

EVALUATION METHODS FOR CHEMICAL BASED STABILIZATION PROCESSES

Proceedings of the
International Congress
on Waste Solidification-
Stabilization Processes

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Nancy, France
Nov. 28 - Dec. 1, 1995

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ABSTRACT

Cement based processes have been the most common solidification/stabilization (S/S) processes for metal immobilization used in industrial sludge treatment or land reclamation projects. These processes may rely on a silica gel, free hydroxide, and cement structure to immobilize soluble metals. As the mining industry finds certain mineral forms to present special challenges in extraction, the waste management industry can benefit from incorporating target contaminants into similar waste forms. Chemical based stabilization processes, without cement addition, have been utilized to immobilize metals by precipitation, sorption, or altering the chemical nature of the waste. These stabilization processes include the use of phosphates, carbonates, sulfides, and iron rich clays.

Many of the physical tests that are used to evaluate cement based solidification/stabilization processes may not be appropriate for chemically based processes, since the cement based processes also rely on the physical structure to impede movement of soluble metals. Since soil stabilization can be considered as a metal immobilization process, chemical based testing methodology such as buffering capacity and competing ion availability may be more useful in predicting stabilization process performance over time.

The purpose of this paper is to overview chemical based stabilization processes and present testing methodology for evaluating the chemical durability of the resulting materials.

INTRODUCTION

The waste management industry recognizes that there is an important distinction between the terms solidification and stabilization. Solidification generally means the conversion to a more solid state by the reduction of surface area, which usually results in volume increase. Stabilization generally refers to a conversion of the metal contaminants to a less soluble chemical form. The physical properties of the stabilized-only material may not be changed, nor would volume increases be of the magnitude of cement based solidification processes.

In cement based applications, both solidification and stabilization phenomena may occur. These occur because of the hydroxide available (from the cement) for metal precipitation and the encapsulating silica gel and physical structure produced during hydration. Cement may also include various amounts of carbonate. One potential drawback of such systems, is the rather high range of pH values that can occur in pore fluids, which can result in the solubilization of amphoteric metals.

In chemical stabilization processes, insoluble compounds may be formed, or the metal may be sorbed. These processes may also use the addition of a buffering system to minimize changes from the optimum pH domain for metal insolubility.

DISCUSSION

Phosphate based processes

Orthophosphate forms compounds with many heavy metals that have low solubilities in water at most naturally occurring pH ranges. The lead phosphates have lower solubilities than lead hydroxide or lead carbonate. Phosphates used in waste stabilization processes to reduce soluble lead include hydroxyapatite and triple superphosphate (TSP).

Laboratory studies and geochemical modelling have shown that phosphate immobilizes lead in soils (Ma, et. al., 1993, Ruby, et. al., 1994). An addition of one per cent TSP to a foundry sludge reduced lead levels below regulatory criterion (Etzel, 1988). An addition of one to four per cent TSP reduced metal availability from several leaching/extraction tests for five foundry sludges (Contos and Regan, 1995).

Phosphate has also been effectively used in conjunction with magnesium oxide for metal immobilization. In this system, the magnesium oxide serves to buffer the pH of pore water at levels below about 10.5 (Stanforth, 1991). This process was used to remediate 55,000 cubic yards of soil contaminated by a battery cracking operation. Less than five per cent phosphate was used (Hasbach, 1995).

Sulfide based processes

In general, metal sulfides have lower solubilities than metal hydroxides. Sulfide has been used to stabilize several heavy metal sludges (Conner, 1990). A sulfide based stabilization system reduced leachable levels of lead and copper in sandblasting grit (Means, et. al., 1992). The disposal environment should be reducing for sulfide based processes.

Carbonate based processes

Cadmium carbonate is more insoluble than cadmium hydroxide, therefore cadmium from industrial operations can preferentially precipitate as a carbonate salt at near neutral pH with carbonate present (Patterson, 1985). Cadmium was found to be carbonate bound in several foundry sludges (Contos and Regan, 1995).

Iron rich clays

Approximately 20,000 cubic yards of arsenic contaminated soil from a site in Richmond, Virginia was attenuated with the addition of iron rich clay (Scovazzo, et. al., 1992). Certain soluble metals can co-precipitate with solid phases that contain iron (Patterson, 1985). Arsenic immobilization may be more favored under oxidizing conditions.

EVALUATION METHODS FOR CHEMICAL BASED STABILIZATION PROCESSES

Many solidification/stabilization processes use both physical entrapment and reduction in metal solubility to immobilize metals. Solidification processes have measurable properties including reductions in hydraulic conductivity and an increase in unconfined compressive strength from the original state. Test methods for evaluating these physical properties do not have direct application for stabilization processes.

Stabilization methods should therefore be evaluated with chemical tests that indicate both chemical state and durability. The following broad categories of test methods are suggested:

Buffering Capacity

Buffering capacity tests indicate the ability of the stabilized waste to maintain a pH value when exposed to either an acidic or basic solution. The larger the buffering capacity, the greater the possibility of maintaining the optimal condition for amphoteric metal retention.

pH

While pH control has been presented for controlling metal solubility, it is also an important control parameter for potential emission problems, such as hydrogen sulfide from a poorly buffered sulfide stabilization process that is exposed to acidic conditions.

Analysis for other competing ions

Soluble ligands such as cyanide, acetate, nitrate, or EDTA may be stronger chelators than other stabilization compounds. Even common stabilization compounds such as sulfide or phosphate can compete with each other for metal retention. Therefore these specific ions or compounds should be analyzed in the leachate test(s).

Stabilization compound concentration

Total or un-reacted stabilization compound content analysis in the treated material may be important for several reasons. The reasons for total content include potential ecological impact, amphoteric metal behavior, or process quality assurance. More specifically for phosphorus, excess phosphorus that is un-reacted and available for leaching could be released to ground water or contained in erodible sediment and ultimately contribute to a eutrophication problem in surface water.

Amphoteric metal behavior was observed at TSP dosages less than one percent and higher than five per cent for the treatment of foundry sludge (Regan, 1991). Excess compound may influence the system equilibria.

For process quality assurance, total phosphorus analysis, normally performed by acid hydrolysis, may be used to determine if treated samples are homogeneous for the design phosphorus loading.

Leaching tests

The more comparable the leaching medium is to disposal conditions, the more reasonable the estimate of short-term durability. A broad array of leaching tests exists and a variety of these should be considered rather than focusing on or

mimicking a single release scenario (USEPA, 1991). The release scenario of acid rain increasing the threat of contaminant releases to ground water may be important, however, and should be considered. The Synthetic Precipitation Leaching Procedure (SPLP) (USEPA, 1995) is an example of such a leaching test.

Bioavailability

The bioavailability of a stabilized contaminant may not be accurately predicted using aqueous based leaching tests. At a site contaminated with copper, zinc, and arsenic, diethylenetriaminepentaacetic acid (DTPA) extracts of contaminated soils were found to correlate with metal levels in plant tissue better than did water extracts (Schafer and Smith, 1989). DTPA-triethanolamine and ethylenediaminetetraacetic acid (EDTA) extracts were found to provide a better correlation with seedling emergence in zeolite amended soils contaminated with lead and zinc than did extracts using de-ionized water and 0.1 M hydrochloric acid (Greene and Barich, 1994). Simple whole-organism bioassays can be used to evaluate the relative toxicity of stabilized waste before and after treatment (Barich, et. al., 1992).

CONCLUSIONS

Several chemical parameters may be used for evaluating the long term chemical durability of chemical based stabilization processes. The combination of several of these chemical testing methodologies offer a more realistic evaluation of chemical stability than generic leaching test or physical parameters which do not have direct application to the disposal environment.

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