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EPA Project Summary

Interference Mechanisms in Waste Stabilization/Solidification Processes

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The stabilization/solidification (S/S) of hazardous wastes involves a series of chemical treatment procedures. The wastes are normally treated to complex or to bind the toxic elements into a stable, insoluble form (stabilization) or to entrap the waste material in a solid and/or crystalline matrix (solidi-fication). Hazardous wastes contain many constituents that can interfere with the binding/trapping process. Possible interference mechanisms between particular waste com-ponents and commercially available, waste binding systems should be identified.

The complete report presents background information and a literature review covering portland cement and pozzolan chemistry, the effects of admixtures on concrete setting characteristics, and the effects of common organic waste components on the physical and containment properties of the final treated waste product. These topics are presented so that conclusions may be drawn as to possible types of interferences that may be encountered in typical waste binder systems. A glossary of common cement terminology and three bibliographic appendices covering a compilation of references and annotated citations for both portland cement and asphaltic waste treatment systems are also presented.

This Project Summary was developed by U.S. EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Waste treatment processes that are designed to reduce the toxicity or volume of hazardous wastes (e.g., precipitation or incineration) usually generate persistent

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residues that must be prepared for safe final or ultimate disposal. In most cases, this final disposal is by means of secure, shallow land burial. The disposal problem is most critical in the case of wastes that cannot be destroyed or detoxified, such as heavy metal sludges and brines. Thus, even with new and improved waste treatment methods, there will continue to be a need for technology related to the safe land disposal of toxic wastes. S/S of hazardous wastes before final disposal has been proposed as a method to prevent release of the hazardous waste constituents to the environment.

A thorough understanding of the potential behavior of stabilized/solidified waste is necessary to make judgments about the long-term effectiveness of their containment. The extent to which various contaminants are held securely in stabilized/solidified wastes must be determined for all S/S processes so that individual processes and delisting petitions can be evaluated. There are several available methods for the S/S of hazardous wastes. Some of the chemical components of the complex wastes may interfere with the proposed S/S process and cause undesired results (e.g., flash set, set retardation, spalling, etc.).

Literature

The literature search was conducted with the use of facilities available at the U.S. Army Engineer Waterways Experiment Station (WES). The *Compendex Data Base, National Technology Information Service Data Base,* and *Technical Research Information Service Data Base* were used for two computer searches. Additional computer searches used the Data Base Index (DBI), Chemical Abstracts Data Base, Engineering Information and Technical Meetings Data Base (EIMET), Environment Abstracts Data Based (ENVIROLINE), Electric Power Information Abstracts Data Base (EPIA), and Geological References Data Base (GEOREF) of the American Geological Institute. Three bibliographies developed through these procedures are included in the report as appendices.

Cement and Pozzolan PropertiesThat May Affect Waste Containment

The ability of a stabilized/solidified waste product to retain/contain a given hazardous constituent depends primarily on its resistance to leaching (or volatilization) of waste constituents and on its long-term durability. Some background is necessary to understand factors controlling leaching and durability characteristics of cement and pozzolans.

Portland Cement

Comparison of the finished stabilized/solidified waste product with standard construction materials is not entirely accurate since most hazardous wastes to be stabilized/solidified are liquid slurries with relatively low solids content (10% to 40% solids by weight). The mixture of a solidification agent such as portland cement with a slurried waste more closely resembles a hydrated cement paste rather than a typical concrete with a large proportion of solid aggregate (60% to 80% of the final cement volume).

Voids in Hydrated Cement and Concrete

The several kinds of voids in hydrated cement paste greatly influence its final strength, durability, and permeability properties. The smallest voids, which occur within the calcium-silicate-hydrate gel structure, are 0.5 to 2.5 nm. They account for around 28% of the porosity of the solid product. These small voids have little effect on the strength and permeability of the final product but appear to be important in drying shrinkage and creep.

Capillary voids account for the larger spaces not filled by solid components. In well-hydrated, low water/cement ratio mixes, capillary voids range from 10 to

50 nm, but in high-ratio mixes they may be as large as 3000 to 5000 nm. Pore size distribution and not simply total capillary porosity is generally held to be a better criterion for evaluating the characteristic of a cementitious product; capillary voids larger than about 50 nm are thought to be detrimental to strength and impermeability, whereas, voids smaller than 50 nm are more important to drying shrinkage and creep. Capillary voids limit the strength of concrete by acting as "stress concentrators."

The third type of void, usually called "air void," is generally spherical and usually ranges from 0.05 to 0.2 mm but may range up to 3 mm. Air voids in this size range are usually introduced intentionally into the cement mixture to increase the resistance of the final product to freeze-thaw (frost) damage, even though they typically have an adverse affect on strength and impermeability.

Pozzolanic Materials

By definition, pozzolans are siliceous materials that display no cementing actions by themselves but that contain constituents that combine with lime at ordinary temperatures and in the presence of water to form cementitious compounds. The main pozzolans used commercially, at present, are fly ash from burning of powdered coal, ground blast furnace slag, and kiln dusts from lime or cement kilns. Although pozzolanic reactions are not identical to portland cement reactions, they are thought to resemble them. Pozzolanic reactions are generally much slower than portland cement reactions, and set-times are usually measured in days or weeks instead of hours. Caution must also be exercised concerning additional contaminants introduced through these waste byproducts.

The Strength/Porosity Relationship

Many factors may influence the strength of a waste-cement mass. By far the most important factor in strength of cement is the relationship between the water/cement ratio and porosity. The relationship is usually explained as a natural consequence: the weakening of the cement matrix caused by porosity increases as the water/cement ratio increases, and thus, the cement is weakened.

Water/Cement Ratio and Degree of Hydration

This relationship between concrete porosity and strength is of great importance when predicting the ability of a given waste-cement mixture to contain the waste under leaching conditions. Compressive strength then may be an acceptable indicator of the stabilized/solidified waste's resistance to leaching.

Mineral Admixtures

The use of pozzolanic and cementitious byproducts such as fly ash, blast furnace slag, or kiln dusts as admixtures is an important issue in waste S/S. When used in addition to, or as a partial replacement for portland cement, the presence of the mineral generally retards the rate of strength gain although incorporating them considerably improves the ultimate strength and impermeability (water tightness).

Air Entrainment

Additives causing stable air incorporation into the cement paste are universally deleterious to the ultimate strength and impermeability of the concrete, most likely because of the added large-pore space. The entrained air, however, greatly increases the resistance of the products to freezing, thereby increasing their durability under freeze-thaw conditions.

The Durability/Permeability Relationship

Long-term durability of the stabilized/solidified waste product is a prime consideration in designing and specifying waste S/S systems. Predicting the long-term integrity of the final waste form requires considering all possible modes of failure. For cementitious stabilized/solidified products, water is generally involved in every form of deterioration; and in porous solids, permeability of the material to water usually determines the rate of deterioration. Internal movement and changes in the structure of water are known to cause disruptive volume changes of many types of products. Examples are water freezing into ice, formation of ordered structure of water inside fine pores, development of osmotic pressures because of different ionic concentrations, and hydrostatic pressure buildup by differential vapor pressures. All of these can lead to large internal stresses within a moist solid and to its ultimate failure

Cracking by Crystallization in Pores

Stabilized/solidified waste products often contain substantial amounts of salts, or organic molecules, or both, with appreciable water solubilities. Concentration of these materials at or below the surface of the solid where evaporation of pore water is occurring can cause super-saturated solutions to develop and salt crystals to form in the pores of the stabilized/solidified product, which may disrupt its structure.

Wet-Dry Cycling

Wet-dry cycling of normal concrete products usually does not significantly damage its structure. As the total proportion of cement is reduced or as the water/cement ratio is increased, as is common for economy in waste S/S practices, wet-dry cycling may, however, cause rapid deterioration of the stabilized/solidified waste product.

Freeze-Thaw Damage

Although there is generally a direct relationship between strength and durability, this does not hold in the case of frost damage. In a manner analogous to salt crystals, ice crystals forming at subfreezing temperatures can rapidly deteriorate water saturated concrete products.

The hydraulic pressure generated by freezing pore water depends on the permeability of the material, the distance from the surface (escape boundary), and the rate at which ice is formed. Durability of cement products to freeze-thaw cycles can be provided by entraining small air bubbles into the cement paste. These provide water escape boundaries. In medium and high-strength concretes, however, every 1% increase in the air content reduces the ultimate strength of the final product by about 5% and appreciably increases its permeability.

Deterioration by Chemical Reactions

The effects of internal waste constituents as well as aggressive environmental agents on stabilized/solidified waste products must be adequately known before the long-term stability of the stabilized/solidified product can be assumed. The solid phase of a well-hydrated portland cement paste exists in a stable equilibrium with the high-pH pore fluid. Large concentrations of Na^+, K^+, and OH-ions bring about a pH of 12.5 to 13.5 in the pore fluid. Natural CO_2 sulfates, and chlorides common in ground- and rainwaters may bring about aggressive solutions below pH 6, which can be detrimental to the stabilized/solidified waste product.

Cation-exchange reactions can occur between the external solution and the cement binder. Anions in acidic solutions that form soluble calcium salts (such as calcium chloride, acetate, and bicarbonate) will leach the calcium from the stabilized/solidified product. This is particularly damaging because it increases the permeability of the concrete, which increases the rate of further exchange reactions.

Sulfates attack of waste-concrete products can be a serious problem and is an important consideration in the S/S of sulfate-containing wastes in portland cement. Concentrations of soluble sulfates greater than 0.1% in soil or 150 mg/L in water will endanger cement products, and soils of over 0.5 soluble sulfates or over 2000 mg/L in water can have serious effect. Pozzolanic S/S systems are useful for S/S of high sulfate wastes since they do not contain free calcium hydroxide and, thus, are nonreactive to sulfate.

Radiation and Stabilized/Solidified Waste Products

Large doses of gamma radiation do not appear to affect setting properties or cause appreciable loss of strength or increased leachability in portland cement solidified waste products.

Standard Admixtures for Portland Cement Products

The properties of cement in both the fresh and hardened state are typically modified by adding specific materials to the cement mixtures. The additives vary widely in chemical composition and may modify more than one property of the cement mixture. Cement admixtures are germane to the discussion of stabilized/solidified waste since an understanding of the effects of common, well-studies' admixtures gives a basis for assessing the possible range of effects of waste constituents on the cement or pozzolanic matrix.

Admixtures fall broadly into three categories: (1) surface active molecules that work on the cement-water system immediately on addition by influencing the surface tension of water and by absorbing onto the surface of cement particles; (2) set controlling materials that ionize and affect the chemical reaction between the cement and the water only after several minutes or hours; and (3) finely-ground, insoluble minerals, either natural materials or byproducts, that immediately affect the rheological behavior of the fresh concrete, but whose chemical effects take several days or months to manifest themselves. These types of effects can also be seen in stabilized/solidified waste products.

Possible Mechanisms That Affect Organic Compounds in Portland Cement

Several conceptual models of possible interference mechanisms of organics on cementitious and pozzolanic are addressed.

Adsorption

One possible interfering mechanism is adsorption of added waste molecules on the surface of the cement particles; this adsorption blocks the normal hydration reactions.

Complexation

Conditions in a cement paste are favorable for aluminate, ferrite, and silicate ion complexation. Such complexation possibly delays the formation of hydration products. When cement crystal-forming ions are kept in solution by complexation, hydration barriers are established that may retard the set and weaken the final product.

Precipitation

The formation of insoluble hydration products by waste constituents reacting with cement compounds is not thought to be a realistic mechanism of admixture interference. If the precipitation reaction involves the hydration product itself, however, the precipitated product would be produced preferentially at the surface of the hydrating material. This is thought to be the mechanism of action of phosphates, borates, and oxalates.

Nucleation

The inhibition of nucleation of crystalline calcium hydroxide by soluble silica, which is present in small quantity, is believed to be the self-retarding set feature of tricalcium silicate hydration. It is postulated that organic retarders act much the same as silica ions by being adsorbed onto the calcium hydroxide nuclei. However, organic interfering materials may be adsorbed more effectively and may cover crystal growth surfaces more completely.

Effects of Wastes on Cement/Pozzolan Processes

Acids, salts, bases, and organic materials may be present in hazardous wastes singly or in variable combinations. As such, they present a difficult problem for process designers and regulatory agencies to predict their single and collective effect on the durability and containment of typical cement and pozzolan S/S processes. Long-term effects are especially difficult to estimate because subtle differences in environmental parameters can have significant long-term consequences to the integrity of stabilized/solidified waste. In the full report, the few studies of the effects of organic and inorganic waste constituents on stabilized/solidified waste properties are discussed in some detail.

Asphaltic and Polymeric Binders

Asphalt and bitumens are often suggested as S/S agents for low-level radioactive and soluble hazardous wastes. Bituminous materials, since they are immiscible in water and are quite stable, will effectively isolate soluble components from contacting water for long periods of time. Major drawbacks of the asphaltic S/S process are its flammability, the need to mix at high temperature, and the cost of the raw materials and mixing equipment. The information most pertinent to intermixing waste and asphalt is its viscosity properties and flash point. Studies of the incorporation of hazardous and radioactive waste in asphaltic materials are summarized.

Conclusions and Recommendations

Although chemical S/S of hazardous wastes before disposal is increasing in importance, very little work has been done concerning the effects of specific waste components on the physical and contaminant properties of the treated waste product.

There is a clear need for further experimental work to obtain physical and chemical data about cementitious and asphaltic treatment systems. Sufficient basic information should be developed so that waste/binder interactions can be modeled. This would overcome the current need to test each specific waste/binder combination for possible interferences. The variability and complexity of most waste streams may, however, still preclude such generalizations.

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The complete report, entitled "Interference Mechanisms in Waste Stabilization/Solidification Processes," (Order No. PB90-156 209/AS; Cost: $23.00, subject to change) will be available only from:
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