TREATMENT TECHNOLOGY BACKGROUND DOCUMENT

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4. STABILIZATION OF METALS

4.1 Applicability

Stabilization is a treatment technology applicable to wastes containing leachable metals and having a high filterable solids content, low total organic carbon (TOC) content, and low oil and grease content. This technology is commonly used to treat residuals generated from treatment of wastes such as electroplating wastewaters, incineration ash residues, and characteristic D-metal wastes such as cadmium (D006), chromium (D007), lead (D008), and mercury (D009). For wastes with recoverable levels of metals, high temperature metals recovery and retorting technologies may be applicable.

Stabilization refers to a broad class of treatment processes that immobilize hazardous constituents in a waste. Related technologies are encapsulation and thermoplastic binding. However, EPA considers stabilization technologies to be distinct from the other technologies in that their operational principles are significantly different. Stabilization typically requires a chemical reaction between the waste and the stabilizing agent for effective treatment, while thermoplastic binding and encapsulation usually employ physical containment of hazardous particulates by the encapsulating agent.

4.2 Underlying Principles of Operation

The basic principle of operation for stabilization is that leachable metals in a waste are immobilized following the addition of stabilizing agents and other chemicals. The leachability is reduced by the formation of a lattice structure and/or chemical bonds that chemically bind the metals to the solid matrix and thereby limit the amount of metal constituents that can be leached when water or a mild acid solution comes into contact with the waste material. Stabilization is most effective when the waste metal is in its least soluble state, thereby decreasing the potential for leaching. For example, hexavalent chromium is much more soluble and more difficult to stabilize than trivalent chromium.

The two principal stabilization processes used are cement-based and lime/pozzolan-based processes. A brief discussion of each is provided below. In both cement-based and lime/pozzolan-based techniques, the stabilizing process can be modified through the use of additives, such as silicates, that control curing rates, reduce permeability, and enhance the properties of the solid material.

4.2.1 Portland Cement-Based Process

Portland cement is a mixture of powdered oxides of calcium, silica, aluminum, and iron, produced by kiln burning of materials rich in calcium and silica at high temperatures (i.e., 1,400 to 1,500°C (2,552 to 2,732°F)). When the anhydrous cement powder is mixed with water, hydration occurs and the cement begins to set. The chemistry involved is complex because many different reactions occur depending on the composition of the cement mixture.

As the cement begins to set, a colloidal gel of indefinite composition and structure is formed. Over time, the gel swells and forms a matrix composed of interlacing, thin, densely packed silicate fibrils. Constituents present in the waste slurry (e.g., hydroxides and carbonates of various metals) are incorporated into the interstices of the cement matrix. The high pH of the cement mixture tends to keep metals in the form of insoluble hydroxide and carbonate salts. It has been hypothesized that metal ions may also be incorporated into the crystal structure of the cement matrix, but this hypothesis has not been verified.

4.2.2 Lime/Pozzolan-Based Process

Pozzolan, which contains finely divided, noncrystalline silica (e.g., fly ash or components of cement kiln dust), is a material that is not cementitious in itself, but becomes so upon the addition of lime. Metals in the waste are converted to insoluble silicates or hydroxides and are incorporated into the interstices of the binder matrix, thereby inhibiting leaching.

4.3 Description of Stabilization Process

The stabilization process consists of a weighing device, a mixing unit, and a curing vessel or pad. Commercial concrete mixing and handling equipment is typically used in stabilization processes. Weighing conveyors, metering cement hoppers, and mixers similar to concrete batching plants have been adapted in some operations. When extremely dangerous materials are treated, remote-control and in-drum mixing equipment, such as that used with nuclear waste, is employed.

In most stabilization processes, the waste, stabilizing agent, and other additives, if used, are mixed in a mixing vessel and then transferred to a curing vessel or pad and allowed to cure. The actual operation (equipment requirements and process sequencing) depends on several factors including the nature of the waste, the quantity of the waste, the location of the waste in relation to the disposal site, the particular stabilization formulation used, and the curing rate. Following curing, the stabilized solid formed is recovered from the processing equipment and disposed of.

4.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether stabilization will achieve the same level of performance on an untested waste that it achieved on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration of fine particulates, (b) the concentration of oil and grease, (c) the concentration of organic compounds, (d) the concentration of sulfate and chloride compounds, and (e) the solubility of the metal compound.

4.4.1 Concentration of Fine Particulates

For both cement-based and lime/pozzolan-based processes, very fine solid materials (i.e., those that pass through a No. 200 mesh sieve (less than 74 μm particle size)) weaken the bonding between waste particles and the cement or

lime/pozzolan binder by coating the particles. This coating inhibits chemical bond formation, thereby decreasing the resistance of the material to leaching. If the concentration of fine particulates in an untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Pretreatment of the waste may be required to reduce the fine particulate concentration and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

4.4.2 Concentration of Oil and Grease

Oil and grease in both cement-based and lime/pozzolan-based systems result in the coating of waste particles and the weakening of the bond between the particle and the stabilizing agent, thereby decreasing the resistance of the material to leaching. If the concentration of oil and grease in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Pretreatment may be required to reduce the oil and grease concentration and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

4.4.3 Concentration of Organic Compounds

Organic compounds in the waste interfere with the stabilization chemical reactions and bond formation, thus inhibiting curing of the stabilized material. This interference results in a stabilized waste having decreased resistance to leaching. If the total organic carbon (TOC) content of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. Pretreatment may be required to reduce the TOC and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

4.4.4 Concentration of Sulfate and Chloride Compounds

Sulfate and chloride compounds interfere with the stabilization chemical reactions, weakening bond strength and prolonging setting and curing time. Sulfate and chloride compounds may reduce the dimensional stability of the cured matrix, thereby increasing leachability potential. If the concentration of sulfate and chloride compounds in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Pretreatment may be required to reduce the sulfate and chloride concentrations and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

4.4.5 Solubility of the Metal Compound

The metal to be stabilized should be in its least soluble state, or the stabilized waste may exhibit a potential for increased leachability. Pretreatment may be required to chemically reduce or oxidize the metal to a lower solubility state and achieve maximum stabilization performance. For example, hexavalent chromium is much more soluble and more difficult to stabilize than trivalent chromium.

4.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a stabilization system, EPA examines the following parameters: (a) the amount and type of stabilizing agent and additives, (b) the degree of mixing, (c) the residence time, (d) the stabilization temperature and humidity, and (e) the form of the metal compound.

4.5.1 Amount and Type of Stabilizing Agent and Additives

The stabilizing agent and additives used will determine the chemistry and structure of the stabilized material and therefore its leachability. Stabilizing

agents and additives must be carefully selected based on the chemical and physical characteristics of the waste to be stabilized. To select the most effective type of stabilizing agent and additives, the waste should be tested in the laboratory with a variety of these materials to determine the best combination.

The amount of stabilizing agent and additives is a critical parameter in that sufficient stabilizing materials are necessary to properly bind the waste constituents of concern, making them less susceptible to leaching. The appropriate weight ratios of stabilizing agent and additives to waste are established empirically by setting up a series of laboratory tests that allow separate leachate testing of different mix ratios. The ratio of water to stabilizing agent (including water in waste) will also impact the strength and leaching characteristics of the stabilized material. Too much water will cause low strength; too little will make mixing difficult and, more important, may not allow the chemical reactions that bind the hazardous constituents to be fully completed. EPA evaluates the amount of stabilizing agent, water, and other additives used in the stabilization process to ensure that sufficient stabilizing materials are added to the waste to effectively immobilize the waste constituents of concern.

4.5.2 Degree of Mixing

Mixing is necessary to ensure homogeneous distribution of the waste, stabilizing agent, and additives. Both undermixing and overmixing are undesirable. The first condition results in a nonhomogeneous mixture; consequently, areas will exist within the waste where waste particles are neither chemically bonded to the stabilizing agent nor physically held within the lattice structure. Overmixing, on the other hand, may inhibit gel formation and ion adsorption in some stabilization systems. Optimal mixing conditions are usually determined through laboratory tests. The quantifiable degree of mixing is a complex assessment that includes, among other factors, the amount of energy supplied, the length of time the material is mixed, and the related turbulence

effects of the specific size and shape of the mix tank or vessel. The degree of mixing is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve homogeneous distribution of the waste, stabilizing agent, and additives.

4.5.3 Residence Time

The residence time or duration of curing ensures that the waste particles have had sufficient time in which to incorporate into lattice structures and/or form stable chemical bonds. The time necessary for complete stabilization depends on the waste and the stabilization process used. The performance of the stabilized waste (i.e., the levels of waste constituents in the leachate) will be highly dependent on whether complete stabilization has occurred. Typical residence times range from 7 to 28 days. EPA monitors the residence time to ensure that sufficient time is provided to effectively stabilize the waste.

4.5.4 Stabilization Temperature and Humidity

Higher temperatures and lower humidity increase the rate of curing by increasing the rate of evaporation of water from the stabilization mixtures. If temperatures are too high, however, the evaporation rate can be excessive, resulting in too little water being available for completion of the stabilization reaction. EPA monitors the stabilization temperature and humidity continuously, if possible, to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

4.5.5 Form of the Metal Compound

Ideally, the waste metal to be stabilized should be in its least soluble state to reduce leaching of the stabilized waste. Pretreatment such as chemical oxidation or chemical reduction may be required to oxidize or reduce the metal to a state of lower solubility. Additionally, the solubility of the metal can

be decreased by precipitating it with an appropriate compound. For example, ferric arsenate is less soluble and less leachable than calcium arsenate. EPA can monitor solubility of the metal by performing a standard leaching test (Extraction Procedure (EP) or Toxicity Characteristic Leaching Procedure (TCLP)).