

Overview of waste stabilization with cement

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Abstract

Cement can treat a variety of wastes by improving physical characteristics (solidification) and reducing the toxicity and mobility of contaminants (stabilization). Potentially adverse waste-binder interactions are an important consideration because they can limit solidification. Stabilization occurs when a contaminant is converted from the dissolved (mobile) phase to a solid (immobile) phase by reactions, such as precipitation, sorption, or substitution. These reactions are often strongly affected by pH, so the presence of components of the waste that control pH are critical to stabilization reactions. Evaluating environmental impacts can be accomplished in a tiered strategy in which simplest approach would be to measure the maximum amount of contaminant that could be released. Alternatively, the sequence of release can be determined, either by microcosm tests that attempt to simulate conditions in the disposal zone or by mechanistic models that attempt to predict behavior using fundamental characteristics of the treated waste.

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1. Introduction

Solidification/stabilization (s/s) was used to treat nuclear wastes in the 1950s and then was widely applied to hazardous wastes in the early 1970s (Conner, 1990). It has been used both to treat wastes currently being produced, as well as soils and sediments contaminated by previous improper disposal. S/S has been identified by the US EPA as the Best Demonstrated Available Technology for 57 regulated hazardous wastes (Shi and Spence, 2004) and it is one of the most commonly applied technologies at Superfund sites in the US, being used at 24% of the sites between 1982 and 2002 (US EPA, 2004).

Most applications of s/s are cement-based, in that they rely on Portland cement as the primary binder. However, it can be combined with lime as well as fly ash, blast furnace slag, and other similar materials. The interactions of these binders with waste components determine the extent of treatment. Treatment by s/s combines two interrelated processes that occur simultaneously to produce a material that will have reduced environmental impact when dis-

posed or reused. One of these processes is called solidification and it is the process of producing a solid product with improved physical properties, primarily strength. The other process is stabilization and it is the process of converting the contaminant of concern to less mobile and less toxic forms. This paper will provide an overview of the processes of solidification/stabilization and the methods of characterizing the treated product in ways that facilitate determination of environmental impacts.

2. Solidification

Solidification results in changes in primarily physical properties of the waste material so that a well solidified waste will no longer contain free liquids and will have improved strength. As such, it will be much more easily handled, particularly if the untreated waste was a liquid or sludge. Furthermore, a solidified waste will have less impact on the environment when disposed. It will not contain free liquids that can be more easily transported to contaminate the environment. It will usually be formed into solids forms of larger size than the untreated waste. This will result in smaller area/volume ratios that will result in lower rates of release of contaminants. The treated waste

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will typically have much reduced permeability, which reduces the advective flow through the waste. If the treated material has a substantially lower permeability than the material surrounding it in the disposal zone, fluids will flow around rather than through it, resulting in substantially reduced release of contaminants.

A major factor in applying cement-based s/s to wastes is the extent to which components of the waste interfere with cement hydration reactions. Many of the compounds that are reported to accelerate or retard cement hydration (Taylor, 1990; Conner, 1990; Lea, 1971) are found to cause similar problems in wastes (Taylor and Fuessle, 1994; Trussell and Spence, 1994; Means et al., 1995; Hills and Pollard, 1997). These include organics, particularly polar organics, halides, metals and sulfate. Avoiding adverse waste-binder interactions is a major focus of developing s/s technologies for some wastes. Approaches to managing these problems include adding an accelerator to counteract a retarder and vice-versa. For example, soluble silicate has been used extensively as a s/s admixture to reduce effects of retarders.

The primary method of characterizing the extent of solidification is to measure the unconfined compressive strength of the treated material. This parameter has been incorporated into some specifications for s/s treatment by regulatory bodies; however, the degree of strength required depends on the disposal scenario. Another important application for strength tests is to estimate the long-term stability of the waste form. A stronger waste form will tend to retain its integrity better than a weaker one, although future characteristics cannot be insured by measurement of current characteristics. Long-term integrity is important because a waste form that degrades to small sized particles will release contaminants more rapidly. Wet-dry and freeze-thaw durability tests have also been applied to waste forms to predict durability. Although they have a history of use to predict longer term performance of construction materials, their applicability to waste forms is in doubt because disposal conditions for many wastes are not similar to those simulated in these tests. Permeability to water is another important characterization parameter for wastes treated by s/s, because it predicts the extent to which water will tend to pass through the waste form in a disposal environment. Permeabilities below those associated with clay liners is possible in well-treated wastes (Stegemann et al., 1997; Conner, 1990). The pore structure in a waste treated by cement-based s/s is important in determining the extent of contaminant release, because contaminant transport within the waste form will be primarily by diffusion in the pores. A waste form with highly tortuous, unconnected pore structure will leach contaminants more slowly.

Characterization of a waste treated by s/s is usually conducted shortly after treatment, but the parameters measured are often used to predict performance over long periods into the future. Therefore, the stability of these parameters is of concern. Hydrated cements and concretes change their physical properties over time and wastes treated by cement-based s/s should also be expected to change in sim-

ilar ways (Klich et al., 1999). Hydration reactions can continue over time and result in higher strength and lower porosity. A combination of Portland cement with pozzolanic materials usually results in slower hydration kinetics. Carbonation can also cause similar changes. Reaction with sulfate is known to degrade concrete and the same can be expected for treated wastes. The wide range of constituents in a waste would be expected to cause more long-term changes than are typically observed for construction materials, which are made with more clearly defined constituents. A waste form also interacts with its environment by leaching binder constituents and waste constituents. This can result in reduced strength and increased connected porosity. Contaminants will leach through the modified pore structure, so it should be characterized to predict release rates.

3. Stabilization

Waste stabilization is the result of chemical changes in contaminants and their environment that cause the contaminants to be less mobile or less toxic. Changes in mobility are primarily due to a contaminant being converted from the dissolved phase to a solid phase. In the dissolved phase, a contaminant is free to diffuse down a pore to the external environment. In a solid phase, the contaminant is substantially mobile.

Precipitation is a major reaction that results in immobilization during cement-based s/s. The high pH resulting from cement hydration results in many metal contaminants forming hydroxide or mixed hydroxide solids. Sulfide precipitates are also possible, particularly sulfides are added directly or indirectly through the use of blast furnace slag or similar binders that can produce sulfides (Taylor, 1990; Lea, 1971). Calcium and calcium hydroxide solid phases are possible for anionic contaminants. Although contaminant stabilization is typically considered to be by formation of pure solids, solid solutions can also be formed. The complex mixture of compounds present in wastes and binders may result in substantial formation of solid solutions. A chemical equilibrium model based on solid solutions of cement hydration products was found to do a good job of describing changes in aqueous phase concentrations (Abdel-Wahab and Batchelor, 2005). Formation of solid solutions can be considered a form of substitution. For example, immobilization of chromate has been reported as being the result of a chromate ion substituting for sulfate in ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) (Poellmann et al., 1993; Palmer, 2000; Zhang and Reardon, 2003). This could also be considered a solid solution of ettringite and the chromate analog of ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{CrO}_4)_3 \cdot 26\text{H}_2\text{O}$) (Perkins and Palmer, 2000). Immobilization of boron, molybdenum and selenium has also been attributed to a similar mechanism with ettringite (Aft) and hydrocalumite (AFm) (Zhang and Reardon, 2003; Baur and Johnson, 2003a).

The pore structure of wastes treated by cement-based s/s also provides substantial amounts of surface area to

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