In Situ Remediation of Arsenic in Contaminated Soils

Todd A. Martin
Michael V. Ruby

In situ chemical fixation represents a promising and potentially cost-effective treatment alternative for metal-contaminated soils. This article presents the findings of the use of iron-bearing soil amendments to reduce the leachability and bioaccessibility of arsenic in soils impacted by stack fallout from a zinc smelter. The focus of this investigation was to reduce the lead bioaccessibility of the soils through addition with phosphorus-bearing amendments. However, as phosphorus addition was expected to increase arsenic mobility, the fixation strategy also incorporated use of iron-bearing amendments to offset or reverse these effects. The findings of this investigation demonstrated that inclusion of iron-bearing chemicals in the amendment formulation reduced arsenic leachability and bioaccessibility without compromising amendment effectiveness for reducing lead bioaccessibility. These results suggest that in situ chemical fixation has the potential to be an effective strategy for treatment of the impacted soils. © 2003 Wiley Periodicals, Inc.

INTRODUCTION

Owing to its toxic nature and relative abundance, arsenic is a common contaminant of concern in environmental cleanup. Arsenic is identified as a constituent of concern at 728 National Priorities List (NPL) sites as of fiscal year 1998, and arsenic in soil is specifically identified at 32 percent of these sites (Fiedler, 2001). Exposure to arsenic has been linked to a variety of cancers, cardiovascular disease, diabetes, and anemia, as well as having reproductive, developmental, immunological, and neurological effects (U.S. Environmental Protection Agency [US EPA], 2003). In October 2001, the U.S. Environmental Protection Agency (US EPA) revised the arsenic standard for drinking water from 50 µg/L to 10 µg/L (effective as of 2006)—sparking substantial research into cost-effective methods to reduce arsenic concentrations in drinking water and increasing attention to remediation of arsenic in both water and soil systems.

Soil cleanup levels are often established not only based on direct exposure risks to human and ecological receptors, but also on the potential for the contaminant to be leached from the soil matrix and transported to groundwater and surfacewater resources. As a result, the revised arsenic drinking water standard will result in more stringent cleanup levels for arsenic in soils, to be protective of these resources.

Traditionally, remediation of arsenic-contaminated soils is achieved by excavation and ex situ treatment (most typically solidification/stabilization) and/or disposal. However, the high cost of such practices has fueled the development of in situ alternatives for remediation of contaminated soils that are less disruptive and, often, less costly than conventional treatment. Available treatment technologies for in situ remediation of
arsenic contaminated soils include phytoremediation, solidification/stabilization, fixation, vitrification, soil flushing, and electrokinetic remediation (US EPA, 2002).

In this article, we discuss the application of in situ chemical fixation of arsenic-contaminated soils through amendment with iron-based chemicals. The article summarizes several research investigations available in the literature that have evaluated the application of this technology for treatment of arsenic in soils, and then presents findings from a series of studies in which phosphate- and iron-bearing amendments were evaluated for the fixation of lead and arsenic in soils impacted by stack fallout from a zinc smelter.

**THEORY**

In situ fixation strategies involve the addition of chemical amendments to the soil matrix to “fix” by inducing a targeted chemical reaction or process that renders the contaminant immobile and/or nonbioavailable (in this situation, bioavailability refers to the fractional uptake of arsenic in soil into human or ecological receptors). These strategies are similar to in situ solidification/stabilization technologies, which typically involve the use of binding reagents to both induce chemical reactions to immobilize contaminants and enmesh the contaminants within a solidified bulk matrix. Solidification/stabilization treatment can substantially alter the soil properties, such as increasing the soil volume, reducing the soil permeability, and increasing soil pH. In situ fixation, on the other hand, involves the use of specific chemical amendments to induce chemical reactions that provide for long-term immobilization of the contaminant without substantially altering the soil properties. Such strategies have the potential to be cost-effective alternatives for remediation of soils and are the subject of considerable research—particularly the use of phosphate amendments for the treatment of lead in soils (Berti & Cunningham, 1997; Ruby et al., 1994; Ryan & Berti, 2001).

Iron oxide minerals, most commonly in the form of ferrihydrite (FeOOH), are the dominant sorbents of metals in the environment and can substantially influence the tendency for metals to migrate with flowing water (Stumm, 1992). Ferrihydrite has a large surface area (~600 m²/g), a strong affinity for arsenic and other dissolved metals, and fast metal adsorption kinetics (Dzombak & Morel, 1990; Klaus et al., 1998). These features are well-understood and have long been exploited for the treatment of arsenic in water systems (Pontius, 1990), are frequently used as a chemical additive in ex situ solidification/stabilization of arsenic-bearing wastes (US EPA, 2002), and are increasingly being developed and applied as an in situ strategy for treatment of arsenic in groundwater systems (Martin & Kempton, 2000).

In situ chemical fixation of arsenic-contaminated soils with iron involves application of iron to the soil matrix to supply ferrihydrite and bind arsenic through adsorption and co-precipitation reactions. In doing so, the mobility and bioavailability of arsenic in the soil matrix is reduced—thereby reducing the overall risk posed by the soils. Iron may be injected to the soil system as a solution (e.g., iron sulfate or iron chloride salts) or mixed directly into the soil matrix (e.g., through tilling) in solid form. Several solid forms of iron may potentially be effective for arsenic fixation, including direct addition of ferrihydrite or use of an iron-rich byproduct from an industrial process. Steel shot and zerovalent iron fillings may also be effective, and offer the potential to supply a long-term source of ferrihydrite as these materials corrode.
Ferrihydrite is only sparingly soluble under oxidizing conditions, but is readily reduced to soluble ferrous iron under reducing conditions. As a result, the in situ fixation application discussed in this article is most applicable to oxidized soil systems (e.g., most surficial soils) in which ferrihydrite is stable. Under these conditions, arsenic is predominantly found in its pentavalent state as the anion arsenate (HAsO₄²⁻). As arsenate is strongly adsorbed by ferrihydrite at soil pH levels below 9–10 s.u. (Stumm, 1992), treatment by in situ fixation should be feasible over the typical range of soil pH conditions.

Phosphate and silicate ions are known to compete for available adsorption sites on the ferrihydrite surface. Jain and Loeppert (2000) found that the presence of phosphate can substantially inhibit arsenic adsorption to ferrihydrite. Su and Puls (2003) evaluated the removal of aqueous-phase arsenic by zerovalent iron and found that phosphate and silicate in the solution substantially inhibited arsenic adsorption. These findings suggest that consideration of the relative abundance and long-term supply of phosphate and silicate to the treated soils is an important consideration to the long-term effectiveness of in situ fixation of arsenic through iron amendment.

LITERATURE REVIEW

Various attempts to apply the technology described above are reported in the literature, with varying degrees of success. Vangronsveld et al. (1994) evaluated the effectiveness of various iron-based amendments to reduce the uptake of arsenic by garden vegetables. Bench-scale tests demonstrated that steel shot and ferrihydrite were far more effective than crystalline iron oxide (Fe₂O₃), aluminum oxide, Al-smectite, and lepidocrocite at reducing the water extractable fraction and plant uptake of arsenic from soils (Vangronsveld & Cunningham, 1998). The water extractable arsenic in the soils of 11.75 mg/kg was reduced by 83 and 95 percent following amendment of the soils with 1 weight (wt) percent steel shots or ferrihydrite, respectively.

Based on the findings of the bench tests, the researchers expanded the testing to evaluate the effects of steel shot amendments on uptake of arsenic from soils by garden vegetables in both greenhouse and field tests (Vangronsveld et al., 1994). The researchers found that amendment of the soils with steel shot induced a substantial reduction in the uptake of arsenic by several garden vegetables. In the greenhouse studies, the researchers found that soil amendment with 1 wt percent steel shot reduced uptake of arsenic by radishes and lettuce by an average of 53 percent and 80 percent, respectively. Further, in field tests, the researchers found that arsenic uptake was substantially reduced in radishes (69 percent reduction), lettuce (76 percent reduction), carrots (75 percent reduction), and potatoes (74 percent reduction).

Artiola et al. (1990) evaluated the use of iron amendments for the stabilization of heavy metal–contaminated soil from an inactive pesticide-manufacturing site. Soils collected from this site contained up to 113,300 mg/kg of arsenic. The authors amended samples of the contaminated soils with iron oxide (Fe₂O₃), ferrous sulfate, gypsum, and ferrous carbonate amendments in laboratory bench-scale tests and subjected the amended soils to a series of wet-dry cycles to simulate soil weathering. The treated soils were then subjected to water extractability testing and EP Toxicity testing (US EPA, 1986)—a test designed to simulate leaching of contaminants from a landfill—to assess the effectiveness of each of the amendments. The authors found that the addition of ferrous sulfate at an
amendment rate of 37 wt percent substantially reduced arsenic mobility in the soils—
decreasing the water and EP leachable fractions by 95 percent or greater.

The Electric Power Research Institute and Southern Company evaluated in situ
chemical fixation through the addition of ferrous sulfate as a remediation alternative for
arsenic in soils (Redwine, 2001). Batch and column treatability testing indicated that
treatment by in situ chemical fixation reduced the mass of leachable arsenic by a factor
of 200 to 1,000. The author estimated costs for in situ fixation to be on the order of
$20–$40 per cubic yard of soil treated.

BENCH TESTING OF IN SITU FIXATION SMELTER-IMPACTED SOILS

The effectiveness of chemical amendments for in situ fixation of metals-impacted soils
from a zinc smelter site was evaluated in a series of bench-scale laboratory tests. The
primary focus of this testing was to evaluate the effectiveness of in situ fixation of lead
through the addition of phosphate-based amendments to produce insoluble and non-
bioavailable lead-apatite minerals in the treated soils. However, by displacing adsorbed
arsenic from the soil surface, the phosphate amendments were found to cause the release
of arsenic to soil water and thus increase the risk posed to underlying groundwater from
soil arsenic. As a result, the in situ fixation strategy for the soils was altered to consider
inclusion of iron-based amendments to offset these effects.

The laboratory tests included three phases of study and involved numerous test
procedures and soil samples. Two primary procedures were used to evaluate the effec-
tiveness of the test amendments. Metals’ leachability was evaluated through the use of
the US EPA’s Synthetic Precipitation Leaching Procedure (SPLP; US EPA, 1997). The
bioavailability of arsenic and lead was estimated by the physiologically based extrac-
tion test (PBET; Ruby et al., 1999). This in vitro extraction method is designed to
mimic the physiology and chemistry of the human gastrointestinal process, and to
establish the fraction of a metal that would be available for absorption into the body.
The percentage of metal released during this test is termed the bioaccessible fraction.

Soils from the smelter site are classified as Dystric Crychrepts and consist of sand,
glacifluvial deposits, or colluvium (Jones, 1997). Exhibit 1 summarizes the typical
properties of the soils used in these experiments.

<table>
<thead>
<tr>
<th>Property</th>
<th>500–1,500</th>
<th>20–100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>mg/kg</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Arsenic</td>
<td>20–100</td>
<td></td>
</tr>
<tr>
<td>Cation Exchange Capacity</td>
<td>5–20</td>
<td>meq/100g</td>
</tr>
<tr>
<td>pH</td>
<td>5–6</td>
<td>s.u.</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>1–2</td>
<td>wt%</td>
</tr>
<tr>
<td>SPLP Leachability</td>
<td>2.4</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Lead</td>
<td>Arsenic</td>
<td></td>
</tr>
<tr>
<td>SPLP Bioaccessibility</td>
<td>4.7</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Lead</td>
<td>58</td>
<td>%</td>
</tr>
<tr>
<td>Arsenic</td>
<td>91</td>
<td>%</td>
</tr>
</tbody>
</table>

**Exhibit 1.** Typical properties of the smelter-impacted soils
Phase I Investigation

The Phase I investigation involved both short- and long-term tests. The short-term tests were conducted to identify the most promising amendments in terms of reducing lead bioaccessibility without increasing the leachability and bioaccessibility of arsenic. The long-term tests evaluated the most promising amendments in soils while subjected to an extended period of wet-drying cycles to simulate soil-weathering processes.

The short-term tests involved four amendment formulations—each evaluated at various amendment rates in small batch tests. These formulations included:

- \( \text{Ca(H}_2\text{PO}_4\text{)}_2\ + \text{FeSO}_4\)
- \( \text{Ca(H}_2\text{PO}_4\text{)}_2\ + \text{ferrihydrite} \)
- \( \text{H}_3\text{PO}_4\ + \text{lime} \)
- \( \text{H}_3\text{PO}_4\ + \text{lime} + \text{ferrihydrite} \)
- Sodium silicate

The soil was amended at the selected amendment rate and 60 g of the amended soil was mixed with 250 mL of deionized water. The slurry was shaken for 1 hour, the solids allowed to settle, and the process repeated. The slurry was then dried for 2–3 days and the resultant solids subjected to SPLP and PBET testing.

The long-term amendment tests involved testing of four amendment formulations (wt percent): 0.66 percent \( \text{Ca(H}_2\text{PO}_4\text{)}_2\), 1.31 percent \( \text{Ca(H}_2\text{PO}_4\text{)}_2\), 1.31 percent \( \text{Ca(H}_2\text{PO}_4\text{)}_2\) + 0.5 percent \( \text{FeCl}_3\), and 1.63 percent \( \text{H}_3\text{PO}_4\) + 0.5 percent ferrihydrite + 5.2 percent \( \text{CaOH}/\text{CaCO}_3\). The amended soils were placed in humidity cells and subjected to a two-week wet/dry cycle to accelerate the reaction process. SPLP solution was added to the cells every two weeks to saturate the soils to field capacity. The process was continued for 33 weeks, and samples were collected from the cells periodically and subjected to SPLP and PBET testing.

Phase II Investigation

The Phase II tests were developed based on the findings of the earlier testing and were designed to optimize the amendment addition rates, minimize the release of arsenic from the amended soils, and evaluate the potential effectiveness of a cellulose-based byproduct from a nearby industrial process for fixation of metals in the soils. The Phase II investigation also included short- and long-term testing according to the same procedures used during the Phase I investigation. These tests evaluated amendment formulations consisting of ferrihydrite solely, the cellulose-based material with and without inclusion of phosphate and ferrihydrite, and various combinations of phosphate, ferrihydrite, and lime.

Phase III Investigation

The Phase III investigation involved short-term, bench-scale laboratory testing to compare the optimal amendments identified during the earlier investigation phases to a series of other amendments identified in the literature as being potentially effective for fixation of lead and/or arsenic in soils. Exhibit 2 summarizes the amendment formulations evaluated during the Phase III testing. The testing involved adding the appropriate mass of amendment to 100 g of soil and slurrying the amended soil in 175 mL of deionized water. Each slurry was agitated for one week before being dried and subjected to SPLP and PBET testing.
RESULTS

Phase I Investigation

The initial short-term tests from the Phase I investigation indicated that all phosphate-bearing amendments increased the bioaccessibility and leachability of arsenic; however, the magnitude of these effects was reduced by the inclusion of iron in the amendment formulation (results not shown). Sodium silicate was found to increase arsenic leachability, but decrease its bioaccessibility. Further, the soils amended with silicate formed a hard agglomerate similar to cement, limiting the potential usability of the treated soils.

The amendment formulations for the Phase I long-term tests were selected based on the results of the initial short-term tests. Exhibit 3 summarizes selected results of the Phase I long-term tests and includes the average ratios of arsenic SPLP-leachability and PBET-bioaccessibility in the amended soils to the unamended soils. The testing demonstrated that all four of the amendment formulations were shown to increase both the leachability and bioaccessibility of arsenic in the smelter soils. The degree of increase in arsenic leachability was minimized in the formulations containing iron. However, the level of increase in arsenic bioaccessibility did not appear to be substantially influenced by inclusion of iron in the amendment formulation.

Phase II Investigation

The Phase II short-term tests included evaluation of 24 amendment formulations consisting of five general composition classes: 1) phosphate [as Ca(H$_2$PO$_4$)$_2$ + ferrihydrite]; 2) phosphate [as H$_3$PO$_4$ + Ca(H$_2$PO$_4$)$_2$] + ferrihydrite; 3) ferrihydrite; 4) cellulose-based material; 5) phosphate [as H$_3$PO$_4$] + ferrihydrite + cellulose-based material.

Exhibit 4 presents the findings for arsenic for the optimal amendment formulations:

<table>
<thead>
<tr>
<th>Amendment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amendment 1</td>
<td>Activated alumina (5 wt% as Al) + Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
<tr>
<td>Amendment 2</td>
<td>EnviroBlend, Formula A (22.5% total wt)*</td>
</tr>
<tr>
<td>Amendment 3</td>
<td>EnviroBlend, Formula B (11% total wt)*</td>
</tr>
<tr>
<td>Amendment 4</td>
<td>Ferrihydrite (5 wt% as Fe) + Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
<tr>
<td>Amendment 5</td>
<td>Iron fillings (5 wt% as Fe) + Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
<tr>
<td>Amendment 6</td>
<td>Iron rich (5 wt% as Fe)* + Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
<tr>
<td>Amendment 7</td>
<td>Manganese oxide (5 wt% as Mn) + Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
<tr>
<td>Amendment 8</td>
<td>Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
<tr>
<td>Amendment 9</td>
<td>Portland cement (3% total wt) + Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
<tr>
<td>Amendment 10</td>
<td>MBS (4.6% total wt)*</td>
</tr>
<tr>
<td>Amendment 11</td>
<td>Steel shot (5 wt% as Fe) + Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
<tr>
<td>Amendment 12</td>
<td>Zeolite (2.5% total wt) + Ca(H$_2$PO$_4$)$_2$ (0.5 wt% as P)</td>
</tr>
</tbody>
</table>

*Proprietary amendment developed by RMT, Inc.
*A byproduct from processing of TiO$_2$ pigment.
*CProprietary amendment developed by Solucorp.

Exhibit 2. Amendment formulations from the Phase III testing
Exhibit 3. Results of the Phase I long-term tests

Exhibit 4. Selected results of the Phase II short-term tests
from each of these five classes. The short-term tests confirmed that phosphate addition to the soils increased arsenic leachability and bioaccessibility, but that the addition of iron to the amendment formulations offset these effects. An iron addition rate of 2.5–5 wt percent (as Fe) was found to result in a net reduction in arsenic leachability and bioaccessibility. This rate of addition translated to approximately 0.5–1.7 moles of iron per mole of phosphorus in the amendment formulation.

The six optimal amendment formulations presented in Exhibit 4 were evaluated in the long-term tests to assess their performance under conditions designed to simulate accelerated soil weathering. Exhibit 5 presents the results for arsenic at the completion of the 33-week tests. All of the amendment formulations that included iron strongly decreased the mobility of arsenic in the treated soils—reducing the arsenic leachability in the soils by 75–80 percent. Similarly, arsenic bioaccessibility was substantially reduced in the soils treated with amendment formulations that included iron, with the greatest reduction (84 percent) occurring in the soil amended solely with ferrihydrite (at 5 wt percent).

The single amendment formulation that did not substantially reduce arsenic leachability consisted solely of the cellulose-based material and did not include iron. Although this amendment produced a reduction in arsenic leachability, this reduction was slight (18 percent) relative to that observed when the same cellulose-based amendment was augmented with 5 wt percent (as Fe) ferrihydrite and 0.5 wt percent \( \text{H}_2\text{PO}_4 \) (as P), which resulted in an 87 percent reduction in arsenic leachability. Further, the cellulose-based amendment resulted in a 13 percent increase in arsenic bioaccessibility when iron was not included in the formulation, compared to a 69 percent decrease when iron was included.

Based on the results of the Phase II investigation, it was determined that an amendment formulation consisting of 5 wt percent (as Fe) ferrihydrite and 0.5 wt percent \( \text{Ca(H}_2\text{PO}_4)_2 \) (as P) was optimal for treatment of the smelter-impacted soils. This formu-
lation produced the desired reduction in lead bioaccessibility in the soils and decreased the leachability and bioaccessibility of arsenic.

**Phase III Investigation**

The objective of the Phase III investigation was to compare the optimal amendment formulation identified from the earlier investigations against amendments using three different sources of iron (iron fillings, an iron waste product, and steel shot), three proprietary amendments, activated alumina, manganese oxide, portland cement, and zeolite. This testing demonstrated that several of the amendments had the potential to reduce lead bioaccessibility—the primary objective of the investigation—with a few of the amendment formulations outperforming the 5 wt percent (as Fe) ferrihydrite and 0.5 wt percent Ca(H2PO4)2 (as P) identified in the Phase II investigations as the optimal amendment. However, as was observed in the previous investigations, only those formulations that included iron resulted in a decrease in arsenic bioaccessibility. Exhibit 6 presents the ratio of arsenic bioaccessibility in the amended soils relative to the unamended soils. The amendment formulations 5 wt percent (as Fe) ferrihydrite + 0.5 wt percent Ca(H2PO4)2 (as P) and 5 wt percent (as Fe) iron fillings + 0.5 wt percent Ca(H2PO4)2 (as P) resulted in the greatest reductions in arsenic bioaccessibility.

The study also included an evaluation of arsenic SPLP-leachability. However, the results of this testing were ambiguous due to elevated analytical detection limits associated with the SPLP extracts. Arsenic concentrations were below the analytical detection limit of 1.7 mg/L in the SPLP extracts from all of the soils (including the unamended control samples), with the exception of the soils amended with iron fillings and zeolite. The arsenic concentrations in the SPLP extracts of these amended soil samples were 12.1 and 2.2 mg/L, respectively.

![Exhibit 6. Results of the Phase III tests](image-url)
CONCLUSIONS

In situ chemical fixation represents a promising and potentially cost-effective treatment alternative for metal-contaminated soils and may provide a remedy that is protective of human health and the environment. Fixation of arsenic in soils by amendment with iron-based chemicals relies on well-established principles for treatment of arsenic in aqueous and solid systems to bind arsenic as an adsorbed phase to ferrihydrite mineral surfaces. Several investigations have shown that this approach can be effective at substantially reducing the potential for arsenic to be leached from soils to infiltrating water.

This article presents the findings of an investigation in which in situ fixation was evaluated for treatment of a lead- and arsenic-bearing soil. The primary objective was to reduce the bioavailability of lead through the use of phosphate-based amendments to induce the formation of insoluble lead-apatite minerals. However, phosphate competes strongly with arsenic for sorption sites within the soil matrix, and it was found that amendment of the soils with phosphate resulted in increased arsenic bioaccessibility and leachability.

The increased arsenic leachability and bioaccessibility in response to the phosphate amendment were offset and even reversed by the inclusion of iron-based chemicals in the amendment formulation. For treatment of arsenic alone, amendment with 5 wt percent ferrihydrite was found to produce a five-fold decrease in both arsenic leachability and bioaccessibility. These findings indicate that in situ fixation of arsenic can be achieved by addition of iron amendments to contaminated soils and can reduce risks posed to human health (by reducing arsenic bioaccessibility) and the environment (by reducing arsenic leachability). These findings are consistent with those of other researchers and suggest that, under appropriate conditions, in situ fixation by iron amendment represents a promising remediation strategy for arsenic-contaminated soils.

REFERENCES


---

Todd A. Martin is a senior engineer at Integral Consulting, with eight years of experience specializing in environmental engineering, contaminant fate and transport, and remediation alternatives analysis.
Mr. Martin’s background encompasses engineering design and cost analysis, aqueous and soil geochemistry, hydrogeology, and microbiology. His work has focused on the development of cost-effective alternatives for site remediation that are protective of human health and the environment and consistent with long-term site management.

Michael V. Ruby is a principal with Exponent, with 17 years of experience in the fields of environmental chemistry and toxicology. Over the last 13 years, Mr. Ruby has specialized in the fate and transport of metals in the environment, and in research pertaining to human exposures to contaminants in soil.