction between the apatite and metals is rapid (Ma et al. 1993), and so the treatment is effective immediately, requiring no time for the material to "set up." The results given in this report show that as little as 1% by weight of NC apatite could remediate soils.

This study uses two very important confirmatory tools used by scientists to investigate adsorption and/or precipitation phenomenon. The adsorption isotherm illustrates graphically the precipitation or reduction of the soluble metals when the phosphate is applied to the system. Adsorption is most often described in terms of isotherms, which show the relationship between the bulk activity, or effective concentration in solution, of the species being adsorbed and the actual amount adsorbed at a constant temperature. When plotted, the shape and mathematical expression of the isotherm provide a great deal of information concerning the chemistry and sorption mechanisms within the system. By examining the sharp downward curves of the isotherm, the most effective concentration NC apatite to effect precipitation can be ascertained. The system then can be modeled thermodynamically, by first analyzing the solution equilibrium components, entering the data into the computer program, and then changing the amounts of phosphate in the theoretical system to match those amounts from the adsorption isotherm.

Although current research demonstrates the successful precipitation of soluble heavy metals when hydroxyapatites are added to a contaminated medium (Misra and Bowen 1981; Ma et al. 1993; Xu and Schwartz 1994), very little attention has been paid to the precise calculation of hydroxyapatite needed to affect precipitation or complexation of metals from contaminated mediums. In this report, the amounts of hydroxyapatite (as NC apatite) calculated to precipitate soluble Pb relative to the molar ratios of the precipitated Pb-PO_4 complexes will be illustrated as sharp downward deviations from linearity of the adsorption isotherms, as predicted by MINTEQ-A2, a thermodynamic speciation model. The amounts of apatite required for precipitating the metals in solution then can be extrapolated and scaled for field remediation.

2.0 PRECIPITATION OF SOLUBLE Pb BASED ON MOLAR RATIOS OF Pb-PO_4 COMPOUNDS

The Bunker Hill 4000 soil (BH 4000), so named because of its 4,000 mg kg^{-1} Pb concentration, was used to demonstrate the precipitation and metal-PO_4 stabilization potential of the NC apatite. A 2-week desorption experiment on the BH 4000 resulted in soluble Pb, Zn, Cd, and Mn concentrations presented in graphic and tabular format in Figure 1 and Table 1.

Of particular interest to this study is the type and amount of metals leaching from the BH 4000 soil as a function of time. Particular metals of interest are those that are regulated by federal agencies relative to health impacts. Metals that are regulated in groundwater and drinking water by the U.S. Environmental Protection Agency (EPA) have been correlated to the ICP/MS metal analysis data. Those contaminants that have desorbed from the Bunker Hill 4000 soil that are of EPA regulatory concern are Pb, Zn, Cd, and Mn. These contaminants, which desorb in detectable amounts over the 2-week test duration and are of potential regulatory concern, will be the focus of this study.

Figure 1 represents the desorption of Pb, Zn, Mn, and Cd from the BH 4000 soil during a 2-week desorption period and illustrates that the maximum amount of metal desorption occurs within the first 24 hours of desorption.

By adding PO_4 to a solution containing one or metals, precipitation/formation of minerals containing the PO_4 and the metal(s) can be induced. By knowing the type and concentration of a particular metal and the mineral it will form when PO_4 is added, the precise amount of PO_4 to be added can be calculated. Using Pb as an example, stoichiometric amounts of PO_4 (from NC apatite), determined from the molar ratios of the precipitated minerals, can be added to induce the precipitation. In the case of Pb, molar ratios from minerals known as pyromorphytes will be used.

Chloropyromorphyte and hydroxypyromorphyte are the two most likely Pb-PO_4 minerals to form under the given conditions. These two minerals exhibit the fastest kinetic rate of formation (Nriagu 1974). Although the two minerals are different by chemical formula, both have the same Pb/PO_4 ratios. The following is the calculation for the molar ratio:

Given the chemical formula for pyromorphytes: $Pb_5(PO_4)_3$ (OH, Cl)
(Nriagu 1972, 1973)

The M.W. for Pb: 207.2 (5) = 1,036.
The M.W. for PO_4: 94.93 (3) = 284.79
Molar ratio of Pb: PO_4 = 3.64

Setting x equal to PO_4 gives the equation:

$$6.76 \times 10^{-6}\ M/x = 3.64$$

Solving for x will give the amount of PO_4 needed to drop out Pb:

x = total PO_4 needed to drop out Pb
= 1.86×10^{-6} M

Figure 1. Desorption of Lead, Zinc, Manganese, and Cadmium From the BH 4000 Soil During a Two-week Period.

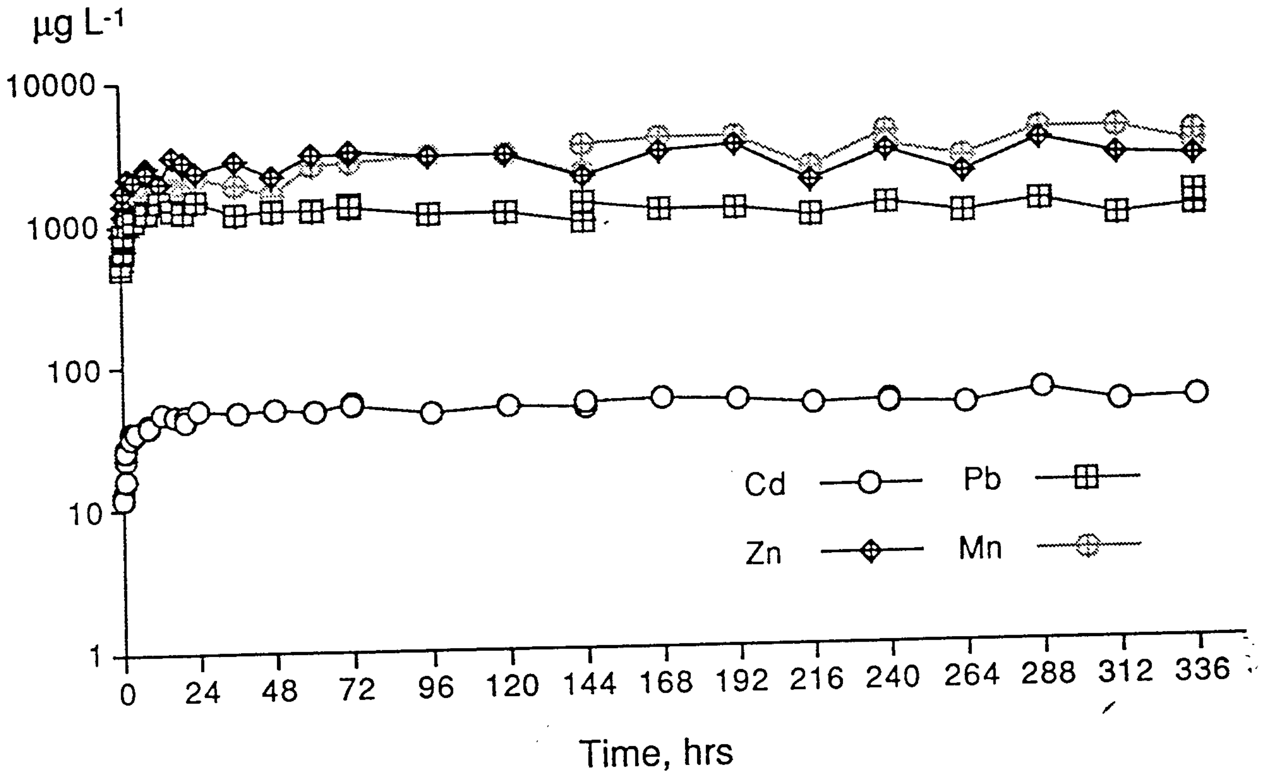


Table 1. Percent Metal Desorption in the BH 4000 Soil After 24 Hours.

Element	Total amount mg kg^{-1}	Amount Desorbed mg kg^{-1}	% Desorbed
Mn	1,031	37.6	3.65
Zn	1,087	30.8	2.83
Pb	4,170	14.4	0.35
Ba	808	4	0.5
Sr	120	1.96	1.63
Cd	17	0.52	3.06
Al	79,000	3.75	0.0047

$(1.86 \times 10^{-6})94.93$ /L = 1.78×10^{-4} g L^{-1}
which = 176μg/1000mL which

= 5.3 μg PO_4/30 mL
= .18 μg PO_4 mL^{-1}

To equate .18 μg PO_4 mL^{-1} to the amount of NC apatite added to cause precipitation, and assuming complete dissolution of the NC apatite, a .01% addition of NC apatite to the 3 g of BH 4000 soil gives:

.01% NC apatite = .0003 g NC apatite = .0001 g PO_4 = ((106).0001g)/30g H_2O=3.3 mg L^{-1}

From a proportional calculation, to obtain the concentration of .18 mg PO_4^- L^{-1} required for the formation of pyromorphytes, .0005% NC apatite must be added.

The resulting concentration of only 0.18 mg PO_4 L^{-1} required for the formation of a pyromorphyte is substantially less than a 1% addition of NC apatite to the 3 g of contaminated BH 4000 soil. There are many other metals in the BH 4000 supernatant that will complex with PO_4, which will reduce the overall concentration of PO_4 in solution. It is hypothesized that, if metal-PO_4 minerals are to form under these conditions, amounts of up to 1% added NC apatite should cause reductions in most or all of the desorbed metal concentrations.

The formation of pyromorphytes calculated from the molar ratios, shown as such by the reduction of desorbed Pb in the adsorption isotherms, is confirmed by the thermodynamic modeling discussed in the following sections. Confirmation of the pyromorphyte formation by this experimental system suggests that PO_4 from the addition of up to 1% NC apatite will also complex with Zn, Mn, and Cd to form stable minerals.

2.1 NC APATITE ADSORPTION ISOTHERM - 24 HOUR REACTION TIME

Using the molar ratio of the pyromorphyte mineral as a beginning concentration range, an adsorption isotherm was conducted to observe the adsorption characteristics of the NC apatite on the desorbed metals from the BH 4000 soil. The nature of the curve, especially the departure from linearity and/or asymptotic characteristics, will determine the NC apatite concentration that induces precipitation of the desorbed metals.

2.1.1 Experimental

Adsorption isotherm tests (Beckwith 1964), using the NC apatite, were performed on the Bunker Hill 4000 soil. For a 24-hour NC apatite adsorption study, 3 g of the BH 4000 were combined with 1%, 5%, 10%, and 20% NC apatite. The NC apatite was ground to pass through a 170-mesh screen and weighed to 3 decimal places. Then, 30 mL of deionized water were added to the mixture in 40-mL polycarbonate centrifuge tubes. The polycarbonate tubes containing the 3 g of BH 4000 soil, incremental percentages of NC apatite, and 30 mL of deionized water were shaken continuously for 24 hours. At the end of 24 hours, the samples were taken from the shaker and centrifuged. The supernatant was filtered at 0.2μ, then analyzed for pH, metals, and anions as described in the elemental analysis section of this report. The data for this analysis are presented in Table 2.

2.1.2 Results

The induced precipitation of desorbed metals by the amendment of NC apatite was evident for many of the analyzed metals. Only the precipitation of metals that desorbed above their regulatory limit will be presented and discussed in this report. Those metals are Pb, Zn, Mn, and Cd, with desorption curves shown in Figure 1.

2.1.2.1 Pb Precipitation. Figure 2 represents the reduction of desorbed Pb with the addition of 1%, 5%, 10%, and 20% NC apatite. At 0% NC apatite, the desorbed amount of Pb in the 24-hour period (control sample) is 1,600 $\mu g\ L^{-1}$. The greatest reduction in Pb occurs with 1% addition of NC apatite, which is a 90% reduction of the desorbed Pb to 154 $\mu g\ L^{-1}$. Increasing the NC apatite concentration to 5%, 10%, and 20% show no significant decrease in the desorbed Pb. Therefore, the precipitation of Pb by the addition of NC apatite occurs at 1% or less.

2.1.2.2 Zn Precipitation. Figure 3 represents the reduction of desorbed Zn with the addition of 1%, 5%, 10%, and 20% NC apatite. At 0% NC apatite, the desorbed amount of Zn in the 24-hour period (control sample) is 2,760 $\mu g\ L^{-1}$. The greatest reduction in Zn occurs with 1% addition of NC apatite, which is an 81% reduction of the desorbed Zn to 536 $\mu g\ L^{-1}$. Increasing the NC apatite concentration to 5% decreases the desorbed Zn amount by 13%. Additions of 10% and 20% show no significant decrease in the desorbed Zn. Therefore, the major precipitation of Zn by the addition of NC apatite occurs at 1% or less.

Figure 2. The Reduction of Desorbed lead by NC Apatite Depicted by 24- and 48-hour Adsorption Isotherms.

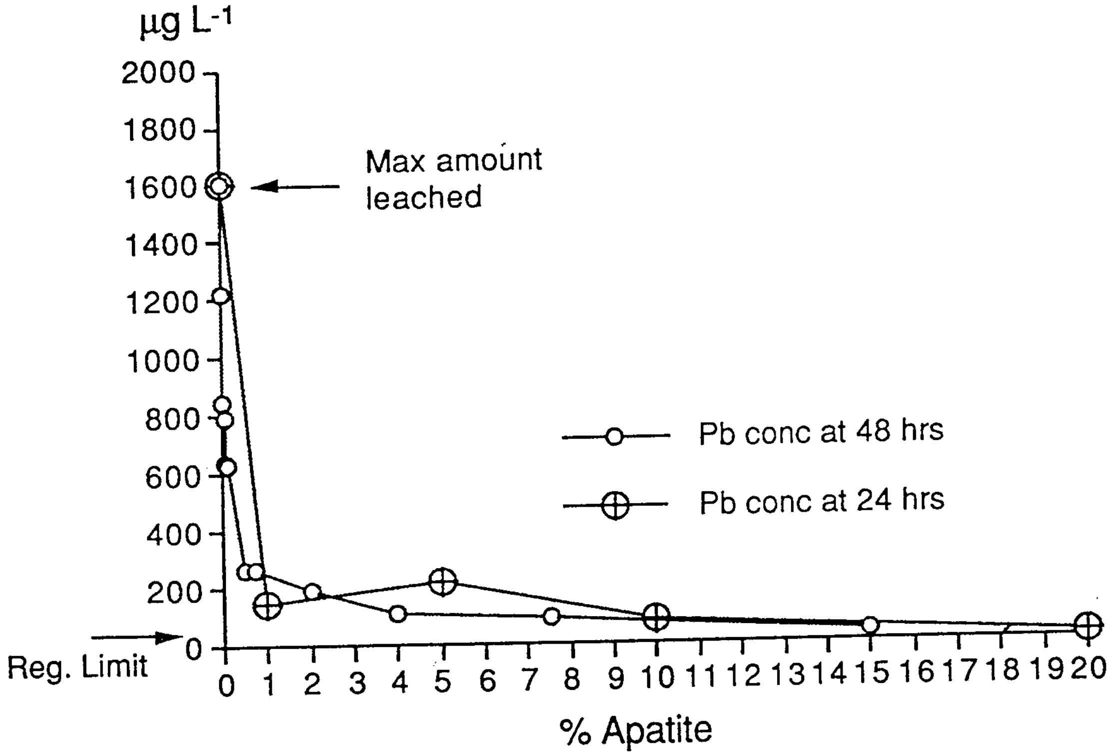


Figure 3. The Reduction of Desorbed Zinc by NC Apatite Depicted by 24- and 48-hour Adsorption Isotherms.

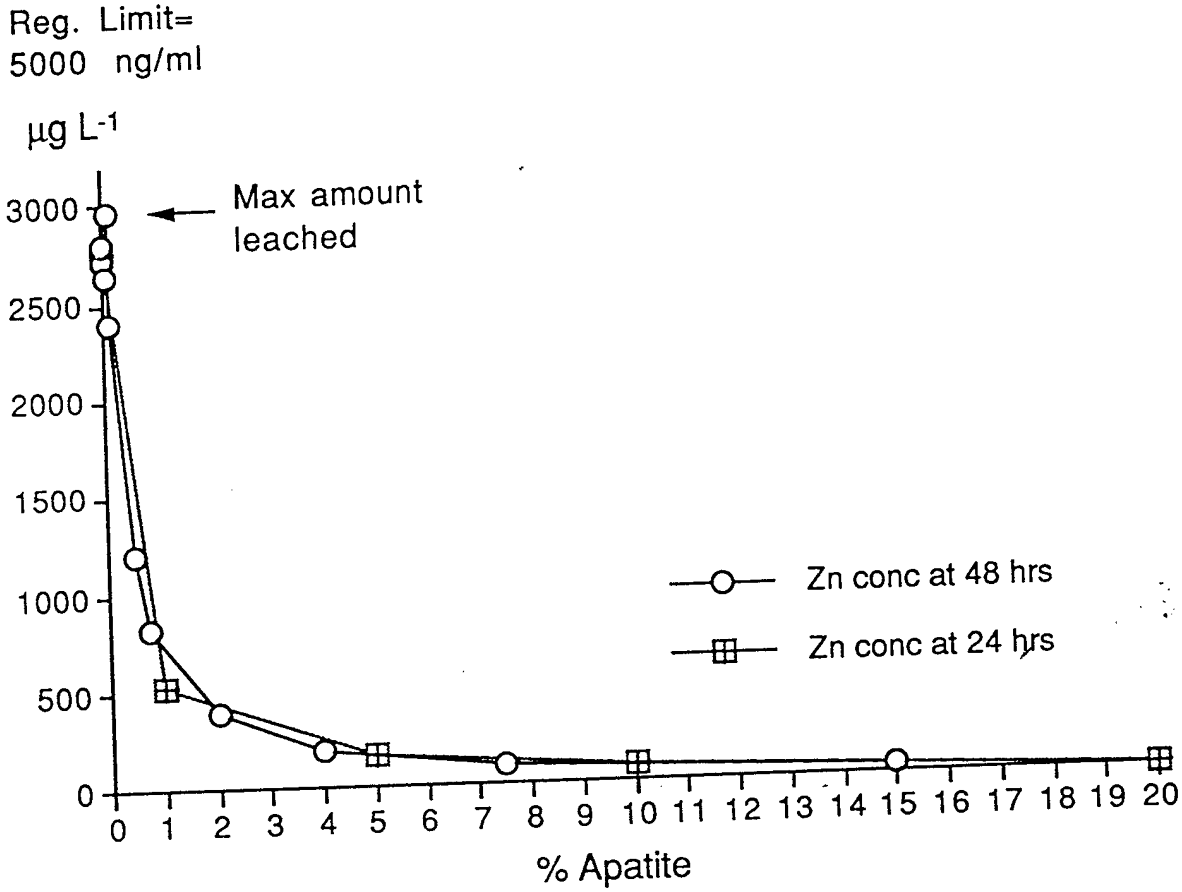


Table 2. Metal Analysis for the 24 Hour NC Apatite Adsorption Isotherm for the BH 4000 Soil ($\mu g\ L^{-1}$).

% NC apatite	Pb	Sr	Ba	Al	Fe	Cd	Zn	Mn
0	1,600	179	486	68	38	53.6	2,760	1,740
1	154	157	152	124	41	8.98	536	875
5	220	303	151	304	185	4.3	165	598
10	86	435	130	123	1	2.1	86.1	490
20	23.3	674	137	25	1	1.7	10	359

2.1.2.3 Mn Precipitation. Figure 4 represents the reduction of desorbed Mn with the addition of 1%, 5%, 10%, and 20% NC apatite. At 0% NC apatite, the desorbed amount of Mn in the 24-hour period (control sample) is 1,740 $\mu g\ L^{-1}$. The greatest reduction in Mn occurs with 1% addition of NC apatite, although not as great a reduction as Pb and Zn. The reduction at 1% addition of NC apatite is 50%, with a Mn concentration of 536 $\mu g\ L^{-1}$. Increasing the NC apatite concentration to 5% decreases the desorbed Mn amount by 16%. Additions of 10% and 20% reduce the desorbed Mn by 6% and 8%, respectively. Therefore, the precipitation of Mn by the addition of NC apatite appears to be greatest at 1% addition of NC apatite, with slight decreases with each incremental addition of the NC apatite.

2.1.2.4 Cd Precipitation. Figure 5 represents the reduction of desorbed Cd with the addition of 1%, 5%, 10%, and 20% NC apatite. At 0% NC apatite, the desorbed amount of Cd in the 24-hour period (control sample) is 54 $\mu g\ L^{-1}$. The greatest reduction in Cd occurs with 1% addition of NC apatite, which is an 83% reduction of the desorbed Cd to 9 $\mu g\ L^{-1}$. Increasing the NC apatite concentration to 5% decreases the desorbed Cd amount by 8.7%. Additions of 10 and 20% show no significant decrease in the desorbed Cd. Therefore, the major percentage of precipitation of Cd by the addition of NC apatite occurs at 1% or less.

2.2 NC APATITE ADSORPTION ISOTHERM - 48-HOUR REACTION TIME

To examine the effect of increasing the contact time between the desorbed metals and the NC apatite, a 48-hour adsorption isotherm was executed. The difference between the 48- and 24-hour adsorption isotherms is the increase in the NC apatite concentration increments.

Figure 4. The Reduction of Desorbed Manganese by NC Apatite Depicted by 24- and 48-hour Adsorption Isotherms.

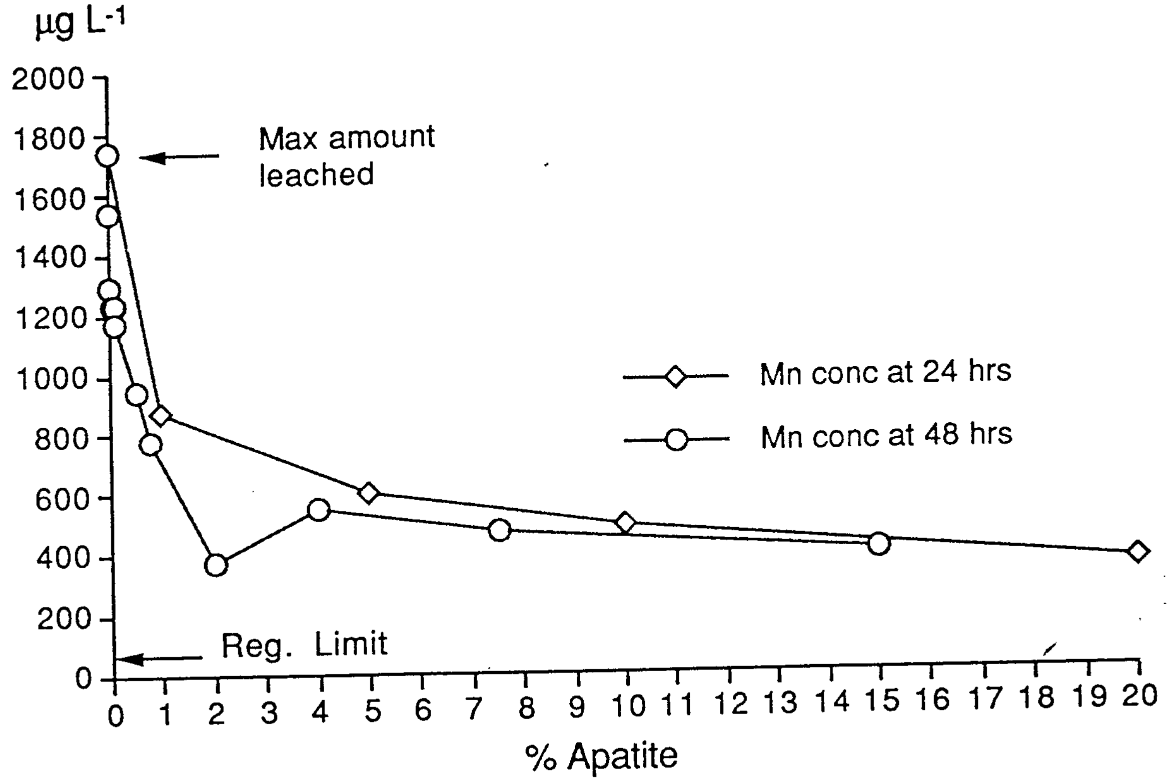
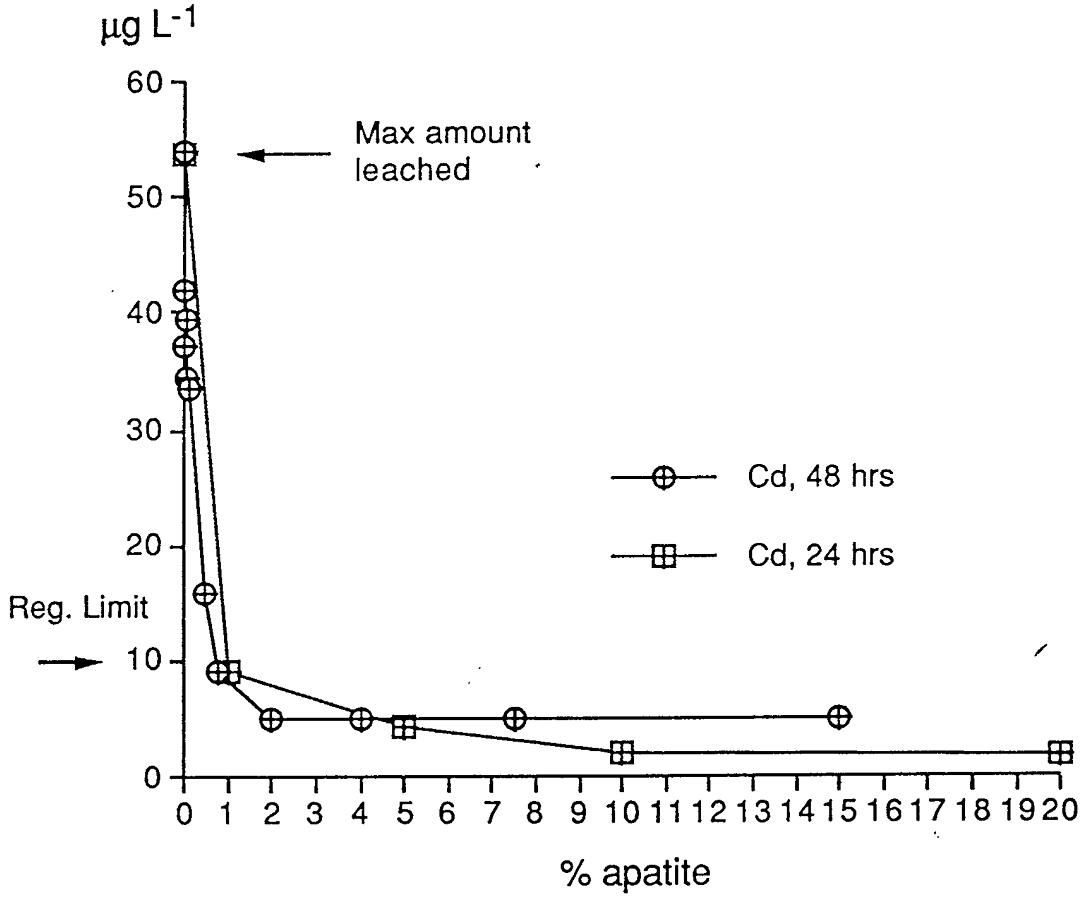


Figure 5. The Reduction of Desorbed Cadmium by NC Apatite Depicted by 24- and 48-hour Adsorption Isotherms.



2.2.1 Experimental

The same NC apatite adsorption isotherm tests were performed on the BH 4000 soil as with the 24-hour isotherm tests; 3 g of the BH 4000 were combined with the percentages of NC apatite listed in Table 3. The NC apatite was ground to pass through a 170-mesh screen and weighed to 3 decimal places. Then, 30 mL of deionized water were added to the mixtures in 40-mL polycarbonate centrifuge tubes. The polycarbonate tubes containing the 3 g of BH 4000 soil, incremental percentages of NC apatite, and 30 mL of DI H_2O were shaken continuously for 48 hours. At the end of 48 hours, the samples were taken from the shaker and centrifuged. The supernatant was filtered at 0.2μ, then analyzed for pH, metals, and anions as described in the elemental analysis section of this report. The data for this analysis are presented in Table 4.

2.2.2 Results

2.2.2.1 Pb Precipitation. Figure 2 represents the reduction of desorbed Pb with the addition of 0.005% through 15% NC apatite, with the precise increments listed in Table 2. At 0% NC apatite, the desorbed amount of Pb in the 48-hour period (control sample) is 1,600 μg L^{-1}. As with the 24-hour isotherm, the greatest reduction in Pb occurs at less than 1% addition of NC apatite, which is an 83% reduction of the desorbed Pb to 266 μg L^{-1}. Increasing the NC apatite concentrations shows no significant decrease in the desorbed Pb. All additions less than 1% reduce the amount of desorbed Pb. The .005% addition of NC apatite reduces the desorbed Pb by 24%, corroborating the molar ratio amount of NC apatite needed to form a pyromorphyte. As also shown by the 24-hour adsorption isotherm, the major percentage of precipitation of Pb by the addition of NC apatite occurs at 1% or less.

2.2.2.2 Zn Precipitation. Figure 3 represents the reduction of desorbed Zn with the addition of 0.005% through 15% NC apatite, with the precise increments listed in Table 2. At 0% NC apatite, the desorbed amount of Zn in the 48-hour period (control sample) is 2,760 μg L^{-1}. As with the 24-hour isotherm, the greatest reduction in Zn occurs at less than 1% addition of NC apatite, which is a 70% reduction of the desorbed Zn to 824 μg L^{-1}. As shown from the adsorption isotherm, increasing the NC apatite concentrations almost parallels the 24-hour adsorption isotherm, strongly suggesting that increasing the contact time to 48 hours does not increase precipitation. As also shown by the 24-hour adsorption isotherm, the major percentage of precipitation of Zn by the addition of NC apatite occurs at 1% or less.

2.2.2.3 Mn Precipitation. Figure 4 represents the reduction of desorbed Mn with the addition of 0.005% through 15% NC apatite, with the precise increments listed in Table 2. At 0% NC apatite, the desorbed amount of Mn in the 48-hour period (control sample) is 1,740 μg L^{-1}. As with the 24-hour isotherm, the greatest reduction in Mn occurs at less than 1% addition of NC apatite, which is a 55% reduction of the desorbed Mn to 776 μg L^{-1}. As in the 24-hour isotherm, the addition of NC apatite is not as great a reduction as Pb and Zn. Increasing the NC apatite concentration decreases the desorbed Mn amount more than in the 24-hour isotherm. The precipitation of Mn by the addition of NC apatite appears to be greatest at less than 1% addition of NC apatite, with a further 12% decrease at 2% added apatite.

Table 3. Percentages of NC Apatite Added to the BH 4000 Soil for 48-hour Adsorption Isotherm.

0	0.005	0.02	0.08	0.1	0.5	0.75	2	4	7.5	15

Table 4. Metal Analysis for the 48-hour NC Apatite Adsorption Isotherm for the BH 4000 Soil ($\mu g\ L^{-1}$).

%NC apatite	pH	Zn	Pb	Ba	Cd	Mn	Al
15	7.5	44.2	36.5	159	5	402	23
7.5	7	100	92.9	163	5	467	88
4	6.5	201	115	148	5	551	112
2	6.4	401	192	146	5	376	216
0.75	5.1	824	266	154	9.1	776	253
0.5	6.3	1,210	270	171	15.9	939	110
0.1	6.3	2,400	635	204	33.6	1,170	92.3
0.08	6.2	2,970	641	345	34.4	1,230	66.7
0.05	5.9	2,640	798	346	39.5	1,230	50.7
0.02	4.95	2,805	846	370	42	1,290	57
0.005	6.8	2,720	1,220	304	37.1	1,540	55
0	5.5	2,760	1,600	486	54	1,740	68

2.2.2.4 Cd Precipitation. Figure 5 represents the reduction of desorbed Cd with the addition of 0.005% through 15% NC apatite, with the precise increments listed in Table 2. At 0% NC apatite, the desorbed amount of Cd in the 48-hour period (control sample) is 54 $\mu g\ L^{-1}$. As with the 24-hour isotherm, the greatest reduction in Cd occurs at less than 1% addition of NC apatite, which is an 83% reduction of the desorbed Cd to 9.1 $\mu g\ L^{-1}$. Increasing the NC apatite concentration to 2% decreases the desorbed Cd amount by 7.6%. Increasing the concentration of apatite past 2% does not reduce the concentration of desorbed Cd. As shown from the adsorption isotherm, the 48-hour isotherm parallels the 24-hour adsorption isotherm, strongly suggesting that increasing the contact time to 48 hours does not increase precipitation. It is suggested that the greatest precipitation of Cd by the addition of NC apatite occurs at 1% or less.

2.2.3 PRECIPITATION OF DESORBED METALS AS DEPICTED IN THE 24- AND 48-HOUR ADSORPTION ISOTHERMS

It can be seen from both the 24- and 48-hour NC apatite adsorption isotherms that very little NC apatite is required to reduce the desorbed concentrations of Pb, Zn, Mn, and Cd from the BH 4000 soil to within or below regulatory limits. In all cases, the greatest reduction in the desorbed metals occurs at 1% or less added apatite. In all cases, the percentage NC apatite increments less than 1% indicate strong and dramatic reductions of Pb, Zn, Mn, and Cd, verifying that NC apatite is causing reduction of the desorbed metals at less than 1%.

Increasing the adsorption isotherm time to 48 hours does not increase the overall effectiveness of NC apatite, except for a slight decrease in the Mn 48-hour adsorption isotherm. Because the increase in contact time to 48 hours does not increase the precipitation for Pb, Zn, and Cd from the 24-hour experiment, it is suggested that the adsorption or formation kinetics of the apatite-metal system for these metals is less than 24 hours. This corroborates the work of other researchers in metal-PO_4 complexation (Ma et al.1993; Ruby et al. 1994; Xu and Schwartz 1994).

2.3 VERIFICATION OF PRECIPITATED METALS USING MINTEQ-A2

In order to gain knowledge about the nature of metal-phosphate complexation and to determine how much PO_4 is needed to complex the desorbed metals of the BH 4000 soil, MINTEQ-A2, a geochemical thermodynamic speciation computer program was used.

The natural soil system has both a solid phase and a solution phase. When chemical equilibrium is assumed to exist between the soil solution and the associated solid phases of the soil, important information about solid phase formations by using thermodynamic calculations performed in geochemical thermodynamic speciation programs can be elicited. MINTEQ-A2 is used to examine the precipitation of selected metals (i.e., Pb, Zn, Mn, and Cd) induced by the application of a specific phosphate compound.

Saturation indices for the BH 4000 soil determined from MINTEQ-A2 indicate whether Pb, Zn, Mn, and Cd-phosphate minerals are present. The saturation index is defined as the Ion Activity Product/Solubility Product, and is a thermodynamic indication of mineral dissolution or formation. Values less than 0 indicate that the mineral is undersaturated with respect to the equilibrium concentration and should not precipitate; while values greater than 0 indicate saturation with respect to the equilibrium concentration, indicating that precipitation is likely to occur. The higher the number, the greater the probability of precipitation.

2.3.1 Experimental

Input data for the execution of the computer program were acquired from a complete metal and ligand analysis of saturation extracts (Page et al. 1982). The computer program used was MacMINTEQ-A2, acquired from Geochem Software, 1994. Metal concentrations on the extract were obtained by inductively coupled plasma analysis and anions by IC analysis (PNL-AL0-211.2 and PNL-ALO-212).

2.3.2 Results

The MINTEQ-A2 program has the ability to configure "what if" scenarios, based on thermodynamic principles. Data produced from the analysis of the BH 4000 saturation extract were input to the program. Included in the data input was the analysis of the metal and ligand concentration, pH, electrical conductivity, redox conditions, and carbonate content. The input data exhibited a charge balance difference of 11%, which is within acceptable limits for program operation (Geochem Software 1994).

The initial input data for the operation of MINTEQ-A2, derived from the analysis of the saturation extract are presented in Table 5. The "what if" scenario to be analyzed using MINTEQ-A2, from a thermodynamic standpoint, is the effect of increasing amounts of NC apatite added to the BH 4000 soil. The incremental amounts of NC apatite are the same as in the previously described adsorption isotherms; the experimental system is being modeled thermodynamically. By varying the amount of NC apatite PO_4 on the solute composition, solubility products are calculated for possible precipitation reactions of PO_4 with those metals present in the analyzed saturation extract. Each incremental amount of PO_4 added requires a separate execution of the MINTEQ-A2 program. With each program run, the output lists the possible combinations of metal-PO_4 solid phases. The saturation index, described previously, is listed in the output for each of the target metal-PO_4 minerals. As a result, each incremental amount of PO_4 added as NC apatite alters the solute composition favorably or unfavorably with respect to the formation of solid phases. The incremental amounts of PO_4 added as NC apatite and the resulting calculated saturation indexes are listed in Table 6.

Table 5. Metal and Ligand Analysis of the BH 40000 Soil Saturation Extract.

Metal analysis (μg L^{-1})													
Na	Mg	Al	K	Ca	Mn	Fe	Ni	Cu	Zn	Sr	Cd	Ba	Pb
14,350	9,530	79	19,550	95,250	6,760	197	26	48	8,390	556	162	302	581

Anion analysis (μg mL^{-1})					
F	Cl	NO_2	NO_3	SO_4	PO_4
2.49	35.9	0.8	0.3	271	0

pH = 5.6
Electrical conductivity = .984 dS/M
$CO_3^=$ = 3 μg mL^{-1}

Table 6. Saturation Indexes Relative to NC Apatite Concentrations for the Formations of Lead, Cadmium, Zinc and Manganese-Phosphate Minerals.

% NC apatite	PO_4,mg L^{-1}	Sat. index $Pb(PO_4)_2$	Sat. index $PbHPO_4$	Sat. index $PbAL_3(PO_4)_2(OH)_5H_2O$
0	0	-6.206	-4.076	-10.505
0.02	9.4	1.74	-0.102	-2.559
0.05	23.5	4.065	0.661	1.762
0.07	32.9	4.727	0.893	2.925
0.1	47	5.754	1.209	4.953
0.5	235	7.154	1.91	6.349
1	470	7.759	2.213	6.949
% NC apatite	PO_4mg L^{-1}	Sat. index $Pb_5(PO_4)_3Cl$	Sat. index $Pb_5(PO_4)_3OH$	Sat. index Mn HPO_4
0	0	2.347	-10.646	-0.807
0.02	9.4	14.267	1.273	3.166
0.05	23.5	17.751	5.158	3.933
0.07	32.9	18.744	6.251	4.166
0.1	47	20.283	7.989	4.487
0.5	235	22.382	10.089	5.189
1	470	23.288	10.994	5.492
% NC apatite	PO_4, mg L^{-1}	Sat. index $Zn_3(PO_4)4H_2O$	Sat. index $Cd_3(PO_4)_2$	Sat. index $Mn_3(PO_4)_2$
0	0	-13.359	-18.771	-21.574
0.02	9.4	-5.412	-10.825	-13.628
0.05	23.5	-3.079	-8.492	-11.294
0.07	32.9	-2.413	-7.825	-10.627
0.1	47	-1.372	-6.784	-9.585
0.5	235	0.03	-5.382	-8.183
1	470	0.636	-4.776	-7.576

Figure 6 shows the graphic representation of saturation indexes of Pb-PO_4 minerals relative to increasing amounts of PO_4 from NC apatite, and Figure 7 shows the graphic representation of saturation indexes of Zn, Mn, and Cd phosphate minerals relative to increasing amounts of PO_4 from NC apatite.

2.3.2.1 Pb-Phosphate Predictions. The Pb-PO_4 minerals depicted in Figure 6 are all common minerals known to form under the given conditions. The chloro- and hydroxypyromorphytes, with the chemical formula $Pb_5(PO_4)_3(OH, Cl)$, are indicated as having the most positive saturation indexes, and are therefore most likely to form. This is substantiated by X-ray diffraction results on the BH 4000 soils after treatment with apatite and by other researchers (Nriagu 1974; Ma et al. 1993; Ruby et al. 1994). Plumbogummite ($PbAl_3(PO_4)_2(OH)_5 H_2O$) is also indicated as a possible precipitated mineral, as are two unnamed complexes, $Pb(PO_4)$ and $PbHPO_4$. For all of the Pb-PO_4 minerals presented in the MINTEQ-A2 output, the thermodynamic predictions occur at less than 0.1% addition of NC apatite. This thermodynamic prediction agrees with the previously calculated NC apatite amount from the Pb/PO_4 molar ratios of pyromorphytes and the adsorption isotherm data presented in Figure 2.

2.3.2.2 Mn-Phosphate Predictions. Figure 7 shows the graphic representation of saturation indexes of Zn, Mn, and Cd phosphate minerals relative to increasing amounts of PO_4 from NC apatite. Rhodochrosite ($MnHPO_4$) shows the highest degree of supersaturation. Based on the solubility reported for $MnHPO_4$, this mineral is very stable in soils. The $MnHPO_4$ mineral is more stable than strengite ($FePO_4$ $2H_2O$), an important competing phase, at most pH and redox conditions of soils (Lindsay 1979). The saturation index for strengite at .02% NC apatite is 2.910 and 3.166 for Rhodochrosite. The higher saturation index indicates a more likely formation for $MnHPO_4$ and suggests that the prediction is credible. As depicted in Figure 7, supersaturation with respect to $MnHPO_4$ formation exists at concentrations of less than 0.1% NC apatite. This thermodynamic prediction agrees with the NC apatite amounts shown to reduce desorbed Mn concentration in the adsorption isotherm data presented in Figure 4.

2.3.2.3 Zn-Phosphate Predictions. The mineral hopeite ($Zn_3(PO_4)_2$ $4H_2O$) is reported to have a very low solubility, with a Log K° of -35.3 (Nriagu 1973). This would indicate extreme stability in the soil environment. As can be noted from the thermodynamic prediction of MINTEQ-A2, the incremental additions of NC apatite raise the saturation index to 0 at 0.5% NC apatite. This condition is favorable for the formation of ($Zn_3(PO_4)_2$ $4H_2O$) but not as positive as Mn or Pb, discussed previously. However, the adsorption isotherm presented in Figure 3 shows a drastic reduction of Zn at less than 1% addition of NC apatite, which would indicate a highly supersaturated condition with respect to the formation of ($Zn_3(PO_4)_2$ $4H_2O$). This discrepancy is best explained by the different solubilities for this mineral presented in the literature by various researchers. The values range from Log K° of -35.3 (Nriagu 1973) to Log K° of 3.80 (Lindsay 1979).

Observing the upward trend toward supersaturation at less than 0.1% NC apatite, the thermodynamic prediction partially agrees with the NC apatite amounts shown to reduce desorbed Zn concentration in the adsorption isotherm data presented in Figure 3.

Figure 6. Saturation Indexes Relative to Increasing Amounts of NC Apatite for the Formation of Lead-Phosphate Minerals.

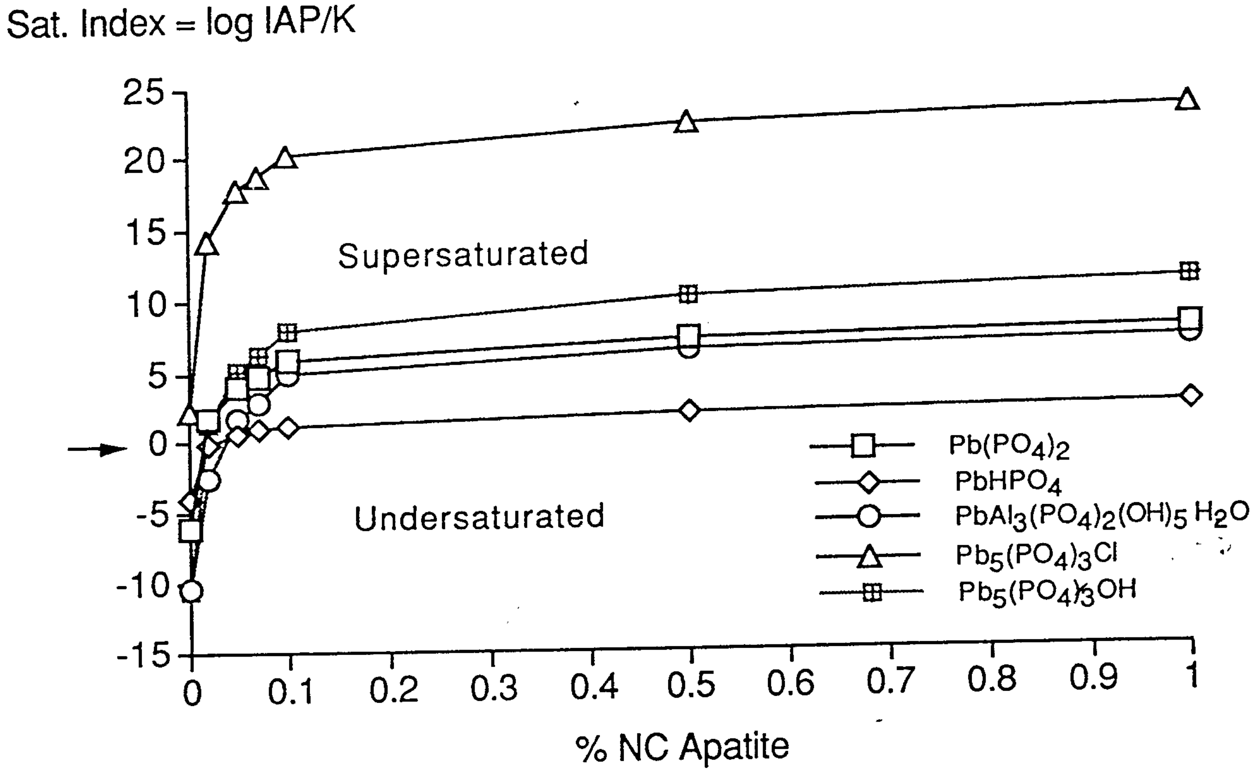
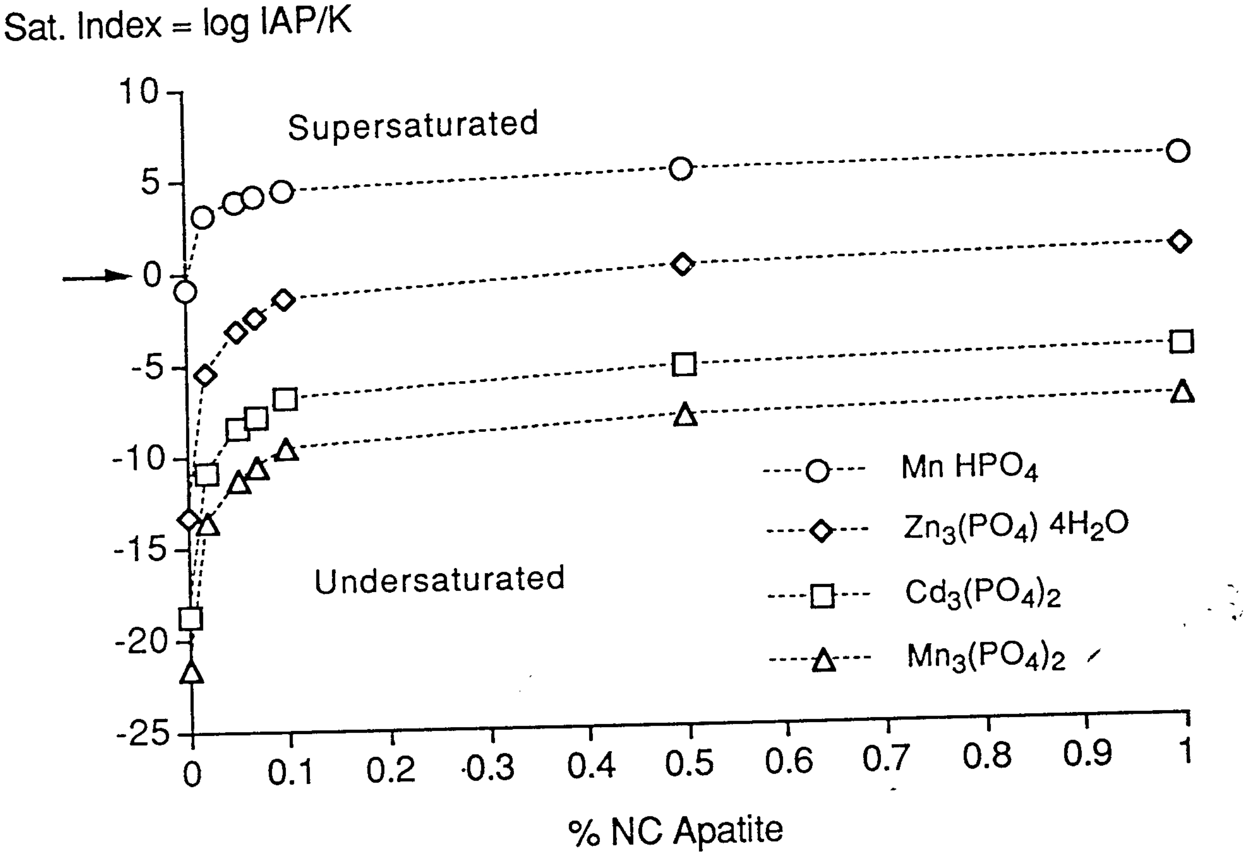


Figure 7. Saturation Indexes Relative to Increasing Amounts of NC Apatite for the Formation of Manganese, Zinc, and Cadmium-Phosphate Minerals.



2.3.2.4 Cd-Phosphate Predictions. As indicated in Figure 7, the formation $Cd_3(PO_4)_2$ is not predicted to occur. The saturation indexes at all increments of less than 1% NC apatite are less than 0, indicating undersaturation with respect to the mineral. This is in contradiction to the adsorption isotherm presented in Figure 5, which depicts an 83% reduction of desorbed Cd at less than 1% addition of NC apatite. As with Zn, this discrepancy is best explained by the different solubilities for $Cd_3(PO_4)_2$ presented in the literature by various researchers. The values range from Log K° of -32.61 (NBS) to Log K° of 1.0 (Lindsay 1979).

3.0 CONCLUSIONS

The 24- and 48-hour NC apatite adsorption isotherms and the modeled thermodynamic system result in the following conclusions.

- During the 24-hour adsorption isotherm, the greatest reduction of desorbed Pb, Zn, Mn, and Cd by the addition of NC apatite is at 1% or less.
- During the 48-hour adsorption isotherm, the greatest reduction of desorbed Pb, Zn, Mn, and Cd by the addition of NC apatite is at 1% or less and is depicted by the NC apatite concentrations of .005%, .002%, and .08%.
- The greatest reduction of desorbed Pb at less than 1% added NC apatite confirms the molar ratio calculation scenario of $Pb:PO_4$ for pyromorphytes.
- The kinetics of formation for Pb, Zn, and Cd phosphate complexes are 24 hours or less.
- Thermodynamic predictions for the formations of pyromorphytes at less than 1% addition of NC apatite confirm the molar ratio calculation scenario of $Pb:PO_4^-$ for pyromorphytes and also confirm the precipitation of Pb at less than 1% NC apatite in the adsorption isotherms.
- Thermodynamic predictions for the formation of rhodochrosite ($MnHPO_4$) at less than 1% addition of NC apatite confirm the precipitation of Mn at less than 1% NC apatite in the 24- and 48-hour adsorption isotherms.
- Thermodynamic predictions for the formation of Hopeite ($Zn_3(PO_4)_2\ 4H_2O$) at less than 1% addition of NC apatite confirm the precipitation of Zn at less than 1% NC apatite in the 24- and 48-hour adsorption isotherms.
- The thermodynamic prediction for the formation of $Cd_3(PO_4)_2$ is not substantiated by MINTEQ-A2. However, the adsorption isotherm shows an 83% reduction of desorbed Cd at less than 1% addition of NC apatite.

4.0 REFERENCES

Beckwith, R. S., 1964, "Sorbed Phosphate at Standard Supernatant Concentration as an Estimate of the Phosphate Needs of Soils," *Aust. J. Exp. Agr. and An Hus.* 5:52-58.

Davis, A., M. V. Ruby, and P. D. Bergstrom, 1992, "Bioavailability of Arsenic and Lead in Soils from the Butte, Montana, Mining District," *Environmental Science and Technology*, 26:461-468.

Geochem Software, Inc., 1994, *Mac MINTEQ-A2: Aqueous Geochemistry for the Macintosh*, Published by Geochem Software, Inc., Reston, Virgina.

Lindsay, W. L., 1979, *Chemical Equilibria in Soils*, John Wiley & Sons, New York, New York.

Ma, Q. Y., S. J. Traina, and T. J. Logan, 1993, "In Situ Lead Immobilization by Apatite," *Environ. Sci. Technol.*, 27:1803-1810.

Misra, D. N. and R. L. Bowen, 1981, *Adsorption from Aqueous Solutions*, P. H. Tewari (ed.), Plenum, New York.

Moody, T. E., J. V. Wright, E. Wyse, X. Chen, and J. Leather, 1994, "Sorption/Desorption Geochemistry of Apatite and Phosphate Minerals in Metal-Contaminated Soils," *American Geophysical Union Annual Meeting Abstracts* (in press).

NBS (National Bureau of Standards), Wagman et al. (1968, 1969, 1971), and Parker et al. (1971).

Nriagu, J. O., 1974, "Lead Orthophosphates, IV, Formation and Stability in the Environment," *Geochim. Cosmochim. Acta*, 38:887-898.

Nriagu, J. O., 1972, "Lead Orthophosphates, I, Solubility and Hydrolysis of Secondary Lead Orthophosphate," *Inorg. Chem.*, 11(10):2499-2503.

Nriagu, J. O., 1973, "Solubility Equilibrium Constant of Hopeite," *Geochim. Cosmochim. Acta*, 37:2357-2361.

Nriagu, J. O., 1973, Lead Orthophosphates, II, Stability of Chloropyromorphite at 25°C," *Geochim. Cosmochim. Acta*, 37:367-377.

Page, A. L. et al., 1982, "Methods of Soil Analysis," *Agronomy 9*, Part 2, p. 167-179.

PNL-ALO-211.2, *Determination of Elements by Inductively Coupled Argon Plasma Atomic Emissions Spectrometry* (Rev. 0, 1993).

PNL-ALO-212.1, *Determination of Inorganic Anions by Ion Chromatography* (Rev. 1, 1994).

Ruby, M. V., A. Davis, J. H. Kempton, J. W. Drexler, and P. D. Bergstrom, 1992, "Lead Bioavailability: Dissolution Kinetics Under Simulated Gastric Conditions," *Environmental Science and Technology*, 26:461-468.

Ruby, M. V., A. Davis, and A. Nicholson, 1994, "In Situ Formation of Lead Phosphates in Soils as a Method to Immobilize Lead," *Environ. Sci. Technol.*, 28:646-654.

Wright, J. V., H. Schrader, and W. T. Holser, 1978, "Paleoredox Variations in Ancient Oceans Recorded by Rare Earth Elements in Fossil Apatite," *Geochim. Cosmochim. Acta*, 51:631-644.

Wright, J. V., 1990, "Conodont Apatite: Structure and Geochemistry," *Biomineralization: Patterns, Process and Evolutionary Trends*, Joseph Carter (ed.), Van Nostrand Reinhold, New York, 445-459.

Xu, Y. and F. W. Schwartz, 1994, "Lead Immobilization by Hydroxyapatite in Aqueous Solutions," *J. Contaminant Hydrology*, 15:187-206.