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This document focuses on the utility of North Carolina apatite and the ability of this mineral to immobilize lead in situ. The stabilization of lead will prevent transport of the lead in the vadose zone, which could subsequently lead to groundwater contamination. The stabilization of surface lead by the application of North Carolina apatite will also reduce the risk of airborne dust particulates containing lead.

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CONTENTS

1.0 OBJECTIVE

This document focuses on the utility of North Carolina apatite and the ability of this mineral to immobilize lead in situ. The stabilization of lead will prevent transport of the lead in the vadose zone, which could subsequently lead to groundwater contamination. The stabilization of surface lead by the application of North Carolina apatite will also reduce the risk of airborne dust particulates containing lead.

2.0 BACKGROUND

Phosphate materials have been proven by various researchers as chemical compounds that can passively complex lead in solution to form lead-phosphate minerals (pyromorphytes) that are stable and insoluble under normal soil conditions (Nriagu 1974; Lindsay 1979; Ma et al. 1993; Ruby et al. 1994). The reactive phosphate compounds responsible for causing the precipitation of metals into insoluble minerals are constituents in geologic or synthetic compounds. These are 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. Their primary constituents are the calcium and phosphate ions, with a molar ratio similar to HA. 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. For the objective of this concept paper, a North Carolina apatite, with the general formula $Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}$, will be used to demonstrate the lead immobilization utility. The North Carolina apatite is supplied from the Texasgulf Mining Company of North Carolina. Because of the carbonate component of this apatite, the North Carolina apatite is one of the most reactive apatites (Chien et al. 1980). For this reason, it is mined extensively for use as a fertilizer for crop production.

3.0 APPLICATION UTILITY

The utility of North Carolina apatite as a waste minimization, waste encapsulation, and soil treatment technology is demonstrated via the following scenario.

1. Add 5% North Carolina apatite to spent decontamination water. This will precipitate the lead and extraneous heavy metals. This scenario will serve as a waste minimization technology allowing the water to be recycled for further decontamination use. The small amount of precipitated metals can then be shipped to a repository or facility for containment.

2. Use a 5% apatite solution in place of the water to control the lead dust while excavating. Because of the short time period required for the formation of lead phosphate (less than 24 hours), the airborne lead complexed with the PO_4 will exhibit less risk for human

ingestion. Pyromorphyte (lead phosphate) minerals synthesized by scientists at PTI Environmental Services, Colorado, were modeled emulating the environment of the human stomach. Their results indicate that pyromorphytes have limited solubility at pH values of 1.5-2 and 4-6, representative of the human stomach during fasting and fed conditions (Ruby et al. 1992).

3. Before excavation of the lead source, apply 5% apatite slurry injected (if below surface) or rototilled into the known areas where the lead contamination might be. Stabilization of soluble lead will reduce the risk to workers and the environment by reducing airborne dust and immobilizing soil lead, thus preventing transport through the vadose zone to the groundwater.

4. Before placement of the lead contamination in a repository, construct an apatite barrier beneath the lead source. This will prevent transport through the vadose zone to the groundwater. Before the lead source is placed in the repository, the source could be encapsulated in an apatite grout, thereby ensuring long-term containment.

5. The application of North Carolina apatite to stabilize and immobilize vadose zone and aquifer lead contamination can be accomplished by the following techniques:

   a) Direct well injection of a 5 to 10% solution of North Carolina apatite

   b) Step-wise vertical injection of North Carolina apatite slurry into aquifer up through the vadose zone using cone penetrometer or similar device

   c) Vadose zone in situ mixing of North Carolina apatite slurry to construct a permeable barrier to depths of 100 ft, using large-diameter augers (3 to 5 ft). The augers are designed with pressurized injection jets (200 lb/in^2) to facilitate the in-place mixing.

3.1 ESTIMATED COST

The cost of the North Carolina apatite as shipped from North Carolina is $85/ton, with an approximate $100/ton freight charge. However, considering that effective concentrations for soil lead remediation would be in the 1% to 5% range (Moody et al. 1994), the raw cost of materials would be $9.25/ton of soil for a 5% addition of North Carolina apatite. At the Wisconsin lead battery and lead arsenate remediation sites, the total cost of remediation for surface application of phosphate was *$50/ton* (Stanforth and Chowdhury 1994). Treatment of 100 gal of decon water (contaminated with lead) at 5% apatite addition would be $3.85.

3.2 CURRENT PO_4 REMEDIATION SUCCESS

- ^{85}Sr co-precipitation: In bench-scale column tests using 15 g soil, Kim, Lee, and Ammons (1990) successfully precipitated 95% of leachable ^{85}Sr using aluminum-phosphates.

- **Plutonium removal from Plutonium Finishing Plant (PFP) wastewaters using bone char (calcium phosphate):** In bench-scale adsorption tests, Barney, Lueck, and Green (1992) found that plutonium removal from low-level wastewater effluents at the Hanford Site was faster and more complete using a bone char (calcium phosphate) adsorbent than for other commercially available adsorbents tested. Those absorbents tested were resin anion exchangers activated aluminia, resin cation exchangers, and chelating adsorbents.

- **B-5 Reverse Well pump-and-treat technology:** Because of the previous bench-scale success in removing plutonium from PFP wastewaters, bone char is being used in conjunction with ion exchange resins as the treatment technology for the removal of plutonium and strontium in the current B-5 Reverse Well pump-and-treat groundwater remediation project. This treatment technology is described in greater detail in *Pilot-Scale Treatability Test Plan for the 200-BP-5 Operable Unit* (DOE-RL 1994).

- **Stabilized lead from used battery and lead arsenate sites using phosphate fertilizer:** Using ordinary calcium phosphate fertilizer, Stanforth and Chowdhury (1994) successfully treated farm orchard soil contaminated by lead arsenate and a highway waste site contaminated with lead from spent car batteries. The initial surface concentrations of lead were 48,000 ppm at the orchard site and 1,000 ppm at the battery site. Concentrations of 10% calcium phosphate rototilled into the surface of both sites rendered the sites compliant with toxic characteristic leach procedure.

- **Current Hanford work on phosphate immobilization of heavy metals:** This work is being executed by a team consisting of scientists at Bechtel Hanford, Inc., Pacific Northwest Laboratory, and Washington State University. Soils from the Bunker Hill, Idaho, mining area contaminated with 4,000 ppm lead were subjected to increasing amounts of North Carolina apatite adsorption. The results indicate that 95% of the soluble lead was precipitated in less than 24 hours with the addition of only 1% of the North Carolina apatite (Moody et al. 1994). The formation of stable, insoluble pyromorphyte minerals was confirmed by utilizing a computer chemical speciation program. This computer program utilizes thermodynamic principles of the system in question to predict the formation of the minerals.

3.3 BENEFITS

- **Apatite is a natural occurring phosphate mineral, no synthetics:** The North Carolina apatite is currently being mined from repositories in North Carolina for agricultural use. There is currently an infinite supply.

- **Technology transfer from agriculture:** Chemical characterization of the mineral, soil reactions, transportation, mode of surface application, slurry, and liquid formulations currently exist from agricultural usage.

- **Stability pH 2-10 (extremes of soil environments):** The formation of the lead phosphate mineral is extremely stable and insoluble under extreme soil pH conditions. The following represents the solubility of the mineral relative to common minerals such as quartz and table salt:

$Pb_5(PO_4)_3(OH,Cl)$ pyromorphytes	$\log K_{sp} = -76.5 \Rightarrow -84.4$
Salt (NaCl)	$\log K_{sp} = 0.0$
Quartz	$\log K_{sp} = -4.0$

- **Easy implementation:** Because of the easy formulation, flowability and non-caustic nature of the apatite, the following applications are easily implemented:

  -- surface application
  -- horizontal drilling
  -- soil auguring
  -- slurry walls/barrier configuration

- **Immediate results:** The reaction kinetics are short in duration, with formation of insoluble lead-phosphate minerals within 24 hours of application (Moody et al. 1994; Nriagu 1974; Ma et al. 1993).

- **Cost effective ($50/ton surface application):** The cost of the North Carolina apatite as shipped from North Carolina is $85/ton, with an approximate $100/ton freight charge. However, considering that effective concentrations for soil remediation would be in the 1% to 5% range (Moody et al. 1994), the raw cost of materials would be $9.25/ton of soil for a 5% addition of North Carolina apatite. At the Wisconsin lead battery and lead arsenate remediation sites, the total cost of remediation for surface application of phosphate was $50/ton (Stanforth and Chowdhury 1994). Treatment of 100 gal of water contaminated with lead at 5% apatite addition would be $3.85.

- **No secondary or tertiary wastes (apatite maintains neutral pH):** Because the Ca/PO_4 molar ratio is 2 to 1, the excess calcium acts as a buffer to maintain a neutral pH. The pH buffering ensures that other metals soluble at the pH extremes will not dissolve during treatment, adding further to metal contamination.

- **No reduction of hydraulic conductivity:** Similar in function and purpose to in situ grouting, this process has the advantages of treating soils in place, immobilizing the lead into apatite grains without cementing the soil into a solidified mass.

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