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Revision Memo

- 03/04** Highlights of these revisions are:
1. Additional definitions.
 2. Discussion (and Tables 6 and 7) of applications of S/S technologies at USA Superfund sites.
 3. Additional references.



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SCOPE

This section describes the solidification and stabilization (S/S) of contaminated soils and wastes. The technology is important for rendering wastes non-hazardous (including delisting hazardous wastes prior to land disposal in the United States) and for remediation of contaminated soils. Information is provided to help assess the technology's potential role in managing hazardous wastes and remediating contaminated sites. General background and information are provided for the selection, use, and evaluation of solidification and stabilization technologies.

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BACKGROUND

Solidification and stabilization (S/S) involves adding stabilizing agents and/or solidifying binders, such as cement, lime, and organic polymers, to contaminated soil or waste. Treatment of contaminated soils can be performed in situ or ex situ. In traditional S/S processes, hazardous contaminants are physically and chemically immobilized rather than destroyed. The final product of an S/S treatment process is a soil-like or solid material that is less hazardous and more stable than the original material under expected environmental conditions.

S/S has been successfully demonstrated on soils and wastes that contain metals, acids, alkalis, organics, hydrocarbons, and oil, even when constituent concentrations vary widely. S/S is well suited for soils and wastes containing high concentrations of metals that are not amenable to thermal or biological oxidation. Occasionally pretreatment is required (e.g., neutralization, oxidation/reduction, chemical sorption, and dewatering) to achieve regulatory limits. Enhanced treatment can also be obtained through the use of additives such as flyash, soluble silicates, clay, activated carbon, and ion exchange resins.

While the broad objective of S/S is to protect the environment, particularly groundwater or surface water, from released pollutants, the main purposes for using S/S processes are to:

- Stop migration of contaminants (leaching) by reducing the solubility of hazardous constituents and the surface area across which transfer occurs.
- Strengthen or solidify sludges in situ so that they can be capped and managed in place ("chemical dewatering").
- Improve the physical properties of soil or waste so that it may be easily excavated and transported to a secure landfill.
- Delist hazardous wastes, since thermal and biological treatment cannot destroy metals (In the U.S. only).

Within the Exxon circuit, a common use of S/S is site closures of inactive impoundments and lagoons (e.g., Singapore Aromatics, Baton Rouge Refinery, Bayway Refinery, and Montreal Refinery). Onsite treatment and closure also minimizes liability by maintaining control over the entire operation, and it eliminates transportation and disposal costs at multi-user facilities.



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DEFINITIONS

Accelerator

Any substance which increases the setting/curing rate of solidifying reagent, resulting in a hastened set. In cement- and lime-based S/S processes, accelerators increase the rate of hydration. Accelerators can be beneficial or disruptive to the S/S process.

Absorption

Refers to bulk uptake of liquid by a solid. Absorption alone is not an acceptable means of S/S treatment. Solidification must also occur.

Adsorption

Refers to surface retention of solid, liquid, or gas molecules, atoms, or ions. Adsorption is due to imbalance of charges at a surface.

Binders

Binder systems can be placed into broad categories: inorganic or organic. Most inorganic binding systems include varying combinations of hydraulic cements, lime, pozzolan, gypsum, and silicates. Organic binders include epoxy, polyesters, asphalt/bitumen, polyethylene, polyethylene-polybutadiene, and urea-formaldehyde.

Chelating Agent

An organic compound that bonds with metal ions at two or more sites, resulting in increased solubility of the metal. Chelating agents generally decreases the effectiveness of the S/S process for metals.

Cone Index

The force per unit basal area required to push a cone penetrometer through a specified increment of soil. Cone Penetrometer

Cone Penetrometer

An instrument in the form of a cylindrical rod with a cone-shaped tip designed for penetrating soil and for measuring the end-bearing component of penetration resistance. The resistance to penetration developed by the cone equals the vertical force applied to the cone divided by its horizontally projected area.

Dispersant

Any substance that serves to dissipate grains of a solidifying agent. This process is vital to successful growth of hydrated cement- or lime-based structures. Dispersants are beneficial to most S/S processes.

Encapsulation

Refers to the physical isolation of hazardous constituents from the environment by a very low permeability matrix. It can be categorized roughly by the scale of the process:

Microencapsulation

The encapsulation of individual particles.

Macroencapsulation

The encapsulation of an agglomeration of soil or waste particles or microencapsulated materials.

Flocculent

Any substance that prevents the dispersion of grains of a solidifying reagent. Dispersion is a vital process for successful growth of hydrated cement- or lime-based structures. Flocculents are generally disruptive to S/S processes.

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Hydration

The incorporation of molecular water and the molecules or units of another species into a complex molecule.

Land Disposal

Means placement in or on the land and includes, but is not limited to, placement in a landfill, surface impoundment, waste pile, injection well, land treatment facility, salt dome formation, salt bed formation, underground mine or cave, or placement in a concrete vault or bunker intended for disposal purposes.

Leaching

The process whereby a liquid agent will dissolve hazardous materials within a waste mass and transport these materials through the mass and beyond. Leachant is the water that does the leaching, while the contaminated water that leaves the waste is the leachate.

Matrix Disrupter

Any substance that prevents a desirable lattice of an S/S binding reagents from forming.

Pozzolan

Any pulverized substance (typically siliceous and/or aluminous) that reacts chemically with slaked lime at ordinary temperature and in the presence of moisture to form a cementitious compound.

Retarder

Any substance that decreases the setting/curing rate of solidifying reagent resulting in a delayed set. In cement- and lime-based S/S processes retarders reduce the rate of hydration. Retarders can be beneficial or disruptive to the S/S process.

Set

The hardening or solidifying of a plastic or liquid substance.

Solidification

Is the process of producing a soil-like material having some integrity from liquid, sludge, or loose solids. Occasionally, solidification may refer to the process that results in a monolithic structure rather than a soil-like material. Solidification does not necessarily chemically bond hazardous materials. However, when a waste is solidified, its mass and structure are altered, decreasing migration of solutions within the mass.

Sorption

A collective term that refers to the combined effects of absorption and adsorption.

Stabilization

Refers to a beneficial chemical reaction that makes waste constituents less leachable. Stabilization may or may not result in improvements to the physical characteristics of the waste. The terms fixation and chemical fixation are often used synonymously with stabilization.

Treatment

Any method of modifying the chemical, biological, and/or physical characteristics or composition of a waste.

Wetting Agent

A substance that renders a surface non-repellent to a wetting liquid. In the context of oils and grease, it is a substance that emulsifies the hydrocarbons, which can coat particles preventing necessary hydration reactions from occurring. Wetting agents are generally beneficial to S/S processes.

SOLIDIFICATION / STABILIZATION MECHANISMS

This section attempts to consider some of the important mechanisms, which contribute to successful solidification and stabilization, on an individual basis. It should be understood that actual S/S systems are extremely complex and multiple mechanisms will be acting at any one time. Multiple mechanisms may exist in a beneficial manner or they can serve to counteract one another.

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INORGANICS

In most S/S treatment process, metals are the primary inorganics of concern. While more is known about S/S treatment of metals than any other hazardous constituent, successful S/S of metals can be difficult because they can exist as complexes and they can have variable oxidation states.

In general, successful solidification and stabilization of metals involve:

1. Controlling the pH (typically excess acidity).
2. Destroying metal complexes.
3. Controlling the oxidation state as needed.
4. Converting to insoluble species.
5. Solidifying the material.

Controlling the pH is perhaps the easiest and most common technique used for S/S treatment of metals. It is well known that the solubility of metals in S/S systems is a function of the pH ([Figure 1](#)). The pH dependence is related primarily to the formation of metal hydroxides. In general, a high pH (7.5 - 11) is desirable since most metal hydroxides have a minimum solubility. Any alkali can be used for the purpose of pH control, but the most common are lime (CaO or Ca(OH)_2), soda ash (sodium carbonate, Na_2CO_3), and sodium hydroxide (NaOH).

Another technique used for S/S treatment of metals is control of the redox potential. Oxidizing and reducing agents can be used to convert metals to more desirable valence states. The converted metal species are generally less toxic than the unconverted metal and will form insoluble species more readily. Some of the more common reducing agents used in S/S systems include ferrous sulfate, sulfides, sodium metabisulfite/bisulfite, sodium hydrosulfite, and sodium borohydride.

Ferrous sulfate is probably the most widely used reducing agent. Ferrous sulfate can safely and effectively reduce certain metal species to a lower valence state that can then readily form metal hydroxides. Unfortunately, the use of ferrous sulfates can result in large volume increases and the reduction process must be conducted under acidic conditions ($\text{pH} < 3$) to achieve reasonable treatment times. The low pH is not conducive to cement- and lime-based treatment processes.

Sulfides have also been used extensively as reducing agents because of their ability to form extremely insoluble metal sulfides. The formation of metal sulfides is advantageous over the formation of metal hydroxides for several reasons. Metal sulfides are typically several orders of magnitude less soluble than metal hydroxides ([Figure 1](#)). In addition, the solubility of metal sulfides is considerably less sensitive to changes in pH.

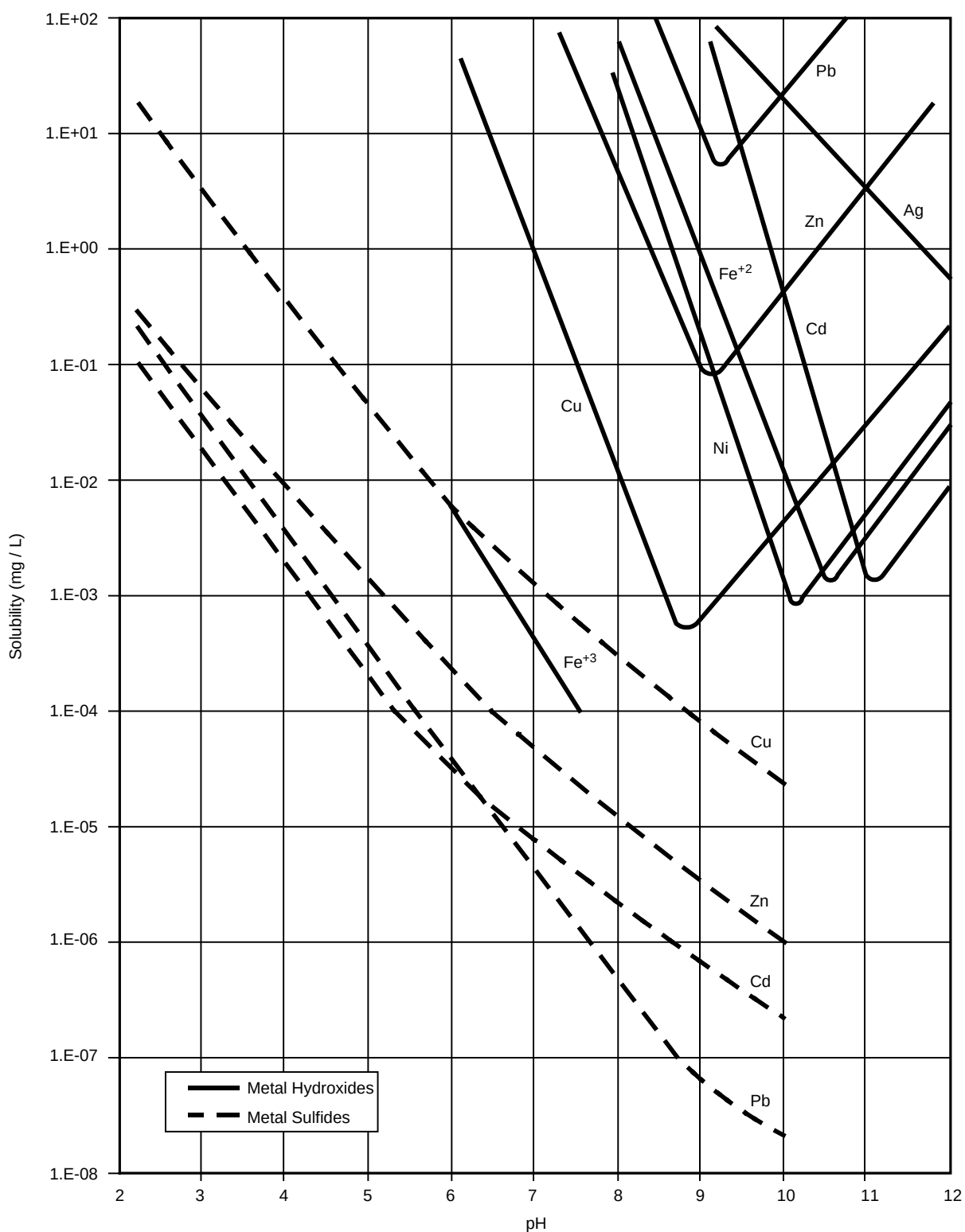
In cement-based systems, silicate precipitation has also been identified as an important mechanism. Calcium silicate hydrate, a compound that constitutes approximately 75% of cement, has been shown to react with some metal ions to form insoluble metallic calcium silicate hydrates.

It should be noted that the solubility curves shown in [Figure 1](#) were determined in a laboratory setting, and may not be representative of field conditions. S/S systems may have other soluble species that can alter the actual solubilities of the metals. Since all metals do not reach minimum solubility at the same pH, the optimum pH of an S/S system with multiple metal constituents will be a compromise.

The resulting metal precipitates are solids that can be easily solidified and are relatively stable under most environmental conditions. A concern exists in acidic environments where the buffering action of an alkali S/S system may be overcome. In the event that acidic conditions prevail in an S/S product, previously insoluble species may be resolubilized, which can then be leached into the environment. This is a common problem with wastewater plant metal-hydroxide sludges where pH is adjusted to achieve minimum solubility of the metals, thus precipitating them and allowing discharge of a clear water phase of the waste stream. The sludge, then, as it is fed into the system is essentially nonleachable. However, under acidic or specific alkaline conditions, these metals may be resolubilized.

Sorption and ion exchange may also play minor roles in the treatment of metals with traditional S/S systems. There is also evidence that some metallic compounds may be incorporated into the crystalline matrix of the solidified S/S reagent.

Figure 1 - The Dependency of Metal Hydroxides and Metal Sulfides Solubility on PH



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Adapted from: EPA Federal Register 52(155):29999⁽⁸⁾

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ORGANICS

While S/S processes can handle a wide variety of soils and wastes, S/S treatment of organic constituents remains a controversial issue. In general, organics are not as reactive as inorganics. Therefore, organics are typically immobilized by physical mechanisms (encapsulation) rather than through chemical reactions. In some instances, successful S/S of organic constituents will be limited by the ability of the final product to maintain its structural integrity.

In addition to the non-reactive nature of organic constituents, many organic compounds interfere with the S/S treatment process. Oil and grease can coat S/S reagents preventing important reactions such as hydration from occurring. Other organics can serve as flocculating agents, thus destroying the dispersion of binding agents, a necessary process for successful matrix formation.

Another problem encountered with organics is volatilization. The agitation of the soil or waste alone often enhances the rate of volatilization. Furthermore, when cement- and lime-based reagents react with water, heat is given off during the hydrolysis reactions. This heat can be significant, resulting in temporary volatilization of semi-volatile and non-volatile organic compounds. The use of retarding agents and slow setting cements can dissipate this heat release and minimize volatilization.

In addition to physical encapsulation, the following mechanisms contribute to successful S/S of organic constituents:

Sorption - Many S/S treatment processes use additives such as flyash, activated carbon, or clays to adsorb and absorb organics contaminants. In general, sorbents are not suitable for high concentrations of organics, because the large amount of sorbent required makes the process economically unfeasible. Furthermore, bonding mechanisms (hydrogen bonds and Van der Waals forces) that are responsible for sorption processes are relatively weak, and can be easily reversed if pH changes or temperature increases.

Hydrolysis - Some organic compounds will react with water under specific conditions to form less toxic or less soluble species. Hydrolysis reactions involving organic compounds are typically catalyzed by basic conditions.

Oxidation - Some organic compounds can be oxidized, resulting in a net decrease of electrons, through natural oxidants or deliberately introduced oxidants such as potassium permanganate, hydrogen peroxide, or ozone. While oxidation reactions are capable of completely destroying some organics, incomplete reactions can sometimes form more hazardous intermediate compounds. Thus, when using oxidants with organic compounds the products of the reaction must be well characterized. Oxidation can also be used to control formation and liberation of hydrogen sulfide (H₂S).

Salt Formation - Many organic acids will readily react with metal ions or other cationic species to form salts that are considerably less soluble than the parent acid. In some situations, organic contaminants can be oxidized to organic acids and then converted to insoluble salts.

SOLIDIFICATION / STABILIZATION PROCESS SELECTION

GENERAL APPROACH

Each S/S project has some combination of product requirements, treatment objectives, and physical, mechanical, and economical considerations that makes it unique. A general approach consisting of four basic steps can be used to select an S/S process:

1. Define the problem and collect data on the important design parameters and project considerations.
2. Analyze the data and compare with past experiences (Note: Some vendors use a computerized "expert system," along with personal experience and knowledge).
3. Conduct and refine laboratory treatability studies using test formulations and actual soil or waste samples (typically 1-5 gallons).
4. Interact with local regulatory agencies, particularly early in the planning and design phases, to obtain approval.

In applications within EXXONMOBIL, the first three steps will most likely be done with vendors. Therefore, vendor selection is key to successful implementation of an S/S system. In determining the technical and economical feasibility of an S/S system, consider the treatment objective, chemical and physical characteristics of the soil or waste, binders, and additives, processing requirements, regulatory requirements, and economics. Site specific factors, such as location conditions, climate, and hydrogeology are also relevant in assuring acceptable performance. The vendor must prove the mechanical and leachate performance of the product. Note that:

- Soils and wastes with an organic concentration greater than 10% are difficult to treat because certain organics may interfere with the hydration of cement- and lime-based stabilizer. However, techniques have been developed for successful S/S of non-hazardous oily soils and wastes (< 25% oil).
- In the U.S., landban regulations prohibit S/S treatment of soil or waste with a hazardous organic content greater than 1% when they are removed from the site. In situ treatment may still be possible.