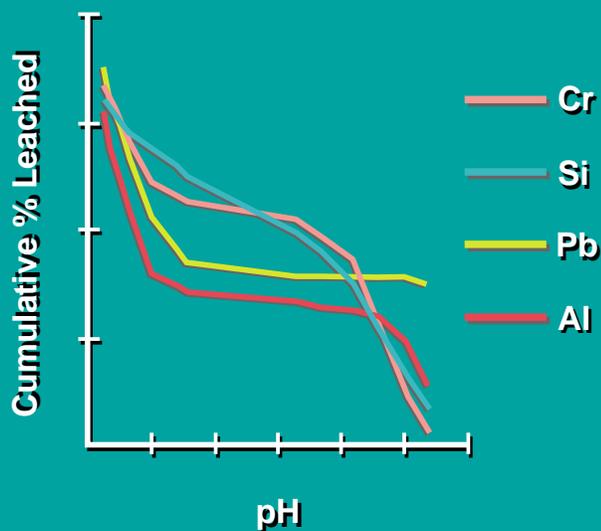


Guide to Improving the Effectiveness of Cement-Based Stabilization/ Solidification



Guide to Improving the Effectiveness of Cement-Based Stabilization/Solidification

This engineering bulletin was authored by:

Jesse R. Conner
Conner Technologies
214 Field Club Rd.
Pittsburgh, PA 15238
USA
(412) 963-6358

Edited by:

Charles M. Wilk, Program Manager, Waste Management,
and
Natalie C. Holz, Editorial/Administrative Assistant
Public Works Department,
Portland Cement Association

Published by:

Portland Cement Association
5420 Old Orchard Rd.
Skokie, IL 60077-1083
USA
(847) 966-6200

© 1997 Portland Cement Association

All rights reserved. No part of this publication may be reproduced in any form without permission in writing from the publisher, except by a reviewer who wishes to quote brief passages in a review written for inclusion in a magazine or newspaper.

Printed in the United States of America

This publication is intended SOLELY for use by PROFESSIONAL PERSONNEL who are competent to evaluate the significance and limitations of the information provided herein, and who will accept total responsibility for the application of this information. The Portland Cement Association DISCLAIMS any and all RESPONSIBILITY and LIABILITY for the accuracy of and the application of the information contained in this publication to the full extent permitted by law.

Caution: Contact with wet (unhardened) concrete, mortar, cement, or 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 concrete, use waterproof boots that are high enough to keep concrete from flowing into them. Wash wet concrete, mortar, cement, or 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 concrete, mortar, cement, or cement mixtures from clothing. Seek immediate medical attention if you have persistent or severe discomfort.

Cover photo courtesy of Geo-Con, Inc.

Guide to Improving the Effectiveness of Cement-Based Stabilization/Solidification

by Jesse R. Conner

Contents

I. INTRODUCTION	1
II. PROBLEMS IN SOLIDIFICATION AND PHYSICAL PROPERTY DEVELOPMENT	3
Setting Problems	3
Compressive Strength Development Problems	6
Permeability Development Problems	7
Durability Problems	7
III. PROBLEMS IN TARGET CONSTITUENT STABILIZATION - CHEMICAL PROPERTIES	7
Metals	8
Organics	12
Organo-Metallics	14
Soluble Salts	14
IV. ADDITIVES USED IN CEMENT-BASED STABILIZATION/ SOLIDIFICATION	15
Metal Stabilization	15
Immobilization of Organic Constituents	20
Processing and Anti-Inhibition Aids	21
V. PHYSICAL/CHEMICAL TECHNIQUES USED IN CEMENT-BASED STABILIZATION/SOLIDIFICATION	22
Anti-Inhibition Aids	22
Physical Property Development	22
Processing Aids	22
Mixing Techniques	23
VI. REFERENCES	24

Guide to Improving the Effectiveness of Cement-Based Stabilization/Solidification

by Jesse R. Conner

I. INTRODUCTION

Stabilization/solidification (S/S) is a very effective tool in the treatment of various wastes, hazardous and non-hazardous. These wastes are commonly generated in ongoing commercial and industrial operations, and are also encountered in remedial activities at old dump sites and other contaminated media. They are usually concentrated residuals from air or water pollution control processes, direct process streams, or contaminated media such as soil. Generally, wastes selected for S/S have already been concentrated to the maximum extent that is economically feasible, and S/S technology is used to prepare the waste for final land disposal. Such preparation requires transforming the waste into a physically acceptable, mechanically stable form, and converting toxic constituents into minimally mobile species.

The United States Environmental Protection Agency (EPA) considers S/S an established treatment technology (USEPA, 1995). For remediation (cleanup) sites, 29 percent of source control Records of Decision (RODs) signed from 1982 through 1994 in EPA's Superfund program include S/S as part of the selected remedy (USEPA, 1995). This makes S/S the most frequently selected technology for treating the source of contamination. In the treatment of industrial hazardous wastes, the EPA has identified S/S as Best Demonstrated Available Technology (BDAT) for 57 Resource Conservation & Recovery Act (RCRA) listed wastes (USEPA, 1993).

Portland cement* alone accomplishes these objectives to a high degree in many instances, but some situations (because of the waste itself, the disposal scenario, and/or the regulatory requirements) require the use of additives or physical/chemical techniques to provide improved properties in the waste form or to

counter problems in solidification caused by the waste itself. The purpose of this Guide is to explain these additives and techniques, the problems encountered in S/S that may require their use, and how they are applied in treatment operations. The Guide is intended to be a practical tool. It is not a discussion of mechanisms and theory.

There are a number of standard types of portland cement, categorized as ASTM Types I through V, with sub-types within some of these. While there has been some investigation of the efficacy of using different cement types in S/S, experience to date indicates that this is not a common practice, and there is often little difference between the types for S/S work. Generally, Type I is used because it is readily available everywhere and is often the least expensive. However, in certain geographical areas, Type II or other types may be more available and/or cheaper, and therefore more practical.

The American Society for Testing and Materials (ASTM) Designation C 150, Standard Specification for Portland Cement, provides for eight types of portland cement as follows:

Type I	normal
Type IA	normal, air-entraining
Type II	moderate sulfate resistance
Type IIA	moderate sulfate resistance, air-entraining
Type III	high early strength
Type IIIA	high early strength, air-entraining
Type IV	low heat of hydration
Type V	high sulfate resistance

* In this Guide, the term "cement" will refer to Type I Portland Cement, unless otherwise stated.

The use of cement in S/S has different requirements than its common use in concrete and mortars — for example:

- S/S has much lower strength requirements than concrete - normally less than 100 psi vs thousands of psi;
- Fast set and high early strength are usually not required, and may not be desirable, in S/S;
- Long term physical durability - resistance to freeze/thaw and wet/dry cycling, and immersion in water - are not normally important, although they may be required in some specifications;
- Physical properties, in general, usually are less important in S/S work than are the system's ability to immobilize hazardous constituents in the waste;
- Concrete chemistry is complex. The chemistry of waste-cement systems is even more so, due to the very complex nature of most wastes.

Many additives have been tried out in cement-based S/S processes. A listing of the most important, most commonly encountered additive types is given in Table 1 (pp 28-32). Many of these have been used commercially or at pilot scale; some have only been tested in the laboratory. There are also a number of proprietary additives and formulations available commercially, but these are generally based on the generic categories listed here. For this reason, and because the composition of the proprietary products is usually not given, these products are not discussed as such unless no generic equivalent is available. In addition to additives, various physical/chemical techniques are also used for similar purposes. Table 2 lists these techniques.

The problems encountered in S/S can be broadly classified into *solidification* problems, i.e., obtaining the required physical properties in the resultant waste form; and *stabilization* problems, i.e., adequately immobilizing the waste constituents. To more effectively discuss the subject, this Guide is organized in the following manner:

1. Problems in Solidification and Physical Property Development:
 - Setting Problems
 - Compressive Strength Development Problems
 - Permeability Development Problems
 - Durability Problems

The challenges described here are those of development of physical properties in the *solidified* waste form, and the term *solidification* is used to describe the process. Table 3 (pp 33-37) lists the additives and techniques that are most important in solidification, or have been proven for this use in actual applications. Other possible solutions to these problems are discussed and referenced in the text.

2. Problems in Target Constituent Stabilization - Chemical Properties:
 - Metals
 - Organics
 - Organo-Metallics
 - Soluble Salts

The challenges described here are those of development of chemical properties, i.e., immobilization of certain species, in the *stabilized* waste form, and the term *stabilization* is used to describe the process. Tables 7 and 9 (pp 38-39, 43-44) list the more important additives and techniques used in stabilization, or those that have been proven for this use in actual applications. Other possible solutions to these problems are

Table 2. Physical/Chemical Techniques Used in Cement-based S/S

TECHNIQUE	EFFECT	RELATIVE COST
Aeration:	Alteration of biological status; removal of interfering volatiles	Low
Temperature Control:	Acceleration of reaction rate to counter retarding effect; improvement of leaching characteristics	Low
Viscosity/Pumpability Alteration:	Important for some applications where pumping of treated waste before curing is necessary	Low to Moderate
Humidity Control:	Prevention of excessive drying during curing	Low
Dewatering:	Removal of excess free water	Low to Moderate
Air Entrainment:	Addition of air into the structure to provide better freeze/thaw durability	Low
Mixing Type and Degree:		
Ex-Situ	Prevent over-mixing, assure adequate mixing	Low
In-Situ	Necessary for proper slurry-grout formulation	Low to Moderate

discussed and referenced in the text.

3. Additives Used in Cement-based Stabilization/Solidification:

Metal Stabilization

Immobilization of Organic Constituents

Processing and Anti-Inhibition Aids

Additives of commercial importance are discussed individually, or by chemical type, in more detail.

4. Physical/Chemical Techniques Used in Cement-based Stabilization/Solidification:

Anti-Inhibition Aids

Physical Property Development

Processing Aids

Mixing Techniques

Various physical/chemical techniques other than the use of additives are discussed in more detail.

A great deal of attention has been paid to "interference mechanisms" in cement-based systems. Considerable experimental work was done for the EPA at the U.S. Army Corps of Engineers Waterways Experiment Station (WES) on the causes, effects, and cures for this problem (United States Environmental Protection Agency, 1982; U.S. Army Corps of Engineers Waterways Experiment Station, 1990; Battelle Columbus, 1993). Conner (1990) describes the various additives used in S/S and summarizes the chemical factors that affect solidification. Other individual investigators and summaries (Coté, 1986; Eaton et al., 1987; El-Korchi et al., 1990; Spence, 1992) have contributed to the knowledge base on this subject, and the reader is referred to these sources for further detailed information.

II. PROBLEMS IN SOLIDIFICATION AND PHYSICAL PROPERTY DEVELOPMENT

There are many factors which retard, inhibit and accelerate the setting and curing of S/S systems. Some also affect the final strength, permeability and other physical properties of the fully cured S/S product. Others affect chemical properties, which will be discussed in Section III, Problems in Target Constituent Stabilization - Chemical Properties. Many of the compounds, materials and factors which are known to have such solidification effects were described by Conner (1990), Battelle Columbus (1993), U.S. Army Engineer Waterways Experiment Station (1990), U.S. Army Engineer Waterways Experiment Station (1990), and Eaton et al. (1987); some are general knowledge in the field of cement technology (Portland Cement Association, 1979).

The effects are many and varied, but in spite of our knowledge about them, these effects are not simple to

predict and sort out from knowledge of the composition of the waste, even when that information is available. Most often, a number of species are present in the waste, sometimes with opposing effects. The same species may have opposite effects depending on concentration. This latter phenomenon has been found with calcium chloride, calcium sulfates, sodium hydroxide, sodium silicate, lead, copper and tin salts, amines and hexachlorobenzene. For example, ion exchange can inhibit or retard S/S reactions by removing calcium from solution, preventing it from entering into the necessary cementitious reactions (Conner, 1990). It can also accelerate the process by removing interfering metal ions from solution. Which occurs may depend on the selectivity of the ion exchange material. Other examples are metals that may retard and inhibit the reactions by substituting for calcium in the cementitious matrix, which may explain the effect of magnesium in dolomitic lime and lime products. Certain substances are natural or synthetic complexing agents which remove calcium from availability in the setting and curing reactions. On the other hand, alcohols, amides and specific surfactants can aid in wetting solids and dispersing fine particulates and oil which interfere with reactions by coating the reacting surfaces. Flocculants can also serve this purpose. Some of these materials and techniques are discussed in sections IV and V.

Specific problems and solutions which have been used are discussed below. They are also summarized and tabulated in Table 3.

Setting Problems

Will not set. Waste form remains non-solid even after curing for up to 28 days.

Cause:

Fine particulates coating cement particles, preventing or slowing reaction: silt (Kitsugi, 1976) (Kitsuge and Kozeki, 1976), clay (Kitsugi, 1976) (Kitsuge and Kozeki, 1976), colloidal matter (Kitsugi, 1976) (Kitsuge and Kozeki, 1976)

Possible Solution:

Use surface active agents: wetting agents (amides, alcohols), dispersants (carboxylic acids, carbonyls, sulfonates), flocculants (amines, iron salts, magnesium salts, silica) to remove and coagulate fine particulates

Cause:

Anaerobic conditions

Possible Solution:

1. Aerate
2. Add oxidizer
3. Add lime, soluble silicate (Conner, 1990)

(Conner, 1974) (USEPA, 1982)

4. Add biocide — commercial products are available

Cause:

Calcium removers in the waste: phosphates

Possible Solution:

Replace lost calcium

Sets, but does not harden. Waste form undergoes an initial set, but does not harden further even after curing for up to 28 days.

Cause:

Fine particulates coating cement particles, preventing or slowing reaction: silt (Kitsugi, 1976) (Kitsuge and Kozeki, 1976), clay (Kitsugi, 1976) (Kitsuge and Kozeki, 1976), colloidal matter (Kitsugi, 1976) (Kitsuge and Kozeki, 1976)

Possible Solution:

Use surface active agents: wetting agents (amides, alcohols), dispersants (carboxylic acids, carbonyls, sulfonates), flocculants (amines, iron salts, magnesium salts, silica) to remove and coagulate fine particulates

Cause:

Anaerobic conditions

Possible Solution:

1. Aerate
2. Add oxidizer
3. Add lime, soluble silicate (Conner, 1990) (Conner, 1974) (USEPA, 1982)
4. Add biocide — commercial products are available

Cause:

Calcium removers in the waste: phosphates, glucose

Possible Solution:

Replace lost calcium

Set is retarded. Waste form set and hardening are retarded, but both take place more or less normally after curing for up to 28 days. Set retardation may last for a week or more.

Cause:

Fine particulates coating cement particles, preventing or slowing reaction: silt (Kitsugi, 1976) (Kitsuge and Kozeki, 1976), clay (Kitsugi, 1976) (Kitsuge and Kozeki, 1976), colloidal matter (Kitsugi, 1976) (Kitsuge and Kozeki, 1976)

Possible Solution:

Use surface active agents: wetting agents (amides, alcohols), dispersants (carboxylic acids, carbonyls, sulfonates), flocculants (amines, iron salts, magnesium salts, silica) to remove and coagulate fine particulates

Cause:

Presence of sugar, sugar derivatives (Portland Cement Association, 1979) (Kitsugi, 1976) (Kitsuge and Kozeki, 1976)

Possible Solution:

1. Add more sugar - 0.2%; an optimum level of sugar may be difficult to achieve. (Portland Cement Association, 1979)
2. Add a sorbent: clay, flyash, diatomaceous earth, carbon
3. Chemical oxidation with potassium permanganate, sodium persulfate, calcium or sodium hypochlorite

Cause:

Presence of phosphates (Kitsugi, 1976) (Kitsuge and Kozeki, 1976)

Possible Solution:

Add calcium ion in excess (cement kiln dust, hydrated lime)

Cause:

Presence of sulfur (Battelle Columbus, 1993)

Possible Solution:

None established

Cause:

Presence of bicarbonates of sodium and potassium (Portland Cement Association, 1979)

Possible Solution:

Pretreat with acidic material to decompose bicarbonate

Cause:

Presence of other chemical interference - inorganics, general (U.S. Army Engineer Waterways Experiment Station, 1990) (Battelle Columbus, 1993) (Cullinane et al., 1986) (Cullinane et al., 1987); presence of certain inorganic salts (Cullinane et al., 1986) (Cullinane et al., 1987): salts of magnesium (Battelle Columbus, 1993), tin (Battelle Columbus, 1993), zinc (Battelle Columbus, 1993) (ASTM, 1985) (Cullinane et al., 1987), arsenic (El-Korchi, 1990), chromium (El-Korchi, 1990), cadmium (El-Korchi, 1990), copper (Battelle Columbus, 1993) (Cullinane et al., 1987) and lead (Battelle Columbus, 1993) (El-Korchi, 1990) (Cullinane et al., 1987), sodium iodate (Battelle Columbus, 1993), sodium phosphate (Battelle Columbus, 1993), sodium arsenate (Battelle Columbus, 1993), sodium borate (Battelle Columbus, 1993), sodium sulfide (Battelle Columbus, 1993), sodium hydroxide (Cullinane et al., 1987), sodium sulfite (Cullinane et al., 1987)

Possible Solution:

Add sulfates (Kitsugi, 1976) (Harada et al., 1977),

soluble silicates (Conner, 1990) (Conner, 1974) (USEPA, 1982), aluminates (Kitsuge and Kozeki, 1976) (Harada et al., 1977), phosphates (Carlson, 1987), hydroxylated organic acids (Bonnell and Hevanee, 1972), glycols (U.S. Patent 3,642,503) (Harada et al., 1977), amines (Harada et al., 1977), iron compounds (for sulfides, tin lead, arsenates) (Conner, 1990) (Electric Power Research Institute, 1996), ASTM set accelerators (U.S. Army Engineer Waterways Experiment Station, 1990), other organics.

Cause:

Presence of other chemical interference - chelating agents (Battelle Columbus, 1993) (U.S. Army Engineer Waterways Experiment Station, 1990): ethylenediaminetetracetic acid (EDTA), nitrilotriacetic acid (NTA), lignins, tannins, glucose, starch

Possible Solution:

See possible solutions above under inorganics

Cause:

Presence of other chemical interference - organics, general: oil, grease, tars, resins, carbohydrates, phenol, trichloroethylene, hexachlorobenzene, coal, lignite, general organics (Cullinane et al., 1987) (El-Korchi, 1990) (Eaton, 1987) (Cullinane et al., 1986) (Battelle Columbus, 1993) (U.S. Army Engineer Waterways Experiment Station, 1990)

Possible Solution:

1. Add sorbent (cement kiln dust, clays, lime, limestone, flyash, carbon)
2. Evaporate VOCs
3. Chemical oxidation with hydrogen peroxide, potassium permanganate, sodium persulfate, calcium or sodium hypochlorite
4. See also possible solutions above under inorganics

Cause:

Mild anaerobic conditions

Possible Solution:

1. Aerate
2. Add oxidizer
3. Add lime, soluble silicate (Conner, 1990) (Conner, 1974) (USEPA, 1982)
4. Add biocide — commercial products are available

Cause:

Insufficient cure time

Possible Solution:

Cure longer

Cause:

General retardation of set

Possible Solution:

Add calcium chloride (<2%) (Blake, 1975), sodium silicate (Conner, 1990) (Conner, 1974), lime (Conner, 1990)

Supernatant liquid on surface, or softer surface layer, after setting.

Large differences in specific gravity between the waste and the reagent result in a tendency toward phase separation. Most reagents used in S/S have particle specific gravities much larger than the waste density as a whole: >2.0 versus 1.0 to 1.5 in most systems. Although reagent particle size is generally small, it is not usually sufficient to make up for this difference, and some settling will occur unless viscosity is sufficient to prevent phase separation until the initial setting reaction can physically immobilize all components in place. Alternatively, sufficient reagent can be added to quickly take up all the free water, or a viscosity-increasing agent can be added. Rheological agents which accomplish the latter technique are available, but add significantly to the cost of the process and sometimes can interfere with the reactions which must subsequently take place for proper curing. Gellants such as soluble silicates do this by causing an almost immediate thickening or gelling reaction between free calcium ion from the cement and the silicate, creating an elastic silica gel which does not interfere with cement or pozzolanic reactions.

Cause:

Set is too slow

Possible Solution:

Add set accelerator: calcium chloride (<2%) (Blake, 1975) (U.S. Army Engineer Waterways Experiment Station, 1990); sulfates, soluble silicates (Conner, 1990) (Conner, 1974), aluminates (Kitsuge and Kozeki, 1976) (Harada et al., 1977), hydroxylated organic acids (Bonnell and Hevanee, 1972), or glycols (U.S. Patent 3,642,503) (Harada et al., 1977); amines (Harada et al., 1977); other organics

Cause:

Water content is too high

Possible Solution:

1. Dewater. Decant water; filter raw waste
2. Add sorbent
3. Add bulking agent
4. Add low-cost, reactive bulking agent: cement kiln dust, flyash, blast furnace slag (Chudo et al., 1981)

Cause:

Viscosity of system is too low

Possible Solution:

Increase viscosity of system, using gelling agent or sorbent: soluble silicates, flyash, clay (dried or

expanded), organic sorbents (wood chips, corn cob, etc.)

Sets too rapidly for satisfactory processing. Some wastes contain, or act as, cement setting accelerators, causing the set to be so rapid that the cement cannot be uniformly mixed into the waste in the desired treatment scheme, or the waste cannot be handled as required after mixing. The former problem is especially important in ex-situ batch mixing, and in some in-situ processes.

Cause:

Presence of accelerating agents: sulfates; soluble silicates, aluminates, phosphates; hydroxylated organic acids, glycols, other organics; ion exchange material

Possible Solution:

1. Use a proprietary, concrete set retarder
2. Add zinc, copper or lead oxide/hydroxide; calcium chloride (>4%); magnesium and tin salts; phosphates, chlorides, sugars (Metcalf and Eilers, 1980), clays
3. Lignosulfonic acid salts and derivatives, hydroxylated carboxylic acids, polyhydroxy compounds (ASTM C494, Types A and B) (U.S. Army Engineer Waterways Experiment Station, 1990)

Cause:

Presence of carbonates and bicarbonates of sodium and potassium (Portland Cement Association, 1979)

Possible Solution:

Decompose or neutralize with acid or acidic additive

Cause:

Presence of sugar at high level (0.2% or more) (Portland Cement Association, 1979)

Possible Solution:

1. Add a retarder (see above)
2. Chemical oxidation with hydrogen peroxide, potassium permanganate, sodium persulfate, calcium or sodium hypochlorite

Compressive Strength Development Problems

Insufficient unconfined compressive strength. The final waste form has insufficient unconfined compressive strength (ASTM D-2166, D-1633) for the intended disposal scenario, even after full curing.

Cause:

Insufficient cement to develop desired strength

Possible Solution:

Use more cement

Cause:

Presence of salts of manganese, tin, zinc (Cullinane et al., 1987), copper (Cullinane et al., 1987) and lead (Portland Cement Association, 1979) (Cullinane et al., 1987)

Possible Solution:

Add sulfates (Kitsugi, 1976) (Harada et al., 1977), soluble silicates (Conner, 1990) (Conner, 1974), aluminates (Kitsugi and Kozeki, 1976) (Harada et al., 1977), phosphates (Carlson, 1987), hydroxylated organic acids (Bonnell and Hevane, 1972), glycols (U.S. Patent 3,642,503) (Harada et al., 1977), amines (Harada et al., 1977), other organics.

Cause:

Presence of sodium sulfide (Portland Cement Association, 1979), sodium sulfite (Cullinane et al., 1987) and sodium hydroxide (high concentrations) (Cullinane et al., 1987)

Possible Solution:

1. Chemical oxidation with hydrogen peroxide, potassium permanganate, sodium persulfate, calcium or sodium hypochlorite
2. Neutralization (sodium hydroxide)
3. Add iron salts: ferrous sulfate to immobilize sulfide ion

Cause:

Presence of sugar (Portland Cement Association, 1979)

Possible Solution:

Chemical oxidation with hydrogen peroxide, potassium permanganate, sodium persulfate, calcium or sodium hypochlorite

Cause:

Presence of algae (Portland Cement Association, 1979)

Possible Solution:

1. Add sorbent (clays, limestone, flyash, carbon)
2. Chemical oxidation with hydrogen peroxide, potassium permanganate, sodium persulfate, calcium or sodium hypochlorite
3. Add lime
4. Add a biocide — commercial products are available

Cause:

Anaerobic conditions

Possible Solution:

1. Aerate
2. Add oxidizer
3. Add lime, soluble silicate (Conner, 1990) (Conner, 1974) (USEPA, 1982)
4. Add biocide — commercial products are available

Cause:

Presence of oils (Portland Cement Association, 1979) and grease (Cullinane et al., 1987)

Possible Solution:

1. Add sorbent: bentonite (Gilliam and Wiles, 1996, p. 584), limestone, flyash (Gilliam and Wiles, 1996, p. 584), carbon
2. Evaporate VOCs
3. Chemical oxidation with hydrogen peroxide, potassium permanganate, sodium persulfate, calcium or sodium hypochlorite
4. Add quicklime (CaO)
5. Add phosphorus pentoxide and a stearate (Takashita, 1979)

Cause:

Water content is too high

Possible Solution:

Dewater, use a water reducing agent (ASTM C-494 Types A, D, F and G) if applicable (U.S. Army Engineer Waterways Experiment Station, 1990)

Permeability Development Problems

High Permeability. Permeability of the final waste form is too high (SW846, Method 9100).

Cause:

Incomplete curing of waste form

Possible Solution:

Cure for at least 28 days before testing

Cause:

Insufficient cement to develop the required matrix

Possible Solution:

Use more cement

Cause:

Waste has natural high permeability

Possible Solution:

1. Add bentonite clay (Conner, 1990)
2. Add hydrophobizing agent (Conner, 1986)
3. Add a stearate (Portland Cement Association, 1974)(Takashita, 1979)
4. Add a pore filling and/or hydrophobic organic polymer compatible with cement
5. Develop better microstructure with flyash ((Gilliam and Wiles, 1996, p. 251), slag (Gilliam and Wiles, 1996, p. 251), silica fume (Gilliam and Wiles, 1996, p. 135)

Durability Problems

Poor durability, stability, or strength. Final waste form has poor freeze-thaw or wet-dry durability

(ASTMD-4842-90, D-4843-88), poor immersion stability (10 CFR 61, Regulatory Guide, May 1983), or poor strength (see Compressive Strength Development Problems Sections above).

Cause:

Insufficient cement

Possible Solution:

Add more cement

Cause:

Poor microstructure

Possible Solution:

1. Add flyash ((Gilliam and Wiles, 1996, p. 251), slag (Gilliam and Wiles, 1996, p. 251), silica fume (Gilliam and Wiles, 1996, p. 135), etc. to improve microstructure
2. Air entrainment (U.S. Army Engineer Waterways Experiment Station, 1990)

Cause:

Excessive porosity, due to non-optimum water content

Possible Solution:

1. Modify water content by addition or removal
2. Add bulking agent or water absorber
3. Add a pore filling and/or hydrophobic organic polymer compatible with cement
4. Add wood resins, proteinaceous materials, synthetic detergents (ASTM C-260) (U.S. Army Engineer Waterways Experiment Station, 1990)

Cause:

Presence of large amounts of soluble salts: sulfates, nitrates, chlorides

Possible Solution:

For treatment of waste in saline or brackish environments, as near a coast, some projects have specified Type II or Type V sulfate resistant cements

III. PROBLEMS IN TARGET CONSTITUENT STABILIZATION - CHEMICAL PROPERTIES

In contrast to solidification, there is only one basic problem in stabilization — the degree of immobilization of the target constituents of concern: metals, organics, organo-metallics, and salts. In most cases, these are entities that are hazardous to human health and the environment. The solutions to the problem, however, depend on the particular inorganic or organic compound of interest. Therefore, discussion of additive use in stabilization is organized along the lines of particular chemical species.

Metals

The stabilization of metals in hazardous wastes has been done at remedial operations and at fixed treatment sites in the U.S. for more than 20 years. Many private companies have been running stabilization operations for metals at RCRA Treatment, Storage and Disposal Facilities (TSDFs) for decades, treating literally thousands of different waste streams. Government and private research and testing laboratories have done tens of thousands of treatability studies to develop formulations for all RCRA metals, as well as for the more recent constituents of concern: copper, nickel, zinc, antimony, beryllium, and vanadium.

Table 4 is a list of metals which are regulated by federal or state agencies in the United States. These are the metals of primary concern in stabilization technology, and are commonly referred to as the "toxic metals" or "RCRA metals." Those marked with an asterisk are the Toxicity Characteristic (TC) metals for which EPA established required treatment levels using the Toxicity Characteristic Leaching Procedure (TCLP) (USEPA, 1990). The other metals have been controlled under the Land Disposal Restrictions (LDRs) (USEPA, 1985), the Universal Treatment Standards (UTS) (USEPA, 1994), or state regulatory systems.

Table 5 lists many of the types of metal compounds that may be found in waste streams. The asterisk denotes the more common species. This listing does not include anions containing the toxic metals themselves, or individual organic complexes.

More is known about metal stabilization than about the stabilization, destruction and immobilization of any other hazardous constituent group encountered in stabilization technology. The mobility of these metals in a landfill situation, as measured by leaching tests such as the TCLP, is greatly reduced in the vast majority of treatment scenarios by simple stabilization with cement-based S/S systems, with or without additives or special techniques. Some metals and metal species may require more complex formulations or pre-treatment. Species that have been encountered in actual wastes are listed in Table 6. In addition, non-additive methods such as temperature adjustment (Vejmelka et al., 1985) and control of free

Table 4. Toxic Metals

Antimony	Lead*	Vanadium
Arsenic*	Mercury*	Zinc
Barium*	Nickel	
Beryllium	Selenium*	
Cadmium*	Silver*	
Chromium	Thallium	* TC Metals

Table 5. Metal Species

Acetates	Ferrocyanides	Phosphates*
Bromides	Fluorides	Silicates*
Carbonates*	Hydroxides*	Sulfates*
Chlorides *	Iodides	Sulfides*
Citrates	Nitrates*	Organic Complexes
Cyanides	Oxalates	
Ferricyanides	Oxides	

water may be used. Most of these special situations require either changing the valence state of the metal, or dealing with metal complexes. Methods for reducing mobility of these species are discussed under the following individual metal headings, and are summa-

Table 6. Potential Problem Metal Species

Arsenic trisulfide - As_2S_3	Organo-mercury compounds
Trivalent arsenic compounds - As^{+3}	Nickel cyanide
Organo-arsenic compounds	Organo-nickel compounds
Hexavalent chromium and its compound - Cr^{+3}	Hexavalent selenium and its compounds - Se^{+6}
Metallic lead	Finely divided elemental metals
Organo-lead compounds	
Metallic mercury	

rized and tabulated in Table 7 (pp 38-39); metals or metal species that are adequately stabilized by cement alone, and do not require additives, are shaded in the table. Table 8 (pp 40-42) provides a general summary of actual, commercial additive utilization for various metals and metal species. It should be noted that flyash or bedash is often used in commercial processes, especially at TSDFs, for a variety of reasons other than metal stabilization, but it is difficult to separate out the actual purpose in most cases. Additives per se will be discussed in Section IV. Following are brief discussions of the various metals of concern, and their stabilization treatment.

Antimony. Antimony may exhibit a valence of -3,+3, or +5, and is classified as a non-metal or metalloid; the trivalent state exhibits metallic characteristics. It forms a number of inorganic and organic compounds, many of complex structure. Until the LDRs, antimony compounds in wastes were hazardous only under California regulations, with a reasonably high allowable leaching level. Very little information is available on stabilization methods (although leachate analyses often include antimony) and problems with antimony stabilization were rarely, if ever, encountered. An

internal study at Chemical Waste Management (Chemical Waste Management, 1992) on K061 waste (Electric Arc Furnace Dust) and soil spiked with antimony chloride showed that simple stabilization with cement provided excellent reduction in mobility, with leaching levels below 0.11 mg/l, the Level of Quantification (LOQ) for analysis. Higher cement content (up to mix ratios of 1.0 at least) did not increase leachability, indicating that antimony is not sensitive to over-treatment.

Arsenic. Arsenic is also classified chemically as a nonmetal or metalloid, although it is grouped with the metals for most environmental purposes. Its principal valence states are +3, +5 and -3. The compounds of arsenic listed below are those commonly found in waste materials.

Arsenic trioxide, As_2O_3

Cacodylic Acid and Sodium Cacodylate

Metal Arsenates

$Ca_3(AsO_4)_4$

$PbHAsO_4$ - acid lead arsenate

$Pb_4(PbOH)(AsO_4)_3 \cdot H_2O$ - basic lead arsenate

$Cu(CuOH)AsO_4$

$5ZnO \cdot 2As_2O_5 \cdot 4H_2O$

Na_2HAsO_4

$MnHAsO_4$

Metal Arsenites

Sodium arsenite, $NaAsO_2$

Copper acetoarsenite,

$(CH_3CO_2)_2Cu \cdot 3Cu(AsO_2)O_3$, or Paris green

Arsenic Sulfides

Arsenic trisulfide, As_2S_3

Arsenic sulfide, As_4S_4

Arsenic pentasulfide, As_2S_5

The oxide is amphoteric and thus is soluble in both acids and bases. Arsenites are often present as complexes such as Scheele's green, $CuHAsO_3$, and copper acetoarsenite described previously. Arsenates derived from the arsenic acids are oxidizing agents. Arsenic forms the three sulfides described above. The trisulfide is soluble only in bases. It is often encountered in waste from phosphoric acid manufacture where it is precipitated from strong acid solution. This property is an unusual one for metal sulfides, which are usually decomposed by acids, but are stable and have low solubility in bases.

Normally, traditional chemical stabilization processes are able to immobilize arsenic in contaminated soils, incinerator ashes and other wastes to well below regulatory requirements (Conner and Lear, 1992). Certain arsenical species—arsenic trisulfide and organic arsenicals, primarily—are very difficult to stabilize by conventional, chemical means. One solution to this problem has been the use of alkaline oxidation, hydro-

lyzing the sulfide and oxidizing As^{+3} to As^{+5} with subsequent precipitation as calcium arsenate, a relatively insoluble species (Conner, 1993a). Another is the use of ferrous sulfate as an additive (Electric Power Research Institute, 1996). Young (1979) reported improved resistance to arsenic leaching by the addition of calcium and manganese chlorides, sulfates, and acetates. The organic arsenical problem is discussed below in the section on Organo-Metallic Compounds.

Barium. Barium is classed as an alkaline earth metal (Group IIA of the periodic table), along with calcium whose chemical behavior it resembles. Its valence state is +2. Barium is present in many waste streams, and is also easily stabilized to well below RCRA levels. Barium leaching is not a problem in any experience to date. Even with extremely high barium wastes, it is sufficient to add sodium sulfate or gypsum to any standard stabilization formulation to precipitate barium as the sulfate. Very often, even drinking water standards can be achieved in the leachate.

Beryllium. Beryllium, along with thallium and zinc, appeared in the RCRA Listed Waste K061 LDRs. It rarely has been analyzed for in other non-wastewater hazardous wastes, so there is little data on its stabilization. In one study (Chemical Waste Management, 1992), K061 waste and soil spiked with beryllium were easily stabilized to below LOQ (<0.01 mg/l) with cement alone, with greater than three orders of magnitude reduction in TCLP leachability. Higher cement content (up to mix ratios of 1.0 at least) did not increase leachability, indicating that beryllium is not sensitive to over-treatment.

Cadmium. Cadmium is a Group IIB element, with only one valence state for all practical purposes (+2). Cadmium compounds present in wastes may include:

Cadmium Arsenides, Antimonides, and Phosphides

Cadmium Borates

Cadmium Carbonate

Cadmium Complexes

Cadmium Halides

Cadmium Hydroxide

Cadmium Nitrate

Cadmium Oxide

Cadmium Selenide and Telluride

Cadmium Sulfate

Cadmium Sulfide

Cadmium Tungstate

Unlike zinc, the cadmium ion is not very amphoteric and its hydroxide, $Cd(OH)_2$, has quite low solubility in an alkaline medium. In view of the low solubility

of most cadmium species in alkaline systems, and the non-amphoteric nature of Cd, the primary treatment method has been precipitation with nearly any alkali, including cement and lime. In the presence of complexing agents, such as cyanide, the cadmium ion will not precipitate (Weiner, 1967). It is then necessary to destroy the cyanide complex, usually by alkaline chlorination, which precipitates the Cd as the hydroxide. Oxidation of cyanide by hydrogen peroxide is also reported to break the complex and precipitate CdO. In most cases, even the lowest LDR level can be met with standard stabilization formulations, especially cement-based formulations. High pH caused by over treatment (excessive mix ratios) is not a problem with cadmium as it is with chromium and lead.

Chromium. Chromium belongs to Group VIB of the periodic table. It has three valence states, +2, +3, and +6, but the latter two are the most common. Cr⁺⁶ is acidic, forming chromates (CrO₄)⁻² and dichromates (Cr₂O₇)⁻², while the other valence states are basic. The major chromium compounds encountered in stabilization work are composed of Cr⁺³ and Cr⁺⁶ valence states in the following compounds:

- Pigments - lead chromate, chromium oxide greens
- Chromium sulfate
- Chromated copper arsenate (CCA)
- Chromium lignosulfonates
- Sodium or potassium dichromate
- Chromic acid
- Ammonium dichromate
- Chromic nitrate

Cr⁺⁶ compounds are usually reduced to the trivalent state and precipitated with bases. The resultant Cr(OH)₃ is the form in which the majority of chromium is encountered in stabilization treatment. Because of its low solubility, fixation of chromium as this species has not been a problem, even though chromium is nearly ubiquitous in waste streams. As long as chromium is speciated as Cr⁺³, stabilization of characteristic wastes to the Toxicity Characteristic level is easy if the final leachate pH is maintained above 6.0. In wastes, this generally requires cement mix ratios above 0.2, or cement kiln dust above 0.5, the latter depending heavily on the alkalinity of the dust.

The hexavalent form is encountered in a number of wastes, either by mixing of untreated chromate solutions with wastewater treatment sludge or because it is intrinsic to the waste, as in some incinerator residues and in wood-treating wastes. It is also a major problem where soil has been contaminated with chromate or chromic acid solutions, a frequent situation with old plating operations. The classical way to manage Cr⁺⁶ has been a two-step process:

reduce the chromium to the trivalent state and then precipitate it as the hydroxide. However, especially when the Cr⁺⁶ level is low, reducing agents such as ferrous sulfate, sodium metabisulfite, or sodium hydrosulfite may be added directly to the cement or cement kiln dust based stabilization system.

Chromium is amphoteric, and so exhibits minimum solubility at around pH 9, with increasing leachability at higher pH. However, empirical measurements in cement-based stabilization systems (Cote 1986) have shown that leachability of Cr⁺³ compounds does not increase substantially below pH 12+. Therefore, over-treatment is normally not a problem and high reductions in mobility of Cr⁺³ compounds can be achieved at almost any mix ratio.

Lead. Lead is a member of Group IVA of the periodic table. It has two valence states, +2 and +4, with the +2 state being the most common. Pb⁺⁴ compounds are regarded as being covalent, while Pb⁺² compounds are primarily ionic. Lead is amphoteric and forms soluble, anionic plumbites and plumbates as well as both cations. Lead compounds encountered in stabilization include:

- Halides
- Oxides
- Sulfide
- Sulfate
- Nitrate
- Acetates
- Carbonates
- Silicates
- Organolead Compounds

In lead stabilization, pH control is more important than with most metals. Minimum lead leaching in nearly all stabilization systems occurs when the pH is maintained between about 8 and 10 in the leachate, but substantial reduction in leachability can be attained in most instances up to pH 12. In most wastes, lead is easily stabilized to the TC requirements, and leaching reductions of two or more orders of magnitude are common in cement-based systems. Research on stabilization of F006 and, especially, K061 wastes, has often focussed on lead, and as a result there are large data bases on lead stabilization. In some cases, remedial projects require the achievement of very low lead levels, sometimes at the drinking water level. This may necessitate the use of additives such as carbonates or sulfur compounds.

The use of calcium carbonate has become common practice in treatability studies on lead-contaminated soils and many other wastes. The function of carbonate is not clear. It may result in the formation of lead carbonate or basic lead carbonate

[$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$], which are much less soluble than lead hydroxide. It also buffers many systems to more moderate pH, but simple buffering action does not explain all of the effects of calcium carbonate. Because they are inexpensive, cannot cause over-treatment, and are applicable to a very wide range of lead-contaminated wastes, cement-calcium carbonate formulations are often the best overall choice for lead-contaminated soil and debris treatment.

Mercury. Mercury salts exist in two valence states, +1 and +2. Many mercury compounds are volatile; they are also labile and easily decomposed by light, heat, and reducing agents, even weak reducing agents such as amines, aldehydes, and ketones. Because of their covalent nature and ability to form a variety of organic complexes, mercury compounds have unusually wide solubility. Compounds that may be found in wastes are:

- Mercuric Chloride
- Mercuric Oxide
- Mercuric Nitrate
- Mercuric Sulfate
- Mercuric Sulfide
- Organomercury Compounds

Mercury concentrations found in most wastes are quite low, and substantial reduction in mercury leachability is easily accomplished in most stabilization processes. Even at higher levels—100 mg/kg or more—stabilization is very effective. If necessary, lower leachability—to the 0.01 mg/l level or below—can be attained by additions of inorganic or organic sulfides or elemental sulfur. The only area where stabilization difficulty might be encountered is where elemental mercury or organo-mercury compounds are present, but this appears to be quite uncommon.

Nickel. Nickel is a Group VIII transition element, along with iron and cobalt. It forms compounds in which the nickel atom has the oxidation states of -1, 0, +1, +2, +3 and +4. The Ni^{+2} valence state, however, represents the majority of all nickel compounds. Nickel is not amphoteric, but the ease with which it forms coordination complexes at high pH gives it the appearance of being so. $\text{Ni}(\text{OH})_2$ has low water solubility, which accounts for the adequate fixation of nickel in most wastes by simple pH control. Nickel compounds encountered in wastes include:

- Nickel Oxide
- Nickel Sulfate
- Nickel Nitrate
- Nickel Halides
- Nickel Carbonate
- Nickel Hydroxide

- Nickel Fluoroborate
- Nickel Cyanide
- Nickel Sulfamate
- Nickel Sulfide

Where proper pH control is exercised, there is usually no difficulty in fixing nickel, but more recent LDR requirements sometimes are difficult to meet without additives. The simplest approach in this situation is the addition of organo-sulfur compounds. The most common difficulties that are encountered have been caused by the presence of complexed nickel, either a cyanide complex or an organo-complex, especially the latter (see organo-metallics below). Non-complexed nickel species do not appear to be sensitive to over-treatment.

Selenium. Selenium is next to sulfur in group VIA, and between arsenic and bromine in period 4 of the periodic table. It forms compounds, both inorganic and organic, similar to those of sulfur. Its valence states are -2, 0, +4, and +6. The most important compounds of selenium are halides, oxides, oxyacids (H_2SeO_3 - selenious, and H_2SeO_4 - selenic), and selenides. Selenates, if known to be present at high levels, would pose a potential leaching problem because of their solubility. Possible treatment would be either reduction to the selenite form, or precipitation with strontium to produce the low solubility strontium selenate.

Rarely is selenium found in industrial wastes in appreciable amounts, and selenium leaching above the RCRA level of 1.0 mg/l, even from the untreated waste, is seldom encountered. In stabilization-treated wastes, leaching is usually below detection limits, with substantial reductions in mobility. Selenium at high levels or in some complex species that might prove difficult to stabilize have not been reported in the literature (Conner 1990). However, the selenate ion appears to have been encountered in at least one instance (Conner, 1994). Ferrous sulfate, probably as a co-precipitant, is believed to be useful for selenates, and precipitation as strontium selenate has been proposed. In most instances, selenium stabilization with simple cement or pozzolan systems appears to be straightforward.

Silver. Silver is a noble metal with only one normal valence state. Most of its compounds are relatively insoluble, especially the halides, cyanide, sulfide, and thiocyanate. Because of the value of silver, and the ease with which most dissolved species can be precipitated by chloride ion, fixation of silver in stabilization systems is rarely a problem since very little is normally present. Leaching results are normally be-

low regulatory levels. If wastes with high silver levels are encountered, very low leachabilities can be attained by the simple expedient of adding chloride ion, either as sodium chloride or hydrochloric acid. This has been done at TSDFs.

Thallium. Thallium is a member of group IIIA of the periodic table with boron, aluminum, gallium, and indium (Cote, 1986). Unlike the others, it exists in both monovalent and trivalent forms, with the former being generally the most stable. It is used in alloys and in electrical applications. Virtually nothing appears in the literature on stabilization treatment or stabilization of thallium. In the treatability study referenced previously (Chemical Waste Management, 1992), K061 waste and soil spiked with thallium were stabilized to less than 1.0 mg/l with cement alone, or nearly two orders of magnitude reduction in TCLP leachability. The higher the cement content (up to mix ratios of 1.0 at least) the lower the leachability. This indicates that thallium is not sensitive to over-treatment.

Vanadium. In the treatability study referenced previously (Chemical Waste Management, 1992), K061 waste and soil spiked with vanadium were easily stabilized to less than 0.1 mg/l with cement alone, or nearly three orders of magnitude reduction in TCLP leachability. The higher the cement content (up to mix ratios of 1.0 at least) the lower the leachability. This indicates that vanadium is not sensitive to over-treatment.

Zinc. There is considerable data on zinc stabilization, all of it indicating the substantial reduction in leachability is achieved with simple pH control, using simple cement-based stabilization systems. While complexation with cyanide is common in electroplating wastes, the data on treatment of electroplating sludges and other wastes indicate no problems with stabilization of zinc in these residuals.

Finely Divided Elemental Metals. Particulate, elemental metals may be divided into three categories.

- Very finely divided metals are often pyrophoric, and must be handled as D003 Reactive Waste. The usual way to de-activate these wastes would be to react the metals to a higher valence state; care should be taken due to the possibility of hydrogen gas formation, an explosion hazard. In this process, the metal could be speciated in a relatively insoluble form and may or may not require further special treatment.
- Non-reactive elemental metals with low solubility in the TCLP test—beryllium, cadmium, chromium, nickel, silver, zinc—would likely pose no

difficulty stabilized or not stabilized.

- Metals with higher solubility in the test—lead, mercury and selenium—should experience substantial reduction in leachability in stabilized debris because the metal, as it dissolves, reacts with the alkalinity in the cement or pozzolan to form low-solubility hydroxides.

Organics

Organic stabilization, although more recent than metal stabilization, has been shown in numerous studies (Conner, 1990) (Gilliam et al., 1986) (Caldwell et al., 1990) (Soundararajan et al., 1990) to be capable of considerably reducing the mobility of organic constituents. In 1990-1991, a massive study was conducted on the stabilization of low-level organic contaminants in soils (Conner and Lear, 1991). It demonstrated that the mobility of nearly all classes of organics could be substantially reduced by the proper choice of additive, as measured either by the Toxicity Characteristic Leaching Procedure (TCLP) or by Total Waste Analysis (TWA). In view of the most recent regulatory stance on organic stabilization, it is necessary in many cases to conduct both Total Constituent Analysis (TCA) and TCLP analyses on samples before and after stabilization to prove the effectiveness of the treatment.

Stabilization, with additives, can meet the present TC standards for all TC-constituents (USEPA, 1990). S/S can also meet the Proposed Universal Treatment Standards (UTS) (Federal Register, 1993) (USEPA, 1994) based on Total Constituent Analysis (TCA) for most of the 50 constituents tested in the Conner and Lear (1991) study. Reductions in TCLP leachability ranged from a minimum of 90% to better than 99%. Reductions in TCA ranged up to 99.9%, with some reduction in all cases.

One surprising result of the above and other recent experimental work (Spence et al., 1990) has been the fact that Volatile Organics (VOCs) are not necessarily lost by volatilization during S/S, as was previously thought (Weitzman et al., 1987). TCA reduction levels suggest that VOCs sorbed onto or associated with soil particles may be less susceptible than expected to volatilization during stabilization, at least in these slow exotherm, cement-based systems under relatively static air flow conditions. Some additives, such as rubber particulate, have been shown in independent studies (Environmental Technologies Alternative, 1994) to substantially reduce the evaporation rate of VOCs so that air pollution is minimized, and also reduce the flash point of the system, thus providing an additional safety factor in treatment and disposal. This property

is expected to be of increasing importance as the new air pollution control requirements (USEPA, 1991) for treatment units come into effect.

Based on the work by Conner and Lear (1991), three additives —activated carbon, organoclays, and a proprietary rubber particulate formulation —all are broadly useful with specific contaminants in specific test methods, and none works best for all. Carbon is effective overall for reduction in TCLP leachability but not for reduction in TCA. Particulate rubber is not as effective in TCLP reduction, but is the only additive that was broadly useful for TCA reduction, especially for the low-volatility compounds. Organo-clays are effective with specific contaminants.

In addition to these three additives, some others have been found to have very narrow applicability for specific situations. Tables 9 - 11 (pp 43-46) list a number of organic compounds that have been stabilization-tested with various additives (Gilliam et al., 1986) (Conner and Lear, 1991) (Conner, 1995) (Conner et al., 1990) (Conner and Smith, 1993). Unless otherwise stated, the test work was performed on natural soil spiked with the indicated concentrations of target organic compounds. The spiked soil was stabilized with 20% cement alone, and with 20% cement plus a number of generic and proprietary additives. In most cases, the additive was used at the 10% addition level because the total level of target constituents approached the 10,000 mg/kg (1%) level. This results in very expensive formulations. However, in practice it is probable that much lower levels can be used in most instances - most likely in the 1% to 5% range, which would result in additive costs of about \$5 to \$100 per ton of waste treated.

All samples were subjected to both TCLP and TCA testing. The tables give the best level achieved in TCLP and TCA testing, respectively, for each target compound, and the additive and addition ratio used to attain that level (in a few instances, designated by "none," no additive was required). Because of the uncertainty at this time as to what the final regulatory stance will be regarding organics, it is difficult to state how useful S/S would be in any given scenario. However, the achievable TCLP and TCA levels shown here should allow the reader to determine whether S/S may be effective in a given waste/treatment/disposal situation once the requirements are established. Table 12 (page 47) summarizes reagent utilization, showing the most useful additives for various organic groupings. In using these tables, it is important to understand that, in addition to the additive that gave the best result, other additives usually also produced improved results for a given combination of target constituent and test method. In practice, the actual selection of additive(s) must be determined by treatability testing with actual wastes.

Volatile organics (VOCs). Although there is no one admixture that produces the best results for all constituents or combination thereof, activated carbon works best for TCLP reduction of VOCs overall (Conner and Lear, 1991). Although some volatilization undoubtedly takes place, comparison of the TCA and TCLP results shows that this is a minor effect in most instances. Carbon has now been used successfully in a number of specific remediation treatability studies (Chemical Waste Management, 1994) (Siegrist et al., 1992) (Morse and Dennis, 1994). Organo-clays have also been used successfully in organic VOC stabilization. A modified rubber particulate, KAX-100TM, also worked well for VOC stabilization, especially for TCA reduction. Table 9 lists the most effective additives for the various organic compounds that have been tested.

Semi-volatile organics (SVOCs). Conner and Lear (1991) showed that, for SVOCs, carbon produces the best TCLP mobility reductions, but rubber particulate (Environmental Technologies Alternatives, Inc., 1994a) provides the best reductions in TCA (Conner and Smith, 1993). A mixture of carbon and rubber particulate would seem to be way to go for SVOCs, dependent on what EPA finally does in the way of organic stabilization regulations. Rubber particulate is surface treated, finely ground tires or other rubber scrap, with particle sizes in the range of 10 to 60 mesh. It is generally less expensive than carbon, especially virgin carbon. Thus a mixture of the two would be cost effective. Table 10 lists the most effective additives for the various semi-volatile organic compounds that have been tested.

Mixtures of VOCs and SVOCs. This common situation seems to be best handled by a mixture of carbon and rubber particulate, by a modified rubber particulate (Environmental Technologies Alternatives, Inc., 1995), or by organo-clays for specific compounds. The best additive or combination of additives can be determined by comparing the mixture of target compounds to be treated with Tables 9 and 10.

Polychlorinated biphenyls (PCBs). PCBs are well known to be immobile in virtually any stabilization system. There is considerable literature (Conner, 1990) showing the latter effect. Therefore, PCB stabilization can be effectively accomplished in simple cement-based systems.

¹ KAX-50TM and KAX-100TM are proprietary rubber particulate-based additives manufactured by Environmental Technology Associates, Inc., Port Clinton, OH.

Pesticides, herbicides. Conner and Lear (1991) found that pesticides and herbicides are easily immobilized leachability-wise with cement plus carbon formulations, and in many cases, by cement alone. TCA reductions range from 50% to greater than 99%. A general formulation here would again be a cement/carbon/rubber mixture; however, depending on the regulatory interpretation of what test method constitutes “mobility reduction” for organics, cement alone might be used in many cases. Table 11 lists the most effective additives for the various pesticides and herbicides that have been tested.

Organo-Metallics

Many industrial waste streams contain soluble metal complexes that are very difficult to treat because of their stability. Simple complexes such as cyanides can be destroyed by alkaline chlorination. More stable complexes such as citrates, EDTA chelates, and a wide variety of non-chelate organometallics may require strong oxidants such as potassium permanganate or potassium persulfate, and possible use of elevated temperature. Other problems complicate the oxidative destruction of complexes. If chromium is present it will be oxidized to Cr^{+6} and must then be reduced before precipitation. With either oxidizing or reducing agents, species other than the target compound may compete for the reagent; large additions of oxidizing agent may be necessary and this becomes very expensive and time consuming. Therefore, a non-oxidative method for handling complexed nickel is desirable. Recently, another approach was used with nickel chelates—sorption on activated carbon. This reduced the leachability of nickel substantially and met the required regulatory level. Additional studies have shown that this technique also works with chromium, and should work with arsenic and cadmium. The sorbed organometallic compounds may then be solidified using portland cement. Table 7 lists the additives used for organo-metallic compounds.

Organo-arsenic compounds. The organic arsenicals are of special interest in stabilization because they are often found in wastes, especially in remediation work at old lagoons and other contaminated disposal sites. Arsenic combines readily with carbon to form a wide variety of compounds many of which are manufactured and used commercially, but may also be formed as waste products in manufacturing and during waste treatment processes.

Organo-cadmium compounds. A number of organic ligand complex systems involving cadmium are known:

acetic acid, dimethylglyoxime, EDTA, glycolic acid, methylamine, oxalic acid, pyridine, sulfamic acid, tartaric acid, and thiourea. Dialkyl cadmium compounds are used as polymerization catalysts in organic and polymer synthesis, and as heat and light stabilizers in plastics. The major complex in use, however, is inorganic $Cd(CN)_4^{2-}$, which is used in electroplating and is treated with alkaline chlorination.

Organo-lead compounds. Tetraethyllead (TEL), used as an antiknock additive in gasoline until recently, is the most important organo-lead compound from a stabilization standpoint. While TEL has undoubtedly been present in various waste streams, there does not seem to have been a reported leachability problem traceable to it. This may be due to its low solubility, or to low levels in the wastes.

Organo-nickel compounds. Organo-nickel complexes include salts such as acetate, formate, oxalate and stearate, and nickel chelates. Nickel acetate is found in metal finishing operations such as aluminum anodizing and electroplating. The fatty acid salts are used in dyeing of synthetic fibers. Various soluble chelates are formed, and these are the source of most of the problems encountered in fixation of nickel. Organo-nickel complexes such as EDTA, citrate, and gluconate may require high temperature oxidation with strong oxidizing agents. Nickel cyanide complexes can be broken with alkaline chlorination, leaving a nickel species which can be stabilized to low leaching levels.

Organo-silver compounds. In cases where a stable, soluble silver complex is present in large amounts, several techniques are available. Magnesium sulfate and lime can be used to precipitate a mixed sulfate-oxide. Alkaline chlorination can be used to break the complex and precipitate silver chloride. Sulfides and hydrosulfites are also used to treat silver complexes.

Soluble Salts

Chlorides, nitrates, sulfates. While it is possible to insolubilize these anions (e.g., silver for chloride, barium for sulfate, etc.), there is no practical way to do so within the realm of S/S processes. The best approach is to produce a low permeability matrix, and/or one that is hydrophobic, to limit the diffusion of the solute out of the stabilized mass. However, this technique will not be effective with crushed or ground material, as is deliberately done in the TCLP test. Actual field leaching of stabilized masses should be much lower than TCLP tests indicate, because of the monolith effect.

Cyanides. This issue has been in dispute between industry and EPA. As we understand it, the dispute centers around whether one-step alkaline chlorination as presently used constitutes "destruction" in EPA's meaning of the word, i.e., conversion to CO_2 and nitrogen. This also affects the use of calcium polysulfide, which converts the cyanide to thiocyanate. EPA has said that stabilization is not permitted for cyanide treatment, and that these two processes may constitute stabilization, especially if they are used in conjunction with normal cement or pozzolan treatment. Therefore, while cyanide standards can be met with additive-enhanced stabilization, the regulatory situation is unclear at this time.

IV. ADDITIVES USED IN CEMENT-BASED STABILIZATION/SOLIDIFICATION

Many additives have been tried out in S/S processes, and a number are used commercially, especially at TSDFs. A summary of the most commonly encountered additives and the characteristics of their use is given in Table 1. In this section, specific additives are underlined for easier identification in the text. References to the use and properties of many of these additives have been given in earlier sections; where no reference is given, refer to Conner (1990), Battelle Columbus (1993), U.S. Army Corps of Engineers Waterways Experiment Station (1990), and United States Environmental Protection Agency (1982). Stabilization additives can be categorized in three basic ways: metal stabilization; immobilization of organic constituents; processing and anti-inhibition aids.

Metal Stabilization

pH control and buffering. Acids, alkalies and salts, such as lime, caustic soda, and ferrous sulfate, can be used to control the pH of the system. Buffers such as calcium carbonate and magnesium oxide are used to keep it within the desired range after the leaching test is complete. Control of pH can also effect the removal of interfering substances from solution in certain cases, e.g., destruction of gels and film-formers.

Lime

The most common alkali used in stabilization is lime (either quicklime (CaO) or hydrated lime ($\text{Ca}(\text{OH})_2$)), because it is the most cost effective in most instances. Lime also supplies additional calcium for cement reactions and may react with certain interfering organics. Lime products may

be either high calcium or dolomitic. The latter contains substantial amounts of MgO or $\text{Mg}(\text{OH})_2$ in place of some of the calcium.

Sodium Hydroxide (NaOH)

In addition to neutralizing acids and raising pH, NaOH may also solubilize silica for quicker reactions of the pozzolanic type. One problem with the use of sodium alkalies is that the cementitious reactions which serve to moderate high pH in those systems (Cote, 1986) are counteracted by the presence of sodium ion.

Magnesium Oxide (MgO)

Acts as a pH control, buffering agent. MgO has also been found to be useful as an additive to portland cement solidification in the nuclear waste area (Carlson, 1987).

Sodium Carbonate (Na_2CO_3)

Also known as soda ash, Na_2CO_3 is much less frequently used than lime in S/S work, but is sometimes present in raw wastes where it was used for neutralization of wastewaters or other process wastes. Sodium carbonate also may be used in lead stabilization, and as a buffer in achieving more precise pH control.

Sodium Bicarbonate (NaHCO_3)

Acts as an accelerator (Shinoki et al., 1980) as well as a pH control, buffering agent.

Reduction. Reducing agents are used for the treatment of hexavalent chromium (Cr^{+6}). The most common are ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$). With ferrous sulfate, the additive is mixed in first with the system preferably at low pH, then the portland cement is added and mixed in. With sodium hydrosulfite, the reagents and additive can be added in any order.

Ferrous Sulfate

Probably the most widely used metal reducing agent in the S/S field, primarily on wastes containing Cr^{+6} . It is safe to use, inexpensive (as reducing agents go), and often produces additional benefits by co-precipitating the toxic metals. Its main drawbacks are large volume increase and the requirement of low pH for acceptable treatment times. The latter problem is especially acute in the case of wastes with high alkalinity, where very large quantities of acid may be required for pH adjustment. Reduction with ferrous sulfate is a three step process: 1) pH adjustment to <3 , 2) addition of ferrous sulfate and mixing until reaction is complete, and 3) raising pH to >7 with portland cement to precipitate metal as the hydroxide or as a co-precipitate with ferric and ferrous iron. The last step allows oxida-

tion of ferrous iron to the Fe^{+3} valence state by oxygen in solution, and any residual reagent should be destroyed. Reduction occurs over a wider pH range, but at lower rates (Allied Chemical Co., 1976) (Eary and Rai, 1988).

Sodium Metabisulfite/Sodium Bisulfite

These two additives react in the same way, since metabisulfite is the anhydrous form of bisulfite. The former is often used because it does not cake in storage. These reagents are effective reducing agents for Cr^{+6} and require much less acid and alkali than does ferrous sulfate, thereby generating less sludge. While considerably more expensive than ferrous sulfate, which can often be obtained as a waste product, much less is used. The overall cost of bisulfite reduction is often less than that of ferrous sulfate. The principal objection to the use of the bisulfites in S/S systems is their tendency to generate sulfur oxides in volume on contact with acids, a very serious problem. The solids in waste residuals seem to increase the evolution of SO_2 , perhaps by a surface catalysis reaction. This is especially evident when treating Cr^{+6} contaminated soils. Reduction rate depends on pH (Allied Chemical Co., 1976).

Sodium Hydrosulfite

This additive is effective at the alkaline pH of many waste residuals, hence it normally does not require pH adjustment before addition. Also, it remains effective after addition of the usually highly alkaline solidification reagents. This allows the addition of both types of reagent in rapid sequence, or even together. The major drawback to the use of sodium hydrosulfite is cost; it is several times as expensive than the metabisulfate and more of it is required, although no acid is used. Nevertheless, where the Cr^{+6} level in the waste is not too high, the additional cost may be justified by simplification of the process (Allied Chemical Co., 1976).

Metallic Iron

Iron filings have been tested successfully for use in reduction, but commercial use to date is not documented.

Other Reducing Agents

Sulfides, sodium borohydride, reductive resins, and hydrazine have all been suggested for use in S/S, but have found little or no commercial application.

Oxidation. Oxidizing agents are used for several purposes: to increase the oxidation state of certain metals such as arsenic (converting As^{+3} to As^{+5}); to destroy soluble complexes such as organo-metal compounds (so that they can be precipitated as a less

soluble species), cyanides, hydrogen sulfide and phenol; to destroy interfering substances in the waste, such as algae; to alter the biological status of the system. There are many oxidizing agents which could, in principle, be used but most are impractical for one reason or another, usually cost. For As^{+3} oxidation and amenable cyanide destruction, a hypochlorite ($\text{Ca}(\text{OCl})_2$ or NaOCl) is normally used. For destruction of organo-metal compounds, a more powerful oxidant such as potassium permanganate (KMnO_4) or ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) is used. Hydrogen peroxide may be used for biological control. Major problems in the use of oxidants are non-specificity and competing constituents. If a waste contains both nickel chelate and Cr^{+3} ion, oxidizing the chelate to release nickel may also oxidize the chromium to Cr^{+6} , which must subsequently be reduced again. This is costly not only in the extra processing required, but in the use of oxidizing agent where it is not needed or wanted. Organics such as oil and grease will compete for the oxidizing agent, making oxidation a very costly procedure if a selective agent cannot be found.

Sodium or Calcium Hypochlorite

Hypochlorites are the most common oxidizing agents in S/S, having been used commercially primarily for cyanide destruction and for trivalent arsenic compounds (Conner, 1993a).

Potassium Permanganate

A powerful oxidizing agent, potassium permanganate is used for destruction of certain organics. Commercially, it has been used for phenol destruction (Conner, 1990).

Ammonium/Sodium Persulfate

Persulfates are effective in some instances where permanganates are not as effective. No commercial use has been documented.

Speciation, Re-Speciation. By far the most important fixation mechanism for metals in S/S systems is chemical precipitation as low-solubility species. All of the cement-based S/S processes and methods precipitate dissolved metals as hydroxides, silicates, or sulfides, and less frequently as carbonates, phosphates, or various complexes. However, few of these systems are really as simple as they appear. Usually, a combination of mechanisms is active and the products of treatment are frequently not simple compounds. Equally important, the wastes being treated by S/S technology often are already speciated as relatively insoluble compounds in sludges, filter cakes, and soils.

Carbonates

In certain cases, metal carbonates are less soluble than their corresponding hydroxides. In cement chemistry, the natural formation of carbonates

from carbon dioxide from the air is termed "carbonation" (Cote 1986). Patterson et al. (1977) found that the formation of hydroxide precipitates controlled the solubility of zinc and nickel over a range of pH values, but cadmium and lead solubilities were controlled by carbonate precipitates in a narrower range. This is in keeping with the results of treatability tests conducted by the author on lead-bearing wastes, using soluble and "insoluble" carbonates. One problem is that the carbonates are decomposed at low pH, such as that encountered in the TCLP test, if the pH of the leaching solution in contact with the solid actually drops too low. If CO_2 is evolved, the reaction is irreversible even if the final pH of the leachant is high, and the final speciation of the metal will be as the hydroxide. This may explain the widely varying results reported (informally) by investigators testing carbonates, since the efficacy of carbonate precipitation would seem to be unusually sensitive to test variables; the sample being tested could either lose carbonate as CO_2 , or gain it in the same way from the atmosphere (air) in the test container. The most common carbonate used in S/S is calcium carbonate (limestone or agricultural lime) because it is so inexpensive. While its solubility is low, calcium carbonate can precipitate even less soluble carbonates such as those of lead and barium. More soluble carbonates such as those of sodium or potassium may be more effective, but are also more expensive.

Sulfur-Based Agents

Other than precipitation as hydroxides, sulfide precipitation of metals has probably been the most widely used method to remove metals from wastewater. This method has been successfully applied in S/S treatment as well, especially for achieving regulatory limits for wastes containing mercury. Unlike water treatment, S/S treatment requires the use of cement, either concurrently with the sulfide treatment or afterwards, to produce a stable product. Most metal sulfides are less soluble than the hydroxides at alkaline pH (arsenic is an exception). Another interesting exception in sulfide precipitation is that of chromium, which does not precipitate as the sulfide, but as the hydroxide. Therefore, chromium leaching will be controlled by hydroxide precipitation, and hence by pH, at least in theory. Metal sulfide solubilities are not as sensitive to changes in pH. There are three classes of sulfide precipitation reagents which have been investigated and used in S/S work:

Soluble inorganic sulfides

Sodium sulfide (Na_2S) and calcium polysulfide

(CaS_x) are the primary examples of commercial use of this class of sulfides in S/S. In some cases, the soluble sulfides will precipitate chromium directly without pretreatment to reduce it to the trivalent state, and sulfides are claimed to precipitate complexed metals (Cherry, 1982). It is necessary to maintain pH 8 or above to prevent evolution of H_2S . While excess sulfide ion is necessary for the precipitation reaction, the excess must be kept to a minimum so that free sulfide removal treatment is not required before the waste can be landfilled. The sulfide is added before any of the solidification reagents, since the latter contain calcium, magnesium, iron and other metals which will compete for the soluble sulfide. However, calcium sulfide, which has limited solubility, may act as a sulfide buffer to maintain a small excess available sulfide level in the system, similar to the action of the alkalis in hydroxide precipitation.

"Insoluble" inorganic sulfides

One answer to the problems encountered with use of soluble sulfides is the use of very low-solubility species such as FeS or elemental sulfur. In the case of FeS, its solubility is about 0.0001 mg/l in water. The former technology has been commercialized as the Sulfex™ process (Knocke et al., 1977) (Feigenbaum, 1977). The advantage of this approach is that very little excess sulfide is present in the system at any time, so the problem of H_2S odor and toxicity is eliminated. The combination of elemental sulfur + alkali (Ader et al., 1989) has also been tested in S/S systems. The principle here is that sulfide ion is generated as it is used up in metal-sulfide reactions, but only a small amount of S^{2-} ion is present at any one time, thereby minimizing risk.

Organo-sulfur compounds

In principle, organo-sulfur compounds may have certain advantages over the inorganics. Several investigators (Yagi and Matsunaga, 1976) (Yagi, 1975) have found thiourea to be useful in reducing mercury leaching from caustic-chlorine production wastes and other residues to very low levels, 0.0001 mg/l, in water. Nakaaki et al. (1975) lowered the mercury leachability of seabed sludge with a fixing agent containing polydithiocarbamates and an iron or copper salt. Notably, all of these applications of organo-sulfur compounds have been on mercury. This may be due to the extremely low regulatory leaching levels for mercury, or to the basic insolubility of mercury sulfides, or both. Little has been reported on the use of these reagents for other

metals in sludges and other waste residuals. One vendor (Chemical Engineering, 1988) has a line of organosulfur reagents for use in wastewater treatment, and there are a number of other reagents of this class offered on a proprietary basis.

Silicates

The reactions of polyvalent metal salts in solution with soluble silicates have been studied extensively over many years (Conner, 1990). Nevertheless, the "insoluble" precipitates which result from such interactions are not usually well characterized, especially in the complex systems representative of most wastes. Metal silicates are non-stoichiometric compounds in which the metal is coordinated to silanol groups, SiOH, in an amorphous silica matrix. The reactions of soluble silicates in solution is best summarized by Vail (1952), who states, "The precipitates formed by the reaction of the salts of heavy metals with alkaline silicates in dilute solution are not the result of the neat stoichiometric reactions describing the formation of crystalline silicates, but are the product of an interplay of forces which yield hydrous mixtures of varying composition and water content." In any case, metals in solution can be effectively precipitated by soluble silicates, and the reaction products tend to be less sensitive to pH variations in the environment than are hydroxide species. However, metals already in relatively insoluble form are generally not re-specified by soluble silicates. Nevertheless, there is evidence that such species can be re-specified in situations where silicates are constantly being formed. Bishop (1988) postulated that the observed low leaching of metals in portland cement CFS systems was due to the association of the metals with silica, possible as silicates. Perhaps most interesting is a patent application (Conner and Rieber, 1992) which claims the continuous production of soluble silicates from biogenetic, amorphous silica and alkali.

For S/S work, the soluble silicate is used along with portland cement and/or cement kiln dust, normally with the cement or kiln dust being added first and mixed into the waste before the silicate is added. The cement provides the physical properties required in the treated waste, due both to the action of the cement itself, and to its release of calcium ion to react with the excess silicate, forming a solid calcium silicate gel. It also results in better overall chemical properties in the waste form, moderating the high pH conditions in the soluble

silicate itself and interacting with waste constituents in ways already discussed.

Phosphates

Phosphate chemistry is very complex and varied. Compounds containing monomeric PO_4^{3-} are called orthophosphates or simply phosphates. The simple phosphate salts of the toxic metals have low water solubility, although they are soluble in acids. For lead immobilization, either phosphoric acid or a sodium phosphate is used. For most S/S work, the phosphate is used along with portland cement and/or cement kiln dust, normally with the phosphate being added first and mixed into the waste before the cement is added. As is the case with soluble silicates, the cement provides the physical properties required in the treated waste. While phosphate is sometimes used alone where lead is the only constituent of concern and where physical property development is not required, the immobilization of other RCRA metals requires the properties of cement.

Iron Compounds

The removal of toxic metals from wastewater with systems which co-precipitate and/or flocculate them with iron salts is well known and widely used (Sittig, 1973) (Swallow et al., 1980). More recently, it has been used to reduce the solubility of various toxic metals in hazardous waste treatment (Pojasek, 1980). The ratio of Fe^{+2} to Fe^{+3} is important, with ratios of 1:1 to 1:2 reported as yielding optimum results. Sano et al. (1975) attribute the removal of zinc and cadmium to the formation of ferrite crystals which could subsequently be removed magnetically. The crystals capture the other metals in the lattice, or adsorb them on the surfaces. This mechanism has not been confirmed by others, who ascribe the results obtained to co-precipitation followed by flocculation. Sols of hydrous metal oxides are stabilized by the presence of excess ferric ion, but acquire a negative charge, destabilize and flocculate under alkaline conditions. As the system becomes alkaline, the ferrous ion is also easily oxidized to ferric, and precipitates as the hydroxide. These reactions remove other metal ions from solution, reducing their concentrations to levels below those obtained with simple hydroxide precipitation. Whatever the mechanism, the net effect is reduction of leachability in many instances. In addition to the iron species, co-precipitation with calcium carbonate and other species has been reported (Envir. Sci. Tech., 1982).

Again, for S/S work, the iron compound is used along with portland cement and/or cement kiln dust, normally with the iron salt being added at the same time as the cement. Where ferrous iron salts are used for electrochemical reduction, the iron salt is normally added first, and the cement added after reduction is complete. The cement provides the physical properties required in the treated waste, as well as the alkalinity and other properties of cement necessary for immobilization of RCRA metals.

Xanthates

Cellulose and starch xanthates have been used for the stabilization of a number of metals in waste streams, especially cadmium, chromium, nickel, and mercury (Bricka and Hill, 1989). The most widely publicized additive has been insoluble starch xanthate (ISX) (Wing, 1975). ISX is produced by treating starch with crosslinking agents, then xanthating it with CS_2 in the presence of an alkali metal base such as sodium hydroxide. The resulting product is a particulate solid. Since 1980, ISX has been a commercially available product with usage in the treatment of wastewaters from metal finishing and similar sources. ISX is also reported to act as a reducing agent for Cr^{+6} . Chromium is reduced to Cr^{+3} and removed by neutralization to precipitate the hydroxide. It should be noted that ISX operates at low pH and the process is less effective as pH rises. Tests with selenium (Navickis, 1975) indicated that the metal after immobilization with ISX could not be extracted with either high or low pH water, but chloride ion does cause some release of selenium. Starch xanthate fixes mercury better than cellulose xanthate, but xanthates alone are not adequate for fixation of cadmium, chromium and nickel—cement also is required. The latter finding probably demonstrates the necessity for pH control in the alkaline range for adequate fixation of cadmium, chromium, and nickel, a result that is not surprising.

Insoluble Substrates

Rather than precipitate metals from solution in the usual sense—by formation of low-solubility species from ions in solution—another approach is to react the metal with an active area or functional group on the surface of an insoluble substrate. Nelson (1980) used a treated leather waste to remove heavy metal ions, particularly lead and cadmium, from nitrate and acetate solutions. Another process (Chemical Engineering, 1979) uses modified casein to remove cad-

mium, chromium, copper, mercury, nickel, and zinc from wastewater. Chromium reportedly can be removed as directly as Cr^{+6} , without prior reduction, to levels below 1.0 ppm from streams containing up to 500 ppm Cr^{+6} . The casein is modified by treating with formaldehyde to form a cross-linked, insoluble product.

Inorganic Complexation

Many metals exist in ores and rocks as complex crystalline structures. The curing of cement-based solidification systems may eventually result in complexes such as those formed when metals are removed from solution by substitution for calcium, aluminum, etc. in cement hydration products. Another example is the formation of ferrite crystals mentioned previously, if indeed these actually form in CFS systems. Both ferricyanide and ferrocyanide form low-solubility species with a number of metals.

Organic Complexation

Many organic compounds form low-solubility species with certain metals (e.g., tartrates of cadmium, lead, mercury(+1), and nickel). Unfortunately, little information is available on either the actual solubility numbers for metal organic compound in aqueous solution or on the effects of pH and other ions. Manahan and Smith (1973) report that humic acids formed in the decay of vegetable matter immobilize metal ions in sediments and soil.

Miscellaneous

Sodium sulfate (Na_2SO_4) and sodium chloride (NaCl), respectively, are used to immobilize soluble barium and silver species. Young (1979) reported improved resistance to arsenic leaching by the addition of calcium and manganese chlorides, sulfates, and acetates. Onoda Cement Co. (1976) used gypsum to produce an improved product from S/S with cement. Chen (1978) reported improved leaching properties by using a mixture of cement and vermiculite. Phosphorus pentoxide and a stearate (Takashita, 1979) were used to treat oily sludges.

Co-precipitation and flocculation. Aggregation of fine particles and film-formers into larger size flocs that are removed from the reactive cement particle surfaces can prevent the inhibition of cement setting and hardening. There are many organic surfactants that might be used for this purpose, and a few inorganic additives. Co-precipitation can be very useful in immobilizing metal and organic compounds in a complex structure. It is difficult to separate the effects of co-precipitation from those of sorption in systems

where the sorbent is formed in-situ.

Ferrous Sulfate

In addition to its use as a reducing agent, ferrous sulfate is used as a co-precipitant and flocculating additive, primarily in lead stabilization and especially where mobile colloidal species are present. It can also be used for the same purpose for other metals such as arsenic, if necessary.

Organic Flocculants, Surfactants

There is a large variety of organic surfactants that can be used to remove fine particulate matter from the surfaces of the reactive cement particles, thereby preventing their inhibiting effect. Alcohols, amides, lignosulfonates (Kokusai, 1981) (Veda and Ito, 1977), and other specific surfactants can aid in wetting solids and dispersing fine particulates and oil which interfere with reactions by coating the reacting surfaces. Flocculants can also serve this purpose.

Other surface effects. Dispersion of oils, greases, and fine particulates away from reacting surfaces, and precipitation of interfering substances have effects analogous to the use of flocculation on interfering particulate matter. Generally, a wide variety of commercial organic surfactants can be used for this purpose.

Ion Exchange. Ion exchange can be either beneficial or detrimental to cement-based S/S. It can inhibit or retard S/S reactions by removing calcium from solution, preventing it from entering into the necessary cementitious reactions. It can also accelerate the process by removing interfering metal ions from solution. Which occurs may depend on the selectivity of the ion exchange material.

Substitution. Certain metals may retard and inhibit the reactions by substituting for calcium in the cementitious matrix, which may explain the effect of magnesium in dolomitic lime products. Certain substances are natural or synthetic complexing agents which remove calcium from availability in the setting and curing reactions. However, cement can also improve metal immobilization when the metals substitute for calcium in the hydrated cement matrix.

Sorption. Here, the term "sorption" is used to cover adsorption at surfaces, absorption into the interior of solid substrates, and chemisorption. Often, it is impossible to distinguish between these various effects in real, complex systems, and in the practical sense, it does not matter anyway. An example of sorption of metals on active oxides is given by Posselt and Anderson (1968). They used hydrous manganese dioxide formed

in-situ by reduction of permanganate ion (Mn^{+7}). Metal ion sorption was rapid, with equilibrium attained within minutes. Dzombak and Morel (1987) found considerable data which show that metals adsorb strongly to iron and aluminum oxides. Lagvankar et al. (1986) described an interesting process using iron filings which are activated by the waste stream itself. Metal sorbents can be broken down into a number of classes or groupings:

Metal Oxides

Iron, manganese, aluminum, etc.

Clays

Bentonite, montmorillonite, attapulgite, illite, kaolinite - all natural and modified.

Natural Materials

Peat moss, natural zeolites, sawdust, vermiculite, sand, etc.

Synthetic Materials

Zeolites, flyash, cullite, activated alumina, organic polymers, etc.

Activated Carbon

Cement Hydrate Phases

Chan et al. (1980) evaluated ten potential sorbents, natural and synthetic, for their ability to remove a variety of pollutants from landfill leachate. They found that no single sorbent is effective in removing all pollutants, and some were not attenuated by any of the materials tested (bottom and flyashes, vermiculite, illite, sand, activated carbon, kaolinite, natural zeolite, activated alumina, and cullite). As expected, activated carbon was most effective for organics, with illite also being successful. Specific sorbents were effective on fluoride and cyanide, but not on chloride. Activated alumina was moderately effective in removing nickel, but none of the other sorbents achieved any success with this metal. None of the sorbents tested were effective for lead. Other investigators have found that flyash, kaolin, and sawdust (Benson, 1980), and a calcined mixture of bentonite and flyash (Japan Kokai, 1980) were effective in immobilizing a variety of metals.

Immobilization of Organic Constituents

Sorption. Sorbents are used for immobilization of organics and organo-metallic compounds (arsenic, chromium, lead, and nickel). While many sorbents have been tested, the most effective overall are activated carbon, organo-clays, and rubber particulate. From a practical standpoint, a combination may be the best single sorbent where a variety of organic constituents of concern are present. Sorbents can also immobilize organo-metallic species, especially those complexed forms which are otherwise difficult to

precipitate. Sorbents can also be used for removal of interfering substances from reacting surfaces.

Activated Carbon

One of the earliest mentions of the use of activated carbon for immobilization of organics (primarily phenol) was by Chappell (1980). Since then, carbon has been used for this purpose in a number of commercial projects (Lawson et al., 1996) and has been demonstrated in many treatability studies (Conner and Lear, 1991).

Clays

Natural clays are not very effective stabilization agents for organics, less so than for metals. However, treated clays – the so-called organo-clays – are effective (Boyd and Mortland, 1987). These are natural clays that have been reacted with various reagents, primarily quaternary ammonium compounds and derivatives, to render them organophilic on internal as well as external surfaces. The organophilic groups attached to the clays attract and hold organic contaminants in the waste. Organo-clays have been used for this purpose in a number of commercial projects (Lawson et al., 1996) and have been demonstrated in many treatability studies (Conner and Lear, 1991).

Rubber Particulates

These are proprietary formulations (Environmental Technologies Alternatives, Inc., 1994a) – KAX-50™ and KAX-100™ – based on rubber particulate derived from ground scrap tires, and were reportedly specifically formulated for this purpose. KAX-50™ was most effective with semi-volatile organics (Conner and Smith, 1993), while KAX-100™ worked best for mixtures of VOCs and SVOCs, as well as the pesticides/herbicides group.

Oxidation of unwanted species. Powerful oxidizing agents such as potassium permanganate and sodium persulfate are effective in destroying certain organic contaminants in wastes. See “Oxidation” in the previous section, Metal Stabilization, for more information on these additives. However, there are a number of drawbacks to the use of oxidizers for this purpose. The primary problem is cost. Since these additives are generally non-selective in their action, all oxidizable species in the waste will compete for the additive; examples are oils, biological materials, vegetative matter, metal species such as Cr^{+3} and many other common waste components. Thus, a very large excess of additive may be required. Secondly, the oxidation process is exothermic and considerable heat is often generated, which will tend to vaporize VOCs rather than destroy them, and cause air pollution problems. Also, any

chromium in the waste will be oxidized to the Cr^{+6} valence state, and then require reduction so that it can be stabilized. For these reasons, oxidation has been little used for organic treatment, except in instances where the constituent is easily oxidized and present at low levels and there is little other oxidizable species in the waste. One successful use has been for phenol destruction in metal finishing wastes (Conner, 1990).

Processing and Anti-inhibition Aids

More and more, additives are being used in chemical systems for purposes other than stabilization. Cement-based systems, especially, are sensitive to many waste components discussed previously in their setting and strength development. Additives such as lime and sodium silicate are often used to counter these inhibition effects. On the other hand, some waste components cause premature setting and require the use of set retarders commonly used in making concrete. The latter effect must also be controlled in some delivery systems, especially in in-situ S/S. Other processing aids are sometimes used: “water-reducing agents” or surfactants to lower viscosity, or clays and polymers to increase viscosity. This subject is covered in some detail in Section II, and will only be discussed briefly here.

Acceleration. There are many compounds that have been reported for their ability to accelerate the setting and/or hardening of cement. Many of these may be effective also in cement-based S/S systems. Common additives and groups of additives, along with references to their use, are listed as follows:

- Calcium Chloride (Kantro, 1975)
- Dispersants/Water Reducing Agents (Falcoux et al., 1980)
- Magnesium Oxide (Kawasaki Steel Corp., 1980)
- Lime (Falcoux et al., 1980)
- Calcium Aluminate Minerals
- Amines (Wagner and Ellis, 1980)
- Organic Acids and Salts (Falcoux et al., 1980) (Yamagishi et al., 1980) (Bonnell and Hevanee, 1972)
- Glycols and Related Compounds (Wagner and Ellis, 1980)
- Calcium Tetraformate (Berry, 1980)
- Asphalt Emulsion
 - Combined with cement, calcium aluminate minerals, and calcium sulfate (Higuchi, 1978)
- Metal Ions
 - Mechanism unclear

Cement Kiln Dust

Source of lime

Of all of these additives, calcium chloride, lime, cement kiln dust, sodium silicate (see below), and the proprietary concrete set retarders have been most used in S/S technology.

Anti-Inhibition. These additives function in the same manner as accelerators in many cases, and thus are basically the same materials. However, some additives not normally used in concrete technology are used in S/S. An example of this is sodium silicate, which reacts with interfering metals and other waste components and also causes acceleration of initial set by very rapidly forming a silicate gel.

Retardation. To date, most applications of set retarders in S/S systems have been with the proprietary set retarders commonly used in concrete ready-mix batch plants. These applications have been for in-situ S/S where the pumpable grout is made up first, and then injected into the waste, requiring it to remain pumpable for up to several hours before beginning to set. Other retarders are:

Sugars and Derivatives

(Metcalf and Ellers, 1980) (Industrial Water Engineering, 1970)

Excessive Water Content. Excessive water in the waste can result in supernatant liquid on the surface after setting and in low strength in the cured waste form. Additives used to counter these problems are of three types: accelerators to reduce set time; bulking agents or sorbents to reduce the free water; and gellants to increase viscosity of the system. Accelerators were discussed in Section IV, gellants in Section II. Bulking agents commonly used are listed below:

Flyash

Cement Kiln Dust

Blast Furnace Slag (Chudo et al., 1981)

Corn Cob, Wood Chips, etc.

V. PHYSICAL/CHEMICAL TECHNIQUES USED IN CEMENT-BASED STABILIZATION/SOLIDIFICATION

In addition to additives, other techniques are used in S/S to improve the properties of the product, to aid in processing, and to immobilize or destroy various constituents of concern.

Anti-Inhibition Aids

There are some physical, non-additive techniques that can be used to counter the effects of inhibiting materials in the waste.

Aeration. Aeration can serve several purposes: alteration of biological status of the waste, which may prevent the formation of inhibiting film formers on the surfaces of the cement binder; and removal of interfering VOCs.

Temperature Adjustment. This technique can be used both to improve the leaching characteristics of the waste form produced by S/S (Vejmelka et al., 1985), and to accelerate the reaction rate to counter retarding effects.

Physical Property Development

Humidity Control. Ambient humidity in the curing area must be kept high if the product is to cure properly. Evaporation of water from the surface will inhibit or stop solidification, and perhaps some fixation reactions in the surface layer. In the laboratory, samples are normally cured at about 95% relative humidity to prevent this effect from masking the real solidification reactions. In very hot and dry field conditions, especially where the layer of curing S/S product is thin, it may be necessary to keep the waste moistened as it cures, much as is done with concrete under the same conditions.

Dewatering. Removal of excess water by physical means is often less costly than the use of additives to absorb the water.

Air Entrainment. This technique may be useful in some cases where maximum freeze/thaw resistance is required. It generally employs additives to aid in entrainment of air. Air entrainment is not known to have been deliberately applied in the field.

Processing Aids

Viscosity/Pumpability Alteration. Water reducing agents, flyash (Industrial Water Engineering, 1970), and natural clays (attapulgitic and illite) (Industrial Water Engineering, 1970) have been used to adjust the viscosity of grout formulations, especially for in-situ S/S applications.

Elevated Temperature. S/S processes are chemical

reactions and would be expected to follow the general rules of such – that reaction rate usually increases with temperature, perhaps according to the old rule-of-thumb that reaction rate doubles with each 10°C rise in temperature. S/S reaction rates do increase with temperature, but there are limitations. Below freezing temperatures can cause irreversible changes in the final product by breaking gel structures at a critical stage, much as can happen with concrete. At very high temperatures, release of steam can actually break up the solid mass, and the loss of water can interfere with subsequent curing reactions. This latter phenomenon is of concern in cement-based systems which are exothermic. Some additives also generate a large exotherm and very rapidly. This must be considered when designing the mechanical aspects of the system. Also, the low heat transfer rate from a large mass of treated waste while curing can drive the internal temperature to unacceptable levels, even though a laboratory test did not indicate a potential problem. This, also, must be taken into consideration in the system design. Self heating of the mass, however, is a valuable aid to curing if it is kept under control and within limits. To be assured that cementitious reactions will start, the temperature should be maintained above -3°C.

Mixing Techniques

Mixing is an important, sometimes critical, element of any S/S process. While it seems obvious that thorough dispersion of the S/S reagents in the waste is important, it is also possible to over-mix certain systems. Fluid wastes such as low-solids sludges are usually easiest to mix, while sticky sludges and filter cakes with the consistency of peanut butter are the most difficult. Soils, solid particulates, and granular materials fall in-between. Selection of a mixer is not only determined by the physical characteristics of the waste, however. Some wastes and some processes are quite sensitive to the energy input and shear rate of the mixer. Use of a high-shear mixer with some wastes may irreversibly alter their properties, causing phase separation. On the other hand, high-shear mixing may be required to completely homogenize other mixtures—for example, to incorporate non-polar organics in aqueous systems. High energy input may help with some plastic, pseudoplastic, or thixotropic wastes by decreasing their viscosity temporarily, and by aiding in the reactions (Kitsugi, 1978) (Munster, 1982). In rare cases, dilatant materials may literally solidify in the mixer before reagents are even added.

Over-mixing, either by using the wrong mixer or mixing too long, interferes with the initial gel forma-

tion of cementitious S/S systems, causing delayed set, slow curing and even the loss of final physical properties. An extreme example of this is seen in the use of soluble silicates, where it irreparably destroys the silica gel structure, preventing the process from working properly at all. Over-mixing can also go the other way. Many a processor has had to dig out a mixer because the blend set up before it could be emptied. This usually happens in batch systems, but has also been observed in continuous mixers when the mixer is stopped while full.

While it is widely assumed that very thorough and intimate mixing is required to assure that reaction will take place and fixation of hazardous constituents will be complete, it is known that such mixing does not happen with most in-situ techniques and still the end result may be satisfactory. One investigation (Chemical Waste Management, 1987) tentatively reached the conclusion that complete mixing at the microscopic scale is not always necessary in commercial S/S systems. Other scientists have recently realized this as they began to look at the microstructures of solidified wastes (Eaton et al., 1985). At this level, apparently unreacted waste conglomerates are evident, as are areas of unmixed reagent. The question now remains: At what size level can inhomogeneities exist and still not prevent the process from achieving its function? There is probably no single answer; it varies from waste to waste and process to process.

Ex-Situ Mixing. The choice of mixer is determined by the rheological properties of the waste, the reagents to be added (including how many and in what order), the mode of operation (batch, continuous, or in-situ), the through-put rate, and the waste conveyance methods. For large volume operations with a continuous, reasonably consistent feed, continuous mixing usually gives the best results at the lowest cost. For smaller projects, and where the waste feed is very variable, batch mixing may be the only feasible method. Sometimes the two are combined by accumulating a large batch of waste and homogenizing it to provide a uniform feed to a low through-put, continuous mixer until the batch is processed.

In-Situ Mixing. In-situ mixing is a special case unto itself. The equipment used is not generally thought of as a mixer, but has some other primary function as, for example, a backhoe, a drilling auger used for stabilizing foundations, or a rock cutting head used in mining. More recently, specialized equipment has been applied more and more to this area, most of it being constructed by or for the S/S contractor himself. Several requirements for state-of-the-art in-situ S/S that are peculiar to

in-situ work are deliberate retarding of the set to allow time for handling, injection and mixing of a grout into the waste, and the formulation of that grout.

VI. REFERENCES

- Ader, M., Glod, E.F., and Fochtman, E.G., *U.S. Patent 4,844,815*, Jul. 4, 1989.
- Allied Chemical Co., *Treatment of Chromium Waste Liquors*, New York, 1976.
- American Society for Testing and Materials (ASTM), *Temperature Effect On Concrete*, Philadelphia, PA, 1985, p.104.
- Ashworth, R., "Some Investigations into the Use of Sugar as an Admixture to Concrete," *Proc. Inst. of Civil Engineering*, London, 1965.
- Battelle Columbus, *Technical Resource Document Solidification/Stabilization and Its Application to Waste Materials 4-29-4-44*, EPA/530/R-93/012, United States Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, Jun. 1993.
- Benson, R.E. Jr., "Natural Fixing Materials for the Containment of Heavy Metals in Landfills," *Proc. Mid-Atlantic Industrial Waste Conf.*, 1980, pp. 212-15.
- Berry, D., *U.S. Patent 4,191,584*, Mar. 4, 1980.
- Bishop, P.L., "Leaching of Inorganic Hazardous Constituents from Stabilized/Solidified Hazardous Wastes," *Hazardous Wastes & Hazardous Materials* 5, No. 2, 1988, pp.129-43.
- Blake, L.S., ed., *Civil Engineer's Reference Book*, Butterworths, London, 1975.
- Bonnel, B. and Hevane, C., *U.S. Patent 3,656,985*, Apr. 18, 1972.
- Boyd, S.A. and Mortland, M.M., "Use of Modified Clays for Absorption and Catalytic Destruction of Contaminants," *13th Annual Research Symposium at Cincinnati*, U.S.EPA, Cincinnati, Jul. 1987.
- Bricka, R.M. and Hill, D.O., "Metal Immobilization by Solidification of Hydroxide and Xanthate Sludges," *Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Sludges*, ASTMSTP 1033, American Society for Testing and Materials, Philadelphia, PA, 1989, pp. 257-272.
- Caldwell, R.J., Cote, P.L., and Chao, C.C., "Investigation of Solidification for the Immobilization of Trace Organic Contaminants," *Hazardous Waste & Hazardous Materials* 7, No. 3, pp. 273-282.
- Carlson, J.E., "The Chemistry of Processing Nuclear Waste with Portland Cement," *Chemical Waste Management Stabilization Seminar*, Jun. 4-5, 1987.
- Chalasan, D., Cartledge, F.K., Eaton, H.C., Tittlebaum, M.E., and Walsh, M.B., "The Effects of Ethylene Glycol on a Cement-Based Solidification Process," *Hazardous Wastes & Hazardous Materials*, 3, No. 2, 1986.
- Chan, P.C., Liskowitz, J.W., Perna, A., and Trattner, R., *Evaluation of Sorbents for Industrial Sludge Leachate Treatment*, EPA-600/2-80-052, U.S. EPA, Cincinnati, 1980.
- Chappell, C.L., *U.S. Patent 4,230,568*, Oct. 28, 1980.
- Chemical Engineering*, May 2, 1979, pp. 83-4.
- Chemical Engineering*, Feb. 15, 1988.
- Chemical Waste Management, *Internal Study*, 1987.
- Chemical Waste Management, *Stabilization of Sb, Be, Tl and V Using AA100*, Geneva Research Center, Geneva, IL, 1992.
- Chemical Waste Management, *Private Communication*, 1994.
- Chen, K.S., *U.S. Patent 4,113,504*, Sep. 12, 1978.
- Cherry, K.F., *Plating Waste Treatment*, Ann Arbor Science Pub., Ann Arbor, MI, 1982.
- Chudo, A., Sugi, T., and Katsoka, K., *U.S. Patent 4,266,980*, May 12, 1981.
- Conner, J.R., *U.S. Patent 3,837,872*, Sep. 24, 1974.
- Conner, J.R., *U.S. Patent 4,518,508*, May 21, 1985.
- Conner, J.R., *U.S. Patent 4,623,469*, Nov. 18, 1986.
- Conner, J.R., *U.S. Patent 4,600,514*, Jul. 15, 1986a.
- Conner, J.R., *U.S. Patent 5,078,795*, Jan. 7, 1992.
- Conner, J., *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, NY, 1990, pp. 77-102, 298-304.
- Conner, J.R. and Lear, P.R., "Immobilization of Low-Level Organic Compounds in Hazardous Waste," *Proc. Air and Waste Management 84th Annual Meeting*, Vancouver, BC, 1991.
- Conner, J.R. and Lear, P.L., *Treatment of Landbank-Varianted Arsenic Wastes at TSDFs*, Chemical Waste Management, Geneva, IL, 1992.
- Conner, J.R. and Rieber, R.S., *U.S. Patent 5,078,795*, Jan. 7, 1992.
- Conner, J.R., "Advanced Stabilization Methods for Treatment of Hazardous Wastes," *Conference on Chemical-Physical Treatment of Industrial Wastes*, Univ. of Brescia, Italy, Jun. 17-18, 1993a.
- Conner, J.R., "Recent Findings on Immobilization of Organics as Measured by Total Constituent Analysis," *Waste Management* 15, Nos. 5/6, 1995, pp.359-369.
- Conner, J.R. and Smith, F.G., "Immobilization of Low-level Hazardous Organics Using Recycled Materials," *Third International Symposium on Stabilization/Solidification of Hazardous, Radioactive, and Mixed Wastes*, Williamsburg, VA, Nov. 1-5, 1993.
- Conner, J.R., Private Communication, 1993.
- Conner, J.R., Li, A., and Cotton, S., "Stabilization of

- Hazardous Waste Landfill Leachate Treatment Residue," *Journal of Hazardous Materials* 24, 1990, pp.111-121.
- Coté, P., *Contaminant Leaching From Cement-Based Waste Forms Under Acidic Conditions*, PhD Thesis, McMaster Univ., Hamilton, ON, Canada, 1986.
- Cullinane, J.M., Jr., Jones, L.W., and Malone, P.G., *Handbook for Stabilization/Solidification of Hazardous Waste*, EPA/540/2-86/001, U.S. EPA, Cincinnati, OH, 1986.
- Cullinane, M.J., Bricka, R.M., and Francingues, Jr., N.R., "An Assessment of Materials That Interfere with Stabilization/Solidification Processes," *In Proc. 13th Annual Research Symposium*, U.S.EPA, Cincinnati, OH, 1987, pp. 64-71.
- Dzombak, D.A. and Morel, F.M., "Development of a Data Base for Modeling Adsorption of Inorganics on Iron and Aluminum Oxides," *Environmental Progress* 6, No. 2, 1987, pp. 133-7.
- Eary, L.E. and Rai, D., "Chromate Removal from Aqueous Wastes by Chromium Reduction with Ferrous Ion," *Environmental Science Technology* 22, No. 8, 1988, pp. 972-7.
- Eaton, H.C., Walsh, M.B., Tittlebaum, M.E., Cartledge, F.K., and Chalasani, D., "Organic Interference of Solidified/Stabilized Hazardous Wastes," *Environmental Monitoring and Assessment* 9, 1987, pp. 133-142.
- Eaton, H.C., Walsh, M.B., Tittlebaum, M.E., Cartledge, F.K., and Chalasani, D., "Microscopic Characterization of the Solidification/Stabilization of Organic Hazardous Wastes," *Energy Sources and Technology Conference and Exhibition*, ASME Paper No. 85-Pet-4, 1985.
- Electric Power Research Institute, *In-Situ Solidification/Stabilization of Arsenic Contaminated Soils - Draft Report*, Palo Alto, CA, Apr. 1996.
- El-Korchi, T., Melchinger, K., Kolvites, B., and Gress, D., *The Effect of Heavy Metals and Organic Solvents on the Microstructure of Cement Stabilized Hazardous Waste*, University of New Hampshire, 1990.
- Environmental Science Technology* 16, No. 12, 1982, 641a.
- Environmental Technologies Alternatives, Inc., *Control of Air Emissions in Hazardous Waste Stabilization Operations*, KAX-50™ Technical Bulletin TB-214, Port Clinton, OH, 1994.
- Environmental Technologies Alternatives, Inc., *Immobilization of Organics in Debris and Characteristic (D-code) Wastes*, Technical Bulletin TB-234, Port Clinton, OH, 1994a.
- Environmental Technologies Alternatives, Inc., *KAX 100™ Technical Bulletin*, Port Clinton, OH, 1995.
- Falcoux, P., Filhol, R., and Communal, J., *U.S. Patent 4,238,236*, Dec. 9, 1980.
- Federal Register*: 48(176), Sep. 14, 1993, pp. 48092-48204.
- Feigenbaum, H.N., "The Sulfex™ Process for Removal of Heavy Metals in a Textile Waste Stream," *Proc. Textile Wastewater Treatment and Air Pollution Control Conference*, Jan. 1977.
- Gilliam, T.M., Dole, L.R., and McDaniel, E.W., "Waste Immobilization in Cement-Based Grouts," *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume*, ASTM STP 933, American Society for Testing and Materials, Philadelphia, PA, 1986, pp. 295-307.
- Gilliam, T.M. and Wiles, C.C., eds., *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, 3rd Volume, STP 1240, ASTM, West Conshohocken, PA, 1996.
- Harada, Y., Itai, N., Uchikawa, H., Kato, H., Sato, K., and Itoh, A., *U.S. Patent 4,060,425*, Nov. 29, 1977.
- Higuchi, Y., Harada, Y., Nakagawa, K., Kawaguchi, I., and Kasahara, Y., *U. S. Patent 4,084,981*, Apr. 18, 1978.
- Industrial Water Engineering*, Oct. 1970.
- Japan Kokai 70/40,797*, Oct. 20, 1980.
- Kantro, D.L., "Tricalcium Silicate Hydration in the Presence of Various Salts," *ASTM Journal Of Testing and Evaluation*, July, 1975.
- Kawasaki Steel Corp., *Japan Kokai 80,136,166*, 1980.
- Kitsuge, K. and Kozeki, S., *U.S. Patent 3,947,283*, Mar. 30, 1976.
- Kitsugi, K., *U.S. Patent 3,947,284*, Mar. 30, 1976.
- Kitsugi, K. and Shimoda, M., *Japan Kokai 78 12,770*, Feb. 4, 1978.
- Knocke, W.R., Croy, L.P., and Kelley, R.T., *An Evaluation of the Solids Handling Characteristics of Sludge Produced by Two Metals' Precipitation Techniques*, Virginia Polytechnic Institute, Blacksburg, VA, 1977.
- Kokusai, G., *Japan Kokai 81 53,796*, May 13, 1981.
- Lagvankar, A., Mayenkar, K., and Pherson, P.A., "An Innovative Process for Removing Heavy Metals from Wastewater," *59th Annual Meeting Central States Water Pollution Control Association*, May 14-16, 1986.
- Lawson, M.A., Venn, J.G., Pugh, L.B., and Vallis, T., *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, 3rd Volume, ASTM STP 1240, West Conshohocken, PA, 1996.
- Manahan, S.E. and Smith, M.J., "The Importance of Chelating Agents," *Water and Sewage Works*, 1973, pp. 102-6.
- Metcalf, A.S. and Ellers, L.H., *U.S. Patent 4,210,455*, Jul. 1, 1980.
- Morse, J.G. and Dennis, D., "Assessment and Cleanup of Soils Using In Situ Stabilization at a Manufactured Gas Plant Site," *At 87th Annual Meeting &*

- Exhibition, AWMA, Cincinnati, Jun. 19-24, 1994.
- Munster, L., *U.S. Patent 4,338,134*, July 6, 1982.
- Nakaaki, O., Horie, Y., Idohara, M., and Shiraogi, J., *Japan Kokai 75,99,962*, Aug. 8, 1975.
- Navickis, L.L., Wing, R.E., and Bagley, E.B., "AISX Reduces Selenium Count in Process Wastewaters," *Industrial Wastes*, Jan./Feb. 1979, pp. 26-30.
- Nelson, D.A., "Removal of Heavy Metal Ions from Aqueous Solution with Treated Leather," *American Chemical Society*, Houston, TX, 1980.
- Onoda Cement Co., *U.S. Patent 3,947,284*, Mar. 30, 1976.
- Patterson, J.W., Allen, H.E., and Scala, J.J., "Carbonate Precipitation from Heavy Metals Pollutants," *Journal of the Water Pollution Control Federation* 12, 1977, pp. 2397-410.
- Pojasek, R.B., *Toxic and Hazardous Waste Disposal*, Vol. 1-4, Ann Arbor Science Pub., Ann Arbor, 1980.
- Portland Cement Association, *Portland Cements*, Skokie, IL, 1974.
- Portland Cement Association, *Design and Control of Concrete Mixtures*, Skokie, IL, 1979.
- Posselt, H.S. and Anderson, F.J., "Cation Sorption on Colloidal Hydrous Manganese Dioxide," *Environmental Science Technology* 2, 1968, pp. 1087-93.
- Roskopf, P.A., Linton, F.J., and Pepler, R.B., "Effect of Various Accelerating Chemical Admixtures on Setting and Strength Development of Concrete," *Journal of Testing and Evaluation* 3, No. 4, 1975.
- Sano, M., Sugano, I., and Okuda, T., *Japan Kokai 75,133,654*, Oct. 23, 1975.
- Shinoki, K., Katayama, T., and Yamaguchi, S., *Japan Kokai 80 44,355*, Mar. 28, 1980.
- Siegrist, R.L. et al., "In-situ Treatment of Clay Soils by Physicochemical Processes Coupled with Soil Mixing: Highlights of the X-231b Technology Demonstration," *At I&EC Special Symposium, ACS*, Atlanta, GA, Sep. 21-23, 1992.
- Sittig, M., *Pollutant Removal Handbook*, Noyes Data Corp., London, 1973.
- Soundararajan, R., Barth, E.F., and Gibbons, J.J., "Using an Organophilic Clay to Chemically Stabilize Waste Containing Organic Compounds," *Hazardous Materials Control*, Jan./Feb. 1990.
- Spence, R.D., Gilliam, T.M., Morgan, I.L., and Osborne, S.C., "Stabilization/Solidification of Wastes Containing Volatile Organic Compounds in Commercial Cementitious Waste Forms," *Presented at 2nd International Symposium on S/S of Hazardous, Radioactive and Mixed Wastes*, Williamsburg, VA, May 29-Jun. 1, 1990.
- Spence, R., *Chemistry and Microstructure of Solidified Waste Forms*, Lewis Publishers, Ann Arbor, MI, 1992.
- Swallow, K.C., Hume, D.N., and Morel, F.M., "Sorption of Copper and Lead by Hydrous Ferric Oxide," *Environmental Science Technology* 14, No. 11, 1980, pp. 1326-31.
- Takashita, I., *Japan Kokai 79,162,844*, 1979.
- United States Environmental Protection Agency, *Guide to the Disposal of Chemically Stabilized and Solidified Waste*, SW-872, Office of Solid Waste and Emergency Response, Washington, DC, Sep. 1982.
- United States Environmental Protection Agency, *Federal Register* 50, No. 105, May 31, 1985, pp. 23250.
- United States Environmental Protection Agency, *Cleaning Up the Nation's Waste Sites: Markets and Technology Trends*, EPA 542-H-92-012, Washington, DC, April, 1993.
- United States Environmental Protection Agency, *Federal Register* 55, No. 61, Mar. 29, 1990, pp. 11798-11877.
- United States Environmental Protection Agency, *Federal Register* 56, No. 140, Jul. 22, 1991, pp. 33490-33579.
- United States Environmental Protection Agency, *Technical Resource Document: Solidification/Stabilization and its Application to Waste Materials*, EPA/530/R-93/012, Office of Research and Development, Washington, DC, Jun. 1993.
- United States Environmental Protection Agency, *Land Disposal Restrictions Phase II — Universal Treatment Standards, and Treatment Standards for Organic Toxicity Characteristics Wastes and Newly Listed Wastes, Final Rule*, 40 CFR 148, Sep. 1994, pp. 260-261, 264-266, 268, 271.
- United States Environmental Protection Agency, *Innovative Treatment Technologies: Annual Status Report (Seventh Edition) Applications of New Technologies at Hazardous Waste Sites*, EPA-542-R-95-008, Office of Solid Waste and Emergency Response, Sep. 1995.
- U.S. Army Corps of Engineers Waterways Experiment Station, *U.S. Patent 3,642,503, Interference Mechanisms in Waste Stabilization/Solidification Processes*, EPA 600/2-89/067, United States Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, Jan. 1990.
- Vail, J.G., *Soluble Silicates*, Reinhold, New York, 1952.
- Veda, S. and Ito, M., *Japan Kokai 77 38,468*, Mar. 25, 1977.
- Vejmelka, P.R., Kosher, and Hauler, W., *U.S. Patent 4,533,395*, Aug. 6, 1985.
- Wagner, H.B. and Ellis, J.R., *U.S. Patent 4,211,572*, Jul. 8, 1980.
- Walsh, M.B., Eaton, H.C., Tittlebaum, M.E., Cartledge, F.K., and Chalasani, D., "The Effect of Two Organic Compounds on a Portland Cement-Based Stabilization Matrix," *Hazardous*

- Wastes & Hazardous Materials* 3, No. 1, 1986.
- Weiner, R.F., "Acute Problems in Effluent Treatment," *Plating* 54, 1967, pp. 1354-6.
- Weitzman, L., Hamel, L.E., and Cadmus, S.R., *Volatile Emissions From Stabilized Waste In Hazardous Landfills*, U.S.EPA Contract 68-02-3993, Research Triangle Park, Aug. 28, 1987.
- Wing, R.E., "Corn Starch Compound Recovers Metals from Water," *Industrial Wastes*, Jan./Feb. 1975, pp. 26-7.
- Yagi, T., *Japan Kokai* 75,105,541, Aug. 20, 1975.
- Yagi, T. and Matsunaga, S., *Japan Kokai* 76,123,775, Oct. 28, 1976.
- Yamagishi, H., Sakamaki, S., Nakagawa, K., and Sirasawa, M., *U.S. Patent* 4,190,454, Feb. 26, 1980.
- Young, J.F., "A Review of the Mechanisms of Set-Retardation of Cement Pastes Containing Organic Admixtures," *Cement and Concrete Research* 2, No. 4, 1972.
- Young, D.A., *U.S. Patent* 4,142,912, Mar. 6, 1979.

Table 1. Additives Used in Cement-based S/S

Additive	Effect	Relative Cost
pH Control and Buffering:	pH adjustment; removal of interfering substances from solution; destruction of gels and film-formers	
Lime - CaO or Ca(OH) ₂	Neutralizes acids, raises pH	Low
Sodium hydroxide	Neutralizes acids, raises pH	Low
Sodium carbonate	Neutralizes acids, raises pH	Low
Sodium bicarbonate	Buffer	Low
Magnesium oxide	Buffer	Moderate
Ferrous sulfate	Lowers pH, alkalinity	Low
Sulfuric acid	Lowers pH, alkalinity	Low
Reduction:	Alteration of valence state of metals	
Ferrous sulfate	Reducing agent in acid conditions	Low
Sodium hydrosulfite	Reducing agent in alkaline conditions	Moderate
Sodium metabisulfite	Reducing agent in acid conditions	Low
Blast furnace slag	Reducing agent	Low
Metallic iron	Reducing agent	Low
Oxidation:	Alteration of valence state of metals; destruction/conversion of interfering substances	
Potassium permanganate	Powerful, non-selective oxidizing agent; alteration of biological status	High
Sodium or potassium persulfate	Powerful, non-selective oxidizing agent; alteration of biological status	High
Sodium or calcium hypochlorite	Non-selective oxidizing agent; alteration of biological status	High
Hydrogen peroxide	Mild, non-selective oxidizing agent; alteration of biological status	Moderate
Speciation, Re-Speciation:	Alteration of the species of the constituents of concern to fix metals and other ions	
Carbonates	With lead, forms carbonates, basic carbonates	Low
Iron and aluminum compounds	Various	Low to moderate

Table 1. Additives Used in Cement-based S/S

Additive	Effect	Relative Cost
Phosphoric acid and salts	With lead, forms phosphate compounds that have low solubility through a wide pH range	Low to moderate
Sodium silicate	Forms low-solubility, silicate species with a variety of metals in solution; anti-inhibitor	Low to moderate
Sodium sulfide	Forms metal sulfides, except with chromium	Low
Calcium polysulfide	Forms metal sulfides, except with chromium	Low
Organic sulfur compounds - thiocarbamates	Forms metal sulfides, except with chromium safer than inorganic sulfides	Moderate
Sulfur + alkali	Forms metal sulfides, except with chromium	Low
Xanthates	Form low-solubility starch or cellulose xanthate substrates with metals attached	Moderate
Sodium chloride	Silver fixant	Low
Sodium sulfate	Barium fixant	Low
Ferrous sulfate	Removes sulfide ion from solution	Low
Precipitation and Flocculation:	Aggregation of fine particles and film formers; dispersion of oils and greases and fine particulates away from reacting surfaces	
Ferrous sulfate	Co-precipitating agent	Low
Proprietary organic flocculants, surfactants	Flocculants and dispersants	Low to moderate
Alcohols	Wetting agent	Low to moderate
Amides	Wetting agent	Low to moderate
Carboxylic acids	Dispersants	Moderate
Aldehydes and Ketones	Dispersants	Moderate
Sulfonates	Dispersants	Moderate
Amines	Flocculants	Moderate
Iron salts	Flocculants	Low
Magnesium salts	Flocculants	Low to Moderate
Silica	Flocculants	Low

Table 1. Additives Used in Cement-based S/S

Additive	Effect	Relative Cost
Sorption, Bulking, Structural Modification:	Removal of interfering substances from reacting surfaces; immobilization of organic species; free water reduction; viscosity control; improvement of microstructure	
Activated carbon	Sorbent for organics, especially VOCs, organo-metallics, and some metals	High
Organoclays	Sorbent for organics	High
Rubber particulate	Sorbent for organics, especially SVOCs	Moderate
Fly ash	Sorbent for some metals and organics; pozzolanic reaction with alkalies; bulking agent	Low
Rice hull ash	Sorbent for organics, especially VOCs; reacts with alkalies to form soluble silicates	Moderate
Natural clays	Sorbents for some metals; bulking agent; viscosity control	Low
Expanded minerals	Sorbents for some metals; bulking agent	Low to moderate
Diatomaceous earth	Sorbents for some metals; bulking agent	Low to moderate
Blast furnace slag	Pozzolanic reaction with alkalies; bulking agent; reducing agent; structural modification	Low
Silica fume	Pozzolanic reaction with alkalies; bulking agent; structural modification	Low
Wood chips	Sorbent; bulking agent	Low
Ground corn cob	Sorbent; bulking agent	Low
Cement kiln dust	Pozzolanic bulking agent, as well as accelerator in some cases	Low
Acceleration/ Anti-Inhibition:	Counter the effects of set retarders in waste accelerate the normal set time of cement based systems	
Calcium chloride	Accelerates set	Low
Calcium aluminate	Accelerates set	Low
Calcium sulfate	Accelerates set	Low
Glycols	Accelerates set	Moderate

Table 1. Additives Used in Cement-based S/S

Additive	Effect	Relative Cost
Sugar	Accelerates set	Moderate
Amines	Accelerates set	Moderate
Organic acid salts	Accelerates set	Moderate
Lime	Supplies additional calcium for reaction; reacts with certain interfering organics; anti inhibitor; controls biological status	Low
Sodium silicate	Reacts with interfering metals; anti-inhibitor; causes acceleration of initial set; fixes metals	Low to moderate
Iron compounds	Counters effect of tin, lead arsenates, sulfides by reaction	Low
Triethanolamine	Accelerates set	Moderate
Calcium formate	Accelerates set	Moderate
Phosphates	Accelerates set	Low
Bentonite	Sorbs oils, organics; anti-inhibitor	Low
Cement kiln dust	Accelerator in some cases	Low
Retardation:	Retardation of setting to allow for better processing control	
Sugar	Retards of setting at low levels	Low
Sugar derivatives	Retards setting	Moderate
Zinc hydroxide	Retards setting	Low
Copper hydroxide	Retards setting	Low
Lead hydroxide	Retards setting	Low
Calcium chloride >4%	Retards setting	Low
Magnesium salts	Retards setting	Low
Tin salts	Retards setting	Low
Phosphates	Retards setting	Low
Lignosulfonic acid salts and derivatives	Retards setting	Low to Moderate
Hydroxy carboxylic acids	Retards setting	Low to Moderate
Polyhydroxy compounds	Retards setting	Low to Moderate

Table 1. Additives Used in Cement-based S/S

Additive	Effect	Relative Cost
Free Water Control:	Control (usually reduction) of the free water content of the system	
Slag	Bulking agent; pozzolan	Low
Flyash	Bulking agent; pozzolan	Low
Concrete water reducing additives	Reduce water requirement where applicable	Low to moderate
Cement kiln dust	Bulking agent, pozzolan	Low
Miscellaneous:		
Biocides	Counter biological activity	Moderate
Organic polymers	Fill pores, improve microstructure, improve durability	Moderate to High
Air entrainment additives	Improve durability	Low to Moderate
Wood resins	Improve durability	Moderate

Table 3. Solidification Problems

PROBLEM	PROBABLE CAUSE - WASTE CHARACTERISTICS, INGREDIENTS	APPROACH TO SOLUTION	SPECIFIC ADDITIVES OR TECHNIQUES USED	ADDITION RATIO RANGE (weight %)	COST RANGE (\$ per ton of waste treated)
Will not set	<ol style="list-style-type: none"> 1. Fine particulates: silt, clay, colloidal matter 2. Anaerobic conditions 3. Calcium removers 	<ol style="list-style-type: none"> 1. Surface active agents: wetting agents, dispersants, flocculants 2. Aerate; add oxidizer, lime, biocide 3. Replace lost calcium 	<ol style="list-style-type: none"> 1. Iron salts, ferrous sulfate, magnesium salts, silica, asphalt emulsions, alcohols amides, amines, carboxylic acids, carbonyls, sulfonates 2. Air, oxygen, lime, calcium/sodium hypochlorite, proprietary biocide 3. Lime, calcium chloride, gypsum 	<ol style="list-style-type: none"> 1. 0.01 - 1.0 2. 1 - 5 3. 1 - 10 	<ol style="list-style-type: none"> 1. <1 - 20 2. 1 - 250 3. 1 -25
Sets, but doesn't harden	<ol style="list-style-type: none"> 1. Fine particulates: silt, clay, colloidal matter 2. Anaerobic conditions 	<ol style="list-style-type: none"> 1. Surface active agents: wetting agents, dispersants, flocculants 2. Aerate; add oxidizer, lime, biocide 3. Replace lost calcium 	<ol style="list-style-type: none"> 1. Iron salts, ferrous sulfate, magnesium salts, silica, asphalt emulsions, alcohols amides, amines, carboxylic acids, carbonyls, sulfonates 2. Air, oxygen, lime, calcium/sodium hypochlorite, proprietary biocide 3. Lime, calcium chloride, gypsum 	<ol style="list-style-type: none"> 1. 0.01 - 1.0 2. 1 - 5 3. 1 - 10 	<ol style="list-style-type: none"> 1. <1 - 20 2. 1 - 250 3. 1 -25

Table 3. Solidification Problems (continued)

PROBLEM	PROBABLE CAUSE - WASTE CHARACTERISTICS, INGREDIENTS	APPROACH TO SOLUTION	SPECIFIC ADDITIVES OR TECHNIQUES USED	ADDITION RATIO RANGE (weight %)	COST RANGE (\$ per ton of waste treated)
Set is retarded	<ol style="list-style-type: none"> 1. Fine particulates: silt, clay, colloidal matter 2. Sugar 3. Phosphates 4. Sulfur 5. Bicarbonates of sodium and potassium 6. Chemical interference: <ol style="list-style-type: none"> a. Inorganics: metal salts, sodium iodate, sodium phosphate, sodium arsenate, sodium borate, sodium sulfide b. Chelating agents c. Organics 7. Mild anaerobic conditions 8. Insufficient cure time 9. General set retardation 	<ol style="list-style-type: none"> 1. Surface active agents: wetting agents, dispersants, flocculants 2a. Add more sugar - 0.2% 2b. Add a sorbent 3. Add calcium ion 4. None established 5. Use acidic material to decompose 6a,b. Add an accelerator or anti-inhibitor 6c. Add a sorbent, oxidant, accelerator or anti-inhibitor 7. Aerate; add oxidizer, lime, biocide 8. Cure longer 9. Add a general accelerator Calcium chloride 	<ol style="list-style-type: none"> 1. Iron salts, ferrous sulfate, magnesium salts, silica, asphalt emulsions, alcohols amides, amines, carboxylic acids, carbonyls, sulfonates 2a. Sugar 2b. Clay, flyash, diatomaceous earth, carbon 3. Lime, gypsum, calcium chloride 5. Acids, ferrous sulfate 6a,b. Sulfates, soluble silicates, aluminates, phosphates, hydroxylated organic acids, glycols, amines, iron compounds, ASTM set accelerators 6c. Clay, lime, limestone, flyash, carbon; hydrogen peroxide, potassium permanganate, sodium persulfate, calcium/sodium hypochlorite; also see 6a,b above 7. Air, oxygen, lime, calcium/sodium hypochlorite, proprietary biocide 9. Calcium chloride, sodium silicate, lime 	<ol style="list-style-type: none"> 1. 0.01 - 1.0 2a. >0.2 2b. .5 - 5 3. 1 - 5 5. 0.1 - 10 6a,b. 0.01 - 5 6c. 0.1 - 10 7. 0.1 - 5 9. 1 - 5 	<ol style="list-style-type: none"> 1. <1 - 20 2a. <1 - 20 2b. 1 - 10 3. 1 - 5 5. <1 - 5 6a,b. 1 - 25 6c. 1 - 100 7. 2 - 10 9. 1 - 10

Table 3. Solidification Problems (continued)

PROBLEM	PROBABLE CAUSE - WASTE CHARACTERISTICS, INGREDIENTS	APPROACH TO SOLUTION	SPECIFIC ADDITIVES OR TECHNIQUES USED	ADDITION RATIO RANGE (weight %)	COST RANGE (\$ per ton of waste treated)
Supernatant liquid on surface after setting (Usually due to large particle size and/or high particle specific gravity in low calcium/sodium hypochlorite viscosity medium)	<ol style="list-style-type: none"> Set is too slow Water content is too high Viscosity of system is too low 	<ol style="list-style-type: none"> Add set accelerator or anti-inhibitor: Dewater or sorb water Increase viscosity of system 	<ol style="list-style-type: none"> Sulfates, soluble silicates, aluminates, phosphates, hydroxylated organic acids, glycols, amines, iron compounds, ASTM set accelerators Decant water; filter raw waste; add flyash, clay, slag, silica fume, wood chips, ground corn cob, diatomaceous earth, expanded minerals Gelling agent - sodium silicate; sorbent - see (2) above 	<ol style="list-style-type: none"> 1-10 5-50 1-50 	<ol style="list-style-type: none"> 2-20 0-25 0-25
Sets too rapidly for satisfactory processing	<ol style="list-style-type: none"> Accelerating agents: sulfates; soluble silicates, aluminates, phosphates; hydroxylated organic acids, glycols, other organics; ion exchange material Carbonates and bicarbonates of sodium and potassium Sugar > 0.2% 	<ol style="list-style-type: none"> Add set retarder Decompose or neutralize with acidic additive Add retarder Chemical oxidation 	<ol style="list-style-type: none"> Proprietary, concrete set retarder; zinc, copper or lead oxide/hydroxide; calcium chloride (>4%); magnesium and tin salts; phosphates, clays Ferrous sulfate, sulfuric acid See (1) above Hydrogen peroxide, calcium/sodium hypochlorite, potassium permanganate, sodium persulfate 	<ol style="list-style-type: none"> 0.01 - 5 1 - 10 0.01 - 5 1 - 10 	<ol style="list-style-type: none"> 2 - 5 <1 - 20 2 - 5 5 - 250

Table 3. Solidification Problems (continued)

PROBLEM	PROBABLE CAUSE - WASTE CHARACTERISTICS, INGREDIENTS	APPROACH TO SOLUTION	SPECIFIC ADDITIVES OR TECHNIQUES USED	ADDITION RATIO RANGE (weight %)	COST RANGE (\$ per ton of waste treated)
Insufficient unconfined compressive strength (ASTM D-2166, D-1633)	<ol style="list-style-type: none"> Chemical interference: metal salts, lead nitrate, sodium iodate, sodium phosphate, sodium arsenate, sodium borate, sodium sulfide Sodium sulfide, sodium sulfite, sodium hydroxide Sugar Algae Anaerobic conditions Oil and grease Phenol Water content too high Cement content too low 	<ol style="list-style-type: none"> Add an accelerator or anti-inhibitor Iron salts; chemical oxidation; acid Chemical oxidation Add sorbent Chemical oxidation Add lime Add biocide Aerate; add oxidizer, lime, biocide Chemical oxidation Add sorbent Add chemicals Chemical oxidation Dewater or sorb water Add more cement 	<ol style="list-style-type: none"> Sulfates, soluble silicates, aluminates, phosphates, hydroxylated organic acids, glycols, amines, iron compounds, ASTM set accelerators Ferrous sulfate Hydrogen peroxide, calcium/sodium hypochlorite Hydrogen peroxide, potassium permanganate, sodium persulfate, calcium/sodium hypochlorite Clays, limestone, flyash See (3a) Air, oxygen, lime, calcium/sodium hypochlorite, proprietary biocide See (3a) Flyash, bentonite, limestone Quicklime, stearates Potassium permanganate, sodium persulfate Decant water; filter raw waste; add flyash, clay, slag, silica fume, wood chips, ground corn cob, diatomaceous earth, expanded minerals 	<ol style="list-style-type: none"> 1 - 10 1 - 10 1 - 10 2 - 10 1 - 10 1 - 10 1 - 10 2 - 10 2 - 10 2 - 10 5 - 50 	<ol style="list-style-type: none"> 2 - 20 2 - 20 5 - 200 5 - 250 1 - 5 5 - 250 2 - 10 <1 - 20 5 - 200 5 - 250 1 - 5 2 - 50 5 - 250 2 - 20

Table 3. Solidification Problems (continued)

PROBLEM	PROBABLE CAUSE - WASTE CHARACTERISTICS, INGREDIENTS	APPROACH TO SOLUTION	SPECIFIC ADDITIVES OR TECHNIQUES USED	ADDITION RATIO RANGE (weight %)	COST RANGE (\$ per ton of waste treated)
Permeability too high (SW846, Method 9100)	<ol style="list-style-type: none"> Incomplete curing Insufficient cement High waste permeability 	<ol style="list-style-type: none"> Cure for at least 28 days Use more cement Add low permeability additive Add hydrophobizing agent Fill pores with water resistant material Develop better microstructure 	<ol style="list-style-type: none"> Portland cement Bentonite clay Emulsified asphalt, stearates Latex or other water compatible polymer Flyash, blast furnace slag, silica fume 	<ol style="list-style-type: none"> 5 - 30 1 - 5 5 - 10 	<ol style="list-style-type: none"> 5 - 30 1 - 5 50 - 100
Poor durability (ASTM D-4842-90, D-4843-88)	<ol style="list-style-type: none"> Insufficient cement Poor microstructure Excessive porosity Large amounts of soluble salts sulfates, chlorides, nitrates 	<ol style="list-style-type: none"> Add more cement Add flyash, silica fume Air entrainment Modify water content Add bulking agent or water absorber Add pore filling agent Add hydrophobizing agent None reported 	<ol style="list-style-type: none"> Portland cement Flyash, silica fume Use air entraining agent, process to entrain air Decant water; filter raw waste Flyash, clay, slag, silica fume, wood chips, ground corn cob, diatomaceous earth, expanded minerals Latex or other water compatible polymer Emulsified asphalt, stearates 	<ol style="list-style-type: none"> 5 - 25 0.01 - 1 5 - 25 5 - 10 1 - 5 	<ol style="list-style-type: none"> 2 - 20 2 - 20 2 - 10 50 - 100 1 - 5

Table 7. Stabilization of Metals

Note: Metals or metals species that are adequately stabilized by cement alone are shaded.

Problem or Target Constituent or Species	Approach to Solution*	Specific Additives Used*	Addition Ratio Range (weight %)	Cost Range (\$ per ton of waste treated)
Antimony				
Arsenic trisulfide	1. Oxidation to As ⁵ followed by precipitation with calcium	1. Calcium/sodium hypochlorite or potassium permanganate 2. Lime	1. 1 - 20 2. 5 - 10	1. 20 - 400 2. 5 - 10
Arsenic complexes	1. Immobilize by sorption 2. Destroy complex by oxidation	1. Activated carbon 2. Potassium permanganate, sodium persulfate	1. 1 - 10 2. 5 - 10	1. 20 - 200 2. 100 - 200
Barium, soluble compounds	Precipitate as sulfate	Calcium sulfate (gypsum)	1 - 5	1 - 5
Beryllium				
Cadmium, simple	Raise pH	Lime, limestone, high-free-lime cement kiln dust	5 - 10	5 - 10
Cadmium cyanide	Destroy complex by alkaline oxidation	Calcium/sodium hypochlorite or hydrogen peroxide	1 - 10	20 - 200
Chromium, simple				
Chromium as Cr ⁶⁺	Reduce to Cr ³⁺	Ferrous sulfate, sodium bisulfite or metabisulfite, or sodium hydrosulfite	5 - 20	10 - 120
Chromium complexes	Immobilize by sorption	Activated carbon	1 - 10	20 - 200
Lead, simple	1. Co-precipitate 2. Speciate as carbonate, basic carbonate 3. Speciate as sulfide	1. Ferrous sulfate 2. Calcium carbonate, sodium carbonate 3. Sodium sulfide or organo-sulfur compounds	1. 5 - 10 2. 5 - 20 3. 0.1 - 5	1. 10 - 20 2. 2 - 10 3. 2 - 40
Lead, complexed	1. Immobilize by sorption 2. Destroy complex by oxidation	1. Activated carbon 2. Calcium/sodium hypochlorite, potassium permanganate, sodium persulfate	1. 1 - 10 2. 5 - 10	1. 20 - 200 2. 100 - 200

Table 7. Stabilization of Metals (continued)

Problem or Target Constituent or Species	Approach to Solution*	Specific Additives Used*	Addition Ratio Range (weight %)	Cost Range (\$ per ton of waste treated)
Lead, elemental	Include a source of carbonate to re speciate lead as it dissolves	Calcium carbonate, sodium carbonate	5 - 20	2 - 10
Mercury, simple	Speciate as sulfide	1. Sodium sulfide or organo-sulfur compounds 2. Sulfur + alkali	1. 0.1 - 5 2. 1 - 10	1. 2 - 40 2. <1 - 5
Nickel, simple	Speciate as sulfide	Sodium sulfide or organo-sulfur compounds	0.1 - 5	2 - 40
Nickel cyanide	Destroy complex by alkaline oxidation	Calcium/sodium hypochlorite or hydrogen peroxide	1 - 10	20 - 200
Nickel complexes	1. Immobilize by sorption 2. Destroy complex by oxidation	1. Activated carbon 2. Potassium permanganate, sodium persulfate	1. 1 - 10 2. 5 - 10	1. 20 - 200 2. 100 - 200
Selenium, simple				
Selenium, selenate	Co-precipitate	Ferrous sulfate	1 - 5	2 - 10
Silver, simple				
Silver, high level	Precipitate as chloride	Sodium chloride	0.1 - 1	<1 - 1
Thallium				
Vanadium				
Zinc				
Metals, elemental, finely divided	De-activate by dissolution if pyrophoric	Acids	1 - 10	<1 - 5

* It is assumed that the treatment is being done in the context of a cement-based S/S system. Therefore, multistep treatment requiring precipitation or speciation by cement in the last step is assumed in the table and is not spelled out.

Table 8. General Additive Utilization List, Metals

Contaminant	Additive Used (X)												
	Flyash/ Bed Ash	Hydrated Lime	FeSO ₄	CaCO ₃	Na ₂ CO ₃	NaCl	Na ₂ SO ₄	Organo- Sulfur	Carbon	Ca(OCl) ₂ / NaOCl	KMnO ₄ / (NH ₄) ₂ S ₂ O ₈	Na ₂ S ₂ O ₄	Na ₂ S/ Sulfur
Antimony													
Arsenic - As ⁺⁵ , conventional	X												
Arsenic - As ⁺³	X	X							X	X			
Arsenic - organo- compounds	X	X						X		X			
Barium	X						X						
Beryllium													
Cadmium	X	X											
Chromium - Cr ⁺³ , conventional	X												
Chromium - Cr ⁺⁶ , hexavalent	X		X								X		
Chromium - complexes								X					
Lead - conventional	X		X	X	X			X					
Lead - organo- compounds									X	X	X		

Table 8. General Additive Utilization List, Metals (continued)

Contaminant	Additive Used (X)												
	Flyash/ Bed Ash	Hydrated Lime	FeSO ₄	CaCO ₃	Na ₂ CO ₃	NaCl	Na ₂ SO ₄	Organo- Sulfur	Carbon	Ca(OCl) ₂ / NaOCl	KMnO ₄ / (NH ₄) ₂ S ₂ O ₈	Na ₂ S ₂ O ₄	Na ₂ S/ Sulfur
Lead - elemental			X										
Mercury - conventional	X						X						X
Mercury - organo- compounds										X			X
Mercury - elemental													X
Nickel - conventional	X							X					
Nickel - cyanide complexes	X								X				
Nickel - organo- compounds	X							X			X		
Selenium - conventional	X												
Selenium - selenate *			X										
Silver	X												
Thallium													

Table 8. General Additive Utilization List, Metals (continued)

Contaminant	Additive Used (X)												
	Flyash/ Bed Ash	Hydrated Lime	FeSO ₄	CaCO ₃	Na ₂ CO ₃	NaCl	Na ₂ SO ₄	Organo- Sulfur	Carbon	Ca(OCl) ₂ / NaOCl	KMnO ₄ / (NH ₄) ₂ S ₂ O ₈	Na ₂ S ₂ O ₄	Na ₂ S/ Sulfur
Vanadium													
Zinc	X												

* Strontium is reported to be useful in stabilization of selenate ion

Table 9. Stabilization of Volatile Organics

TARGET CONSTITUENT	UTS LEVEL	TCLP TESTING (mg/l)				TCA TESTING (mg/kg)			
		Un-treated	Treated	Additive	Addition Ratio (%)	Un-treated	Treated	Additive	Addition Ratio (%)
Acetone	160	120.5	17.25	KAX-50™	10	918	<200	KAX-100™	10
Benzene	10	26.5	<1.25	Carbon	10	418	26.4	KAX-100™	10
2-Butanone (Methyl ethyl ketone)	36	68.0	6.0	Carbon	10	430	95.8	Carbon	10
Carbon Disulfide	4.8*	5.0	<0.25	***	10	83	<0.25	None	-
Carbon Tetrachloride	6	18.0	<1.25	Carbon	10	429	14.5	KAX-100™	10
Chlorobenzene	6	35.5	<1.25	Carbon	10	1400	402	Carbon	10
Chloroform	6	48.5	<2.5	KAX-100™	10	431	9.8	KAX-100™	10
1,2-Dichloroethane	6	68.5	<2.5	KAX-100™	10	654	<0.25	KAX-100™	10
1,1-Dichloroethylene	6	-	-	-	-	2.24	<0.25	O-clay	10
Ethyl Acetate	33	29.5	<0.25	KAX-50™	10	258	<0.25	**	10
Ethyl Benzene	10	11.0	<2.5	****	10	1040	2.63	Carbon	10
Methylene Chloride	30	15.0	<0.25	KAX-50™	10	62	<0.25	KAX-100™	10
4-Methyl-2-Pentanone (Methyl isobutyl ketone)	33	104.5	<2.5	Carbon	10	1030	610	KAX-100™	10
Tetrachloroethylene	6	22.0	<1.25	Carbon	10	1980	615	KAX-100™	10
Toluene	10	33.5	<1.25	Carbon	10	938	256	KAX-100™	10
1,1,1-Trichloroethane	6	34.5	<0.25	KAX-50™	10	550	<0.25	KAX-100™	10
Trichloroethylene	6	44.5	<1.25	Carbon	10	881	89.1	KAX-100™	10

Table 9. Stabilization of Volatile Organics (continued)

TARGET CONSTITUENT	UTS LEVEL	TCLP TESTING (mg/l)				TCA TESTING (mg/kg)			
		Un-treated	Treated	Additive	Addition Ratio (%)	Un-treated	Treated	Additive	Addition Ratio (%)
Trichlorofluoromethane	30	-	-	-	-	0.49	<0.25	None	-
1,1,2-Trichloro-1,2,2-Trifluoroethane	30	-	-	-	-	9.1	<0.25	***	10
Total Xylenes	30	11.0	<1.25	Carbon	10	1070	174	Carbon	10
N-Butanol	2.6	55.0	31.4	KAX-50™	10	3350	<5	KAX-100™	10
Cyclohexanone	0.75*	-	-	-	-	536	<5	KAX-100™	10
Iso-Butyl Alcohol	170	-	-	-	-	2100	<5	KAX-100™	10
Methanol	0.75*	233.0	50.4	Carbon	10	2337	444	KAX-100™	10

Note: "O-clay" = organoclay * = TLCP ** = Carbon, O-clays, or KAX-100™ *** = O-clay or KAX-100™ **** = Carbon or O-clays

Table 10. Stabilization of Semi-Volatile Organics

TARGET CONSTITUENT	UTS LEVEL	TCLP TESTING (mg/l)				TCA TESTING (mg/kg)			
		Un-treated	Treated	Additive	Addition Ratio (%)	Un-treated	Treated	Additive	Addition Ratio (%)
Anthracene	3.4	0.032	<0.02	**	10	544	6.9	KAX-50™	10
Bis(2-Ethylhexyl) Phthalate	28	0.52	<0.02	KAX-50™	10	776	<0.99	KAX-50™	10
1,2-Dichlorobenzene	6	2.1	<0.02	Carbon	10	429	6.78	KAX-50™	10
1,4-Dichlorobenzene	6	1.86	<0.02	Carbon	10	461	6.03	KAX-50™	10
2,4-Dinitrotoluene	140	6.26	<0.02	Carbon	10	438	<0.99	KAX-50™	10
Hexachlorobenzene	10	-	-	-	-	440	6.96	KAX-50™	10
Hexachlorobutadiene	5.6	0.14	<0.02	*	10	620	10	KAX-50™	10
Hexachloroethane	30	0.38	<0.02	Carbon	10	381	6.46	KAX-50™	10
4-Methyl phenol	5.6	12.2	<0.1	**	10				
Naphthalene	5.6	2.1	-	-	-	584	6	KAX-50™	10
Nitrobenzene	14	11.6	0.05	Carbon	10	372	3.66	KAX-50™	10
Pentachlorophenol	7.4	2.3	<0.2	***	10	152	<1.8	*	10
Pyridine	16	30.2	28.2	Carbon	10	1900	35.1	KAX-50™	10
2,4,5-Trichlorophenol	7.4	8.2	<0.5	*	10	132	3.37	Carbon	10
2,4,6-Trichlorophenol	7.4	13.7	<0.1	KAX-50™	10	952	<0.99	KAX-50™	10

Note: * = Carbon or KAX-50™/KAX-100™ ** = Carbon, O-clays, or KAX-100™ *** = Carbon or O-clays

Table 11. Stabilization of Pesticides and Herbicides

TARGET CONSTITUENT	UTS LEVEL	TCLP TESTING (mg/l)				TCA TESTING (mg/kg)			
		Un-treated	Treated	Additive	Addition Ratio (%)	Un-treated	Treated	Additive	Addition Ratio (%)
gamma-BHC (Lindane)	0.066	1.5	<0.2	*	10	25	<5.0	KAX-100™	10
Heptachlor	0.066	0.4	<0.008	**	10	163	54	O-clays	10
Endrin	0.13	0.3	<0.02	**		2.6	0.8	Carbon	10
Methoxychlor	0.18	<10.	<0.2	**	10	1.1	0.28	Carbon	10
Chlordane	0.26	<0.03	<0.03	***	10	52	5.6	Carbon	10
Toxaphene	2.6	<0.5	<0.5	***	10	68	26	Carbon	10
2,4-Dichlorophenoxyacetic acid	10	<0.1	<0.1	***	10	26000	17	KAX-100™	10

Notes: "O-clay" = organoclay * = O-clay or KAX-50™/KAX-100™ ** = Carbon *** = Carbon, O-clay or KAX-50™//100™

Table 12. General Additives Utilization List, Organics

TARGET CONSTITUENT	CARBON		ORGANO-CLAY		RUBBER PARTICULATE KAX-50™		MODIFIED RUBBER PARTICULATE KAX-100™	
	TCLP	TCA	TCLP	TCA	TCLP	TCA	TCLP	TCA
VOCs	X	X	X	X	X		X	X
Semi-VOCs	X	X	X	X	X	X	X	X
PCBs	NR	ND	NR	ND	NR	ND	NR	ND
Pesticides, Herbicides	X	X	X	X	X	X	X	X
Organo-metallics	X	ND	ND	ND	X	ND	X	ND
Poly Nuclear Aromatics (PNAs)	X	X	X	X	X	X	X	
Alcohols	X		ND	ND	X			X

NR = Not Required ND = No Data

KEYWORDS: additives, cement, compressive strength, durability, fixation, heavy metals, immobilization, metals, organics, organo-metallics, permeability, portland cement, solidification, soluble salts, stabilization.

ABSTRACT: Portland cement-based stabilization/solidification (S/S) has been used to successfully treat a wide variety of wastes. Some situations (because of the waste itself, the disposal scenario, and/or the regulatory requirements) require the use of additives or physical/chemical techniques to improve the effectiveness of cement-based S/S. The problems encountered in S/S can be broadly classified into *solidification* problems, i.e. obtaining the required physical properties in the treated waste, and *stabilization problems*, i.e. adequately immobilizing the hazardous constituents of the waste. The Guide lists additives and techniques that can be applied to specific solidification problems such as problems in development of set, compressive strength, and free liquids. Also included are lists of additives and techniques that can be applied to immobilization of specific hazardous constituents such as lead, cadmium, and chromium, as well as classes of constituents such as volatile organics, organo-metallics and soluble salts. The Guide lists a variety of generic additives for specific desired stabilization/solidification effects, including those that can be used to control the pH of wastes; to reduce, oxidize, and co-precipitate constituents; and to accelerate or retard set.

This publication is intended SOLELY for use by PROFESSIONAL PERSONNEL who are competent to evaluate the significance and limitations of the information provided herein, and who will accept total responsibility for the application of this information. The Portland Cement Association DISCLAIMS any and all RESPONSIBILITY and LIABILITY for the accuracy of and the application of the information contained in this publication to the full extent permitted by law.

Portland Cement Association 5420 Old Orchard Road, Skokie, Illinois 60077-1083, (847) 966-6200, Fax (847) 966-9781



An organization of cement manufacturers to improve and extend the uses of portland cement and concrete through market development, engineering, research, education and public affairs work.