Portland Cement Association

WASTE MANAGEMENT INFORMATION

Stabilization of Heavy Metals with Portland Cement: Research Synopsis

by Charles M. Wilk*

Introduction

This publication summaries research on establishing the mechanisms by which portland cement and portland cement-based reagents immobilize certain toxic heavy metals in inorganic form by solidification/stabilization (S/S) treatment. The metals studied included lead (Pb), chromium (Cr), cadmium (Cd), arsenic (As), and mercury (Hg). This work demonstrates the effectiveness of portland cement systems in stabilizing wastes. It confirms that cement-based stabilization involves far more than simple pH control, and suggests some possible mechanistic explanations for the effectiveness. The research also investigated certain additives designed to enhance stabilization mechanisms, and suggests modifications to further improve the immobility of metals.

The complete report on the research is available as *Stabilization of Heavy Metals in Portland Cement, Silica Fume/Portland Cement and Masonry Cement Matrices*, by Javed I. Bhatty, F. MacGregor Miller, Presbury B. West, and Börje W. Öst, PCA publication RP 348.

Cement-Based Solidification/Stabilization

Solidification/Stabilization (S/S) is a widely applied treatment for the management and disposal of a broad range of wastes, particularly those classified as toxic or hazardous. The U.S. Environmental Protection Agency considers S/S an established treatment technology. *Solidification* refers to changes in the physical properties of a waste. The desired changes usually include increase of the compressive strength, decrease of permeability, and encapsulation of hazardous constituents. *Stabilization* refers to chemical changes of the hazardous constituents in a waste. The desired changes include converting the constituents into a less soluble, mobile or toxic form.

Portland cement is a versatile S/S binding reagent with the ability to both solidify and stabilize a wide variety of wastes. Portland cement has been applied to a greater variety of wastes than any other S/S binding reagent. Cement-based S/S has been used to treat both inorganic and organic hazardous waste constituents. Generally, for inorganic-contaminated wastes, the hazard resides in the heavy metals content. S/S is often the only reasonably available technology to treat significant amounts of heavy metals-contaminated soil, sludge, or sediment.

Cement is uniquely suited for use as a S/S reagent; it not only provides the alkaline pH conditions for the precipitation of many heavy metals as insoluble hydroxides, but also provides a strong chemical bonding, physical encapsulation, and strength development.

Stabilization of Metal Salts and Oxides

Metals in contaminated wastes usually do not exist in elemental form, but usually exist as compounds of oxides, hydroxides or salt solutions. The research showed that the oxides and salt solutions of the metals studied (lead, cadmium, chromium, and mercury) were well stabilized. The stabilization of cadmium and chromium was particularly good. The metal oxide and salt solutions typically, decreased the workability of Type I cement pastes. For metals that caused set retardation (particularly lead), the decreased workability effect was more pronounced for the oxide form than for the salt. The chromium (III) salts in solution accelerated both setting time and strength development, whereas both variables were retarded with lead salts addition. As judged by compressive strength development, although these metals influence early hydration reactions, ultimate cement hydration was as complete as in control samples.

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Effect of pH on Metals Stabilization

It has long been held that the principal stabilization mechanism of certain heavy metals is based on reduction of the solubility of these metals through control of the pH of treated wastes. These metals frequently appear in wastes in the form of hydroxide sludges, or are rapidly converted to that form by addition of portland cement. The hydroxides of these metals are amphoteric. The term "amphoteric" means that the hydroxides are least soluble at a specific intermediate pH. These hydroxides are more soluble at both lower pH (more acidic) conditions and at higher pH (more basic) conditions. Lead (Pb) and chromium (Cr) are heavy metals that have amphoteric hydroxides. The hydroxide of cadmium (Cd) is weakly amphoteric. Figure 1 depicts this amphoteric nature of certain metal hydroxides by plotting the solubility (theoretical) of the hydroxides versus pH. Mix designs to stabilize these metals in wastes usually count on utilizing this amphoteric nature. Designs involve adding the right amount of cement so that the pH of the waste form during testing is maintained at the level where the subject metal hydroxide's solubility is at its lowest. The present research established that the effectiveness of cement in stabilization was greater than could be attributed to mere pH control.

Stabilization Mechanism Beyond pH Control

Lead, cadmium, and chromium often occur in wastes in the form of hydroxide sludges, or are rapidly converted to that form by portland cement. For this reason, most of the research used the metals in hydroxide form. Initially, the metals were studied individually in paste matrices. Sequential batch leaching using nominally 0.1 M acetic acid was carried out on mature pastes. Metals mobility as a function of decreasing pH (increasing acidity) was in general far less than would be predicted by the theoretical solubility of the corresponding metal hydroxide. It was apparent from this phase of the study that the stabilization of the metals and in particular lead, was far better than would be anticipated from pH considerations alone.

A contributing mechanism to the better-than-expected stabilization of certain heavy metals may be attributed to the incorporation of those metals into the cement hydration products. Results of the sequential leaching experiments indicated a correlation between the leaching of lead and the leaching of alumina from the cement paste (Figure 2). There was also evidence of a correlation between chromium and silicon (Figure 3). These two metals may be bound by incorporation in the cement hydration products and not released from the matrix until the breakdown of the products. The pH at which these cement hydration products break down and release these metals is much lower than the pH at which the same level of metal would be released if the metals were bound solely as hydroxides.

Further evidence of the stabilization effect of cement hydration products is a measured difference in the stabilization performance between types of portland cements. There are five major types of portland cement. Each type develops cement hydration products in different proportions and at different rates. A comparison of lead stabilization in Type V and Type I portland cements was made. Lead appeared to be better stabilized by a small but measurable amount with Type V cement compared to Type I. The difference was not attributable to pH, but most likely related to the influence of differences in the cement hydration products.

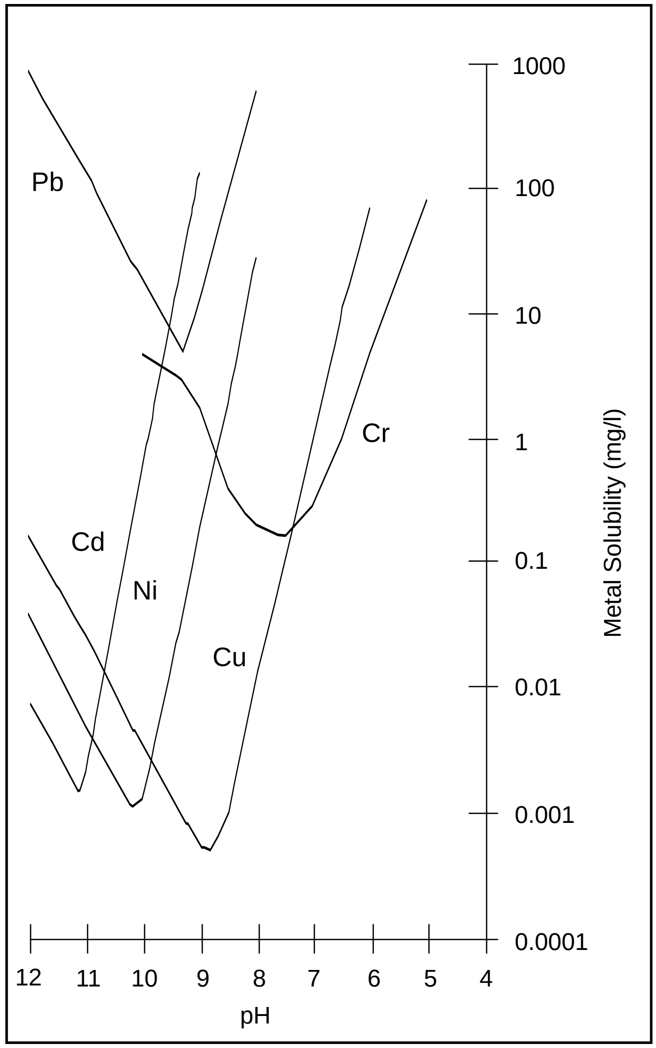

Figure 1. Solubilitites of metal hydroxides as a function of pH.

In the next phase of research, three metals (lead, cadmium, and chromium) were added together to cement paste at the 0.1% and 1% levels by mass, and the batch leachability was determined, using 0.1 M acetic acid, distilled water, and synthetic acid rain as leachants. With the exception of the early high-pH leachability of lead, very little of any of the metals were dissolved by increments of the latter two leachants. The effectiveness of stabilization of the other metals was, in most cases, orders of magnitude better than projected from the respective hydroxide solubility. Lead showed the greatest improvement in stabilization, followed by chromium and then cadmium. Even though the stabilization of cadmium was better than predicted, the solubility of cadmium still appears to be most strongly determined by the pH of the system. Combinations of the three metals were shown to be slightly better-

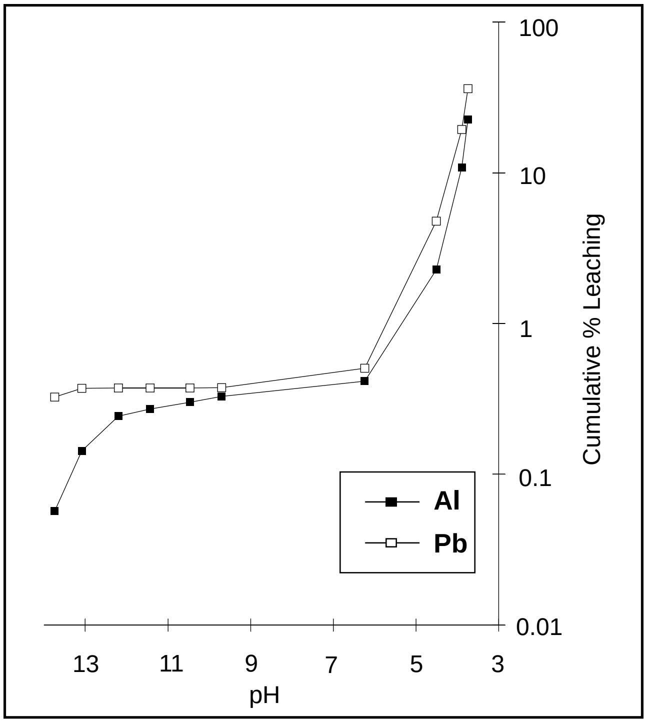

Figure 2. Al/Pb leaching, 1% lead, Type I cement.

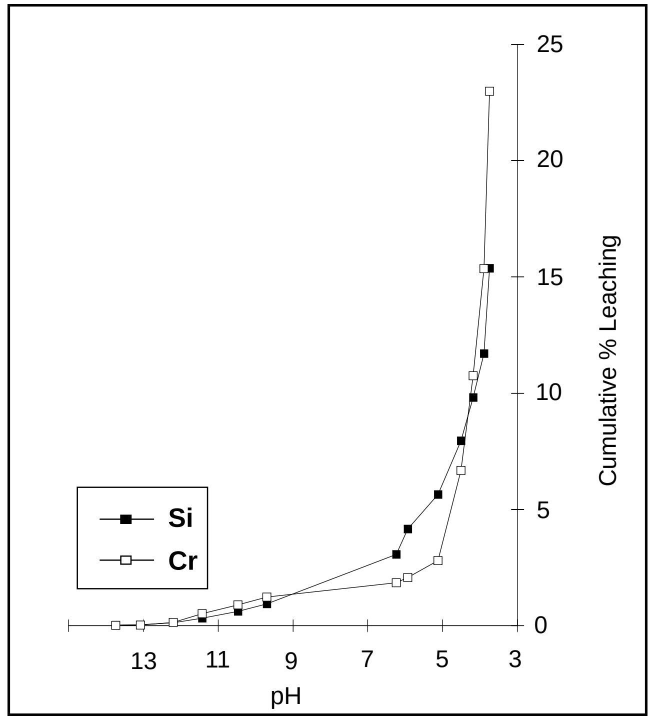

Figure 3. Si/Cr leaching, 1% chromium, Type I cement.

stabilized in a cement matrix than were the individual metals. Figures 4 through 6 compare the observed solubilities of the three metals versus their theoretical solubilities. For each metal, the curve for the observed solubility is broader than the theoretical solubility curve. Generally, at any one pH level the observed solubility of a subject metal was lower than the theoretical solubility.

Metal Stabilization in Soil and Oily Soil Matrix

Another phase of the study focused on stabilization in standard soil matrix, both dry and oil-contaminated. Two types of soils were choosen: a dolomitic soil and a siliceous soil. Type I cement was added to the soils at an 8% cement content by weight of dry soil. The systems were moist cured for 28 days before leaching tests were begun. Stabilization of the metals in a soil matrix was at least as good as in cement paste, after accounting for differences in the cement content. In fact, chromium was less soluble in the soil matrix than in the cement paste. Generally, metals were stabilized better in the dolomitic soil than in the siliceous soil due in part to pH effects. For oily soil experimentation, oil-contaminated soils were simulated by adding 8% by weight of aged SAE 10 W machine oil to the two soil types. Use of appropriate emulsifiers avoided early phase separation, and the metal leaching results with added oil were essentially comparable to those without oil.

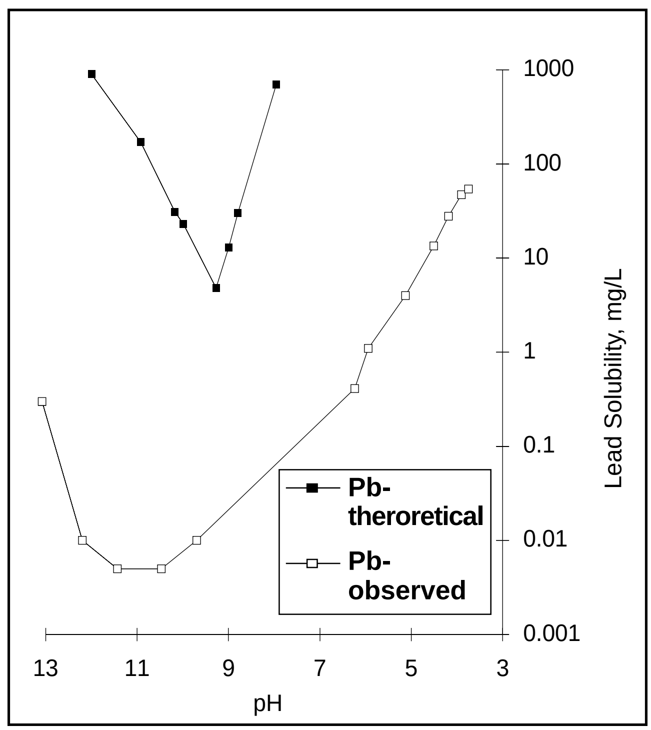

Figure 4. Solubility of lead hydroxide theoretical vs observed (S/S matrix).

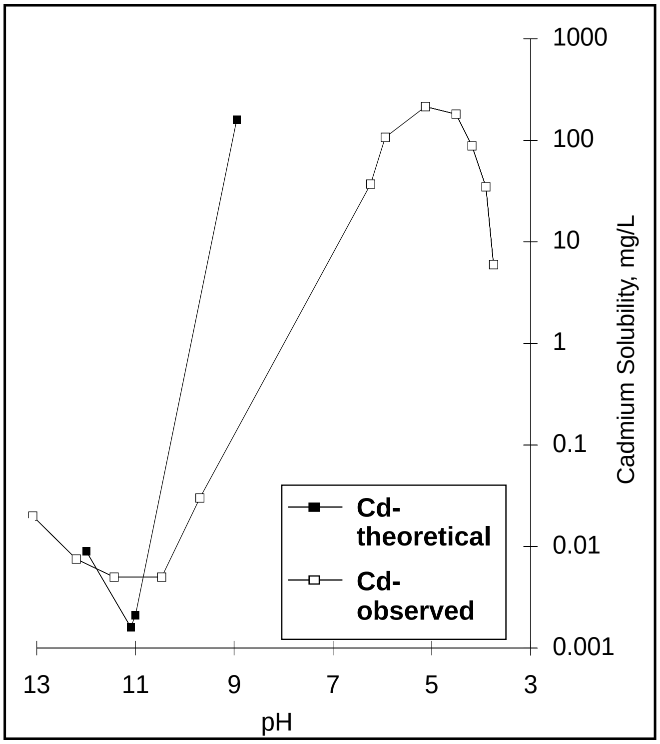

Figure 5. Solubility of cadmium hydroxide theoretical vs observed (S/S matrix).

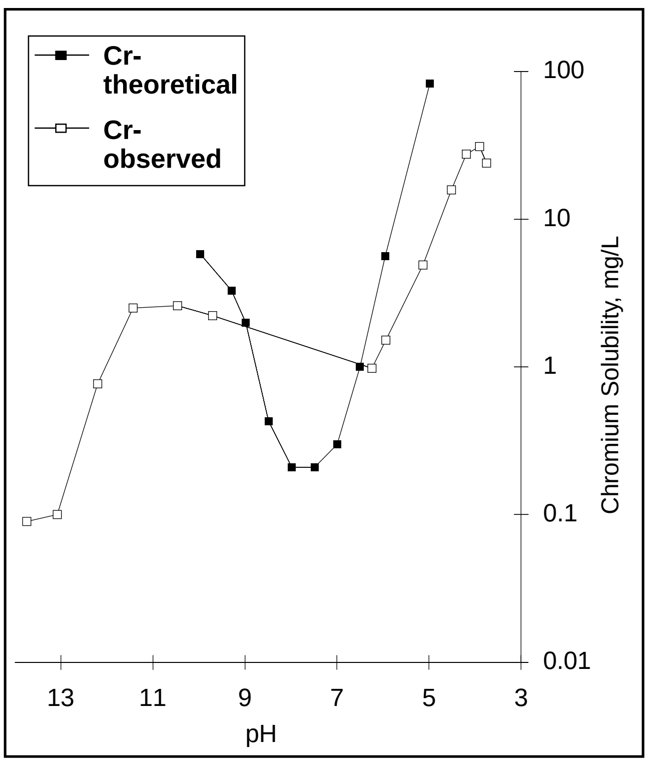

Figure 6. Solubility of chromium hydrous oxide theoretical vs observed (S/S matrix).

Additives

Attempts to suppress the initial high-pH leachability of lead and chromium were another phase of the study. Additional gypsum was added to the cement to create the potential for more ettringite formation on hydration of the cement. Under certain conditions, particularly at high pH, the additional gypsum suppressed metals leachability. An additional series of tests employing silica fume was carried out to discover if removing the calcium hydroxide from hydration products would inhibit calcium ion replacement of the metals in hydration products. This would avoid resolubilization. Silica fume was very effective under certain circumstances, particularly for lead at high pH, and for all metals at low pH after almost all calcium had been leached out. Practical applications undoubtedly exist for this technique, especially for lead stabilization where the use of added silica fume, or other pozzolan alternates such as Class F fly ash, may be appropriate. However, the materials should optimally be cured for a long enough period that the silica fume or fly ash has time to react with the calcium hydroxide generated from cement hydration. If only a short curing time can be allowed, it may be preferable to consider using alkali silicate solutions as the source of reactive silica to tie up calcium hydroxide.

Arsenic-Contaminated Soils

The next phase of the study involved the stabilization of arsenic in siliceous soils. Arsenic is generally more difficult to stabilize than lead, cadmium, or chromium, at least in part because it forms oxy-anions in aqueous systems, not hydroxides. Further complexity is derived from the various oxidation states in which arsenic can be found. The study verified that it is beneficial to oxidize arsenic to the higher oxidation state (arsenate) before attempting stabilization. Effective stabilization can be achieved by pretreating arsenic with the use of ferrous salts, together with a relatively high binder-to-waste ratio. For long term stabilization, it may be necessary to increase both the binder-to-waste and iron-to-arsenic ratios. At a higher binder-to-waste ratio of perhaps about 0.4, and the use of iron salts at a molar ratio of iron to arsenic of at least 6, better stabilization might be expected. Use of ferrous sulfate caused water demand, perhaps as a result of precipitation of gypsum on addition of $FeSO_4 \cdot 7H_2O$. Further work is needed to address this high water-cement ratio when using ferrous sulfate. A common retarder such as citric acid or a superplasticizer could be used, or perhaps a non-sulfate ferrous compound could be substituted. One issue of concern with arsenic stabilization is the fact that arsenic shows a maximum solubility around pH 9.5. This is the pH at which the solubility of lead and chromium is near a minimum. When wastes contain arsenic and either lead or chromium, it is necessary to be especially careful in the design of the S/S composition.

Table 1 Qualitative Guide for Stabilization of Metals Studied

Metal	Good	Better	Best
Lead	Type I cement	Type I cement with silica fume	Type V with silica fume and a little extra gypsum
Cadmium	Cement with silica fume	Higher cement factor, no silica fume	Still more cement for long term durability
Chromium	Portland cement	Portland cement with a silica fume	Same, but with oxidation inhibitor to avoid hexavalent chromium
Arsenic	Portland cement with added $FeSO_4$	Portland cement with preoxidation with H_2O_2 and added $FeSO_4$	Same, but with higher cement factor and higher Fe/As ratio
Mercury	Portland cement	Higher cement factor	Even more cement to ensure strongly reduced porosity

Durability

There was only limited work conducted in the area of long term durability of stabilized wastes. The work indicated that carbonation, attack of acidic waters from the decomposition of organic matter, or acid rain have the potential to cause deterioration of cement forms or paste. Acids such as that formed by CO_2 in moist air, may cause degradation of calcium hydroxide and calcium silicate hydrate to calcium carbonate and silica gel, as well as the similar degradation of ettringite, perhaps via the intermediate thaumasite. However, the amount of acidic material required to bring about this transformation is very large. If an adequate amount of cement is used, and if the material is properly cured, durability of stabilized waste for centuries is by no means unrealistic.

Summary

Table 1 summarizes the results obtained by the research that can be applied in the field. It is arranged on the basis of a "good/better/best" method for stabilizing the metals studied. It must be emphasized that the table is based only on the results of this particular study and **should not** be used for design purposes without first testing the particular wastes.

The research conducted demonstrates the effectiveness of portland cement systems in stabilizing wastes. It provides confirmation that portland cement stabilized systems involve far more than simple pH control. The research showed that metals may also be bound in the cement hydration products, and certain additives can be used to enhance the stabilization mechanisms.

Abstract: Portland cement has found increasing use as a binding reagent in solidification/stabilization treatment of wastes contaminated with heavy metals such as Cd, Cr, Pb and As. Recent research demonstrated the effectiveness of cement to treat wastes with these metals. The research also found that the effective stabilization by cement involved more than simple pH control and suggests that the metals are incorporated into cement hydration products.

Keywords: Fixation, heavy metals, immobilization inorganics, oil, organics, portland cement, solidification, stabilization.

Caution: Contact with wet (unhardened) cement mixtures can cause SKIN IRRITATION, SEVERE CHEMICAL BURNS, or SERIOUS EYE DAMAGE. Wear waterproof gloves, a long-sleeved shirt, full-length trousers, and proper eye protection when working with these materials. If you have to stand in wet cement mixture, use waterproof boots that are high enough to keep the mixture from flowing into them. Wash wet cement mixtures from your skin immediately. Flush eyes with clean water immediately after contact. Indirect contact through clothing can be as serious as direct contact, so promptly rinse out wet cement mixtures from clothing. Seek immediate medical attention if you have persistent or severe discomfort.

Publications on Solidification/Stabilization

Solidification and Stabilization of Waste Using Portland Cement

State-of-the-art report on the characteristics of portland cement and how it can be used effectively to solidify/stabilize various types of wastes. Discusses waste compounds that may interfere with cement hydration reactions. Includes information on several additives that may be used with portland cement to enhance solidification/stabilization reactions.

EB071 16 pages 1991 $12

Solidification/Stabilization of Contaminated Soil

This special report describes a completed Superfund clean-up project. The project used portland cement to treat metals-contaminated soil. Five full-color photographs showing the method of treatment are included.

SR341 4 pages 1994 $2

Cement-Based Solidification/Stabilization of Lead-Contaminated Soil at a Utah Highway Construction Site

Reprint of a technical article on the use of cement to solidify and stabilize lead-contaminated soils at a Superfund emergency response site. Provides detailed information on design and construction aspects of the cleanup. Published by Remediation, The Journal of Environmental Cleanup Costs, Technologies & Techniques.

RP332 8 pages 1995 $4

Potential Solidification/Stabilization Projects Under the Superfund Program

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IS500 112 pages 1994 $40

Potential Solidification/Stabilization Superfund Projects - 1995 Update

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Directory of Cement Sales Offices

A valuable reference for contractors seeking supplies of bulk cement for solidification/stabilization treatment projects and other large projects. The Directory lists cement sales offices grouped by U.S. state and Canadian province served in order to identify cement suppliers in the project area. A listing of cement sales offices is available on PCA's Web Site <www.portcement.org>.

MS123 1997 Free

Guide To Improving the Effectiveness of Cement-based Solidification/Stabilization

Provides information on field techniques and additives that can be used to improve the effectiveness of cement-based solidification/stabilization treatment of wastes. The Guide includes lists of commonly occurring hazardous constituents in wastes and suggests techniques and additives that can be used to successfully stabilize these constituents.

EB211 48 pages 1997 $18

Stabilization of Heavy Metals in Portland Cement, Silica Fume/Portland Cement and Masonry Cement Matrices

Reports PCA-sponsored research in establishing the mechanisms of heavy metals immobilization by portland cement-based solidification/stabilization treatment. This research found that the effectiveness of stabilization is better than could be expected based on the pH effects of cement addition alone. This suggests that certain metals may actually be bound within cement hydration products.

RP348 98 pages 1997 $Call

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