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Ferrous Iron Treatment of Soils Contaminated with Arsenic-Containing Wood-Preserving Solution

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This article discusses the results of efforts to reclaim As-contaminated soil from a former timber-treating plant. The study site, commonly referred to as the Rocker Timber Framing site, is located along Silver Bow Creek approximately 7 miles west of the Butte Mining District, MT, USA. The plant operations resulted in contamination of the soils with a highly caustic solution containing 5% As (III). Contaminated soil resulted in the groundwater plumes that contained up to 25 mg L^{-1} As, with As (V) being the predominant species. The objective of this study was to evaluate the effectiveness of Fe (II) treatment for remediation of As-contaminated soils.

Laboratory-treatability studies were conducted on samples of saturated zone (AS1) and vadose zone (AV1) soils. The AS1 soil was a mixture of coarse alluvium and potentially some mill tailings from adjacent mining operations. The AV1 soil consisted primarily of fill, including soil, construction debris, and timber fragments. Initial concentrations of total As in AS1 and AV1 soils were 683 and 4814 µg kg^{-1}, respectively. Water-soluble As concentrations were 15.4 and 554 µg L^{-1}, respectively, in a 20:1 solution to soil extract. Batch equilibration were performed by placing 10 g of soil into 20 vessels and adding increasing amounts of $FeSO_4 \cdot 7H_2O$. Amendment increments were made as multiples of molar ratios of total As present in each soil. Treatability studies were run with and without a pH buffer of $CaCO_3$ (added at a 2:1 molar ratio to the $FeSO_4 \cdot 7H_2O$ treatment). Solution concentrations of As in the AS1 and AV1 soils (without $CaCO_3$) decreased from 554 to 15.4 µg L^{-1} and 3802 to 0.64 µg L^{-1}, respectively, as the Fe:As molar ratios increased from 0 to 2, whereas for the AS1 soil the solution As concentration increased at the Fe:As molar ratios >2 and reverse trend was observed for the AV1 soils. The decrease in As solution concentration for the AS1 soil is attributable to the dramatic decrease in soil pH with increasing Fe:As molar ratios.

In the case of soils treated with $CaCO_3$, the solution concentrations decreased from 564 to 0.65 µg L^{-1} and 3790 to 0.79 µg L^{-1} for the AS1 and AV1 soils, respectively,as the Fe:As molar ratios increased from 0 to 50. Generally, in both the soils, the $CaCO_3$-treated soil contained significantly more solution As compared with the non-$CaCO_3$-treated soil at the comparable Fe:As molar ratios. This is attributable to higher solution pH on $CaCO_3$ treatment.

Our rapid engineering study indicates that treating both the soils with Fe:As molar ratio of 2 lowered the As water quality limit to < 50 µg L^{-1}, whereas treating the AS1 and AV1 soils with Fe:As molar ratio of 2 and 3, respectively, lowered the As water quality limit to ≤15 µg L^{-1}. The concentrations of the Cu and Zn were below the instrument detection limits for the AS1 and AV1 soils without $CaCO_3$ treatment.

Sequential extraction of Fe-treated soils illustrated that As was relatively stable. Less than 1% of the As was extractable using a modified TCLP approach and <70% of the As was extractable using a harsh acid modified hydroxylamine hydrochloride extraction.

KEY WORDS: *$CaCO_3$, groundwater, metal mobilization, Remedial Investigation (RI), saturated zone, sequential extraction, TCLP, vadose zone.*

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INTRODUCTION

The Rocker Site

The Rocker timber-treating plant operated between 1909 and 1957 to produce structural support timbers for the underground mining industry in the area. The site is located along Silver Bow Creek, approximately 7 miles west of the Butte Mining District, Montana, USA. The plant fabricated and impregnated structural support timbers with a preservative solution. A highly caustic solution containing approximately 5% dissolved As was the primary preservative solution used, although creosote was used for a shorter time during early operations. The impregnating solution was prepared by dissolving As_2O_3 in a heated pH 13 solution of NaOH to achieve a 50% As solution. A diagram of the Rocker site is included in Figure 1. Losses of caustic As (III)-containing solution occurred primarily in the process area. The working solution contaminated vadose zone soils and subsequently resulted in groundwater contamination.

Groundwater gradients are primarily from the southeast to the northwest, resulting in a plume that contains As concentrations as high as 25 mg L^{-1}. The As contamination is restricted to the shallow alluvial aquifer (15 to 90 ft thick). Although this Quaternary alluvium is dominated by fine sands and gravels in the upper portion, sediments are generally coarser (some cobbles) with depth. Below the alluvial aquifer is a Tertiary deposit of alluvial materials that contains primarily weathered tuff, but also have lenses of sand, gravel, and lacustrian sediments.

The entire treatment process area of the Rocker site was constructed of mixed fill material placed between the railroad tracks to the south and Silver Bow Creek to the north (Figure 1). Fill materials consisted primarily of local soils, but also contained brick and construction debris, treated timbers and wood fragments, and coal cinders. The fill materials are generally from 4 to 12 ft thick (Figure 2). Fill materials rest on alluvium that might contain some mineralized tailings from the Bluebird Mill located a short distance up Silver Bow Creek. The water table occurs in the alluvium, approximately 2 ft below the fill/alluvium contact. The alluvium has some natural $CaCO_3$ and $MnCO_3$ minerals from the weathering of uplifted carbonate formations in the basin. The fill materials may not have been calcareous originally, but currently have some carbonate minerals in the treatment area because of being impacted by the caustic treatment solution.

In 1989, action was taken at the site to prevent exposure of humans to As-contaminated surface soils. A soil cap approximately 1 ft in thickness was installed and vegetated with wheatgrass and legumes. A Remedial Investigation (RI) was performed in 1995, and it was determined that, although the contaminant plume was at a steady state and isolated to a small portion of the shallow aquifer, future modifications to the hydrology such as installation of high-capacity wells for commercial purposes adjacent to the site could potentially result in off-site migration of contaminated waters. Pump tests of a new well drilled adjacent to the site

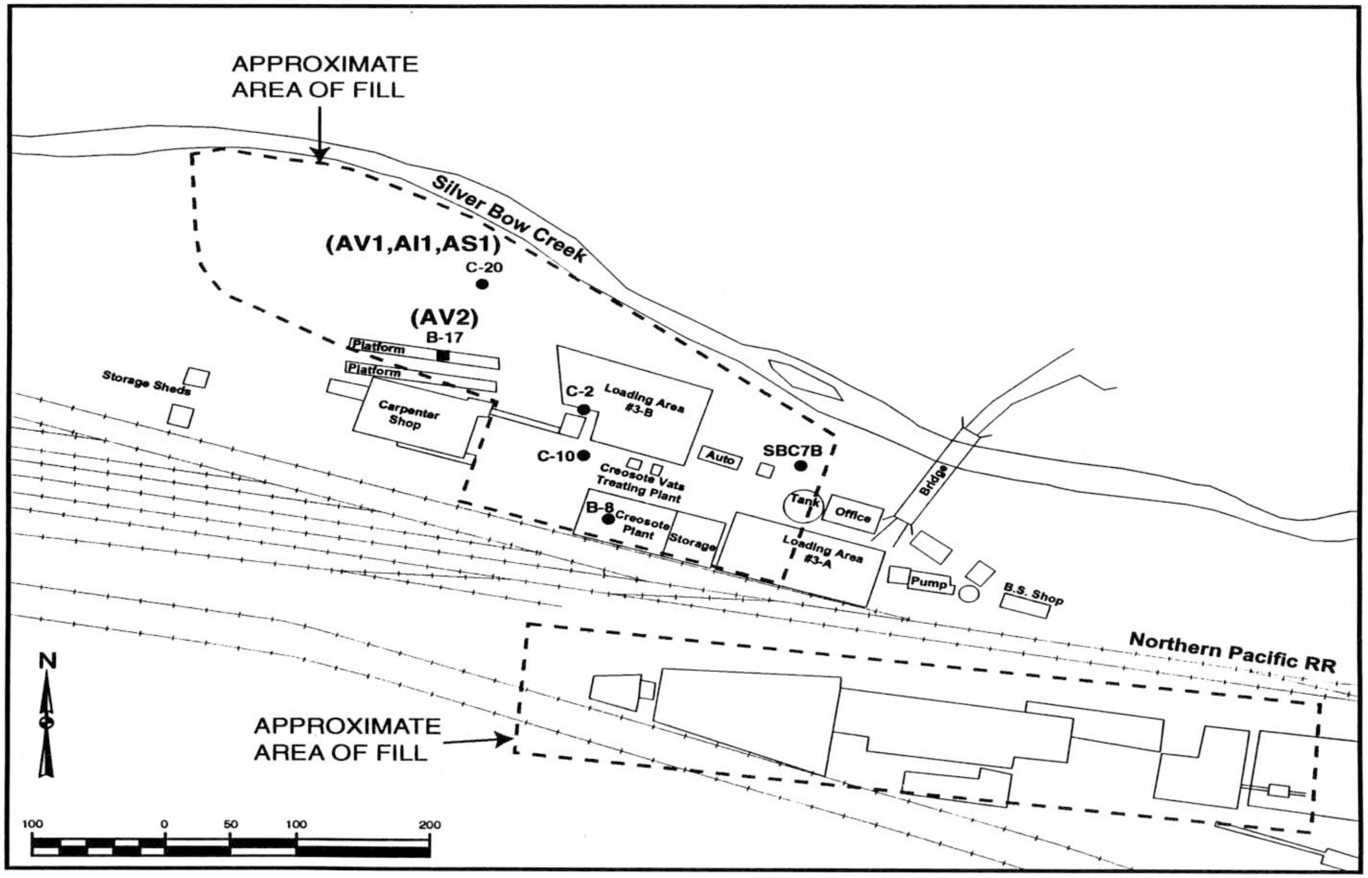

FIGURE 1

Plain view of Rocker, MT site.

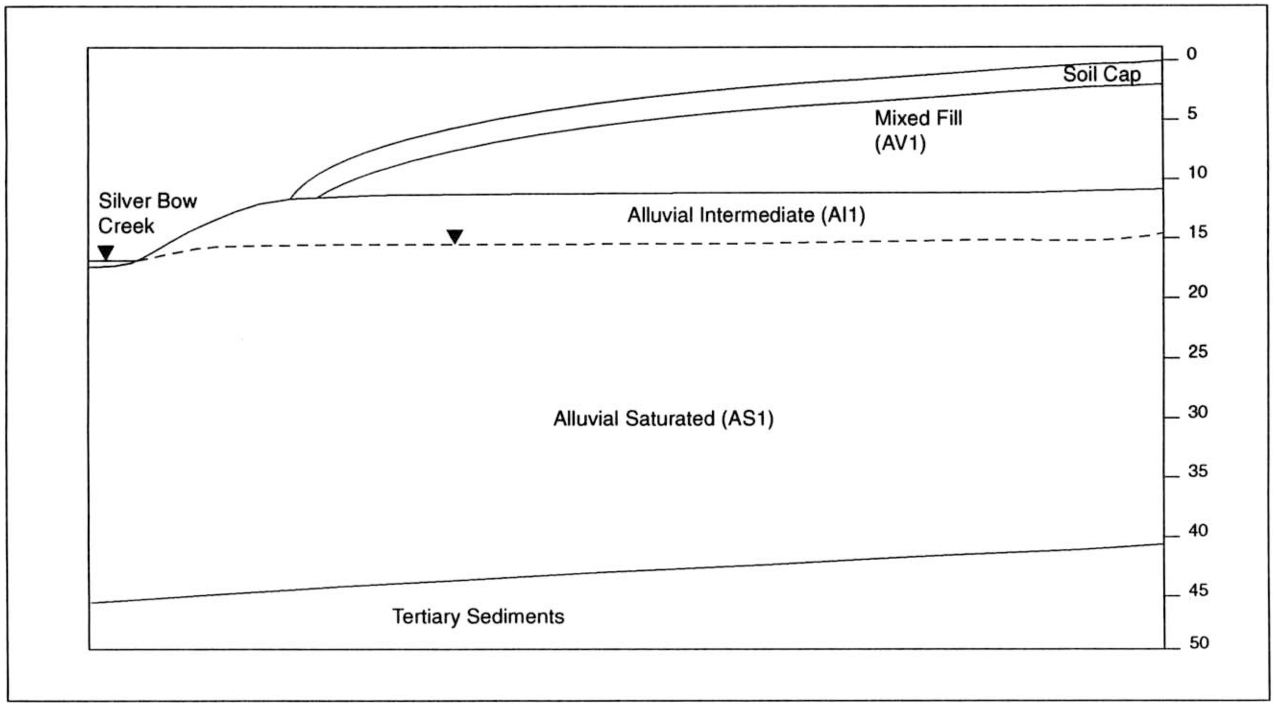

FIGURE 2.

Rocker shallow stratigraphy (typical).

and completed in the Tertiary sediments were interpreted to illustrate hydraulic connectivity with the shallow alluvial aquifer. The United States Environmental Protection Agency (USEPA) determined that the source of groundwater As should be attenuated or removed.

Alternatives to pump-and-treat groundwater remediation systems were immediately sought. Chemical stabilization of As has been studied extensively from a water treatment standpoint (Datta, 1989; Fox, 1989; Varsányi *et al.*, 1991; Jekel, 1994). Chemical stabilization of As in contaminated soils is less well documented. References to soil treatment were often anecdotal and did not provide information as to rates of application, achievable endpoints, and potential problems that the treatment might pose.

As Solution Chemistry

Speciation of As is dependent on the Eh and pH of the aqueous system (Peterson and Carpenter, 1983; Reimer and Thompson, 1988; Xu *et al.*, 1991; Bowell *et al.*, 1994). The dominant As (III) species are H_3AsO_3, $HAsO_3^{2-}$ and AsO_3^{3-}; and As (V) species are H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} (Korte and Fernando, 1991). The organic As compounds monomethylarsonic acid, dimethylarsinic acid, and trimethylarsinic acid can be produced biologically under reducing conditions (Johnson, 1972; Bowell, 1994). In the present system, the organic As species is not considered because we are dealing with a system that has minimal organic contents and microbial activity. The pK of the inorganic species are given in Eqs. 1 to 6 (Sadiq *et al.*, 1983):

$$H_3AsO_3 \rightleftharpoons H_2AsO_3^- + H^+ \qquad pK=9.22 \qquad [1]$$

$$H_2AsO_3^- \rightleftharpoons HAsO_3^{2-} + H^+ \qquad pK=12.13 \qquad [2]$$

$$HAsO_3^{2-} \rightleftharpoons AsO_3^{3-} + H^+ \qquad pK=13.4 \qquad [3]$$

$$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+ \qquad pK=2.22 \qquad [4]$$

$$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+ \qquad pK=6.97 \qquad [5]$$

$$HAsO_4^{2-} \rightleftharpoons AsO_4^{3--} + H^+ \qquad pK=11.53 \qquad [6]$$

The regions of thermodynamic stability of the inorganic As species are given in Figure 3. The dominant As (V) species at various pH values in an oxidized environment are as follows: $H_3AsO_4^0$ at pH <2.5; $H_2AsO_4^-$ in the pH range of 2.5 to <7, $HAsO_4^{2-}$ in the pH range of 7 to 11.5 and AsO_4^{3-} at pH >11.5. As (III) primarily exists as neutral $As(OH)_3^0$ species at pH <9.5. Therefore, As (III) is mobile under most soil conditions at pH < 7 and As (V) is retained by amphoteric

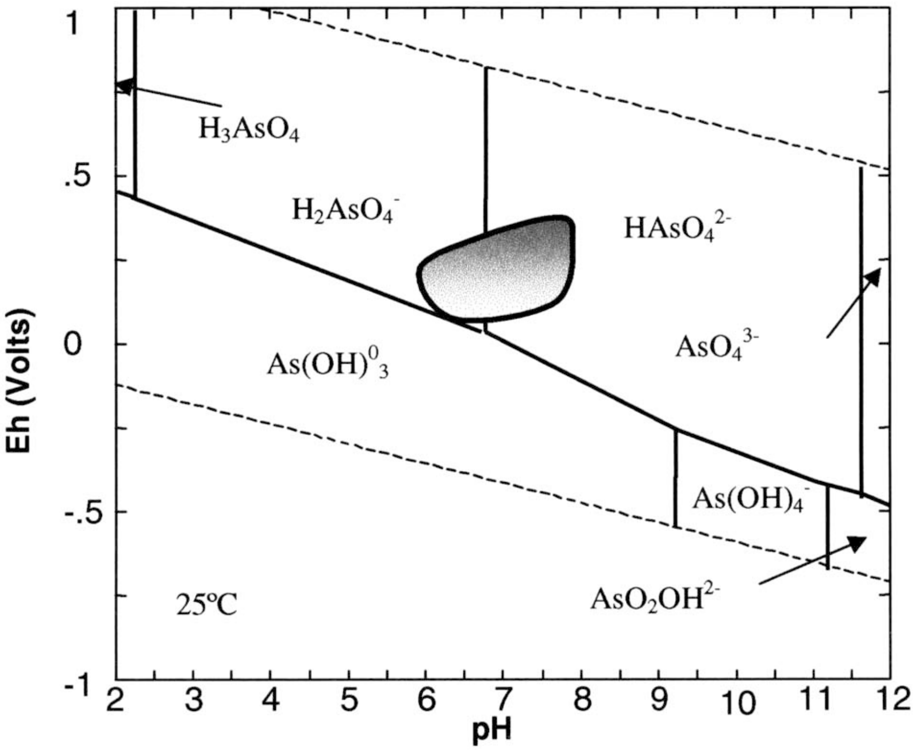

FIGURE 3

Eh and pH diagram for As species at 298K and 100 kPa with total As concentration of 10^{-4} moles per liter. Generated using Geochemist's workbench (Bethke, 1994). The shaded portion in the figure is the Eh and pH of the soils under study.

oxides of Fe and Al (Korte and Fernando, 1991; Raven *et al.*, 1998) at pH < 6. The dominant species of As under the present soil conditions are $H_2AsO_4^-$ and $HAsO_4^{2-}$, the proportion of which depends on the pH conditions (Figure 3).

Arsenic Interaction with Solid Phases

Arsenic adsorption has been studied extensively using several adsorbents, for example, phyllosilicates, silica, Al oxides, Fe oxides and Mn oxides, soils, and sediments (Frost and Griffin, 1977; Anderson and Malosky, 1979; Pierce and Moore, 1980; Stumm and Morgan, 1981; Elkhatib *et al.*, 1984; Brannon and Patrick, 1987; Moore *et al.*, 1988; Seyler and Martin, 1989; Singh *et al.*, 1988; Fuller *et al.*, 1993; Bowell, 1994; Manning and Goldberg, 1997; Raven *et al.*, 1998; Jain *et al.*, 1999). The adsorption of As (V) on amorphous and crystalline Al oxides indicates that the maximum adsorption takes place in the pH range of 3 to 4 (Hingston, 1970; Hingston *et al.*, 1971; Anderson *et al.*, 1976; Anderson and

Malotsky, 1979). The adsorption of As (V) was 1500 mmol kg^{-1} by amorphous Al hydroxide compared with 40 mmol kg^{-1} by gibbsite. Also, the adsorption capacity decreased with increasing pH. The studies on Mn (IV) oxides suggest that As (III) is oxidized to As (V) by a surface reaction mechanism (Oscarson *et al*., 1981; Scott and Morgan, 1995). The surface reduction of Mn (IV) to Mn (II) results in its dissolution, and the process is commonly referred to as reductive dissolution (LaKind and Stone, 1989). A study by McKenzie (1981) suggests that Mn oxides and hydroxides are not good scavengers of As (V) because the zero point of charge (ZPC) of these oxides are ~2.3, and therefore carry a net negative surface charge well below pH 7. There are reports of As incorporating into the structure through coprecipitation with hydrous Mn oxides (Masscheleyn *et al*., 1991).

$$3MnOOH + 2HAsO_4^{2-} + 7H^+ + 3e^- \longrightarrow Mn_3(AsO_4)_2 + 6H_20 \quad [7]$$

There has been recent interest in the understanding of adsorption of As (V) on ferrihydrites (Waychunas *et al*., 1993; Fuller *et al*., 1993; Raven *et al*., 1998; Jain *et al*., 1999), because this oxyhydroxide has high surface reactivity. More As (V) is adsorbed in the pH range of 4 to 6 (Leckie *et al*., 1980; Pierce and Moore, 1980; Goldberg, 1986), that is, below the ZPC of the amorphous Fe Oxide (ZPC = 8), because the oxides are positively charged below the ZPC (Motts, 1978).

At pH 4.6, the adsorption maxima for As (III) and As (V) were 0.60 and 0.25 mole As per mole of Fe, respectively; at pH 9.2 the adsorption maxima for As (III) and As (V) were 0.58 and 0.16 mole As per mole of Fe, respectively (Raven *et al*., 1998). The ligand exchange mechanisms involve replacement of anionic As species for OH_2 and OH^- in the coordinate spheres of surface structural Fe or Al atoms, resulting in monodentate, bidentate, and/or binuclear bridging complexes. The ligand exchange mechanisms have been confirmed by extended X-ray absorption fine structure spectroscopy (EXAFS) (Waychunas *et al*., 1993; Fendorf *et al*., 1997) and infrared spectroscopic techniques (Harrison and Berkheiser, 1982; Sun and Doner, 1996). Furthermore, Fendorf *et al*. (1997) reported that in the case of goethite, arsenate (adsorbed in the pH range of 6 to 9) is predominantly adsorbed as monodentate complexes at low coverage, bidentate complexes at intermediate coverage, and bidentate complexes, including binuclear bridging complexes at high coverage.

Adsorption vs. Co-Precipitation

Fuller *et al*. (1993) conducted an experiment on As (V) adsorption on ferrihydrite during co-precipitation (CPT) and post-synthesis adsorption (PSA) in the pH range of 7 to 9. For the CPT sample, the ferrihydrite samples were prepared from Fe (II) and Fe (III) salts. The sorption of As (V) was greater in CPT samples compared with PSA samples. The adsorption densities were as high as 0.7 mol As (V) per mole of Fe in CPT compared with 0.25 mol As per mole of Fe in PSA. The As sorption in the CPT was consistently higher at all pH levels compared with PSA. In the case of CPT synthesized using Fe (II), the sorption of As (V) was slightly less than with Fe(III), but the desorption was slower upon aging. In addition, the release of As was slower in the CPT compared with PSA. Furthermore, using EXAFS spectroscopy, they concluded that in CPT samples the As-O-Fe bond distances and coordination numbers for the CPT were significantly different than that of ferric arsenate (scorodite), As-bearing precipitates, or solid solution (Waychunas *et al*., 1993). No As-O-As bonds were observed, corroborating the absence of precipitated As minerals.

Arsenic Stabilization Reactions

The current study was designed to investigate Fe (II) treatment of As-contaminated soils. The process involves amending soils with a ferrous iron salt (ferrous sulfate) and allowing the iron to oxidize and precipitate (see Eq. 8). Arsenic is either adsorbed and/or co-precipitated, as the iron is precipitated. The chemical reaction describing oxidation and precipitation of iron with and without $CaCO_3$ are as follows:

$$4\ FeSO_4 + O_{2(g)} + 6\ H_2O \longrightarrow 4\ FeOOH + SO_4^{2-} + 8H^+ \qquad [8]$$

$$FeSO_4 + 1/2\ O_{2(g)} + CaCO_3 + 5/2\ H_2O \longrightarrow FeOOH + CaSO_4\bullet 2H_2O + CO_2 \qquad [9]$$

Two moles of acidity are generated for each mole of iron oxidized and this acidity is of concern at the Rocker site, because alluvium may contain mineralized tailings. Acidification of these tailings-containing sediments could potentially mobilize other metals (e.g., Cu, Zn, etc.). This study contained provisions for monitoring treatment-induced mobilization of metals. In the presence of calcite (Eq. 9), the stoichiometric reaction indicates that 1 mol equivalent of $CaCO_3$ is consumed per mole of Fe (II). Therefore, calcite in such a system will serve as a proton sink and prevent formation of acid conditions.

Fe (II) Salts and $CaCO_3$ Interaction

Loeppert and Hossner (1984) reported that the interaction of $Fe(ClO_4)_2$ with calcite in air containing 0.03% CO_2 or 20% CO_2 (balance air) resulted in formation of lepidocrocite and goethite, respectively. The reaction of $Fe(ClO_4)_3$ with $CaCO_3$ resulted in the formation of ferrihydrite. However, studies have shown that the adsorption of specific oxyanions, for example, sulfate, silicate, phosphate, will retard or inhibit the formation of more crystalline phases (Schwertmann and

Thalmann, 1976; Vempati and Loeppert, 1986). Furthermore, Manceau (1995) suggested that the poisoning of the A-type OH^- groups at the Fe oxide surface by the specific adsorption of anions, such as silicate, phosphate, and sulfate, at the edge sites results in retardation of the crystal growth processes. Therefore, in the current study the formation of crystalline oxides or oxyhydroxides is unlikely. This is important because the formation of crystalline Fe oxide will result in lower surface area and reactivity for adsorption of As.

Selective Extraction Procedures

Sequential extraction procedures have been used routinely to determine the relative influence of various soil colloids, for example, carbonates, Fe, and Al oxides, layered silicates in maintaining adsorbates of interest (Chang and Jackson, 1957; Woolson *et al*., 1973; Parfitt, 1978; Tessier *et al*., 1979; Chang *et al*., 1984;). The sequential extraction if used with discrimination and care can provide useful information regarding the metal partitioning in soils and sediments despite their inherent limitations (Martin *et al*., 1987).

An As fractionation scheme similar to that developed for soil-P by Chang and Jackson (1957) was adopted by several workers (Woolson *et al*., 1973; Koyama, 1975; Li, 1982). The fractionation scheme is as follows: water-soluble As fraction are extracted by water, Al-bound As by 0.5 M NH_4F solution, Fe-bound As by 0.1 M NaOH extractant, and Ca-bound As by 0.5 M H_2SO_4 extractant. Based on the fractionation scheme, they concluded that As was predominantly associated with Al and Fe oxides. Additionally, Woolson *et al*. (1973) showed that 77% of the adsorbed arsenate was extractable by 0.05 M KH_2PO_4. Depending on the soil characteristics, there were several modifications to the fractionation scheme. The sequential extractions adopted in the current study were as follows: (1) three times water extraction, (2) modified toxicity characteristic leaching procedure (MTCLP) extraction solution # 1, (3) pH 5 sodium citrate extraction, and (4) modified acidified hydroxylamine hydrochloride ($NH_2OH{\bullet}Cl$). The reasons for use of citrate and $NH_2OH{\bullet}Cl$ are summarized below.

Phosphate sorbed to Al and Fe oxides and gel can be extracted using 0.2 M sodium citrate at pH 5. The citrate ions likely compete with phosphate for adsorption site on Al oxides (Sposito, 1996). Citrate is known to dissolve the surface oxides, oxyhydroxides, or hydroxides of Al and Fe oxides, resulting in release of phosphate into the solution (Sposito, 1996). However, the reaction with Fe oxides is light dependent (Loeppert, R. H., personal communications). Because phosphate adsorption mechanisms are similar to arsenate, this extraction procedure was adopted. Studies have shown that phosphate can displace arsenate from the Fe oxide sites (Woolson *et al*., 1973; Parfitt, 1978, and references therein). The hydroxylamine hydrochloride ($NH_2OH{\bullet}Cl$) is commonly used for determining quantitatively the amount of Mn oxides present in soil. Chao and Zhou (1983) have modified $NH_2OH \bullet Cl$ to determine the presence of amorphous Fe oxides. They recommended the use of 0.1 *M* $NH_2OH \bullet Cl$ solution prepared in 0.01 *M* HNO_3 acid (pH 2) and a shaking time of 30 min. This extraction recovered 85 and 5% of total Mn and Fe, respectively (Chao, 1972). Tessier *et al*. (1979) reported the use of 0.04 *M* $NH_2OH \bullet Cl$ with 25% (v/v) acetic acid extractant (pH of the system was 2) to recover both the reactive Fe and Mn oxides from the sediment. Complete extraction of these oxides occurred within 6 h.

Our modified $NH_2OH \bullet Cl$ extraction contained 0.15 *M* hydroxylamine hydrochloride prepared in 25% acetic acid with pH adjusted to 2.05 and shaking time of 18 h. This extractant is harsher than that adopted by the previous workers.

The objectives were to conduct a rapid engineering study to:

- Immobilize solution As concentration in the vadose (AV1) and saturated (AS1) zone soils using $FeSO_4$ treatment.
- Understand As fixation by soil minerals so as to prevent significant As from re-entering the soil solution.
- Understand the immobilization of the USEPA priority metals, that is, Cu and Zn in the AV1 and AS1 zones after addition of $FeSO_4$ with and without $CaCO_3$.
- Evaluate the most effective rates of $FeSO_4$ amendments with and without $CaCO_3$ for attenuation of As and other soil metals so as to meet the USEPA water quality requirements.

MATERIALS AND METHODS

Sample Collection and Preparation

Two soil samples were collected from the Rocker Site for the screening study. A backhoe was used to open a soil pit in the central, contaminated portion of the site. Samples were collected at four depths: (1) AV1 — vadose zone sample was collected between 2 and 5 ft of depth, which represents the original soil that was contaminated due to contact with As–impregnating solution, and (2) AS1–saturated zone sample was collected from 2 ft below the water table, which represents an area that has acted as an attenuation zone for many years.

Samples were collected in 5-gallon plastic containers, sealed with lids, and transported to the laboratory where they were stored at 277 K. The saturated zone sample settled significantly during transportation; water was drained from this sample and subsequently analyzed for As. The percent solids were determined by drying triplicate 10-g samples at 333 K for 24 h and reweighing. The procedure was repeated until a constant weight was obtained. The total quantity of As removed with the water phase was 1.2 mg of As from the 5-gallon container, which was insignificant for our analysis. Large gravel and wood fragments were removed from soil samples at the laboratory by sieving through a 1/8-in. stainless steel sieve. Soils were homogenized as thoroughly as possible during the mixing and sieving process.

Total Metals Analysis

The USEPA Method 3050A acid digestion method was used to determine total concentrations of As and other metals in treated and untreated soil samples. One to two grams of representative sample were digested in a 1:1 HNO_3 and H_2O_2 solution to extract metals. The digest was refluxed with HNO_3 or HCl, depending on the analytical instrument usage. Then H_2O_2 is added to achieve complete oxidization of the organic substrate.

Additionally, soils were extracted in 4 *M* HCl to minimize alteration of valence state in the determination of Fe (II) and Fe (III) and As (V) and As (III) states. A 20-ml aliquot of 4 *M* HCl was added to a 1- to 2-g sample and heated to near boiling. The solutions were cooled and brought to 100-mL volume. Total As and arsenite were analyzed using hydride generation atomic absorption. The detection limit for total As and arsenite is 0.1 and 0.3 $\mu g\ L^{-1}$. The Fe(II) and total Fe were determined by the 1,10-phenanthroline colorimetric method (Eaton *et al*., 1995). The detection limit is 10 $\mu g\ L^{-1}$

Water and TCLP-Extractable As

The AS1 and AV1 samples were extracted four times with deionized water to determine the release of As from the solid phase. Ten grams of each sample were placed in a 125-mL HDPE bottle and 100 mL of 18 Mohm deionized water was then added. The samples were shaken on a wrist-action shaker for 18 h, centrifuged for 30 min at 1500 rpm, and the supernatant was passed through a 0.45-μm nominal pore-size membrane filter. In addition, TCLP Method 1311 of SW-846 was performed to determine the amount of As extracted by this procedure. (SW-846 is the acid digestion protocol for aqueous samples and extracts for total metal analysis.) The acetic acid extraction was performed in a manner that simulated TCLP analysis. The TCLP extraction is commonly used to simulate the leaching intensity of a municipal landfill leachate and is commonly used to evaluate the toxicity of waste materials. The extracting solution was sodium acetate solution. This solution was prepared by mixing 11.4 mL of 17.4 *M* glacial acetic acid to 1 L of deionized water containing 128.6 mL of 1 *M* NaOH, and the pH was adjusted to 4.93 before the final volume was made to 2 L. Ten grams of soil were placed in a 250-mL HDPE bottle, and 200 mL of the extracting solution was added. Each sample was equilibrated for 18 h on an orbital shaker, centrifuged, decanted, filtered, and acidified pH before instrumental analysis.

Soil Ferrous Treatment

Soil samples AV1 and AS1 were subjected to ferrous iron treatments with and without $CaCO_3$. This set of treatment represented four different batch equilibration. For each titration, 20 gram samples (calculated on a dry-weight basis) were placed into 20, 250-mL HDPE bottles. Ferrous sulfate amendment rates were calculated based on stoichiometric multiples of the total As content of the soil samples. The Fe:As molar ratios used include: 0, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12.5, 15, 20, 30, 40, and 50 and the treatments were not replicated. Dry ferrous sulfate heptahydrate with a molecular weight of 278.02, supplied by Fisher Scientific, was added directly to bottles containing the soil samples. Calcium carbonate, with a molecular weight of 100.09, from Mallinckrodt, was included in one of the ferrous iron treatments. Calcium carbonate was added to each container in dry form at a molar ratio of two times the ferrous iron to neutralize the acidity associated with iron oxidation for AV1 samples and 1.8 for the AS1 samples. Slight errors associated with the determination of water content of the soil caused the $CaCO_3$:Fe molar ratio to be 1.8 for the AS1 soil compared with 2.0 for the AV1 soil. After soil and dry amendments were added to the 250-mL bottles, 200 mL of deionized water was added and equilibrated for 48 h on an orbital shaker at a speed of 275 rpm. Containers were left open to the atmosphere to facilitate oxidation of iron.

After 48 h of the reaction time, samples were centrifuged at 1500 rpm for 30 min to facilitate settling of soil particles and precipitated iron oxide. The pH of each bottle was measured. A plastic syringe was then used to carefully remove clear solution from each bottle. The technique allowed removal of all but approximately 20 mL of the supernatant solution. Soil samples were then allowed to air dry in preparation for sequential extraction techniques.

Most of the sequential studies performed on soils and sediments were on air-dried soils. However, it has been observed that the rewetted soils usually resulted in increase in metal concentrations due to increase in microbial concentration (Bartlett and James, 1980).

Supernatant solutions were filtered through a 0.45-μm nominal pore-size membrane filter and acidified by the addition of 2% HCl in preparation for instrumental metals of As, Al, Ca, Cd, Cu, Fe, Pb, Mg, Mn, Ni, and Zn.

Sequential Extraction of Treated Soils

Selected samples were air dried following treatment and analyzed using sequential extractions to determine how strongly As was retained by the treated soil. Ferrous iron treatments were conducted on 20-g soil samples in 250-mL HDPE bottles, as described above. The sequential extraction scheme included: (1) three successive deionized water extractions, (2) acetic acid (MTCLP) extraction, (3) extraction with citric acid, and (4) modified hydroxylamine hydrochloride (pH 2) extraction. The extraction procedures are summarized below:

1. **Deionized Water Extractions**. Each water extraction was conducted by adding 200 mL of deionized water to the sample container containing 20 g of soil and equilibrating on an orbital shaker for 18 h. Following equilibration, the pH of the suspension was measured using a glass electrode. The sample was centrifuged at 1500 rpm for 30 min, then the supernatant solution was removed using a plastic syringe, filtered through a 0.45-μm nominal pore size membrane filter and acidified by bringing the solution to 2% HCl. The supernate was then submitted for analysis. A total of three sequential water extracts were obtained to determine the fraction of As that might be mobile following ferrous iron treatments with and without $CaCO_3$ addition.
2. **Modified TCLP Extraction (MTCLP)**. To the residue of the above water treatment, 200 mL of sodium acetate extracting solution was added. In the MTCLP method, the solid to solution ratio was 1:10 instead of the 1:20 ratio utilized for the original TCLP. Each sample was equilibrated for 18 h on an orbital shaker, centrifuged, and decanted, and the supernate was filtered and acidified by bringing the extract solution to 2% HCl before analysis.
3. **Sodium Citrate Extraction.** Two hundred mL of 0.2 *M* sodium citrate adjusted to pH 5 was added to the above residue. Samples were equilibrated for 18 h on an orbital shaker, centrifuged, decanted, and the supernate was filtered and acidified before analysis.
4. **Modified Hydroxylamine Hydrochloride Extraction (M-$NH_2OH{\bullet}Cl$).** The modified hydroxylamine hydrochloride (*M*-$NH_2OH{\bullet}Cl$) extracting solution consisted of 0.15 *M* hydroxylamine hydrochloride prepared in 25% acetic acid and the pH adjusted to 2.05 using 1 M NaOH. To a previous sodium citrate residue, 200 mL of the $NH_2OH{\bullet}Cl$ solution was added and the suspension was shaken for 18 h with a wrist action shaker. The suspension was centrifuged and the supernatant saved for analysis. The supernatant collected in the sequential extraction was preserved by adding 2 mL of concentrated HCl before analysis.

Instrumental Analysis

The pH of extracting and treatment solutions was monitored using a glass pH electrode with a Ag/AgCl reference electrode. Metals were determined using inductively coupled plasma emission spectroscopy atomic emission spectroscopy (ICP-AES). The As and Fe estimated detection limits are 53 and 7 μg L^{-1}, respectively. For speciation studies, solutions were analyzed for total As and arsenite using atomic absorption (hydride generation) spectroscopy. Fe(II) and total Fe were measured by the 1,10 phenanthroline colorimetric method (Eaton *et al.*, 1995).

RESULTS AND DISCUSSION

Arsenic Content of Untreated Soils

The As concentrations of the two soils in the study were based from the averages of the two different procedures adopted in the study (see Table 1). In the case of AS1 and AV1, higher amounts of As were extracted with the 4 *M* HCl extraction. The residual standard deviation (RSD) of the data is provided. Average As concentrations ranged from 683 to 4814 mg kg^{-1} in the central portion of the Rocker site (Table 1). Concentrations were greatest near the surface or the AV1 zone (4814.5 mg kg^{-1}), where exposure to As-containing preservative solution occurred.

USEPA 3050A Total Metal Concentration

The total metal concentrations extracted by USEPA 3050A is presented in Table 2. The total Fe concentration was highest in the AS1 sample (49.4 g kg^{-1}) when compared with the AV1 (27.9 g kg^{-1}) sample. The concentrations of Al (11.43 g kg^{-1}) and Ca (67.16 g kg^{-1}) were high in the AV1 samples compared with the AS1 sample with concentrations of 2.32 and 3.44 g kg^{-1}, respectively. The concentration of Mn was 0.28 g kg^{-1} and 0.63 g kg^{-1} in the AS1 and AV1 soils, respectively. In addition, other USEPA priority metals, that is, Zn, Cu, and Pb, and alkali, and alkaline metals are reported in Table 2. The values in Table 2 do not reflect total

TABLE 1
Total As Concentration as Determined by the Digestion Procedures

Digestion	AS1	AV1
	mg kg^{-1}	
USEPA 3050A	634.0	4657.0
4 *M* HCl	732.0	4971.0
Average	683.0	4814.0
RSD%	7.2	3.3

TABLE 2
Distribution of Major and Minor Metals in Rocker Site Samples as Extracted by USEPA 3050A Method

Analyte	AS1	AV1
	g Kg^{-1}	
Fe	49.4	27.9
Al	2.32	11.43
Mn	0.28	0.63
Ca	3.44	67.16
As	0.63	4.66
Mg	0.84	1.19
Cu	0.97	1.06
Zn	0.68	1.02
Pb	0.15	0.42
K	0.77	1.30
Na	0.01	0.06

elemental analysis because the soils were not completely dissolved using the USEPA 3050 protocol.

4 *M* HCl Extractable Fe and As

Soil samples were extracted by 4 *M* HCl to determine the oxidation states of Fe and As in the samples. More total Fe was extracted by 4 *M* HCl compared with the USEPA 3050A total metal extractable method (see Tables 1 and 2). About 8.3 to 67.7% more Fe was extracted by 4 *M* HCl compared to the USEPA 3050A method. More Fe was extracted in AS1 soil compared with AV1 soil by 4 *M* HCl extraction. This is due to the fact that HCl extracts more Fe from magnetic Fe oxide phases (maghemite, magnetite, etc.) compared with other Fe oxides (Sidhu *et al*., 1981). This increased extraction efficiency has been attributed to the Fe-Cl complexes that reduce the repulsion between the oxide surfaces and protons attached to the oxide surfaces resulting in more extraction (Cornell *et al*., 1976). Alternately, HNO_3 extractant may form passive oxide and salt films resulting in less dissolution (Krestov *et al*., 1973). The AS1 soil contained large quantities of magnetic particles that could be separated with a hand-held magnet. These particles were observed using scanning electron microscope (SEM) and determined to be fine sand-sized spheres. These spherical particles were analyzed using X-ray diffraction and identified as well-crystallized magnetite. Therefore, the presence of Fe (II) in the 4 *M* HCl extract is likely due to dissolution of Fe (II) from the magnetite structure. Also, the sequential extraction data using sodium citrate and $NH_2OH•Cl$ suggest that <5% of the total native Fe present in both the soils were present in noncrystalline and/or poorly crystalline forms (data not shown).

The As in the wood preservation solution was originally contained in the trivalent form, dissolved in NaOH solution. Extraction of As with 4 N HCl followed by As speciation illustrates that the vast majority of As (97 to 99%) retained by the soils was in the As (V) form (Table 3). Manning and Goldberg (1997) observed that the presence of a trace amount of Mn in the clay-sized faction resulted in the oxidation of As (III) to As (V). Furthermore, they reported that 0.12 mol of As (III) was oxidized per mole of MnO_2. In this study, based on the total Mn reported by USEPA 3050A method, the concentration of Mn in the soil was not sufficient to oxidize As (III) to As (V). Only 2% As (III) and 6% As (III) could have been potentially oxidized by native MnO_2 present in the AV1 and AS1 soils, respectively. The rest of the oxidation must have been brought about by dissolved O_2 in the groundwater.

Untreated soils were leached with deionized water to determine how readily As was desorbed with water alone. Arsenic extracted by four 1:20 (soil:water) extractions ranged from 566 to 3627 μg L^{-1} (Table 4). The AV1 sample showed

TABLE 3
Selected Physical and Chemical Properties of the Samples

Sample	pH	%Solids	Total Fe[a,b] g kg^{-1}	%Fe(III)	%Fe(II)	Total As[a] g kg^{-1}	%As(V)	%As(III)
AS1	7.85	94.2	73	77	23	0.68	97	3
AV1	8.04	78.6	33	82	18	4.81	98	2

[a] 4 *M* HCl extraction.

[b] <5% of the total Fe in the native soils were present as non- and/or poorly crystalline Fe oxides.

TABLE 4
Arsenic Concentrations of Soils From the Rocker Site

Sample	Total As[a] μg kg^{-1}	Water Soluble As μg L^{-1}				%Total As[b]	TCLP As μg L^{-1}	%Total As
		I	II	III	IV			
AV1	4814	3627	2794	2091	2414	1.78	7250	1.52
AS1	683	566	877	788	811	3.26	885	0.82

[a] Average of two digestion procedures.

[b] Water soluble.

a general decline in As concentration with each successive water extraction, whereas AS1 suggests increasing amounts of As desorbed with successive water extractions. All the soil solution used in the study failed to meet the current USEPA As drinking water standard of 50 µg ml^{-1}. The cumulative As extracted by four successive water extraction was in the range of 1.78 to 3.26% of the total As present in the soil.

The TCLP extractable As was 885 and 7250 µg L^{-1} for the AS1 and AV1 soils, respectively. Only AV1 sample failed to meet the TCLP As limit of ≤5 mg mL^{-1}. The percent As extracted by the TCLP extractant was in the range of 0.82 to 1.52% of the total As present.

As content of Ferrous Iron-Treated Soils

Results of ferrous iron treatments of AS1 and AV1 soils are listed in Table 5. Concentrations of As in the treatment solutions decreased with Fe (II) with and

TABLE 5

Arsenic Concentrations (µg L^{-1}) and pH of Treatment Solutions for the AS1 and AV1 Ferrous Iron-Treated Soils

Treatment Rate Fe:As	AS1 Soil Sample				AV1 Soil Sample			
	Without CaCO3		With CaCO3		Without CaCO3		With CaCO3	
	As (µg/L)	pH	As (µg/L)	pH	As (µg/L)	pH	As (µg/L)	pH
0	554	8.05	564	8.31	3802	8.36	3790	8.43
0.1	343	8.06	300	8.17	2453	8.31	2314	8.26
0.5	132	8.02	168	8.05	339	8.22	363	8.22
1	64.7	7.81	127	8.05	44.4	8.05	71.3	8.07
2	15.4	6.97	35.1	7.93	18.6	7.64	22.8	7.53
3	42.5	5.57	32.6	7.88	10.3	7.49	18.3	7.44
4	37.1	4.75	10.5	7.62	18.3	7.52	18.5	7.47
5	44.8	4.21	13.9	7.55	20.5	7.14	21.2	7.44
6	48.3	4.17	8.74	7.54	0.51	6.36	13.2	7.34
7	62.1	4.06	10.5	7.56	0.39	5.87	8.34	7.44
8	63.3	4.01	9.29	7.6	0.64	5.66	12.5	7.32
9	60.1	3.97	9.08	7.57	1.18	5.53	10.7	7.31
10	72.9	3.9	6.71	7.56	1.31	5.43	5.78	7.31
12.5	76.4	3.77	5.34	7.54	1.62	5.62	6.6	7.25
15	85.8	3.7	6.71	7.54	2.11	5.36	5.63	7.12
20	90.1	3.6	3.32	7.57	4.09	4.38	4.98	6.85
30	99.5	3.46	0.65	7.57	7.28	3.67	1.05	7.09
40	108	3.39	1.23	7.55	3.82	5.32	1.47	6.59
50	88.2	3.42	0.49	4.7	4.09	4.29	0.79	6.83

without $CaCO_3$ treatments for both soils. The pH dependence of As adsorption did cause some differences between treatments (with or without $CaCO_3$). Data are presented graphically in Figures 4 to 7.

Saturated Zone (AS1)

Results of ferrous iron treatment of the AS1 soil without $CaCO_3$ are summarized in Figure 4. For the untreated AS1 sample, the total As in solution corresponds to <1% of that present in the solid phase. The treatment fully reduced As solution concentrations from 554 to 15.4 μg L^{-1} (at a molar ratio of 2 Fe:As). The soil contained predominantly natural $CaCO_3$ that was capable of buffering pH above neutrality up to a Fe:As molar ratio of 2. Past this ratio, however, pH of the treatment solution decreased dramatically, and As in solution increased from 37.1 to 108 μg L^{-1}. The maximum attenuation of As occurred at neutrality.

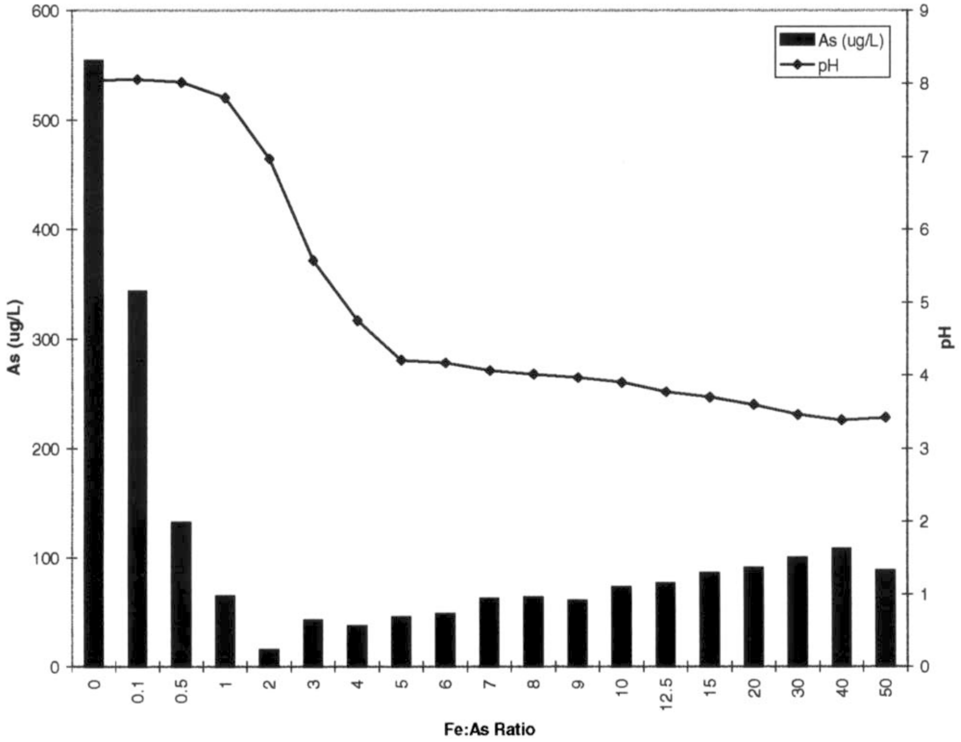

FIGURE 4

Arsenic concentration and pH of treatment solutions for the AS1 soil without $CaCO_3$ amendment.

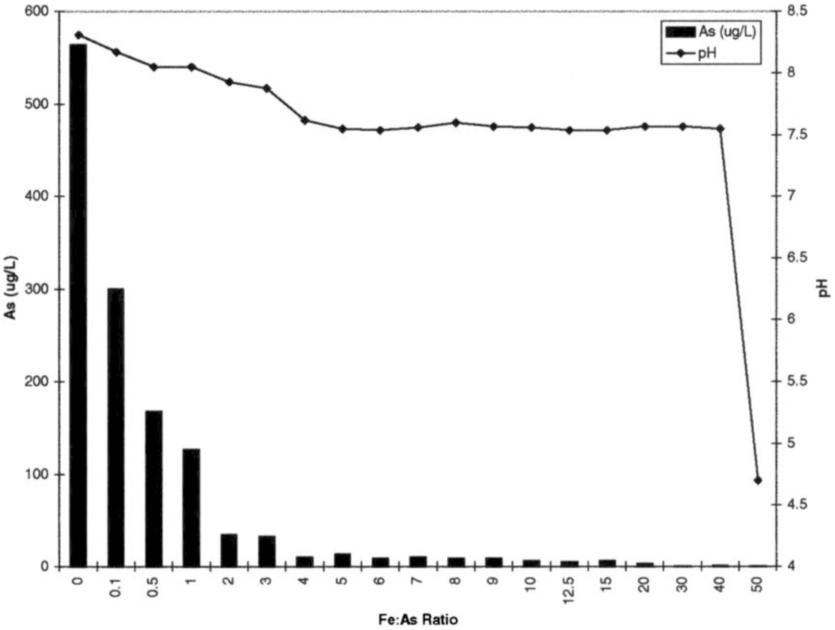

FIGURE 5

Arsenic concentrations and pH of treatment solutions for the AS1 soil with $CaCO_3$ amendment**.**

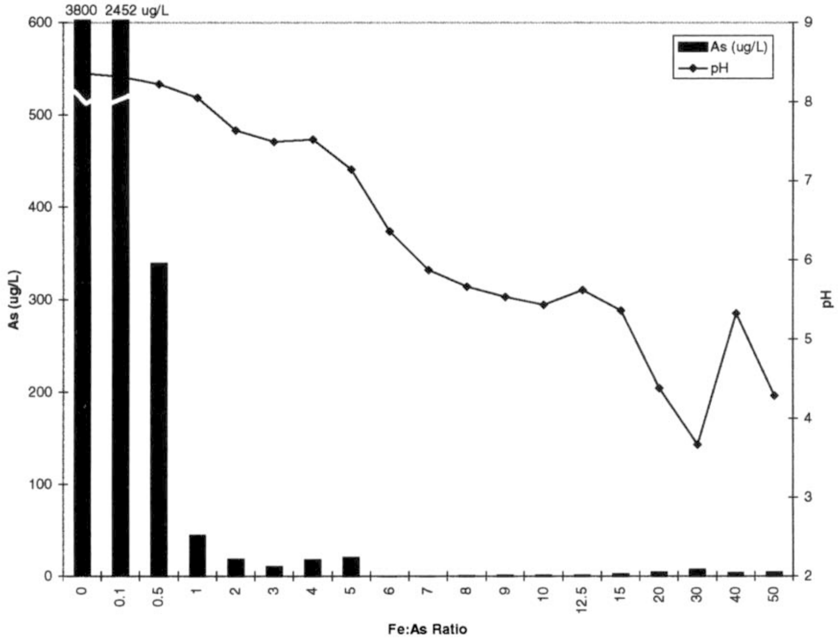

FIGURE 6

Arsenic concentrations and pH of treatment solutions for the AV1 soil without $CaCO_3$ *amendment.*

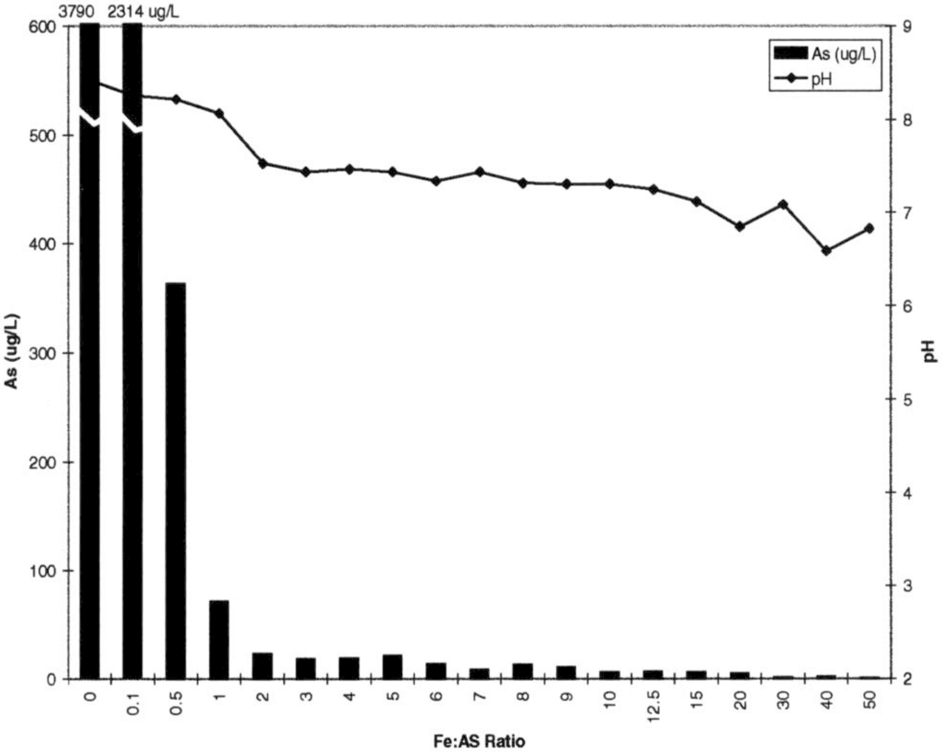

FIGURE 7

Arsenic concentrations and pH of treatment solutions for the AV1 soil with $CaCO_3$ amendment.

Results of the ferrous iron treatment of the AS1 soil, with $CaCO_3$ amended at a rate equal to a $CaCO_3$:Fe molar ratio of 1.8 are summarized in Figure 5. The pH of $CaCO_3$-treated soils did not decrease as dramatically as the untreated soil. The pH of the soil was >7.5 up to Fe:As molar ratio of 40.

Arsenic concentration of the untreated sample (ratio = 0) was 564 $\mu g\ L^{-1}$, and it decreased with increasing Fe:As molar ratio. At Fe:As molar ratio of 2, As concentration was 35.1 $\mu g\ L^{-1}$. This value was slightly higher than that obtained for the treatment without $CaCO_3$ (As = 15.4 $\mu g\ L^{-1}$) and probably results from the higher pH of the treatment with $CaCO_3$ (see Figure 5). Increases in Fe:As molar ratio produced consistently lower As concentrations, for $CaCO_3$-treated soils.

Vadose Zone (AV1)

The total amount of Fe added to the AV1 soil was about seven times that of the AS1 soil, at any given molar ratio. The solution As concentration decreased consistently from 3802 mg L^{-1} to 0.64 $\mu g\ L^{-1}$ with increasing Fe:As molar ratios ranging from 0 to 8 for samples treated without $CaCO_3$ (Table 5). However, the As concentration increased from 1.18 μg L^{-1} to 4.09 μg L^{-1} for samples treated with molar ratios from 9 to 50 without $CaCO_3$. Ferrous iron treatments of the AV1 sample produced very dramatic reductions of As concentration (Figure 5). At the Fe:As molar ratio of 2, the As concentration was 18.6 μg L^{-1}, which is similar to the AS1 soil without $CaCO_3$ treatment. The concentration of solution As was 10.3 mg L^{-1} at Fe:As molar ratio of 3 for soil treated without $CaCO_3$. An interesting shift in As concentration occurred from molar ratios of 6 to 8. A drop of approximately one pH unit resulted in an order-of-magnitude decrease in As concentration to <1 μg L^{-1}. Concentration of As increased from 1.18 μg L^{-1} to 4.09 μg L^{-1} with increasing Fe:As molar ratio (>8), which is attributable to decreasing pH. This may be due to the decreasing negative charge on the oxide surfaces as the pH is below ZPC of the Al and Fe oxides and/or dissolution of oxide and resulting release of As with decreasing pH.

Results of $CaCO_3$ amendments with ferrous iron treatments in the AV1 soil are plotted in Figure 7. The As solution concentration decreased steadily from 3790 to 0.79 μg L^{-1} with increasing Fe:As molar ratios from 0 to 50. As with the AS1 soil, the 2:1 Fe:As molar ratio treatment was effective in lowering dissolved As concentrations to approximately 20 μg L^{-1}. Arsenic concentrations did not fall below 10 μg L^{-1} as readily as the noncarbonate treatment, because pH values remained above neutrality in all except the highest molar ratio treatments.

Mobilization of Other Metals

Fe:As Molar Ratios and Metal Concentration

One objective of this study was to determine if the protons (acidity) generated by iron oxidation and hydrolysis would result in increased mobility of other metals in the fill and sediments comprising the Rocker site (see Eq. 7). Effects of proton generation were greatest in the noncarbonate iron treatment of the AS1 soil, as evidenced by the decrease in the pH of the soil by 4.5 units (see Figures 4 and 8). Copper and Zn concentrations in the soil solution are plotted as a function of Fe:As molar ratios in Figure 8.

Concentration of Cu in the treated AS1 soils (no $CaCO_3$) ranged from 0.02 to 86.7 mg L^{-1} with concentration increasing with decreasing pH. A similar trend was noted for Zn concentration, where the concentration ranged from 0.01 to 42.9 mg L^{-1}. This plot illustrates that Cu and Zn concentrations increased when the pH buffering capacity of the natural sediment carbonates became depleted, that is, when the soil Fe:As molar ratio was >2. In case of $CaCO_3$-treated AS1 soils, the concentrations of Cu and Zn were <1 mg L^{-1} irrespective of Fe:As molar ratio.

The solution Cu concentrations for the AV1 sample were below the instrument detection limit for the treated soils without $CaCO_3$, whereas solution Zn concen-

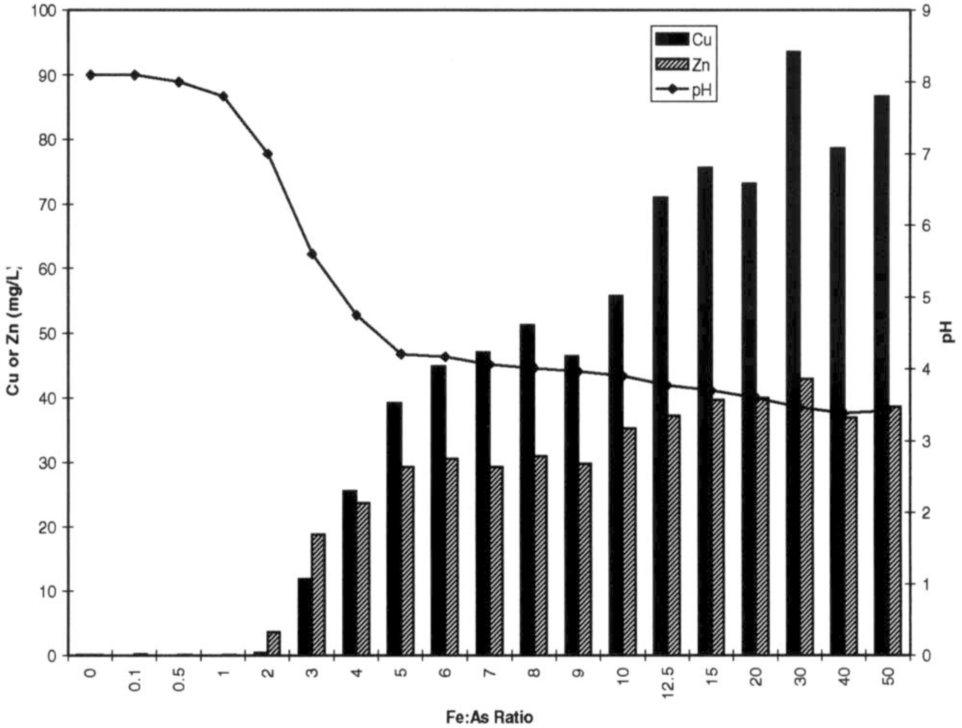

FIGURE 8

Treatment solution concentrations of Cu and Zn for the AS1 sample (without $CaCO_3$ amendment) plotted as a function of Fe:As molar ratio.

tration was in the range of 2 to 30.6 mg L^{-1} for the samples with Fe:As molar ratios of >7 (Figure 9). In case of $CaCO_3$-treated AV1 soils, the concentrations of Cu and Zn were <1 mg L^{-1} irrespective of Fe:As molar ratios.

Retention of As by Treated Soil

The degree with which the treated AS1 and AV1 soils retain As was investigated using the sequential extraction procedure (Table 6). The primary goal of Fe (II) treatment was to decrease mobility of As in the soil aqueous phase and prevent its migration. Calcium carbonate was added to the system to provide a sink for protons generated during the Fe addition. During the three sequential extractions with deionized water, only the AV1 sample treated at the Fe:As molar ratio of 10 had dissolved As concentrations of <50 μg L^{-1}.

Water-soluble As concentrations of treated soils were less than 5% than those of untreated samples in all cases (Table 6). There was a slight increase in As concentration with sequential extractions in water. This trend generally might be

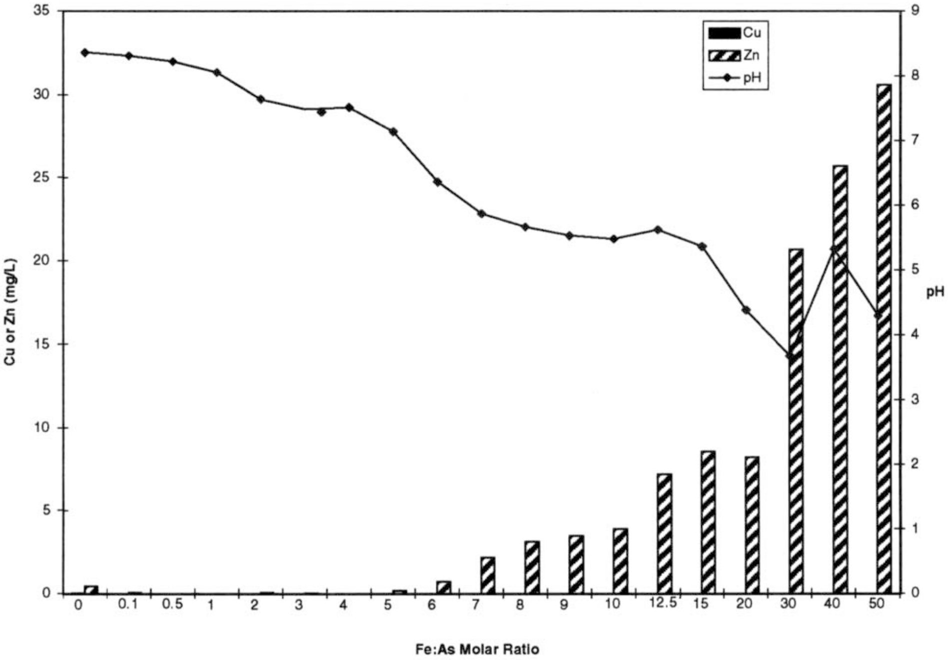

FIGURE 9

Treatment solution concentrations of Cu and Zn for the AV1 sample (without $CaCO_3$ amendment) plotted as a function of Fe:As molar ratio.

related to the increasing pH of samples during sequential water extractions. The increase in pH and/or increase in ionic strength results in increased As desorption (Raven *et al*., 1998; Jain *et al*., 1999). Furthermore, it may have ramification in management of As under field conditions, where it may be essential to maintain lower pH (<8) and higher ionic strength (by addition of gypsum) to prevent As release in a soil environment.

The total As soil extracted by the three sequential water extractions ranged from 0.60 to 4.90% for the AS1 soils and 0.03 to 2.5% for the AV1 soils. Comparison of MTCLP-extractable As for the ferrous iron treated soils and the control (see Table 5) illustrates that treatments were successful in stabilizing As, especially in the highly contaminated AV1 sample. The addition of $CaCO_3$ to the soil containing similar Fe:As molar ratios mostly resulted in increase in solution As. Treatment of the AV1 sample resulted in MTCLP leachate concentrations that were several orders of magnitude lower than those of untreated soils. The concentration of MTCLP extractable As ranged from 171 to 885 μg L^{-1} and 222 to 7250 μg L^{-1} for the AS1 and AV1 soils, respectively.

Stability of As in treated soils was investigated further using extractions of citric acid and hydroxylamine hydrochloride. These extractions would be outside the

TABLE 6
Concentrations of As in Sequential Extractions of Treated and Untreated Samples of the AS1 and AV1 Soil Materials

			Extractions							
Sample	**Fe:As†**	**$CaCO_3$**	**I**	**II**	**III**	**As-MTCLP**	**MTCLP As**	**Citrate As**	**MHAH As‡**	**Total As**
		g	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$	%
			------------------Solution Concentration------------------			------------------μg As released g^{-1} of Soil------------------				
AS1§	0	0	874[8.1](0.1)	1150[8.8](2.2)	1180[8.8](2.3)	885	8.9(1.28)	270(38.9)	150(22.1)	66.8
AS1§	0	0	961[8.3](1.4)	1210[8.7](1.7)	1250[8.8](1.8)	885	8.9(1.28)	250(37.1)	160(23.2)	66.4
AS1§	2	0	77[7.0](0.1)	194[8.5](0.3)	338[8.1](0.5)	300	3.0(0.41)	260(38.5)	160(23.0)	62.8
AS1§	6	0	78[4.2](0.1)	58[6.5](0.08)	76[7.4](0.12)	171	1.7(0.22)	250(37.1)	160(23.6)	61.2
AS1§	6	0.219	58[7.5](0.08)	92[8.5](0.1)	249[8.0](0.42)	193	1.9(0.03)	250(36.8)	160(23.8)	61.2
AS1§	7	0				225	2.3(0.36)	250(39.0)	150(21.8)	61.2
AV1¶	0	0	4460[8.4](0.9)	3180[9.2](0.6)	4200[9.0](0.8)	7250	72.5(1.50)	1350(28.4)	981(20.4)	52.8
AV1¶	0	0	4400[8.4](0.9)	3200[8.9](0.6)	4260[9.0](0.8)	6800	68.0(1.42)	1740(36.5)	940(19.6)	60.0
AV1¶	6	0	79[6.4](0.01)	74[7.4](0.01)	150[8.1](0.04)	335	3.4(0.06)	1500(31.5)	410(8.6)	40.2
AV1¶	7	0				260	2.6(0.05)	12.80(26.9)	490(10.4)	37.4
AV1¶	10	0	41[5.4](0.01)	42[7.5](0.01)	47[7.6](0.01)	222	2.2(0.05)	1220(25.7)	360(7.58)	33.0
AV1¶	10	2.542	46[7.3](0.01)	61[7.9](0.01)	68[7.9](0.01)	268	2.7(0.06)	460(9.3)	1160(24.2)	33.6

† = molar ratios
‡ MHAH = modified $NH_2OH{\cdot}HCl$
§ = total soil As in AS1 is 0.699 mg g^{-1}
¶ = total soil As in AV1 is 4.759 mg g^{-1}
The values in brackets are pH of the extract and values in parentheses are percent As released from the total As sorbed.

range of normal leaching environments, but help to give information concerning the mechanism of As retention. The pH 5 sodium citrate extractant attacks poorly crystalline Al and Mn oxides, resulting in release of ligand bound As (Sposito, 1996). Citrate competes with phosphate and sulfate (Parfitt, 1978 and papers therein) for ligand exchange sites. The citrate-extractable As for the AS1 soils ranged from 250 to 270 μg g^{-1} and for AV1 soils ranged from 460 to 1740 μg g^{-1}. The citrate-extractable As was severalfold greater than the MTCLP-extractable As. Citrate appears very effective in removing As from control and treated soils (Table 6). This probably stems from dissolution of poorly crystalline Mn oxide and to a lesser extent Fe- and Al-oxide and/or oxyhydroxide phases and $CaCO_3$ (Figure 10a,b,c,d), which may be responsible for attenuation of As in soils.

Modified hydroxylamine hydrochloride (pH = 2.05) (M-NH_2OH•Cl) shaken for 18 h produces an even harsher extraction for iron oxides but primarily extracts Mn oxides (Chao, 1972; Tessier *et al*., 1979). The extractant provides a rigorously reducing environment in addition to low pH. The amount of As extracted ranged from 150 to 160 μg g^{-1} for AS1 soils and 360 to 1160 μg g^{-1} for the AV1 soils. Only

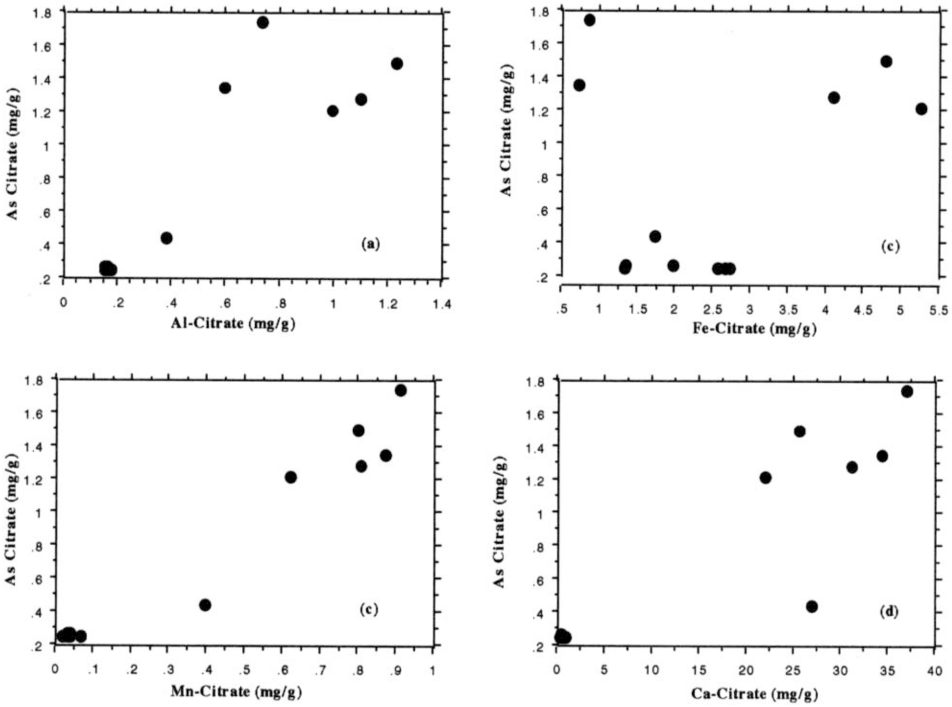

FIGURE 10

Plot of citrate extractable As with (a) citrate extractable Al, (b) citrate extractable Fe, (c) citrate extractable Mn, and (d) citrate extractable Ca. The values below detection limits are not plotted.

the treated AV1 soil showed resistance to the M-NH_2OH•Cl extraction at the Fe:As molar ratio of 10 treated without $CaCO_3$. These results indicate that M-NH_2OH•Cl might not have been effective in dissolving freshly precipitated Fe oxide. The release of M-NH_2OH•Cl-extractable As was related to the M-extractable Mn, Al and Ca (Fig. 11a,b,c,d). This suggests that As was released primarily from these phases. The total amount of As released from AS1 soils ranged from 61.2 to 66.8% compared with 33.6 to 60% from the AV1 soils.

The release of Cu and Zn also was observed during citrate and M-NH_2OH•Cl extractions but may be related to the metals bound to Mn, Al, and Fe oxides. The M-NH_2OH•Cl extracted only 69.4 to 86.8% of the added Fe (II) from the AS1 soil and only 23.3 to 35.7% of the added Fe from the AV1 soil. This is based on the amount of Fe added that was cumulatively extracted during sequential extractions. The total native Fe present in the soils was excluded in the calculation. The question of co-precipitated Fe and As oxides vs. adsorbed As on freshly precipitated Fe oxides could not be concluded from the study. However, based on the

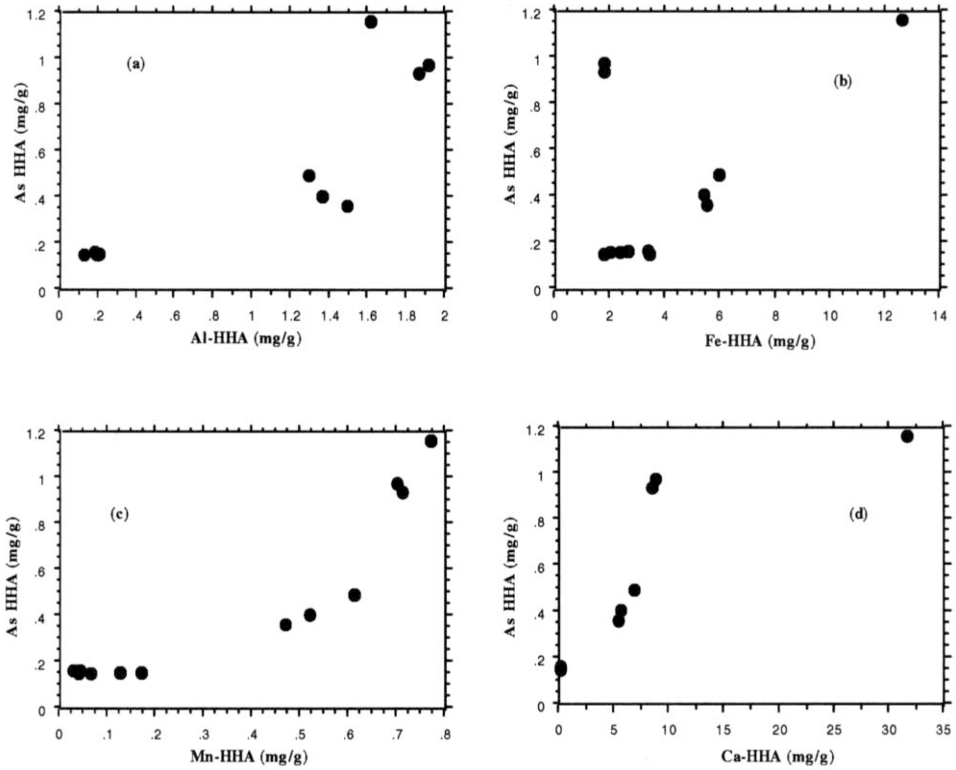

FIGURE 11

Plot of hydroxyamine hydrochloride acid (HAH) extractable As with (a) HAH extractable Al, (b) HAH extractable Fe, (c) HAH extractable Mn, and (d) HAH extractable Ca. The values below detection limits are not plotted.

Waychunas *et al*. (1993) study the formation of ferric arsenate can be ruled out and that ligand bond As is likely to occur.

Effective Treatment to Reduce Solution As Concentration

In both AS1 and AV1 soils, the Fe amendment with Fe:As molar ratio of 2 was effective in reducing the solution As concentration. In case of AS1, the As concentration was reduced from 554 to 15.4 μg L^{-1} without $CaCO_3$ addition, but for the $CaCO_3$-treated soil the concentration was 35.1 μg L^{-1}. This is attributable to increase in soil pH resulting from the addition of carbonates. For the AV1 soils at the comparable Fe:As ratio, the solution As concentration was reduced from 3802 μg L^{-1} to 18.6 for the soil treated without $CaCO_3$ and 22.8 μg L^{-1} for soil treated with $CaCO_3$. Because the AV1 soil had an inherent buffering capacity, the pH (7.54 ± 0.1) did not differ much for the sample treated with $CaCO_3$.

The current water quality As concentration established by Unites States Environmental Protection Agency (USEPA) is 15 mg L^{-1} but at the time the experiments were performed the limit was 50 mg L^{-1}. Therefore, our primary goal was to reduce the solution As concentration to 50 mg L^{-1}. Our rapid engineering study indicates that treating both the soils with Fe:As molar ratio of 2 met the USEPA As water quality limit of < 50 mg L^{-1}. Whereas treating the AS1 and AV1 soils with Fe:As molar ratio of 2 and 3, respectively, met the current USEPA As water quality limit of ≤ 15 mg L^{-1}. The concentrations of the Cu and Zn were below the instrument detection limits for the AS1 and AV1 soils without $CaCO_3$ treatment.

CONCLUSIONS

The study was designed to answer a set of questions posed during the very early stages of feasibility assessment, and it provided the following results:

- The ferrous iron treatment reduced water soluble As to less than 20 μg L^{-1} in all soils studied.
- Sequential extraction with water suggests that As concentrations generally stayed below 100 μg L^{-1} even after leaching with a deionized water volume equivalent to hundreds of years of groundwater or rain water infilteration. Sequential water extractions produced higher pH values and concomitant increases in As concentration. Significant pH increases are not expected in field applications because of the inherent buffering capacity of the soils.
- The sequential extraction illustrated that chemically stabilized As was at least partially resistant to the MTCLP extraction. This result suggests that As will be stable with respect to reasonable changes in the soil or ground-

water environment. Instability of the As occurs when the leaching environment is harsh enough to dissolve iron oxides. This would only occur in very acid conditions, such as those accompanying acid sulfate weathering reactions, or highly reducing conditions.

- Ferrous iron treatment of the AS1 soil (without calcium carbonate) did release some Cu and Zn at the higher amendment rates (higher than optimum rates). These metals were from mineralized tailings or sediments in the sample. Use of $CaCO_3$ with the treatment eliminated the risk of releasing other metals at any ferrous iron amendment rate.
- Ferrous iron rates for soil amendment were calculated based on total As contained in the bulk soils. Therefore, this produced a much higher Fe:As in the actual soil solution. For the AS1 and AV1 soils, Fe (II) amendment with Fe:As molar ratio of 2 was effective in As attenuation and metal immobilization. Bulk soil Fe:As molar ratio values above a range of 2:1 to 6:1, tended to show diminishing returns. The addition of $CaCO_3$ may be unnecessary if it is assured that sufficient amount is present throughout the soil body to stabilize the pH.

This initial study of As stabilization in soils at the Rocker site showed promising results. It subsequently was included in the USEPA Record of Decision for the Site (EPA/ROD/R08-96/110, March 1996). Additional bench- and pilot-scale feasibility studies were conducted and are presented in a latter publication. This initial study provided sufficient data to help focus additional studies on the critical aspects of physical and chemical treatment for a pilot- and full-scale study.

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REFERENCES

Anderson, M. A., Ferguson, J. F., and Gavis, J. 1976. Asenate adsorption on amorphous aluminum hydoxide. *J. Colloid Interface Sci*. **54**, 391–399.

Anderson, M. A. and Maloksky, D. T. 1979. The adsorption of protolyzable anions on hydrous oxides at the isoelectric pH. *J. Colloid Interface Sc*i. **72**, 413–427.

Bartlett, R. and B. James. 1980. Studying dried, stored soil samples — some pitfalls. *Soil Sci. Soc. Am. J*. **44**, 721–724.

Bethke, C. M. 1994. The Geochemist's Workbench™ Version 2.0. A Users Guide to RXn, Act2, Tact, React and Gtplot. University of Illinois.

Bowell, R. J., Morley, N. H., and Din, V. K. 1994. Arsenic speciation in soil porewaters from the Ashanti mine, Ghana. *Applied Geochem*. **9**, 15–22.

Bowell, R. J. 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem*. **9**, 279–286.

Brannon, J. M. and Patrick, W. H., Jr. 1987. Fixation, transformation and mobilization of arsenic in sediments. *Environ. Sci. Technol*. **21,** 450.

Chang, S. C. and Jackson, M. L. 1957. Fractionation of soil phosphorus. *Soil Sci*. **84**, 133–144.

Chang, A. C., Page, A. L., Warneke, J. E., and Grgurevic, E. 1984. Sequential extraction of soil heavy metals following a sludge application. *J. Environ. Qual*. **13**, 33–38.

Chao, T. T. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Sci. Soc. Am. Proc.* **36**, 704–768.

Chao, T. T. and Zhou, L. 1983. Extraction techniques for selective dissolution of amorphous Fe oxides from soils and sediments. *Soil Sci. Soc. Am. J*. **47**, 225–232.

Cornell, R. M., Posner, A. M., and Quirk, J. P. 1976. Kinetics and mechanisms of the acid dissolution of goethite (α-FeOOH). *J. Inorg. Nucl. Chem*. **38**, 563–567.

Datta, A. 1989. Removal of arsenic (III) from groundwater by lime treated with powdered coal additive. M. Tech. Thesis. Indian Institute of Technology, Kanpur, India.

Elkhatib, E. A., Bennett, O. L., and Wright, R. J. 1984. Kinetics of arsenite sorption in soils. *Soil Sci. Soc. Am. J*. **48,** 758.

Eaton, A. D., Clesceri, L. S., and Greenberg, A. E. 1995. In: Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D. C. USA. p-3–68–70.

Fendorf, S., Eick, M. J., Grossl, P., and Sparks, D. L. 1997. Arsenate and chromate retention mechanisms on goethite. I. Surface structure. *Environ. Sci. Technol*. **31**, 315–320.

Fox, K. R. 1989. Field experience with point-of-use treatment systems for As removal. *J. Am. Water Works Assoc*. **81**, 94–101.

Frost, R. R. and Griffin, R. A. 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. *Soil Sci. Soc. Am. J*. **41**, 53–37.

Fuller, C. C., Davis, J. J., and Waychunas, G. A. 1993. Surface chemistry of ferrihydrite II. Kinetics of arsenate adsorption and coprecipitation. *Geochim. Cosmochim. Acta* **57**, 2271–2282.

Goldberg, S. 1986. Chemical modeling of arsenate adsorption on aluminum and iron oxide minerals. *Soil Sci. Soc. Am. J*. **50**, 1154–1157.

Harrison, J. B. and Berkheiser, V. E. 1982. Anion interactions with freshly prepared hydrous iron oxides. *Clays Clay Miner*. **30**, 97–102.

Hingston, F. J. 1970. Specific adsorption of anions on goethite and gibbsite. Ph. D. Thesis. University of W. Australia, Nedlands.

Hingston, F. J., Posner, A. M., and Quirk, J. P. 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. *Discuss. Faraday Soc*. **52**, 334–342.

Jain, A., Raven, K. P., and Loeppert, R. H. 1999. Arsenite and arsenite adsorption on ferrihydrite: Surface charge reduction and net OH^- release stoichiometry. *Environ. Sci. Technol.* **33,** 179–1189.

Jekel, M. R. 1994. Removal of arsenic in drinking water treatment. In: *Arsenic in the environment. Part I. Cycling and Characterization*. J. O., Nriago, Ed., pp. 119–132. John Wiley & Sons, New York.

Johnson, D. L. 1972. Bacterial reduction of arsenate in seawater. *Nature*, **240**, 44–45.

Korte, N. E. and Fernando, Q. F. 1991. A review of Arsenic (III) in groundwater. *Crit. Rev. Environ. Control* **21(1),** 1–39.

Koyama, T. 1975. Arsenic in soil-plant system. *Nippon Dojo Hiryogaku Zasshi*, **46**(11), 491–502.

Krestov, G. A., Shormanov, V. A., and Pimenova, N. I. 1973. Kinetics study of the dissolution of a-iron(III) oxide in aqueous solutions of inorganic acids. *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Technol*. **16**, 377–381.

Lakind, J. S. and Stone, A. T. 1989. Reductive dissolution of goethite by phenolic reductants. *Geochimica et Cosmochimica Acta* **53**, 961–971.

Leckie, J. O., Benjamin, M. M., Hayes, K., Kaufman, G., and Altmann, S. 1980. Adsorption/coprecipitation of trace elements from water with iron oxyhydroxide. Final report CS–1513. Electric Power Research Institute, Palo Alto, CA.

Loeppert, R. H. and Hossner, L. R. 1984. Reactions of Fe2+ and Fe3+ with calcite. *Clays Clay Miner*. **32(3)**, 213–222.

Li, X. G. 1982. Chemical forms and content of arsenic in some soils of China. *Turang Xuebao* **19(4)**, 360–366.

Manceau, A. 1995. The mechanism of anion adsorption on iron oxides: evidence for the bonding of arsenate tetrahedra on free Fe(O, OH)6 edges. *Geochimica et Cosmochimica Acta* **59(17)**, 3647–3653.

Manning, B. A. and Goldberg, S. 1997. Modeling arsenate competitive adsorption on kaolinite, montmorillonite and illite. *Clays Clay Mineral*. **44**, 609–623.

Martin, J. M., Nirel, P., and Thomas, A. J. 1987. Sequential extraction techniques: Promises and problems. *Marine Chem.*, **22**, 313–341.

Masscheleyn, P. H., Delaune, R. D., and Patrick, W. H., Jr. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol*. **25**, 1414–1419.

McKenzie, R. M. 1981. The surface charge on manganese dioxides. *Aust. J. Soil Res*. **19**, 41-50.

Moore, J. N., Ficklin, W. H., and Johns, C. 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. *Environ. Sci. Technol*. **22(4**), 432.

Motts, C. J. B. 1978. Anion and ligand exchange: In: *The Chemistry of Soil Processes*, Greenland, D. J. and Hayes, M. H. B., Eds. John & Wiley, New York, 179–220.

Oscarson, D. W., Huang, P. M., Defosse, C., and Herbillon, A. 1981. Oxidation power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environment. *Nature* **291**, 50.

Parfitt, R. L. 1978. Anion adsorption by soils and soil materials. *Adv. Agron*. **30**, 1–50.

Peterson, M. L. and Carpenter, R. 1983. Arsenic distribution in porewaters and sediments of Puget Sound, Lake Washington, the Washington Coast and Saanich Inlet, B. C. *Geochim. Cosmochim. Acta* **50**, 353–369.

Pierce, M. L. and Moore, C. B. 1980. Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solutions. *Environ. Sci. Technol*. **14(2)**, 214.

Raven, K.P., Jain, A., and Loeppert, R. H. 1998. Arsenite and arsenate adsorption of ferrihydrite: Kinetics, equilibrium and adsorption envelopes. *Environ. Sci. Technol*. **32**, 344–349.

Reimer, K. J. and Thompson, J. A. J. 1988. Arsenic speciation in marine interstitial water. The occurrence of organoarsenicals. *Biogeochem*istry **6**, 211–237.

Sadiq, M., Zaidi, T. H., and Mian, A. A. 1983. Environmental behavior of arsenic in soils: theoretical. *Water, Air Soil Pollut*. **20**, 369.

Scott, M. J. and Morgan, J. J. 1995. Reactions at oxide surfaces. I. Oxidation of As(III) by synthetic birnessite. *Environ. Sci. Technol*. **29**, 1898–1905.

Schwertmann, U. and Thalmann, H. 1976. The influence of Fe(II), Si and pH on the formation of lepidocrocite and ferrihydrite during oxidation of aqueous $FeCl_2$ solution. *Clay Miner*. **11**, 189–200.

Seyler, P. and Martin, J. M. 1989. Biogeochemical processes affecting aresenic species distribution in a permanently stratified lake. *Environ. Sci. Technol*. **23**, 1258.

Sidhu, P. S., Gilkes, R. J., Cornell, R. M., Posner, A. M., and Quirk, J. P. 1981. Dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids. *Clays Clay Mineral.* **29(4)**, 269–276.

Singh, D. B., Prasad, G., Rupainwar, D. C., and Singh, V. N. 1988. As(III) removal from aqueous solution by adsorption. *Water Air Soil Pollut*., **42**, 373–386.

Sposito, G. 1996. *The Environmental Chemistry of Aluminum*. Lewis Publishers, Boca Raton, FL.

Stumm, W. and Morgan, J. J. 1981. *Aquatic Chemistry*. Wiley-Interscience, New York.

Sun, X. and Doner, H. E. 1996. An investigation of arsenate and arsenite bonding structures on goethite by FTIR. *Soil Science* **161**, 865–872.

Tessier, A., Campbell, P. G. C., and Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analy. Chem.* **51(7)**, 844–851.

Varsányi, I., Fodré, Z., and Bartha, A. 1991. Arsenic in drinking water and mortality in the Southern Great Plain, Hungary. *Environ. Geochem. and Health* **13**, 14–22.

Vempati, R. K. and Loeppert, R. H. 1986. Influence of structural and adsorbed Si on the transformation of synthetic ferrihydrites. *Clays Clay Mineral*. **37(3),** 273–279.

Waychunas, G. A., Rhea, B. A., Fuller, C. C., and Davis, J. A. 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geochemistry of coprecipitated and adsorbed arsenate. *Geochimica et Cosmochimica Acta* **57**, 2251–2269.

Woolson, E. A., Axley, J. H., and Kearney, P. C. 1973. The chemistry and phytotoxicity of Arsenic in soils. II. Effects of time and phosphorus. *Soil Sci. Soc. Am. Proc*. **37**, 254–259.

Xu, H., Allard, B., and Grimvall, A. 1991. Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Wat. Air Soil Pollut*. **57-58**, 269–278.