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## Mineral-Based Amendments for Remediation

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### Abstract

Amending soils with mineral-based materials to immobilize contaminants is both old and new. Although mineral amendments have been used for decades in agriculture, new applications with a variety of natural and reprocessed materials are emerging. By sequestering contaminants in or on solid phases and reducing their ability to partition into water or air, amendments can reduce the risk of exposure to humans or biota. A variety of mineral types are commonly used to amend contaminated soils, with different modes of molecular-scale sequestration. Regulatory, social, and economic factors also influence decisions to employ mineral amendments as a treatment technology.

### Keywords

contaminated soil; remediation; in situ amendment; metals; metalloids; Portland cement; reactive capping

## INTRODUCTION

The use of reactive or stabilizing materials for remediation of metal and organic contaminants in soils has been widely studied and is gaining broader acceptance as a remediation technology. The overall aim of in situ amendment technologies is to sequester and stabilize contaminants in soils or sediments in order to reduce their ability to partition to water or biota, and thus their potential for transport and toxicity. Soil amendments have been employed to treat both organic and inorganic contaminants, although the selection of amendment treatment and the mechanism of hazard reduction differ widely depending on the target contaminant, or mixtures of contaminants, at a given site. Metal and metalloid elements, such as lead, cadmium, arsenic, mercury, chromium, and selenium, are especially problematic because they are potentially hazardous at low bulk solid concentrations (i.e. about 1–500 mg kg<sup>-1</sup>) and their speciation and mobility are influenced by environmental factors like pH and oxidation–reduction potential (Eh or pe). They are often widespread in surface and shallow subsurface soils at these low concentrations, making removal and disposal of large volumes of impacted material impractical or prohibitively expensive. Remediation of widespread and persistent organic pollutants that are not readily biodegradable, such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), and dioxins, may be improved by an amendment treatment that collectively enhances immobilization, chemical attack, and microbiological degradation.

The difficulty and expense of remediating soils and sediments contaminated with dispersed, low levels of problematic organic, metal, and metalloid contaminants calls for applications and technologies that are both effective and cost-competitive. Carbonate, lime, or phosphate amendments have long been used in agriculture to raise soil pH, lower metal toxicity to

plants, or add nutrient phosphorus (McBride and Martinez 2000; Bolan and Duraisamy 2003). Other soil amendments in use or under development evolved from stabilization or encapsulation technologies, such as vitrification and cement stabilization, designed for the disposal of radioactive and other hazardous wastes (Conner 1990; Taylor 1997). An important difference between remediation approaches developed for waste streams versus contaminated soils is that waste streams are generally concentrated and spatially contained, and the remediation goal is to limit contaminant dispersal after disposal. For soil contaminants already released and potentially transformed in the environment, the remediation goals are to reduce the risk to humans and biota of exposure, uptake, and assimilation (bioavailability), and to lessen the risk of contaminant leaching or mobilization. Soil amendments can be applied in an “ex situ” process that resembles treatment of a waste stream. In this process, soil is physically removed, in some instances washed to leach soluble contaminants, mixed with a stabilizing amendment, and then returned to its original location. While effective, this type of remediation approach is generally more labor intensive and expensive than the direct addition of an amendment to the soil (“in situ” treatment) (Mulligan et al. 2001; US EPA 2009). A significant challenge to in situ treatments, however, is ensuring adequate mixing, contact, and reaction of amendments with contaminated materials to achieve stabilization.

From a practical standpoint, responsible parties and regulatory authorities have been reluctant to leave contaminated soils and sediments in place for fear of future remobilization (and liability), particularly due to uncertainties in long-term fate after amendment treatment. Several criteria must be met for an amendment technology to be considered successful and safe for remediation of contaminated soils. The treatment must effectively reduce the exposure risk to humans and/or organisms by demonstrating a reduction in bioavailability, potential for mobilization, or transformation to more toxic forms. Treatments generally must have no adverse effects on the reestablishment of biota, on agriculture, or on land reuse after application. For example, restoration of agricultural lands must ensure that crop yields are not reduced by the application of too much salt or by the addition of amendments that result in high pH (“overliming” of soils) or limit nutrient uptake (McBride and Martinez 2000; Lombi et al. 2002). Amended soils must be resistant to chemical alteration, bioturbation, and microbiological transformations that may release contaminants as they are buried or aged. Finally, and perhaps most critically for implementation, treatment must be cost-effective when compared with alternative remediation approaches producing a similar degree of risk reduction and must also be acceptable to regulatory agencies and the public.

## TYPES OF AMENDMENTS AND PRODUCT PHASES

Numerous materials have been investigated for application to surface soils and, to some extent, surface and subsurface sediments (Table 1). The more commonly used amendments include materials such as silicate, aluminosilicate, or clay minerals; forms of phosphate, carbonate, sulfate, oxide, or hydroxide; or organic residues (i.e. various biosolids such as manure or sewage sludge; see Jones and Healey 2010 this issue). For remediation applications, many of these materials have been adapted from agriculture; from industrial processes such as cement making, production of construction materials, and soil stabilization for foundations; or from vitrification and encapsulation technologies associated with the treatment of radioactive and hazardous waste (Mulligan et al. 2001; Guo et al. 2006; Kumpiene et al. 2007). For these borrowed technologies, an important criterion for use in situ is that the material does not require heating or other specialized processing sometimes associated with ex situ treatment. Some mineral amendments, such as clay minerals, zeolites, carbonates, sulfates, and phosphates, may be employed as relatively pure phases, while others, such as Portland cements, are processed materials designed to react with water to produce hardened product phases. Clay minerals (primarily montmorillonite from, for

example, bentonite deposits), zeolites, and activated carbon (black carbon and charcoal) have been used traditionally as high-surface-area, adsorbent materials for filtration and water treatment. These materials are effective sorbents for organic compounds and other contaminants, and they have been widely studied and used in remediation. In pure form, however, they can be relatively expensive for large-scale site remediation. Treatments with phosphate-based or carbonate-based materials, lime (sometimes with organic solids), oxides and hydroxides, zero-valent iron, and calcium silicate cements (with or without sulfate) have been among the most studied and commonly used reactive amendments.

Cementitious amendments have been used for ex situ solidification and stabilization of wastes for encapsulation and disposal (Paria and Yuet 2006) and employed to some extent for in situ soil remediation. Portland-type cements are composed primarily of calcium silicate and calcium aluminate phases formed from the high-temperature reaction of limestone and clay, or other materials of similar bulk composition (Taylor 1997). When reacted with water, they create highly alkaline solutions and form a complex mixture of hydroxides, mainly portlandite  $[\text{Ca}(\text{OH})_2]$ , amorphous calcium silica hydrate phases (C-S-H) of the tobermorite  $[\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$  or jennite  $[\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}]$  types, and siliceous “hydrogarnet” solid solutions  $[\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}]$  (Taylor 1997; Matschei et al. 2007). Depending on the starting composition of the cement, variable amounts of iron, magnesium, carbonate, and sulfate can both shift chemical equilibria and affect the kinetics of formation of solid phases to produce calcite ( $\text{CaCO}_3$ ), carboaluminate phases  $[\text{Ca}_4\text{Al}_2(\text{CO}_3)(\text{OH})_{12} \cdot 8\text{H}_2\text{O}]$ , gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), ettringite  $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}]$  or related sulfoaluminate phases, and hydrotalcite-type phases  $[\text{Mg}_4(\text{Al,Fe})_2(\text{OH})_{14} \cdot n\text{H}_2\text{O}]$  in addition to C-S-H and hydrogarnet phases (Matschei et al. 2007). Although a vast body of research has examined cement and concrete chemistry for industrial and construction applications, fewer studies have looked in detail at the mineralogy and chemistry of the mineral products formed from the reaction of cement-based amendments with contaminated soils (e.g. Voigt et al. 1996; Miller et al. 2000).

Recycled materials, industrial by-products, or residual materials from treatment processes may serve as low-cost, sustainable alternatives to pure solids as source materials for soil amendment treatments. Examples include residues from alumina extraction from bauxite (“red mud”), fly ash from coal combustion, treated coal combustion products (“beringite”), steelmaking slags, and scrap iron (Lombi et al. 2002; Guo et al. 2006; Kumpiene et al. 2007). These materials are often mixed with a reactive activator or “binder” material such as Portland cement (Taylor 1997), or used in combination with an organic solid such as peat or sludge. The use of recycled materials as additives is potentially a beneficial “green” technology that reduces the amount of material destined for landfills while lowering the overall cost of a remediation project (Dermatas and Meng 2003). Fly ash, which is high in aluminosilicate glass (Table 1), has been added to Portland cements for decades to impart strength and durability (Conner 1990). High-silica materials act as a “pozzolan” (from the Latin *pulvis puteolanus*, or “powdery ash”), named for the altered volcanic tuff and ash deposits in the Alban Hills used by ancient Roman builders as a highly durable mortar when mixed with hydrated lime (Jackson et al. 2010). During cement hydration, excess silica and alumina react with hydroxyl and, depending on the availability of alkali cations, shift the reaction products to silica-rich zeolite-type phases. Although soil amendments used for large-scale treatments are relatively low-cost commercial products, their composition can be variable and may not necessarily be well characterized, adding uncertainty to their performance and long-term stability under specific field conditions. Furthermore, waste materials and industrial by-products, such as fly ash, mining residues, incinerator wastes, and metallurgical slags, may themselves contain hazardous constituents, such as arsenic, chromium, vanadium, lead, zinc, and other elements, that could potentially leach from amended soils (Cornelis et al. 2008).

## MECHANISMS OF CONTAMINANT IMMOBILIZATION

Sequestration mechanisms associated with mineral-based amendments to soils fall into two broad categories, surface adsorption and structural incorporation, each of which may have several molecular-scale variations (Fig. 1). In complex mixtures of amendments and soil, both mechanisms may occur and change with time. For many amendment treatments, however, molecular-scale mechanisms have been inferred from laboratory experiments rather than directly verified, which has contributed to a lack of confidence in the long-term effectiveness of amendments to sequester contaminants. For treatments traditionally used to raise the pH of acidic soils, such as the addition of lime or carbonate, reduced leaching or phytoavailability of metal cation contaminants (for example,  $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$ ) probably results from simple adsorption to oxide and silicate minerals as pH is increased. Metal cations tend to form strongly bound, inner-sphere surface complexes with soil minerals (Fig. 1) such that desorption is suppressed under typical soil conditions as long as pH remains high. However, elevated soil pH can mobilize adsorbed anion and oxyanion contaminants, with effects that vary depending on pH and competing species. Many organic compounds are strongly adsorbed by high-surface-area amendments, such as activated carbon, exchangeable clays, and zeolites. Surface-reactive amendments such as zero-valent iron ( $\text{Fe}^0$ ) may provide sites capable of electron transfer with adsorbed species, leading to oxidation state changes for metals or chemical degradation for organic molecules. Since organic contaminants may be degraded by either biological or chemical pathways, an interesting approach is to combine treatments to stimulate both processes by adding, for example, organic carbon to stimulate microbial degradation and zero-valent iron to promote reductive dehalogenation of chlorinated compounds (Boparai et al. 2008). Although adsorption can be an effective immobilization mechanism for metal contaminants, which may undergo changes in speciation but do not degrade, there is an inherent risk that future changes in pH, Eh, ionic strength, or solution composition could shift surface complex equilibria and desorb contaminants.

Some amendments react with soil water and minerals to alter the composition, pH, or Eh of the system, causing dissolution of solids and precipitation of new phases that can structurally incorporate contaminants (Fig. 1). This class of sequestration mechanisms has the potential for more permanent immobilization, compared to surface adsorption or ion exchange, since mineral dissolution is required to partition the contaminant into water. However, the host phase for the contaminant must be stable under the given environmental conditions. Of the amendments summarized in Table 1, phosphate-based treatments, particularly for lead contamination of soils, have been among the most widely studied and used. Application of phosphate minerals or soluble forms of phosphate to soils (Table 1) is intended to sequester toxic divalent cations such as  $\text{Pb}^{2+}$  by precipitation of pure or substituted phosphate phases of the apatite group  $[\text{Ca}_5(\text{PO}_4)_3\text{X}]$ ,  $\text{X} = \text{F}, \text{Cl}, \text{OH}$  (Miretzky and Fernandez-Cirelli 2008). This type of treatment tries to take advantage of differences in the solubility of phosphate minerals to precipitate the contaminant into a more stable phase. For treatment of lead, for example, dissolution of more soluble apatite-group minerals, such as hydroxyl-apatite  $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$  (a primary component of bone meal) or substituted apatites  $[\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3\text{FOH}]$  from natural phosphate-bearing rocks, adds dissolved phosphate to soils and leads to the precipitation of highly insoluble phosphate minerals such as pyromorphite  $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$  (Ma et al. 1995; Miretzky and Fernandez-Cirelli 2008). A potential negative consequence of phosphate remedial amendments, however, is excessive phosphate leaching from soils and runoff to water bodies, which can promote algal blooms and eutrophication.

Cement-based treatments, sometimes together with ferrous sulfate, have been studied as an amendment for immobilization of problematic oxyanion contaminants such as arsenate

(Voigt et al. 1996; Miller et al. 2000). Ettringite-type minerals [Ca-end member:  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ], which form at high pH, have been proposed as a potential host phase for oxyanions (Chrysochoou and Dermatas 2006), as well as for cations (substituting for  $\text{Ca}^{2+}$ ). This mineral class has a channel structure that may allow substitution of sulfate by oxyanions of similar structure and size, such as chromate, borate, arsenate, vanadate, and selenate (Poellmann et al. 1993) (Fig. 2). In the presence of  $\text{Fe}^{3+}$ , Fe-ettringite (where Fe substitutes for Al) has been synthesized experimentally and forms an incomplete solid solution with Ca-ettringite (Möschner et al. 2009). Field samples of arsenic-contaminated soils, collected more than 10 years after treatment with a combination of Portland type-V cement and ferrous sulfate, indicate the formation of ettringite and a close association of arsenic with calcium and iron (Illera et al. 2006) (FIG. 2). Comparison of field samples with laboratory control experiments suggests that arsenic (present only as arsenate) is associated with ettringite, possibly within arsenic-rich domains that locally resemble calcium-arsenate phases.

Microencapsulation (Fig. 1) refers to a mechanism whereby contaminants are bound physically in nano- to microscale inclusions or chemically as sorbed or precipitated nanoparticles within another resistant medium. This mechanism may be more prevalent than currently recognized due to the lack of microscale characterization of reaction products in prior studies. Silica- and cement-based amendments provide an example of microencapsulation that reduces contaminant partitioning into porewater. During hydration of ordinary Portland cement added to soil, abundant neoformed C-S-H gel coats and binds arsenic-contaminated soil particles, thereby acting as a physical barrier to pore-water leaching (Voigt et al. 1996). Microencapsulation may also be an effective mechanism for relatively unreactive contaminants such as mercury if a two-step treatment process is employed—for example, sorption to activated carbon or precipitation as insoluble mercury sulfide, followed by microparticle encapsulation with a more chemically or physically resistant treatment such as a cement-based amendment. Encapsulation-based remedies may also result in permeability reduction, thereby decreasing the flux of water through treated soil and the potential for leaching of stabilized contaminants.

## METHODS OF APPLICATION

Mineral-based remediation strategies rely on adequate contact between amendments and contaminants to promote contaminant transformation and immobilization reactions. As such, delivery and uniform distribution of amendments within the targeted soil volume are often the most significant engineering challenge for successful in situ application. Selection of an appropriate delivery method is dictated by both the physical state of the amendment (e.g. solid phase versus liquid or slurry) and the physical and hydraulic properties of the soil medium. For shallow applications, mixing of amendments using conventional earth-moving equipment has been widely used. Direct subsurface injection of liquid or slurry amendments is commonly used for deeper applications. However, nonuniform amendment distribution can be a problem for subsurface injection, especially in heterogeneous soils or sediments containing low-permeability regions. This can be mitigated to some extent by controlling the injection pressure, pulsing, or adjusting the injectate fluid viscosity to site conditions. Subsurface barriers containing reactive solid phases have been used where contaminant mass-flux reduction is desired. A potential pitfall of this technology is clogging due to infilling of pore spaces by the formation of secondary precipitates or biological fouling over time, which can lead to mobile contaminants bypassing the treatment zone. Another problem is the potential for adverse biogeochemical reactions that may shift pH or redox conditions and thus remobilize contaminants.



In situ soil mixing using specially designed, large-diameter augers has proven to be one of the more successful methods for uniform delivery of chemical amendments to soil depths in excess of 10 m (Fig. 3). Soil is treated by simultaneous mechanical mixing and injection of fluidized amendments in overlapping cells 60 to 140 cm in diameter in 1.5 m depth increments until the desired total treatment depth is attained. A final mixing pass over the entire cell thickness ensures uniform amendment distribution. After amendment application, soils may be covered with an impermeable cap to limit infiltration and leaching, or with clean soil, and then stabilized with vegetation.

The use of reactive amendments to treat subaqueous or subsurface sediments presents significant challenges, and this is an area of considerable research. A crucial difference for the subaqueous environment is the method of amendment delivery, for which site considerations such as water depth, currents, bottom topography, and nature of the contaminants determine method feasibility (Bailey and Palermo 2005). Delivery methods, including release, spreading, broadcasting from the water surface, and the use of subaqueous diffusers, must be designed to minimize sediment resuspension. Amendments must have sufficient contact with contaminants in the sediment, and the intended reactions must proceed under saturated, often reducing, conditions. In shallow marsh or tidal areas, mixing of amendments directly into shallow subaqueous sediments with large-scale mixers or slurry injection from barge- or crawler-mounted equipment is potentially feasible, as demonstrated in a recent pilot study in which an activated carbon amendment was added to PCB-contaminated mudflat sediments (Cho et al. 2009).

Another promising technology for subaqueous sediments is the use of amendment media within an engineered cap to create a reactive geochemical barrier system. New research is examining a variety of reactive materials for this application, including adsorptive media, such as expansive clay minerals, zeolites, or activated carbon, or reactive materials, such as Portland cement or siderite ( $\text{FeCO}_3$ ). Reactive amendments are emplaced either between layers of conventional capping material, such as gravel or coarse sand, or in geosynthetic composite or textile mats. The treated area is then covered with a clean sediment layer for long-term, active contaminant attenuation, physical isolation, and erosion control (Bailey and Palermo 2005).

## REGULATORY FRAMEWORK, ACCEPTANCE, AND ECONOMICS

Development of science and technology for the remediation of contaminated soils and sediments has been driven by environmental regulations enacted in many countries, beginning mostly in the 1970s. Legislation was initially created in response to environmental disasters such as Love Canal (USA) and Minamata Bay (Japan), with the goal of restoring contaminated sites and impacted natural resources to pristine conditions. With the realization during the 1980s and 1990s that such a goal was economically and sometimes technically unfeasible given the sheer number and complexity of contaminated sites, the paradigm has shifted to one of risk management. In many developed countries (e.g. United States, United Kingdom, Canada, Australia, and others), complex, risk-based regulatory policies for site remediation are often implemented at the state or regional government level, and sometimes tailored to specific geographic and political factors. Because standards tend to be site-specific and regulated locally, the use of soil stabilization technologies has increased slowly over the last few decades. For example, at U.S. Superfund sites, the use of an in situ treatment of any kind for source control of contaminants increased from 47% of sites during the period 1982–2005 to 60% of sites during 2002–2005. Solidification–stabilization constituted only about 10% of the in situ technologies applied at all Superfund sites, with the dominant application being remediation of metal and metalloid contaminants (US EPA 2007). These trends suggest increasing interest in using in situ

treatments for site remediation, but also some reluctance to employ them, probably because of an inability to demonstrate effectiveness, uncertainty in long-term performance, or economic factors.

The effectiveness of soil treatment has traditionally been assessed primarily by extraction-based tests such as the Toxicity Characteristic Leaching Procedure (TCLP), the Waste Extraction Procedure (WET), and the Synthetic Precipitation Leaching Procedure (SPLP). These are usually short-term (<24 hours) batch procedures that evaluate contaminant partitioning between the solid and a leaching fluid. Some of these protocols were developed for specific regulatory purposes and thus are not necessarily appropriate for evaluating contaminant fixation under a variety of field conditions. For example, the TCLP, which employs an acidic acetate solution as the leachate, was developed to simulate leaching by dissolved organic compounds in order to determine whether specific waste types are legally acceptable for landfill disposal in the United States. Nevertheless, the TCLP continues to be a widely used test for a range of organic and inorganic contaminants. In Europe, significant effort has been directed toward standardization or “harmonization” of a number of different extraction tests. Post-treatment monitoring of groundwater and surface water is typically conducted to confirm that remediation has reduced contaminant mobility. Although such assessments are useful for evaluating contaminant sequestration following treatment, they do not directly address whether amendments are effectively reducing the risk of contaminant exposure at a site for a sufficiently long period of time. More recently, there has been a regulatory shift towards performance evaluations that are more closely tied to contaminant bioavailability and exposure risk. This effort includes development of extraction tests, such as the Physiologically Based Extraction Test (PBET). The PBET and similar protocols evaluate partitioning between contaminated solids and simulated gastric fluids to assess bioaccessibility, and are compared against relative bioavailability tests that employ animal models, such as swine or mice (Kelley et al. 2002; NRC 2003). More direct evaluations of toxicity reduction include the survival and growth of soil biota (e.g. earthworms) in treated versus untreated soil, the use of plant bioassays as a measure of metal phytoavailability in soil, and the development of methods for using microorganism assays and biomarkers as monitoring tools in the field. Alternative assessment metrics are important for the acceptance and evaluation of mineral amendments as a remediation option.

Another potential barrier to the use of mineral amendments for soil remediation is the overall cost of treatment relative to other methods that provide similar risk reduction. Expenses for mineral-based remediation vary widely depending on the site, contaminants, and ex situ versus in situ treatment. The cost of ex situ treatment of excavated soils depends on the processing rate and volume of soil treated. For example, in the United States, the cost typically ranges from US\$90 to \$190 per cubic meter (m<sup>3</sup>). In situ treatment using auger-based equipment ranges from US\$50/m<sup>3</sup> for shallow contamination to more than US\$300/m<sup>3</sup> for deeper applications (US EPA 2009). When selecting an appropriate remedy for a particular site, the estimated cost for in situ treatment is compared with that of more traditional methods, such as excavation and off-site disposal. The long-term effectiveness and permanence of risk reduction are also factored into the selection process.

## SUMMARY AND OUTLOOK

Remediation approaches need not be restricted to a “one-size-fits-all” methodology in which convenient or inexpensive amendment materials are used regardless of whether the treatment is compatible with the environmental characteristics of a particular site. Rather, remediation strategies can and should be tailored to site-specific biogeochemical and hydrologic factors where existing conditions can modify or enhance the remediation method. Although the effectiveness of mineral amendments in reducing contaminant

mobility has been demonstrated in many instances by operational tests, detailed knowledge of sequestration mechanisms is still lacking, particularly over timescales of years to decades. Better understanding of the chemical and physical controls on contaminant immobilization, together with a framework for site assessment, would aid in selecting amendments that are compatible with, and optimized for, a specific site. Because many amendment technologies were originally developed for the treatment of waste streams before disposal, it can be a challenge to adapt them for in situ treatment of soils and sediments where contaminants have already been released to the environment and where the goal is to limit further dispersal and exposure to humans or biota. Amendment stabilization technologies are particularly useful when combined with conventional methods, such as source-area removal, pump-and-treat, or vapor extraction, or with other in situ technologies, such as bioremediation, phytoremediation, reactive barriers, capping, or monitored natural attenuation in an overall risk-management approach. Better knowledge of contaminant sequestration mechanisms would improve confidence in the use of mineral-based amendments for soil remediation and promote the use of reprocessed and recycled materials as amendments, thereby making this technology more sustainable and economically competitive.

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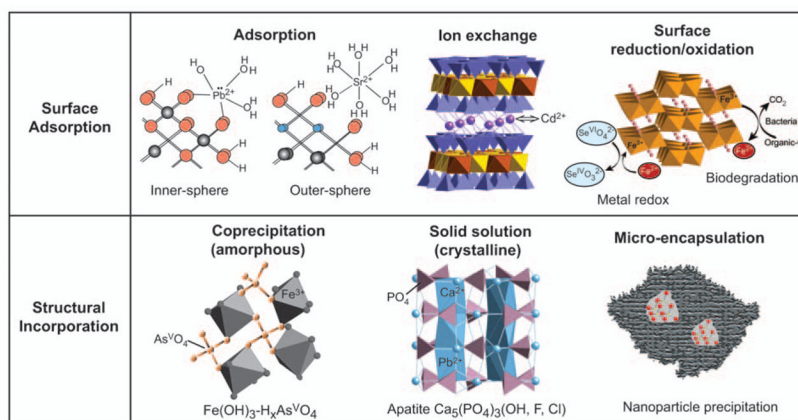
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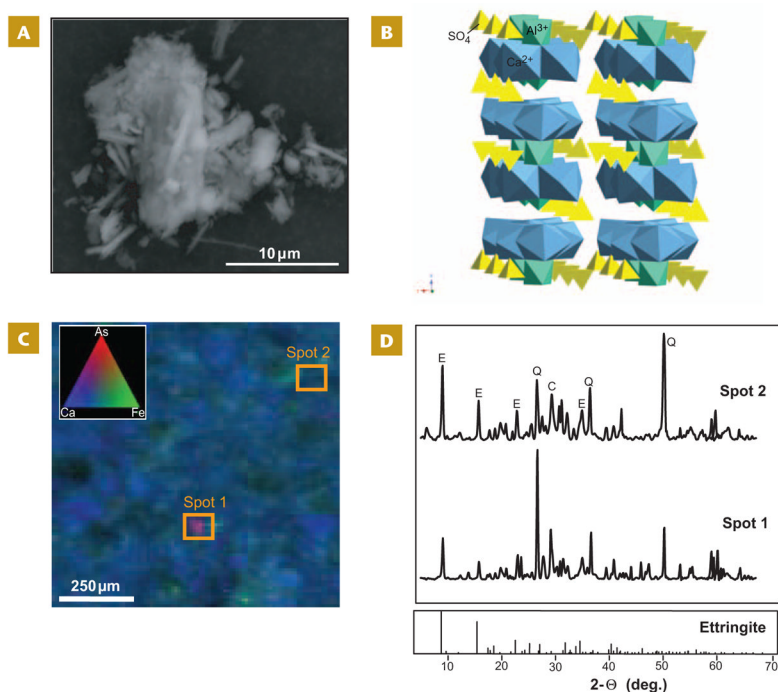
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**Figure 1.** Conceptual models of molecular-scale sequestration mechanisms for representative contaminants and mineral-based amendments. In surface adsorption, “inner-sphere” refers to direct bonding of an ion to atoms on the mineral surface, whereas “outer-sphere” indicates the presence of water or hydroxyl ligands between the metal center and the surface. Ion exchange is typically associated with the exchange of cations in clay mineral interlayers with species in solution. Surface reduction-oxidation processes may involve either microbial biodegradation of organic compounds coupled to mineral reduction, or the oxidation (or reduction) of adsorbed inorganic contaminants. Structural incorporation of contaminants by the precipitation of new phases may involve the formation of either amorphous or crystalline solids and contaminant substitution, or the encapsulation of micro- or nano-scale precipitates containing contaminants into new phases.



**Figure 2.** Formation of ettringite in arsenic-contaminated soil samples amended with a mixture of Portland cement and  $\text{FeSO}_4$ . **(A)** Scanning electron micrograph of ettringite needles in amended soils in laboratory batch experiments. **(B)** Polyhedral model of the ettringite structure,  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$  (hydrogen atoms not shown). **(C)** Synchrotron X-ray fluorescence microprobe map for elemental arsenic, calcium, and iron in a field soil sample that was treated with Portland cement and  $\text{FeSO}_4(\text{s})$  about 10 years before sample retrieval (the sample was impregnated with epoxy and made into a thin section for analysis; spot size  $\sim 2 \mu\text{m}$ ). Spots 1 and 2 with high arsenic concentrations were probed by X-ray microdiffraction **(D)**, which showed diffraction lines for ettringite (E), calcite (C), and detrital quartz (Q).



**Figure 3.** Amendment application by soil mixing using large-scale augers at an arsenic-contaminated site. A sulfate–cement slurry is injected as the augers are advanced into the soil, thoroughly mixing the amendments with the contaminated soil. Photos Courtesy of S.S. Papadopoulos and Associates

Table 1

## SUMMARY OF MINERAL-BASED AND RELATED AMENDMENTS

Amendment Type	Source Material	Primary Contaminant-Stabilization Mechanism <sup>1</sup>	Comments
Clay minerals	<i>Layered aluminosilicates:</i> montmorillonite (bentonite deposits), vermiculite	Adsorption/ion exchange	Natural expandable clays; used in geosynthetic sorptive mats
Zeolites	<i>Framework aluminosilicates:</i> natural (clinoptilolite) and synthesized from coal fly ash	Adsorption/ion exchange	High-surface-area ion exchange; also mixed with cement
Carbon	Activated carbon [C], charcoal	Adsorption	Very high surface area; most effective for organic compounds
Silica	<i>Soluble alkali silicate salts:</i> sodium metasilicate [Na <sub>2</sub> SiO <sub>3</sub> ·xH <sub>2</sub> O]	Adsorption, encapsulation	Forms amorphous silica or silica gel on aging; also used for permeability reduction
Phosphates	<i>Solids:</i> natural and synthetic apatite-group minerals [Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> X, X = F, Cl, OH] <i>Soluble phosphate:</i> phosphoric acid [H <sub>3</sub> (PO <sub>4</sub> )]; sodium, potassium, ammonium phosphate [Na <sub>2</sub> HPO <sub>4</sub> , K <sub>2</sub> HPO <sub>4</sub> , (NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> ]	Solid solution	Solid sources include natural rock, bone meal, fertilizers
Carbonates	Calcite [CaCO <sub>3</sub> ], dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ], magnesite [MgCO <sub>3</sub> ], siderite [FeCO <sub>3</sub> ], soda ash [Na <sub>2</sub> CO <sub>3</sub> ·xH <sub>2</sub> O]	Solid solution	Acid neutralization, pH buffering
Sulfates	Gypsum [CaSO <sub>4</sub> ·2H <sub>2</sub> O], ferrous sulfate [FeSO <sub>4</sub> ·xH <sub>2</sub> O], aluminum sulfate [Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O]	Solid solution	Potential formation of ettringite-type phases; also used for permeability reduction
Iron-based	Zero-valent iron (Fe <sup>0</sup> ), iron(III) oxides	Adsorption, solid solution	Potential for oxidation state changes
Lime	Lime [CaO], portlandite [Ca(OH) <sub>2</sub> ]	Adsorption, solid solution	Highly soluble; produces alkaline pH and variable reaction products
Portland-type cements	Mixture of high-temperature calcium silicates [Ca <sub>3</sub> SiO <sub>5</sub> , Ca <sub>2</sub> SiO <sub>4</sub> ], calcium aluminate [Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> ], calcium aluminoferrite [Ca <sub>2</sub> AlFeO <sub>5</sub> ] with Mg, Na, K substitution	Solid solution, encapsulation	Highly reactive with water; products are mixtures of hydrated CaO–Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub> phases
Residual and by-product materials	Coal fly ash [35% SiO <sub>2</sub> , 20% Al <sub>2</sub> O <sub>3</sub> , 6% Fe <sub>2</sub> O <sub>3</sub> , 5–15% CaO, 0–5% MgO, 0–5% SO <sub>3</sub> ] <sup>2</sup> Blast furnace slag [30–40% SiO <sub>2</sub> , 5–30% Al <sub>2</sub> O <sub>3</sub> , 30–50% CaO, 0–20%, MgO] <sup>3</sup> Bauxite mine residuals, “red mud” (Fe- and Al-oxides); wastewater treatment residuals (Al, Fe-hydroxides)	Adsorption, solid solution, encapsulation	Amorphous and (micro)crystalline phases, variable compositions; commonly mixed with other amendment material

<sup>1</sup> See Figure 1.



<sup>2</sup>Typical values for Class C and Class F fly ash from Conner (1990)

<sup>3</sup>Typical ranges from Taylor (1997)