

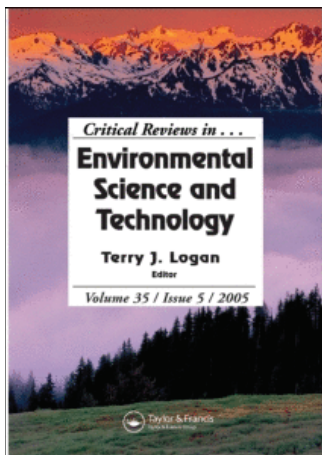
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Remediation of Arsenic-Contaminated Soils by Iron Amendments: A Review

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Arsenic (As) in soil is a serious environmental issue, and although As occurs naturally in soil, anthropogenic activities have greatly increased As soil contamination. Several technologies can be used to reduce arsenic contamination in soils, among them in situ chemical immobilization by application of inorganic amendments, which are incorporated and mixed with the contaminated soil. The binding of As to the additive reduces its mobility and bioavailability in the soil, with the long-term stability of the new compounds formed being an important issue. The objective of this study was to review the literature concerning remediation of As-contaminated soils with different iron sources and to evaluate their effectiveness.

KEY WORDS: arsenic, in situ chemical immobilization, iron amendments, soil contamination

INTRODUCTION

The presence of arsenic (As) in soil is a serious environmental problem for humans and other living organisms due to its high toxicity. Common routes of exposure to arsenic are ingestion and inhalation of arsenic compounds. Even at low concentrations, long-term exposure to inorganic As can lead to several diseases.^{1–3} The As concentration in uncontaminated soils is *ca* 5–6 mg kg⁻¹, with variations of more than an order of magnitude, depending on the type of soil considered.^{4–6}

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The dominant source of arsenic in soils is the parent rock,⁵ but anthropogenic activities such as mining, smelting of sulfide ores, application of agricultural pesticides (e.g., fungicides, herbicides, insecticides), timber preservation, wood preservation, disposal of industrial wastes from tannery industries, disposal of chemical warfare agents, and combustion of fossil fuels^{7–11} can enhance arsenic concentration in soils by factors of 100 to 1000 or even more.¹² While the regulations governing As contamination in waters are well defined, the regulatory cleanup goals for remediation of contaminated soils are still under development and may vary greatly among countries, states, and land uses.⁶ For example, the regulatory limits set by the Ministry of Environment in Canada for As contamination in agricultural, industrial, and residential soils are 25, 50, and 25 mg kg⁻¹, respectively, whereas the current soil cleanup goals set by the Florida Department of Environmental Protection for As in residential and industrial soils are 0.80 and 3.7 mg kg⁻¹, respectively.⁶

Arsenic in soil distributes among various soils components, its mobility and bioavailability being determined by the forms of chemical associations of As with different soil solid phases, rather than its total concentration.⁹ Arsenic in soil is usually found in association with iron, aluminum, and manganese hydroxides; clays and mineral oxyanions (e.g., sulfates, phosphates, and carbonates); and organic matter.^{9,13,14} Iron hydroxides such as goethite and ferrihydrite, commonly found in soils, have very important influence in the mobility behavior of As. Both arsenate (As (V)) and arsenite (As (III)) ions present a strong pH-dependent sorption affinity for iron hydroxides.^{14–17} In addition to sorption interactions with iron oxides, precipitation of iron-arsenate minerals also can control arsenic mobility. The main minerals formed from weathering of primary As sources or from industrial and agricultural products are scorodite (FeAsO₄·2H₂O), pharmacosiderite (Fe₄(AsO₄)₃(OH)₃·6H₂O), and parasymplectite (Fe₃(AsO₄)₂·8H₂O).¹⁸

In addition, soil texture is important for As distribution in soil phases. Lombi et al.¹⁹ reported that As is mobile in coarse textured soils but mainly immobile in the fine textured ones. Due to the fact that the fine grain size fraction of the soil (clay minerals, non-crystalline aluminosilicate phases, and amorphous Fe-oxides and hydroxides) possess a greater surface area, it is expected that anionic contaminants such as HAsO₄²⁻ and HAsO₃²⁻ adsorb preferentially to these mineral phases at pH values in which the surface are positively charged.²⁰

The redox state determines toxicity, bioavailability, and mobility of arsenic, As (III) being 25–60 times more toxic than As(V) and more mobile.²¹ Microorganisms that use As (V) and As (III) as a basis for their metabolism play an important role in regulating the kinetics of arsenic redox reactions in the environment.²² The redox conditions of soils vary widely, from about + 500 mV in surface soils to –300 mV under strong reducing conditions, so

in upland soils, it is unusual to find As sulfides even though they would be stable solids under reducing conditions.²³

It is essential to fully understand the fate and transport characteristics of arsenic in soils in order to achieve soil remediation. The most important issues are arsenic bioavailability, related to its speciation, and the stability of arsenic compounds with time. Although As can be immobilized in mine tailings and soils, changes in the geochemical environment to a more reductive condition may facilitate arsenic dissolution and transport to groundwaters.⁷

Arsenic distribution among different soil phases can be examined by sequential extraction technique (SSE). The fractions, operationally defined, include As, soluble or exchangeable, adsorbed to amorphous Fe oxides, bound to crystalline Fe oxides and residual phase.^{13,19,24–26}

Several technologies can be used to reduce arsenic contamination in soils.²⁷ The remediation of contaminated soil by excavation followed by landfilling with clean soil is a very expensive and arduous task.²⁸ Alternatives techniques are phytoremediation^{29,30}; inorganic solidification/stabilization using inorganic binders such as cement, lime, and pozzolanic materials²¹; soil washing³¹; electrokinetic remediation^{32,33}; and in situ chemical immobilization. The last technique implies the application of inorganic amendments, which are incorporated and mixed with the contaminated soil. Soil amendments can adsorb, bind, or coprecipitate the contaminating elements.³⁴ The binding of As to the additive reduces its mobility and bioavailability in the soil, making the long-term stability of the new compounds formed an important issue.³⁵ The long-term stability of the As compounds depends of the disposal site characteristics, particle crystallinity, grain size distribution, as well as the presence of oxygen, sulfides, and complexing agents such as chloride and organic acids.³⁶

A great number of inorganic amendments has been used to reduce As contamination in soils, such as silica, phyllosilicates, clays, zeolites, amorphous Al and Mn oxides, and nanocrystalline titanium dioxide.^{37–44} Sequential extraction of As-contaminated soils has indicated that arsenic was primarily associated with crystalline and amorphous iron oxides,^{45–47} so As sorption on amorphous and crystalline iron hydroxides has shown great potential to remediate contaminated soils.^{15,34,35,39,43,48–57} Arsenic may also coprecipitate with Fe oxides.^{58–60}

The efficiency of the remediation treatments depends on the soil characteristics, the sorption capacity of the iron source used as amendment, and the environmental conditions to which the treated soil is exposed.⁶¹

There are a number of tests for measuring the availability and bioavailability of arsenic in soils. Leaching potential is frequently estimated by the toxicity characteristic leaching procedure (TCLP),⁶² by the synthetic precipitation leaching procedure (SPLP),⁶³ and by the physiologically based extraction test (PBET).⁶⁴ The U.S. Environmental Protection Agency has specified

As = 5.0 mg L⁻¹ is the maximum allowable concentration that can be released in the TCLP in a treated As-contaminated soil.^{65,66}

As we have already mentioned, although numerous inorganic amendments have been incorporated into As-contaminated soils to reduce As availability, iron minerals and iron industrial byproducts show great potential for in situ remediation.⁶⁷ The aim of this study is to review the literature concerning remediation of As-contaminated soils with different iron sources to evaluate their effectiveness and the sustainability of the treatment over the long term.

ARSENIC SOIL GEOCHEMISTRY IN THE PRESENCE OF IRON

Under the range of Eh and pH common in soil, As is present as As(III) and As(V), usually in association with iron, aluminum, and manganese hydroxides. Iron hydroxides such as goethite and ferrihydrite, commonly found in soils, influence the mobility behavior of As.¹⁷

Two principal processes are responsible for As geochemistry in soils in the presence of iron compounds: adsorption of As(V) and As(III) on iron hydroxides and precipitation of secondary phases such as iron arsenates, including or not including sulfur. The most common iron oxides are ferrihydrite (β -FeOOH), lepidocrocite (γ -FeOOH), goethite (α -FeOOH), and hematite (α -Fe₂O₃), with goethite and hematite the most stable ones. Conversion of ferrihydrite to goethite or to other crystalline iron oxide phase may occur gradually over time,⁶⁸ affecting arsenic adsorption/desorption as density of adsorption sites diminishes with crystallization.⁶⁹

Under oxidizing conditions, As(V) in soil is retained in the solid phases by interaction with Fe(III) oxy-hydroxide coatings on soil particles.⁷⁰ Several types of interactions have been reported: As(V) adsorption on amorphous iron hydroxide,^{71,72} As(V) adsorption on ferrihydrite,^{51,69,73} and co-precipitation of As(III) and As(V) with iron oxy-hydroxide.^{59,60} The mechanism involved in the adsorption of As species into iron oxides, including poorly crystalline oxides such as ferrihydrite, is the replacement of OH₂ and OH⁻ for the anionic As species in the coordinate spheres of surface structural Fe atoms, resulting in monodentate, bidentate, mononuclear, or binuclear bridging complexes.^{15,39,51} The ligand mechanism has been confirmed by extended x-ray absorption fine structure (EXAFS) and infrared (IR) spectroscopic techniques.^{49,50,74}

Several authors have reported that As(V) binds strongly to Fe(III) oxide minerals under fully oxidized conditions, as an inner-sphere complex, probably predominately as a bidentate, binuclear surface complex.^{14,49,50,53,57,75-79} In this case, competition between arsenate and phosphate ions for sorption sites on iron oxides can be a significant factor in decreasing As(V)

adsorption.^{80,81} Fendorf et al.⁵⁰ reported that adsorption of As(V) on goethite is as a monodentate complex at low coverage, bidentate complex at intermediate coverage, and bidentate complexes, including binuclear bridging complexes at high coverage. A change of the environmental conditions to reducing ones such as flooding leads to the dissolution of iron oxides coating and produces release of As(III), As(V), and Fe(II).

Under reducing soil conditions, As(III) in soil is associated with sulfides (arsenopyrite (FeAsS) being the most common, plus realgar (AsS), enargite (CuAsS₄), and orpiment (As₂S₃)).⁷⁰ Once exposed to the atmosphere by natural or anthropogenic activities, arsenopyrite is oxidized releasing As(III), SO₄²⁻, and Fe(II). As(III) can be oxidized to As(V) and Fe(II) to Fe(III) by reactions bacterially mediated.^{82,83}

The adsorption of As(V) and As(III) anions (AsO₄³⁻ and AsO₃³⁻) on iron hydroxides depends also on pH, being higher at pH 4–6, below the pH of zero point of charge (pH_{ZPC}) where the oxides are positively charged (pH_{ZPC} magnetite 6.5, goethite 6.8, hematite 6.7).⁸⁴ Under acidic conditions the protonation of mineral surfaces favors the adsorption of As(V) polyanions H₂AsO₄⁻ or HAsO₄²⁻, while As(III) remains soluble in such conditions as arsenious acid H₃AsO₃.⁸⁵ Instead, under alkaline conditions, As(III) is adsorbed on iron oxides surfaces.

Near neutral pH As(V) and As(III) both adsorb at the surface of hydrous iron oxides and crystalline iron oxides via the formation of strong inner sphere surface complexes.⁸⁶ It has been reported that As(III) adsorbs through a mix of inner and outer sphere surface complex,⁸⁷ bidentate, and binuclear inner sphere complexes,^{59,77,88} although bidentate mononuclear complex of As(III) with hematite and ferrihydrite was also reported.⁸⁸

Pierce and Moore⁷² reported that As(V) is preferentially adsorbed to Fe hydroxides between pH 4 and 7, with an optimal pH about 4, whereas As(III) is adsorbed between pH 7 and 10, pH 7 being the optimal. High-performance liquid chromatography linked to inductively coupled plasma mass spectrometry analysis (HPLC-ICP-MS), sequential extraction experiments, and scanning electron microscopy coupled with energy dispersive spectrometry analysis (SEM-EDS) confirm that As in soils is present in soils as As(V), predominantly associated with amorphous iron oxides containing a more or less important presence of sulfur.⁸⁹ A schematic diagram of the influence of pH and Eh on the As(V) and As(III) adsorption/desorption process onto Fe(III) hydroxides is shown in Figure 1.

The oxidation of As(III) to As(V) by iron oxides and hydroxides has been reported to diminish the toxicity and mobility of As(III).⁹⁰ This oxidation reaction can be catalyzed by the presence of light or hydrogen peroxide (H₂O₂) in alkaline environments.⁷⁸

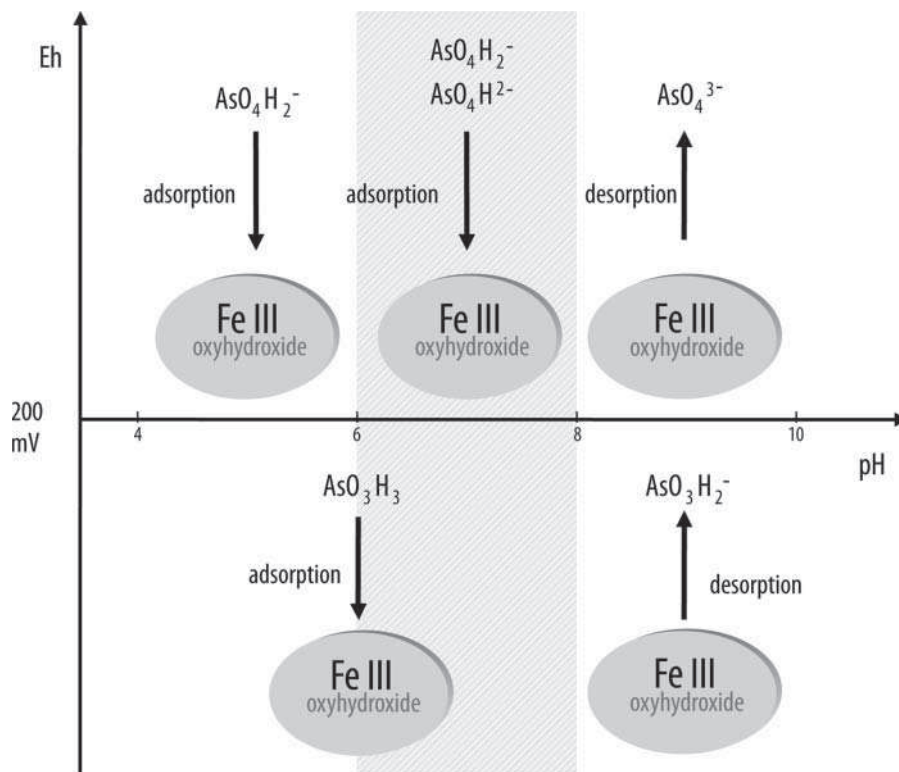


FIGURE 1. Influence of pH and Eh on the As (V) and As (III) adsorption/desorption onto Fe (III) hydroxides.

As we have already mentioned, both As(V) and As(III) have a strong pH-dependent sorption affinity for iron hydroxide and oxyhydroxide minerals such as ferrihydrite and goethite. Surface coatings of these iron oxides on detrital minerals are important sorbents of As in groundwaters and have been exploited as remediation technologies for arsenic removal.^{80,91}

Several Fe arsenates can be formed, including the mineral scorodite $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, parasymplectite/symplectite $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, kaatialite $\text{Fe}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}$, pharmacosiderite $\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_3 \cdot 6\text{H}_2\text{O}$, ferri-symplectite $\text{Fe}_4(\text{AsO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, kankite $\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$, and angellelite $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$.^{89,92}

Under strongly oxidizing conditions and at low pH, scorodite is the principal solid phase precipitated, at low pH and low Eh, and orpiment As_2S_3 , and arsenolite As_2O_3 . At neutral pH and moderate Eh, the principal solid phases are iron(II) arsenate $\text{Fe}_3(\text{AsO}_4)_2$ and under strongly reducing conditions, both arsenopyrite FeAsS and loellingite FeAs_2 are stable.⁹³ Although arsenic sulfides are the less-soluble arsenic solid phase, they easily become soluble due to oxidation of sulfide at very low redox potential, generating

acid drainage.⁹⁴ The best choice for soil remediation is $\text{Fe}_3(\text{AsO}_4)_2$, the most insoluble one with the exception of FeAs_2 , but its formation requires a strong reducing potential. Iron(III) arsenates are too soluble, the As concentration in equilibrium with the solid phase being up to 200 times the maximum contaminant level for total As in potable water. Therefore, iron arsenates are not suitable to provide an adequate decrease of As concentration by precipitation processes, especially taking into account that their formation is highly dependent on pH and Eh.⁹⁴ The principal concern is that changing conditions can significantly change the solubility of arsenic. For example, a rise of pH from 6.2 to 7.2 at fixed Eh can increase the As solubility near 30 times.⁹³

REMEDICATION BY DIFFERENT IRON SOURCES

Amendments with Iron Oxides

Iron oxides have been widely used as agents for in situ remediation of arsenic in polluted soils (see Table 1). At neutral to alkaline pH, Fe(III) salts precipitate as amorphous hydrated oxide or oxyhydroxide, which has stable properties. Gradually, the precipitate transforms into goethite, the crystalline iron oxide form.⁹⁵

The immobilization of arsenate in two weathering soils from mine waste containing arsenopyrite was studied adding synthetic Fe oxyhydroxides, Al hydroxides, and natural clay minerals.⁴³ The As retention was tested by water extraction from the soils after four weeks of treatment. The best results were obtained when synthetic $\text{Al}(\text{OH})_3$ and FeOOH were used. The iron oxyhydroxide maximum adsorption capacity for As(V) was 76 mg g^{-1} at pH 5. At $\text{pH} > 6$, the arsenic retention decreased significantly, and the solubility of scorodite and other arsenates increased.

Adsorption of As by iron(II) and iron(III) hydroxide (green rust) and iron(III) hydroxides such as goethite and lepidrocrocite proved to be two or more orders of magnitude greater than arsenic adsorption by clays and feldspars.⁹⁰ The researchers also reported that desorption of As from iron hydroxides was $<10\%$, resulting in iron-hydroxides capable of providing natural attenuation for arsenic in contaminated subsurfaces.

The use of ochre as a potential amendment for As-contaminated soils was studied by Doi et al.⁵⁶ in different ochre type and soil-ochre ratios experiments. Ochre is the colloquial name given to the characteristic orange Fe(III) oxide-bearing precipitates that accumulate in the outflows of mine systems where Fe(II)-laden water comes into contact with a more oxic environment.⁵⁶ The researchers found that the main mechanism of removal was adsorption of As onto goethite in the ochres. Nevertheless, it must be taken into consideration that in ochre-amended soil, the change to reducing

TABLE 1. Selected references on As immobilization by different Fe sources

Material	Cause of soil contamination	Evaluation of the amendment potential	Principal results	Author
Natural Fe oxyhydroxides and synthetic FeOOH	Mining soils	Iron oxides Water extraction	As (V) adsorption was 76 mg g ⁻¹ on synthetic Fe oxyhydroxide at pH 5. The As water extractable fraction decreased 55–79% by the amendments.	Garcia-Sanchez et al., 2002
Ochre	Soil at a former As smelter	Water extraction, radish growth	Ochre removed As from soil by sorption rather than precipitation, diminishing As uptake by plants	Doi et al., 2005
Soil rich in iron oxides + lime	Pyrite tailing spill	Water extraction	After remediation, the extractable As remained high, indicating insufficient amount of applied iron rich materials	Aguilar et al., 2007
Fe(OH) ₃ + lime + KH ₂ PO ₄	Lead arsenate	Water extraction	Phosphate-arsenate competition resulted in As desorption from soils	Codling and Dao, 2007
FeSO ₄ + Ca(OH) ₂ + Portland cement	As-bearing waste stockpiled onto soils	Ferrous sulphate XRD, SEM, EDX, chemical analysis, sequential extractions	Exchangable As was reduced in the amendment with FeSO ₄ . No evidence for formation of Fe-As phases in amended soils was found	Voigt et al., 1996
FeSO ₄ , Fe ₂ (SO ₄) ₃ ; FeCl ₃ , FeCl ₂ + Type I Portland cement	As(III) oxide as herbicide	TCLP, XRD, SEM, thermal analysis, NMR	Low potential for leaching resulted when soils were amended with a mixture of Type I Portland cement and ferrous sulphate	Miller et al., 2000
FeSO ₄ , FeSO ₄ + lime	As-containing wood-preserving solution	Water, acetate, citrate, hydroxylamine extraction, TCLP	Soil amendment with Fe:As molar ratio = 2 reduced As soluble concentration below 50 mg L ⁻¹	Moore et al., 2000

FeSO ₄ , Fe ₂ (SO ₄) ₃	Tailing from metal mines	NaOCl extraction, sequential extractions	70–80% As reduction was observed in the two treated tailings. Stabilization was related to the amount of Fe added and to a lesser extent to pH.	Kim et al., 2003
FeSO ₄ + lime	Soil at a former As smelter	Vegetable crops growth	Application of ferrous sulphate in solution (0.2% Fe oxides in the soil) reduced As plant uptake in 22%, solid ferrous sulphate (0.5 and 1% Fe oxides in soil) reduced plant uptake in 32%.	Warren et al., 2003
FeSO ₄ + lime	Soil at a former As smelter	Vegetable crops growth	FeSO ₄ 1.89% (w/w) giving Fe oxide concentration 0.54% reduced As lettuce concentrations 84% . Simultaneous addition of lime (0.68% w/w) with FeSO ₄ was essential to prevent metal mobilization	Warren and Alloway, 2003
FeSO ₄ , FeSO ₄ + lime	Sulfur-less minimig waste material	Water extraction	Fe(II) treatment reduced water-extractable As < 10 mg L-1 as Fe:As = 8	Seidel et al., 2005
FeSO ₄	Soil from a former timber preservation and emerald green production site	Sequential extractions	As effluent concentration in the amended soil columns indicated 89.9 to 99.8% immobilization	Gemeinhardt et al., 2006
FeSO ₄ , FeSO ₄ + KMnO ₄ ; FeSO ₄ + KMnO ₄ + lime	Herbicide containing arsenic trioxide	XRD, SEM/EDX, TCLP, SPLP	Soils showed decreases in As leachability for the three treatments, but FeSO ₄ was the best in reducing As mobility. No evidence of newly formed arsenic bearing phases was found.	Yang et al., 2007
Steel shot (SS) 1%; SS 1% + beringite (B) 5%	Contaminated soils	Chemical extractions Fe ^o	BBS resulted in the most promising remediation treatment for As- and metal-contaminated soils	Boisson et al., 1999

(Continued on next page)

TABLE 1. Selected references on As immobilization by different Fe sources (*Continued*)

Material	Cause of soil contamination	Evaluation of the amendment potential	Principal results	Author
5% compost with 5% beringite (CB); 5% compost with 1% steel shots (CS); 5% compost with 5% beringite +1% steel shots (CBSS)	Former gold mine	Short-term plant test, water extractions	After three years, revegetation was excellent with CSS treatment and successful for the CBSS. These treatments were the most effective for long-term As leaching.	Mench et al., 2003
Iron grit (SS) 1%; beringite (B) 5%; iron grit 1% + beringite 5% (BSS)	Soil adjacent to a derelict As smelter	Plant growth, soil microorganisms, and epigeic earthworm; PBET test	After six years of treatment, decrease in As extractable occurred in the BSS-amended soil producing best growth of lettuce and cabbage. As bioaccessibility was reduced from 12% in the untreated soil to 7.4% (BSS) and 3% (SS).	Mench et al., 2006
Iron grit (97% Fe ^o)	Chromated copper arsenate	Leaching under different experimental conditions	As remobilization was controlled by liquid-solid ratio and microbial activity	Kumpiene et al., 2007
Water treatment sludges (WTS), red muds, red gypsum (RG)	Agricultural soil near a Cu and As mine	Fe-rich industrial byproducts Ryegrass and lettuce growth, PBET	As bioaccessibility decreased only with the WTS-A treatment and As concentration in pore water and As extractable decreased with WTS and RG treatments	Lombi et al., 2004
Steel abrasive (SA), oxygen-scarfing granulate (OSG)	Chromated copper arsenate	Field lysimeter experiments	SA and OSG reduced As concentration in pore water by 68 and 92% for the soil with low organic matter content (OM) and 30% for the soil with high OM.	Lidelow et al., 2007

Fe-blaster sand (BS), oxygen-scarfing granulate (OSG)	Chromated copper arsenate	Field lysimeter experiments under different redox conditions	The treatments with high Fe concentration (17% OSG) and small Fe particle size resulted in higher As stabilization. Reduced conditions increased the As (III) fraction and consequently, As mobility	Maurice et al., 2007
Drinking water treatment residuals (WTR)	Arsenical pesticides and triple phosphate fertilizer	KCl extraction test, bioaccessibility and phytoavailability in vitro experiments	Fe-WTR and Al-WTR were able to reduce soil As bioaccessibility irrespective of the presence of P. As phytoavailability also was decreased for both WTR.	Sarkar et al., 2007
α -FeOOH, iron grit, Fe(II) and Fe(III) sulphates plus lime	A former landfill site, a canal embankment augmented with dredgings, a coal fly ash-based soil	Mixed Fe sources Leachate extractions	Iron oxides reduced As concentration but increased the Pb and Cd concentration in leachates from soils	Hartley et al., 2004
α -FeOOH, iron grit, Fe(II) and Fe(III) sulphates plus lime	A former landfill site, a canal embankment augmented with dredgings, a coal fly ash-based soil	Plant growth trials, biomass production	Goethite resulted the best in terms of reduction of plant shoot As content	Hartley and Lepp, 2008
Fe ⁰ ; Fe(II) and Fe (III) halide salts	Soils contaminated by defense-related industrial processes; soil at a former As-pesticide manufacturer; orchard soil contaminated by As-pesticides	PBET	Soluble Fe(II) and Fe(III) salts were more effective than Fe ⁰ to reduce As bioaccessibility.	Subacz et al., 2007

Abbreviations: XRD = x-ray diffraction, SEM-EDS = scanning electron microscopy coupled with energy dispersive spectrometry analysis, TCLP = toxicity characteristic leaching procedure, SPLP = synthetic precipitation leaching procedure, PBET = the physiologically based extraction test.

conditions due to water logging for a period of time may produce ochre dissolution and As release.

The use of local red soils, rich in free-iron oxides (2.26–6.31%), resulted in an appropriate material in the remediation of As-contaminated soils in the Guadiamar River Basin, Spain.¹⁷ Long-term monitoring of the treated soils was recommended. Lead arsenate was extensively used to control insects in apple and plum orchards during the last century. Codling and Dao⁹⁶ studied the effectiveness of lime (CaCO_3), potassium phosphate (KH_2PO_4), and iron hydroxide ($\text{Fe}(\text{OH})_3$) amendments in reducing the As and Pb solubility in lead arsenate treated soils over time. The experimental results suggested that the competition between H_2PO_4^- and H_2AsO_4^- resulted in As desorption from the two soils treated, increasing the risk of contaminating groundwater. Different results were reported by Martin and Ruby.⁹⁷ The researchers used phosphorous-bearing amendments in order to reduce the Pb bioaccessibility in soils near a Zn smelter. Addition of phosphorous was expected to increase As mobility, so they incorporated iron-bearing amendments in their strategy to reverse As mobility. They found that As leachability and bioaccessibility was reduced without compromising the effectiveness on reducing Pb bioaccessibility.

Amendments with Iron Sulfates

The addition of Fe(II) sulfate to As-contaminated soil for immobilizing As is also a valid method of remediation (see Table 1). Fe oxyhydroxides can be formed by direct precipitation from Fe(III) salt solutions or by oxidation followed by hydrolysis of Fe(II) salt solutions.

Iron oxy-hydroxides have been formed in situ when iron(II) sulfate followed by $\text{Ca}(\text{OH})_2$ and Portland cement was applied to As-contaminated soil to create a soil slurry which eventually hardened.⁹² No direct evidence of the formation of FeAsO_4 phases in the fixed soils was found, although the exchangeable As decreased. Also, Miller et al.⁹⁸ amended a contaminated sandy soil first with Fe(II) sulfate and then with type 1 Portland cement. As decreased leachability was studied through TCLP test.

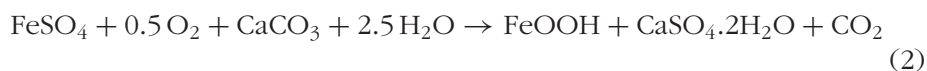
Iron(II) sulfate with and without a pH buffer of CaCO_3 was added to an As-contaminated soil from a former timber-treating plant.⁹⁹ Sequential extraction of Fe-treated soils showed that <1% of As was extractable using a modified TCLP approach, and <70% of As was extractable using a harsh acid-modified hydrochloride extraction.

Iron(II) sulfate and iron(III) sulfate were applied to sequester available As in the solid tailing phase from metal mines at Korea as stabilization treatments through the formation of amorphous iron compounds.²¹ Sequential extraction analysis was applied to obtain information on the binding strength of As to amorphous Fe precipitates.

Warren et al.⁵⁴ and Warren and Alloway⁵⁵ investigated the application of Fe(II) sulfate to soils. Fe(II) sulfate was chosen because it is a commercially available product. Solid Fe(II) sulfate was applied to give concentrations of 0.5 and 1.0% Fe oxides. The Fe (II) was oxidized under field conditions



The effects on As bioavailability were assessed in greenhouse pot experiments and field trials using a range of vegetable crops. The results were successful to a certain extent, because the Fe(II) oxidation caused soil acidification and reduction in crops yields. Two moles of H^+ are generated for each mole of iron oxidized (Eq. (1)) unless accompanied by an application of lime:

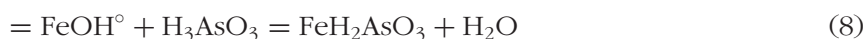
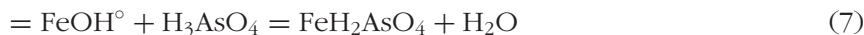


It can be seen that 1 mole of lime is consumed per mole of Fe(II).

Seidel et al.¹⁰⁰ studied the efficiency of Fe(II) treatment in immobilizing As in sulfur-less mine tailings. Fe precipitates were created by aerobic treatment of tailing material at several Fe:As molar ratio, with or without CaCO_3 , followed by aging the Fe-treated tailing material. The Fe:As molar ratio of 4 was the most effective for immobilizing As (water extractable total As of tailings $< 10 \mu\text{g L}^{-1}$).

The effectiveness of iron(II) sulfate as an immobilizing agent for arsenic in the vadose zone of contaminated soils was studied by column experiments.¹⁸ The soils were sampled at a former timber preservation site and a pigment production plant. Possible immobilization mechanisms were the precipitation of FeAs phases, the formation of inner sphere complexes, and/or the occlusion of arsenic in newly formed amorphous/crystalline iron oxides. The decrease in pH during the Fe(II) oxidation produced release of other heavy metals such as Co, Ni, Zn, so the researchers proposed the use of iron(II) sulfate/lime mixtures. Subsurface soils from several industries sites in the United States contaminated with arsenic trioxide were treated with three different amendments: FeSO_4 , $\text{FeSO}_4 + \text{KMnO}_4$, and $\text{FeSO}_4 + \text{KMnO}_4 + \text{CaCO}_3$.¹⁰¹ The molar ratios of each reagent to total soils arsenic content was chosen as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} : \text{As} = 2:1$; $\text{CaCO}_3 : \text{As} = 4:1$, $\text{KMnO}_4 : \text{As} = 5:2$. The design of the remediation experiments was based in the following possible reactions:





MnO_4K was used to help oxidize As(III) in the soils into less toxic and more stable As(V) and to convert soil As species into fairly insoluble $\text{Mn}_3(\text{AsO}_4)_2$. Calcium carbonate was used to increase the pH.

The efficiency of the treatments was investigated through the mobility of As during sequential chemical extraction procedure (SCEP),²⁶ toxic characteristic leaching procedure (TCLP), and synthetic precipitation leaching procedure SPLP, which is the one that better simulates natural weathering. All treatment solutions were found to be effective, reducing As leachability compared to the untreated soils. However, SPLP and TCLP sequential leaching experiment results showed that the effectiveness of each treatments solution varies. Treatment with the Fe(II) sulfate solution produced the best effect in terms of SPLP leaching while treatment with Fe(II) sulfate + KMnO_4 + CaCO_3 produced the best effect in terms of TCLP. The sequential chemical extractions showed that soil As leachability was reduced in 90% after the chemical fixation treatment. No evidence of newly formed arsenic-bearing phases after soil treatment were found by using x-ray diffraction (XRD) and SEM/EDS analysis, so the immobilization mechanism through the formation of insoluble arsenic-bearing phases such as Fe-As or Mn-As (see Eqs. (3–8)) is probably unlikely. Sequential chemical extractions of the treated soils indicated that surface complexation of As on Fe(III) hydroxide was the principal immobilization mechanism. Yang et al.¹⁰¹ reported that the best results were achieved by the use of FeSO_4 , because the permanganate treatment left large portions of the soil arsenic vulnerable to environmental leaching.

Amendments with Zerovalent Iron

Zerovalent iron (Fe°) presents several advantages over other iron amendments (see Table 1). It is a largely available material containing several times more Fe per unit weight than most common Fe salts, and its oxidation has little consequence on soil pH. Boisson et al.⁴² reported that application of steel shot abrasives (SS 1%) and also the combination of steel shot (SS 1%) with beringite (B 5%) to a contaminated soil were both effective in decreasing the mobility of As. Steel shots (iron grit) is an industrial material used for shaping metal surfaces that contains mainly zerovalent iron (97% α Fe) and native impurities such as Mn. Beringite is a mixture of modified aluminosilicates that originates from the fluidized bed burning of coals refuses from a coal mine. Mench et al.¹⁰² performed extraction analysis and short-term plant tests for in situ inactivation of As on a contaminated soil from a former gold mine by use of steel shots (SS), beringite (B), and municipal compost (C). The

CBSS and CSS treatments were the most effective for limiting water-soluble S.

An As-contaminated soil in a field adjacent to a derelict As(III) smelter in Belgium was treated with iron grit (SS 1%) and iron grit 1% + beringite 5% (BBS).¹⁰³ The efficiency of both treatments was evaluated six years after the amendments by terrestrial bioindicators (i.e., three plant species, soil microorganisms, and epigeic earthworm) and As-soluble and -exchangeable fractions in the soil, resulting in the BBS treatment the most effective.

The effect of environmental factors such as pH, Eh, liquid/solid ratio, presence of organic matter, and microbial activity on the immobilization of As in an iron grit (97% Fe^o and Mn as impurity) stabilized soil was analyzed by Kumpiene et al.³⁴ applying a factorial design experiment. The researchers determined that solid/liquid ratio and microbial activity were the most influential factors for As stability, and in the worst-case scenarios, 14% of As could be expected to remobilize from the treated soil.

Amendments with Iron-Rich Industrial Byproducts

Different industrial byproducts were tested for remediation of As-contaminated soils (see Table 1). Two water treatment sludges (WTS-A, WTS-B), two red muds, and red gypsum—all rich in iron oxy-hydroxides—were added to a soil highly polluted with As to reduce metal bioavailability.¹⁰⁴ WTS was the most effective in terms of enhancing plant and microbial growth, decreasing As mobility and bioavailability. Nevertheless, the re-acidification of the treated soils increased As labile fraction and enhanced its transportation to groundwater.

The capacity of two iron-rich industrial byproducts to stabilize soils contaminated by chromated copper arsenate (CCA) resulting from the previous use of the wood impregnation chemical CCA was investigated.⁶¹ One of the byproducts, steel abrasive (SA), consisted mainly of metallic iron (97% Fe^o), which corrodes and oxidizes to produce iron oxides in situ. The other, oxygen-scarfing granulate (OSG), contained mainly crystallized iron oxide (magnetite) (69% Fe₃O₄). The soils amendments were applied at industrial scale, at 1% SA and 8% w/w OSG. Both amendments decreased the concentrations of As in leachates and pore water, but their efficiency decreased in organic-rich soils. In another study conducted to stabilize a CCA-contaminated soil, Maurice et al.¹⁰⁵ used iron blaster sand (BS) and oxygen-scarfing granulate (OSG) at an industrial scale and under different redox conditions. The treatments with high additions of ameliorant and with smaller Fe particle size were more successful. The development of anaerobic conditions simulated by water saturation increased the As(III) fraction and consequently As mobility. The researchers concluded that the final destination of the treated soil should govern the amendment choice; 10% OSG would be suitable if the soil is to be landfilled under anaerobic condition.

Alternatively, the soil mixed with 1% SB could be kept under aerobic conditions in a landfill cover or in situ at a brownfield site.

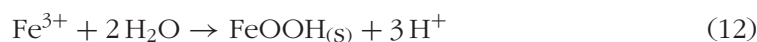
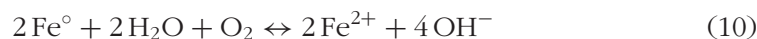
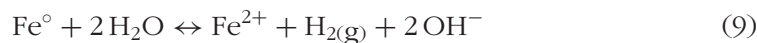
A laboratory incubation study was conducted to determine the effect of drinking-water treatment residual (Al-WTR and Fe-WTR) on As bioaccessibility and phytoavailability in a soil contaminated with arsenical pesticides and fertilized with triple super phosphate.⁸¹ The researchers reported that application of WTRs at a minimal rate of 2.5% could be a viable and effective in situ remediation method for As contaminated soils even in the presence of fertilizer P. Bioaccessibility was measured using an in vitro gastrointestinal test and phytoavailability with 1M KCl extraction test.

Although byproducts seem to be an interesting alternative in terms of low-cost treatment and also from beneficial reuse of them, it must be taken in consideration that there exist differences between materials even within the same class of byproduct due to differences in the process used at industrial level. These differences result in large variability in terms of composition and mineralogy of the byproducts.¹⁰⁴

Amendments with Mixed Iron Sources

Different Fe sources were evaluated for their effectiveness in the immobilization of As in three contaminated soils (see Table 1): goethite (α -FeOOH), iron grit (particle size 2–4 mm diameter), and Fe(II) sulfate heptahydrate and Fe(III) sulfate pentahydrate plus lime, applied at 1% w/w soil.³⁵ Different leachate extraction tests were used to evaluate the immobilizing potential of the different amendments and the durability of their effects. Iron oxides produced in situ by incorporation of iron(III) sulfate and lime were the best option, but careful consideration ought to be taken to heavy metals increased leaching. Hartley and Lepp¹⁰⁶ conducted plant growth trials on the three amended soils mentioned before for a period of three months. The As immobilization potential of the different amendments used before was determined by plant growth and elemental accumulation in plant tissues. As before, Fe-oxides produced the most promising results, reducing both bioavailability and food chain transfer potential, although soil plant transfer was not completely halted.

The use of Fe⁰ + soluble Fe(II) and Fe(III) halide salts was evaluated to reduce As bioaccessibility in contaminated soils.¹⁰⁷ Soluble Fe(II) and Fe(III) salts were more effective than Fe⁰ in reducing As bioaccessibility. The chemical reactions involved were as follows:



As can be seen from Eqs. (9–12), the addition of soluble Fe(II) or Fe(III) salts reduced As bioaccessibility in two ways: by increasing Fe(III) hydroxide content and by lowering soil pH. A molar ratio Fe:As = 100:1 reduced the As bioaccessibility in the soils by approximately a factor of 2. Results of PBET tests suggested that at least 30% moisture was needed to be added along with the amendments.

CONCLUSIONS

These studies suggest that reducing arsenic leachability and bioaccessibility in soil by adding iron amendments may be an effective strategy to remediate As-contaminated soils. Fe(II) sulfate, amorphous iron oxide, and other byproducts rich in Fe present a high adsorptive capacity for soil arsenic and low cost. The acidification problem created by amendments with Fe(II) sulfate that mobilizes heavy metal in soils should be avoided with simultaneous application of lime. The iron-bearing industrial byproducts are effective, but caution is required because of the potential release of their contaminants.

The most probable mechanism for remediation of As-contaminated soils by iron amendment seems to be the adsorption of As on iron hydroxides. Iron(III) arsenates are too soluble to provide an adequate decrease of As concentration by precipitation, and their formation is very pH- and Eh-dependent.

It must be taken into account that the immobilization process by sorption is reversible, and remobilization of sorbed As may occur when the biogeochemical conditions change with time, such as when an amended soil becomes water-logged. Additional investigations ought to focus on the impact of anaerobic conditions on As mobility.

Also, the effect of dissolved organic matter on As immobilization by iron-amended soils has to be considered. Under acidic and slightly acidic conditions, natural organic matter (NOM) (humic and fulvic acids derived from the decomposition of terrestrial and aquatic animals and plants) adsorbs to metal hydroxides mainly through ligand exchange surface complexation competing with As(III) and As(V) anions for active adsorption sites.⁷⁸ Also, due to NOM adsorption, the iron hydroxide surface becomes negatively charged, inhibiting further As anions adsorption and enhancing As mobilization.

The effect of phosphate must also be taken into consideration, as phosphate presents a stronger affinity for iron hydroxide surface than As and can replace it in the iron surface, producing a desorption of arsenic.

Remediation techniques must also consider the solubility and adsorptive properties of As-containing materials and minerals. Long-term monitoring is absolutely necessary to ensure the remediation strategies.

The use of different combinations of iron compounds altogether with other materials as lime and zeolites has also been shown to immobilize As and is worthy of future research.

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