7355 U-007-409.7

PORTLAND CEMENT ASSOCIATION, SOLIDIFICATION AND STABILIZATION OF WASTES USING PORTLAND CEMENT - (USED AS A REFERENCE IN OU 5 FS) - THIS IS COPY RIGHTED MATERIAL, NOT TO BE COPIED - MAY BE VIEWED FROM PUBLIC READING ROOM

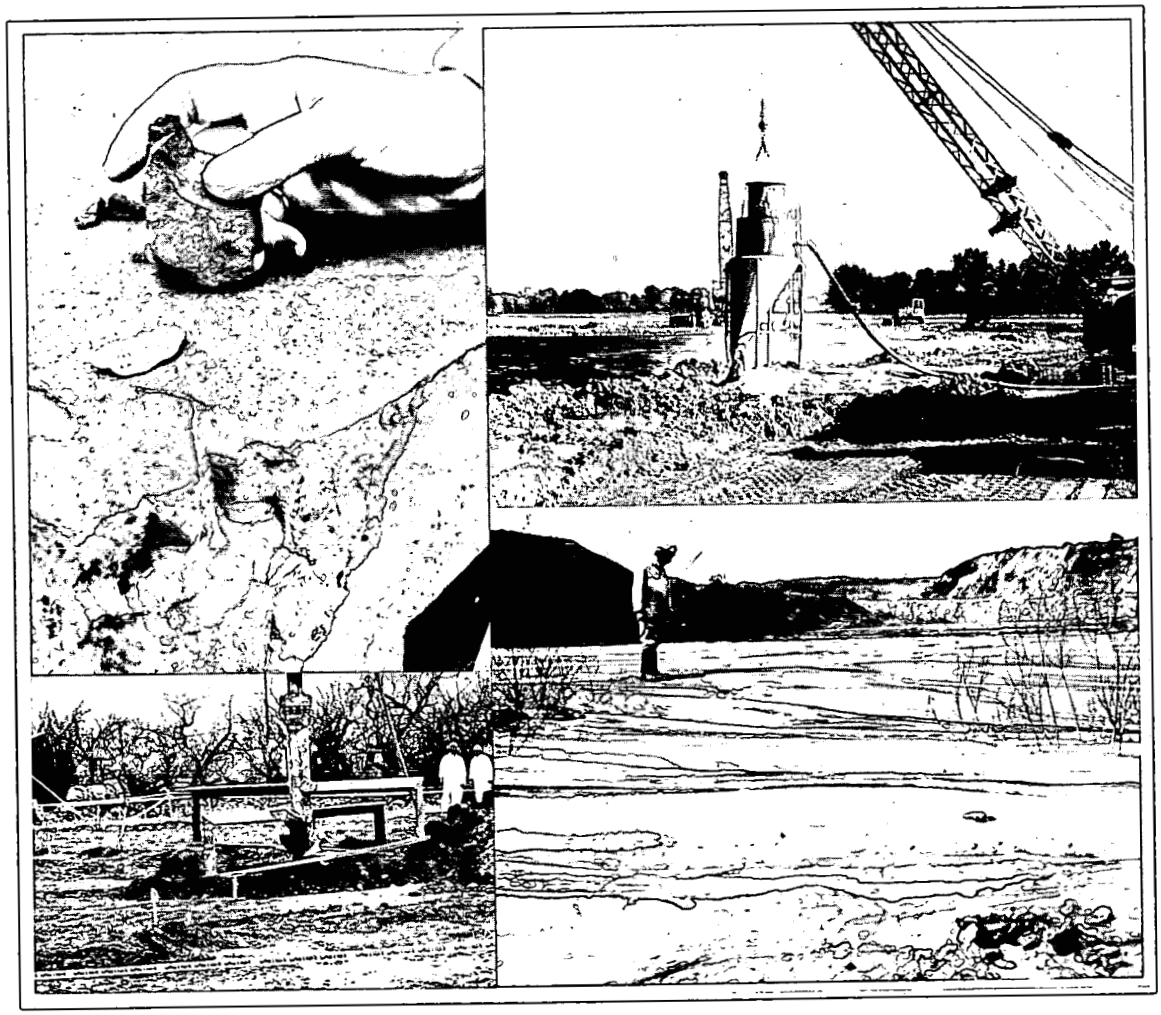
00/00/91

PORT CEMENT ASO
17
REPORT

P-7355

PORTLAND CEMENT ASSOCIATION

Solidification and Stabilization of Wastes Using Portland Cement



Solidification and Stabilization of Wastes Using Portland Cement

This engineering bulletin was authored by Wayne S. Adaska, manager, Water and Waste Facilities Department, Portland Cement Association; Stewart W. Tresouthick and Presbury B. West, director and research chemist, respectively, Materials Research and Consulting Division, Construction Technology Laboratories, Inc.

Portland Cement Association
5420 Old Orchard Rd.
Skokie, IL 60077-1083
(708) 966-6200

© 1991 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.

First edition print history
First printing 1991
Second printing (rev.) 1994
ISBN 0-893120960
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.

Cover page photo credits: upper left; courtesy Stablex Corp., upper right; courtesy Velsicol Chemical Corp., and lower right; courtesy Stablex Corp., lower left courtesy Geo Con, Inc.

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.

EB071.01T

F-7355

CONTENTS

Introduction 1

Terminology 2

Regulatory Basis for Use of S/S Processes 3

Portland Cement 4
- Manufacturing Portland Cement 4
- Cement Kiln Dust 6
- Portland Cement Chemistry 6
  - Compounds Formed in the Kiln 6
  - Cement Hydration 7

Use of Additives in S/S Systems 9

Stabilization of Metals 10
- Role of Calcium Silicate Hydrate in Stabilization of Metals 11
- Individual Metals in Cement-Based S/S Systems 11

Wastes Containing Organic Compounds 12

Waste Components Causing Interference 13

Treatment Characterization 14

References 16

PRINTED WITH SOY INK

Printed on recycled paper with soybean oil based inks.

7355

Solidification and Stabilization of Wastes Using Portland Cement

by Wayne S. Adaska, Stewart W. Tresouthick, and Presbury B. West

Preface

Solidification and stabilization (S/S) technology is currently being used to treat a wide variety of wastes. Although considerable information is available on S/S technology, much of it addresses research work or case studies on specific waste sites. This material usually contains very little on the characteristics of the binding agent used to treat the wastes. In addition, chemical reactions that occur during waste treatment are generally presented for those who are highly technically oriented. As a result, there is still a lack of familiarity with S/S technology among many consulting engineers, material suppliers, government officials, waste site owners, and the general public. This publication is intended to explain what portland cement is and how it can be used to solidify and stabilize various wastes.

The Portland Cement Association contracted Construction Technology Laboratories, Inc., (CTL) to prepare a state-of-the-art report on waste stabilization using portland cement. This engineering bulletin was developed from that report.

The authors wish to acknowledge contributions made by the many individuals who provided valuable assistance in preparing this bulletin. A special thanks to the following for reviewing the CTL draft report: Edwin F. Barth, USEPA; Walter Grube, Jr., USEPA: Jesse R. Conner, Chemical Waste Management; Julia Stegemann, Environment Canada; Alexander J. Fazzini and Robert J. Collins, VFL Technology Corp.; and several cement company representatives too numerous to list.

Solidification and Stabilization of Wastes Using Portland Cement

Introduction

Portland cement is well known for its use in concrete. It is the "glue" that holds the mass together. Concrete's high strength, low permeability, and resistance to most chemicals makes it an ideal material for waste containment. In addition to concrete structures, there are many other applications for portland cement that are worthy of note. Some of these include:

Cement grout is a mixture of portland cement and water. Admixtures are often used to improve certain properties such as flowability, to aid or supply additional cementious reactions or to act as fillers. Depending on the application, it is usually proportioned to produce a flowable consistency without segregation of the constituents. Applications include crack and void fillings in foundations and stabilizing soil and rock in mining and tunneling operations. Grouts have also been used in waste stabilization. Figure 1 shows a method of stabilizing wastes in situ. Grout is fed through the hollow stem of augers, which mix the grout with the waste to depths up to 120 feet.

Cement-bentonite and plastic concrete slurry trench cutoff walls provide an underground barrier to the horizontal flow of water and other fluids. A major application of slurry trenches has been in pollution control, including the containment of hazardous wastes. One of the first "Superfund" projects utilized a cement-bentonite slurry trench to contain the migration of coal tar residue into a nearby stream (Ref. 1) (Fig. 2).

Soil-cement is a thoroughly blended mixture of soil, portland cement, and water, which is compacted and cured to form a hardened material. Soil-cement has been used for over 50 years as a base material under asphalt and concrete pavements. More recently it has been used for environmental applications as slope protection and a liner for wastewater treatment lagoons, sludge drying basins, ash settling ponds, and other waste containment facilities (Fig. 3). The Portland Cement Association has a number of publications available on design, construction, laboratory testing, and field inspection and testing procedures for soil-cement (Ref. 2-5). Much of the information available on soil-cement can be directly applied to the solidification and stabilization of waste contaminated soils.

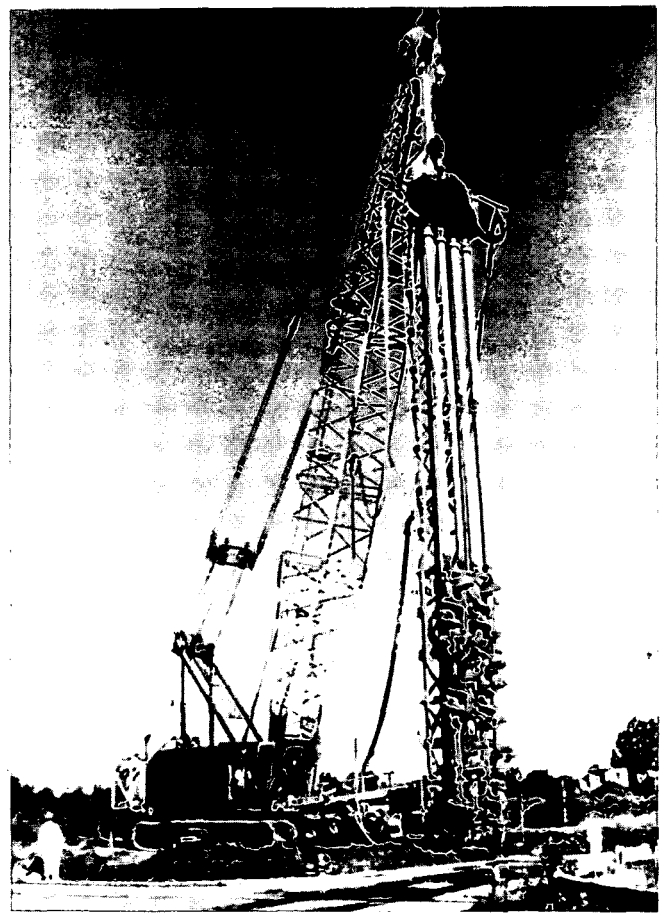


Fig. 1. Stabilization of wastes in situ using a specially developed soil mixing technique. (Courtesy of Geo-Con, Inc.)

Controlled Low Strength Material (CLSM) is a highly flowable material used in lieu of compacted granular material. Primarily used as backfill for utility cuts and filling voids under pavements, buildings, and other struc-

Fig. 2. Cement-bentonite slurry trench being installed for Superfund project in Pennsylvania.

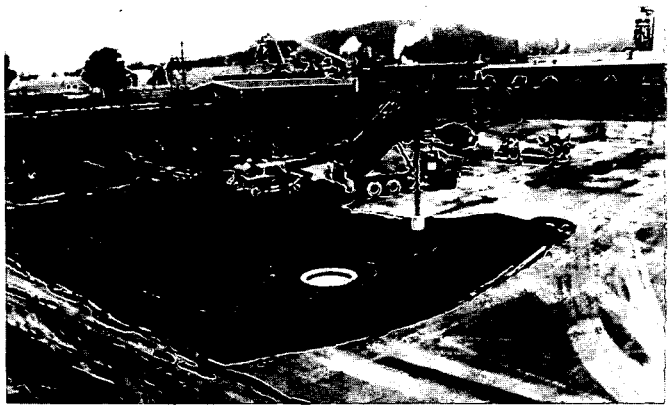


Fig. 3. Soil-cement used to line bottom of industrial wastewater storage lagoon. (Courtesy Solid Seal Systems)

Fig. 4. Backfilling utility cut trench with Controlled Low Strength Material (CLSM).

tures (Fig. 4), CLSM is normally supplied by local concrete ready mixed producers. Depending on the application, compressive strengths can vary from 50 to 1200 psi. CLSM has been found to be an economical alternative to excavating and removing abandoned underground fuel tanks. Rather than remove the tanks, they are left in place and filled with CLSM.

Solidification and stabilization of wastes provide one of the largest uses of portland cement outside the traditional concrete markets. For some 30 years, portland cement has been used to encapsulate nuclear wastes. Many of these wastes are in liquid form and have been taken up in cement-based concrete masses or pumped down bore holes into porous rock as a cement slurry. The wide use of portland cement in S/S systems has come about because it has many advantages, including versatility, over other materials. S/S technology using portland cement provides solidification, stabilization, and, to a limited extent, some sorption of liquids. Portland cement can be used by itself or with additives. Listed below are a few advantages of portland cement for solidification/stabilization.

Advantages of Portland Cement in S/S Systems

- **Manufactured to specifications, which ensures uniformity**
- **Manufactured product, not a waste or byproduct**
- **Binding reagent with more S/S performance data available than any other reagent**
- **Long-term performance record in S/S treatment of nuclear wastes**
- **Minimizes volume increase compared with other reagents**
- **Readily available**
- **Nonproprietary product**
- **Economical**
- **Available in bag or bulk quantities**

Terminology

To better understand the solidification and stabilization process, it is necessary to define certain common terms used in the industry (Ref. 6-8).

Treatment as broadly defined by EPA includes any method of modifying the chemical, biological, and/or physical characteristics or composition of a waste.

Leaching is the process whereby a liquid agent will dissolve hazardous materials within a waste mass and transport these materials through the mass and beyond. The most widely used laboratory leaching test is the TCLP (Toxic Characteristic Leaching Procedure) specified by EPA in several regulations. For many treated and untreated wastes, the results of this test determine whether the EPA considers the material toxic or not.

Solidification is the process of producing from liquid, sludge, or loose solids a more or less monolithic structure having some integrity. Occasionally, solidification may refer to the process that results in a soil-like material rather than a monolithic structure. Solidification does not necessarily reduce leaching of hazardous materials. However, when a waste is solidified, its mass and structure are altered, decreasing migration of solutions within the mass.

Stabilization generally refers to a purposeful chemical reaction that has been carried out to make waste constitu-

F-7355

ents less leachable. This is accomplished by chemically immobilizing hazardous materials or reducing their solubility by a chemical reaction.

Sorption involves adding a solid to soak up liquid present in the waste. Liquid wastes are not allowed in EPA-approved waste storage sites, and regulations now prohibit the use of absorbents alone to treat liquids. The use of reagents that have sorptive properties, including portland cement, must also have other binding capabilities.

Encapsulation refers to the isolation of waste from the environment by a very low permeability matrix, which surrounds the waste. This term can cover a wide variety of meanings, which may be categorized roughly by the scale of the process. Examples of large scale encapsulations include contaminated trash, debris, protective equipment, syringes, etc., which often are embedded in concrete. At an intermediate scale, encapsulation describes processes that coat waste particles with matrices such as plastics, bitumen, or cement. Containing and solidifying treated waste in drums also provide encapsulation. At the microscopic scale and below, an example of encapsulation is metal ions in a cement gel or silicate gel matrix.

Fixation has not been defined by EPA. Its use is rather loose, sometimes referring to solidification, and sometimes referring to stabilization, or both. Most people practicing in the field of hazardous waste treatment, however, use the term more in the context of chemically altering the waste to tie up or immobilize hazardous or toxic components. When used in this context the term "stabilization" is preferred.

Regulatory Basis for Use of S/S Processes

In the early 1970's, legislative action including the Occupational Safety and Health Act of 1970, the amended federal Water Pollution Control Act of 1972, the Safe Drinking Water act of 1974, and the Toxic Substances Control Act of 1976 attempted to address the problem of hazardous waste disposal indirectly by regulating the effects of waste disposal on surrounding air and water quality. Eventually, the basis for the establishment of a national hazardous waste regulatory program was put in place with the passage of the Resource Conservation and Recovery Act (RCRA) of 1976, which regulates current and planned hazardous waste disposal. This bill provided for the development of criteria to determine which wastes were hazardous and to establish standards for siting, design, and operation of disposal facilities.

In 1984, the Hazardous and Solid Waste Amendments (HSWA) to RCRA were passed, which established stricter standards for compliance and more specific criteria. Regulations under both RCRA and HSWA cover in detail matters relating to generation, handling, treatment, and disposal of hazardous wastes.

The goal of Congress in issuing RCRA and HSWA was to restrict the land disposal of untreated hazardous wastes regardless of the liner and leachate collection systems present in a landfill. For example, land disposal of bulk liquid hazardous wastes is prohibited. As a part of the "landban" directive, EPA was required to establish treat-

Table 1. Major Types of Portland Cement

ASTM C 150 Designation	Characteristics and Uses
Type I (Normal)	Type I portland cement is a general-purpose cement suitable for all uses where the special properties of other types are not required. This type is most often used in S/S systems.
Type II (Moderate Sulfate Resistance)	Type II portland cement is used where precaution against moderate sulfate attack is important. Sulfate resistance is obtained by formulating the cement with a low amount of tricalcium aluminate (8% maximum). Type II cement will usually gain strength and generate heat at a slower rate than Type I. In S/S applications this may be a consideration where volatile organics are involved. A lower temperature of the S/S mixture may decrease the release of volatile organic species.
Type III (High Early Strength)	Type III portland cement provides higher early strengths than Type I or II; however, ultimate long-term strengths are about the same. It is chemically and physically similar to Type I cement, except that its particles have been ground finer. Although richer mixes of Type I cement can be used to gain high early strength, Type III may provide it more satisfactorily and more economically. The faster hydration will generally release heat faster and cause a slightly higher temperature rise than Type I.
Type IV (Low Heat of Hydration)	Type IV portland cement is used where the amount of heat generated must be minimized as in the case of massive concrete structures such as dams and large foundations. Availability, however, is extremely limited primarily because similar characteristics can be obtained from a Type IP cement, usually consisting of a blend of fly ash and Type I cement. Because of its lack of availability and suitable replacement, Type IV cement probably has little use in S/S applications.
Type V (High Sulfate Resistance)	Type V portland cement is used when S/S systems contain or are exposed to severe sulfate action - principally where soils, waste, or groundwaters have a high sulfate content. It gains strength more slowly than Type I or Type II cement. It is more resistant to sulfate attack than Type II due to its lower tricalcium aluminate content (5% maximum). Iron content is usually higher in Type V cement, and this may be desirable if species in the waste form insoluble iron complexes.

ment standards, which will render a waste nonhazardous prior to land disposal. The treatment standards may be either specific technologies or standards based on the performance of the Best Demonstrated Available Technology (BDAT) to treat the waste. Because of their technical and economic effectiveness, S/S methods, either alone or in conjunction with other types of treatment such as incineration, are the recommended BDAT for several types of wastes.

In addition to regulating production, treatment, and disposal of hazardous wastes, Congress also addressed the problem of what to do with existing wastes. The Comprehensive Environmental Response Compensation and Liability Act (CERCLA) of 1980, better known as Superfund, and its Superfund Amendments and Reauthorization Act (SARA) of 1986, established a massive remedial program for the identification and cleanup of abandoned or uncontrolled hazardous waste sites created before 1980.

It is estimated that as many as 100,000 sites may eventually require attention. The most severely contaminated sites administered under Superfund are placed on a National Priority List (NPL). Over 1200 sites have been placed on the NPL to date. More than 20 percent of the remedial action decisions on Superfund sites in 1988 included S/S technology for at least part of the treatment process (Ref. 9).

Portland Cement

Portland cement is the most widely used of all S/S binding reagents today. It was originally used for nuclear waste solidification purposes in the 1950's (Ref. 10). Portland cement is not only used alone, but is also used as the major ingredient in a number of proprietary S/S systems. Many formulations combine portland cement with fly ash, lime, soluble silicates, clays, and other materials. For the most part, however, portland cement remains the backbone of S/S technology, whether used alone or in combination with other constituents.

Portland cement is a type of hydraulic cement, a family of materials, which upon addition of water, produces a hardened paste. This paste acts as a strong "glue" to bind together aggregates and other substances to form concrete, grouts, mortars, and stabilized wastes.

Requirements for portland cement are given in ASTM C 150, Standard Specification for Portland Cement (Ref. 11). Within that specification, five major types of portland cement are outlined, each having its own chemical and physical descriptions and limits. Each type of cement is made for a specific purpose and is manufactured to meet the requirements placed on it by the ASTM specification. Table 1 lists the five major types of portland cement with their various characteristics.

All five types of cement may be specified as low alkali, and Types IA, IIA, and IIIA are air-entrained versions of Types I, II, and III. These variations of cement will have virtually no special application in solidification/stabilization systems. The ASTM C 150 specifications are not mutually exclusive, and cements are manufactured to meet requirements of different types of cement. Type I/II and Type II/V are the most common dual designation cements available.

In addition to the familiar portland cement types mentioned above, blended hydraulic cements are also available. These cements are produced by intimately and uniformly blending two or more types of fine materials. The primary blending materials are portland cement, ground granulated blast-furnace slag, fly ash and other pozzolans, hydrated lime, and preblended cement combinations of these materials. Blended hydraulic cements must conform to the requirements of ASTM C 595.

Other hydraulic cements listed as follows are available for specialized purposes, many based on portland cement technology. In general, these cements would have limited use in S/S systems.

Cement Type	Application
Calcium Aluminate	Refractory and acid resistant concretes
Oil-Well	Cementing oil well casing and liners
Masonry	Mortar for structural units and stucco
Expansive	Reduction of shrinkage cracking in concrete
Regulated-Set	Very rapid setting and strength gain
White	Architectural panels; structures; terrazzo

Not all types of cement are available at all locations. Manufacturers may not carry certain types in inventory but may make a desired type upon request. Type I and Type II are normally carried in stock by all plants and are furnished when a type of cement is not specified. If a given type is not available, frequently comparable results can be obtained with an available cement. In such cases, however, it is always wise to perform applicable tests to determine if a substitution is appropriate.

Manufacturing Portland Cement

Portland cement is a manufactured product. It is produced in large, automated plants, which use naturally occurring and secondary raw materials. In 1990 there were 112 portland cement plants in the United States having a total capacity of close to 81.1 million tons of clinker per year. The average capacity of a U.S. plant is about 700,000 tons per year (Ref. 12). A map with the cement plant locations in the United States and Canada is shown in Figure 5.

The four primary chemical elements needed to produce portland cement are: calcium, silicon, aluminum, and iron. Calcium sulfate, usually added as gypsum, is also required in the last stage of production. Almost any raw material, which can supply these chemical elements abun-

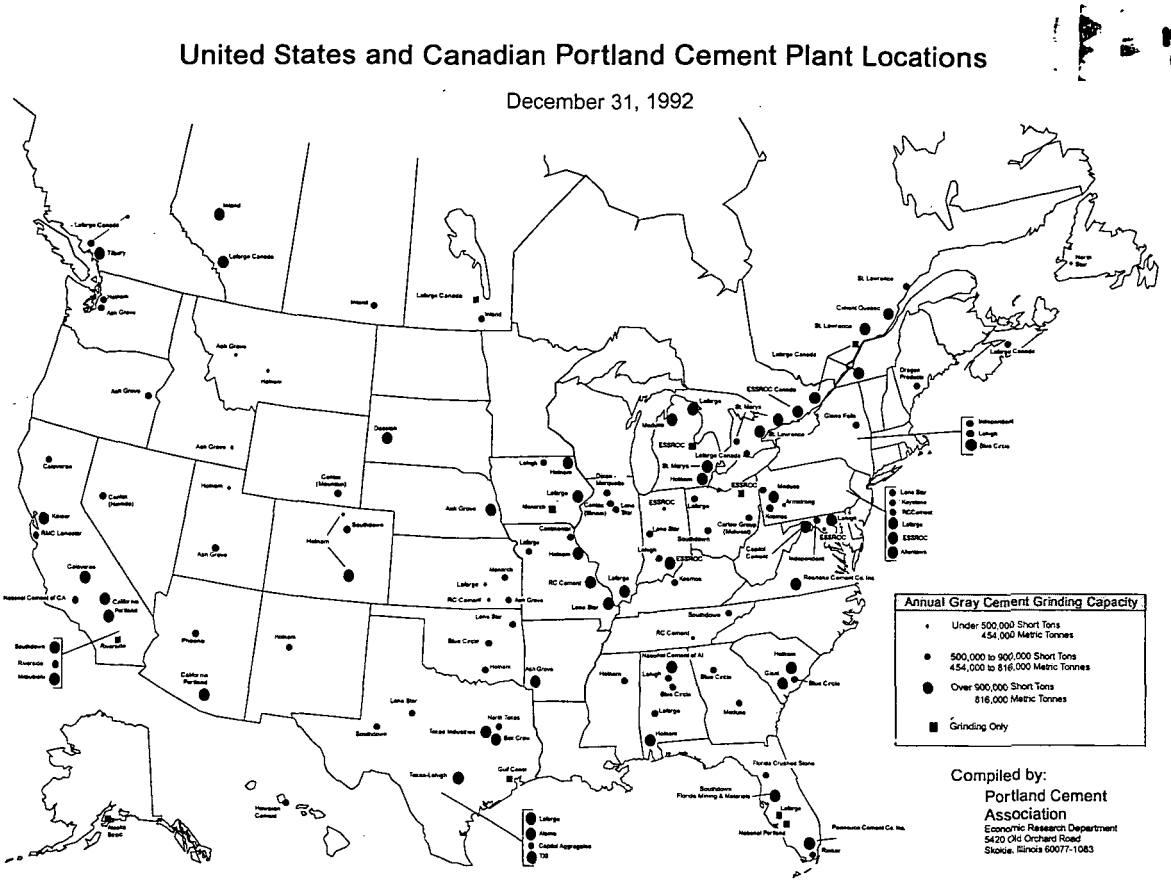


Fig 5. United States and Canadian portland cement plant locations in 1992. (Ref. 12)

dantly and economically without containing deleterious minor constituents, can be used. Because of its abundance, limestone is the principal source of calcium, while shales, clays, silica sand, iron ore, slags, and other materials supply all the other necessary chemical elements (Ref. 13). Table 2 shows typical raw material sources.

Raw materials are quarried usually on the plant site or received by ship, rail, or truck from other sources. Process and quality control begin with the continuous analysis of the raw materials. Based on chemical analyses, the raw materials are accurately proportioned, dried, finely ground, and homogenized. This powdered material is fed to a rotary kiln, which processes the feed at about 2800°F to produce a new series of chemical compounds in the form of walnut-sized nodules called portland cement clinker. Clinker is then finely ground with gypsum to produce portland cement. Gypsum is added during grinding operations to regulate the setting time of the cement. The amount of gypsum added is usually 4 to 7% depending on the chemistry and type of cement. At each step of the way,

Table 2. Sources of Raw Materials Used in Manufacture of Portland Cement (Ref. 13)

Lime, CaO	Iron, Fe_2O_3	Silica, SiO_2	Alumina, Al_2O_3	Gypsum, $CaSO_4 \cdot 2H_2O$	Magnesia, MgO
Alkali waste	Blast-furnace flue dust	Calcium silicate	Aluminum-ore refuse*	Anhydrite	Cement rock
Aragonite*	Clay*	Cement rock	Bauxite	Calcium sulfate	Limestone
Calcite*	Iron ore*	Clay*	Cement rock	Gypsum	Slag
Cement-kiln dust	Mill scale*	Fly ash	Clay*		
Cement rock	Ore washings	Fuller's earth	Copper slag		
Chalk	Pyrite cinders	Limestone	Fly ash*		
Clay	Shale	Loess	Fuller's earth		
Fuller's earth		Marl*	Granodiorite		
Limestone*		Ore washings	Limestone		
Marble		Quartzite	Loess		
Marl*		Rice-hull ash	Ore washings		
Seashells		Sand*	Shale*		
Shale*		Sandstone	Slag		
Slag		Shale*	Staurolite		
		Slag			
		Traprock			

Note: As a generalization, probably 50% of all industrial byproducts have potential as raw materials for the manufacture of portland cement.
*Most common sources

chemical analyses are made to insure uniformity of operation and product. The cement is continuously sampled and then tested according to ASTM specifications and standard testing methods to assure a quality product.

Cement Kiln Dust

Because finely divided powder is fed into the rotary kiln, there is a certain amount of dust produced from this part of the process. This cement kiln dust (CKD) consists of varying amounts of components such as raw feed, calcined limestone, alkali compounds, chloride compounds, and others. CKD varies widely depending on cement kiln operation, type of kiln, type of fuel, and several other factors. Some CKD is almost the same as the raw material fed to the kiln, i.e., principally limestone, clay or shale, and sand. Other CKD contains material exposed to calcining temperatures and, as a result, it contains lime and/or hydrated lime, which is typically present at concentrations from 2 to 5%. Variability is wide, and some CKDs may contain as high as 30% of the two types of lime. Dusts coming from zones of even higher temperatures often contain dicalcium silicate (one of the primary compounds of portland cement), in addition to lime.

Applications for CKD in S/S systems will vary depending on the characteristics of the CKD. For CKDs with a composition close to that of cement raw materials and having a low lime content, the application may be limited to neutralization of acids that would occur because of the reaction between the limestone and the acid. A CKD with some lime can be used by itself, in place of lime, or in addition to cement for waste stabilization. Reactive silica in the CKD or the waste may react with the lime to form a fairly weak binder given a relatively long curing time on the order of days or weeks. A CKD that contains calcium silicate compounds, i.e., dicalcium silicate and lime, is the most desirable for use in S/S processes. This type of CKD will result in a weakly cementitious binder and is the best candidate for use by itself in S/S systems.

All CKDs may and usually do contain calcium sulfate; some contain alkali sulfates and chlorides although for many, these compounds are present at relatively low levels. Variable levels of trace elements are also present in cement kiln dust. These minor components may affect the performance and restrict the applications of some CKDs.

Since the nature of CKD is dependent upon the nature of the raw materials, cement composition, kiln operation, kiln type, type of fuel, and many other factors, CKD may be highly variable between various plants and also within the same plant. Care must be taken to recognize variations occurring in CKD from individual plants and also between plants. For successful utilization of CKD, thorough testing of the material for its suitability to treat specific wastes is required. Despite the necessary precautions, CKD has been and will continue to be used extensively in S/S applications.

Portland Cement Chemistry

Compounds Formed in the Kiln

During the burning operation in the manufacture of portland cement clinker, calcium oxide combines with the acidic components (alumina, silica, and iron oxides) of the raw mix to form four principal compounds that make up about 95% of the clinker by weight. The primary compounds and their abbreviations are as follows:

Tricalcium silicate	**C_3S ***
Dicalcium silicate	**C_2S**
Tricalcium aluminate	**C_3A**
Tetracalcium aluminoferrite	**C_4AF**

The following properties are associated with the four primary cement compounds:

Tricalcium Silicate, C_3S, hydrates and hardens rapidly and is largely responsible for initial set and early strength. In general, the early strength of portland cement concrete is higher with increased percentages of C_3S.

Dicalcium Silicate, C_2S, hydrates and hardens slowly and contributes largely to strength increase at ages beyond one week.

Tricalcium Aluminate, C_3A, liberates a large amount of heat during the first few days of hydration and hardening. It also contributes slightly to early strength development. Gypsum, added during final cement grinding, slows down the hydration rate of C_3A. Without gypsum, a cement with C_3A present would set rapidly. Cements with low percentages of C_3A are especially resistant to sulfates contained in wastes or soils.

Tetracalcium aluminoferrite, C_4AF, reduces the clinkering temperature, thereby assisting in the manufacture of cement. It hydrates rather rapidly but contributes very little to strength.

C_3S and C_2S in clinker and cement are also referred to as alite and belite, respectively. These and other compounds may be observed and analyzed through the use of microscopical techniques (Figures 6 and 7) or X-ray diffraction techniques. The approximate percentage of each compound can be calculated from a chemical analysis of the clinker or cement. Table 3 shows typical compound composition and fineness for each of the principal types of portland cement.

* Within this publication, conventional cement chemistry notation is used, i.e. C = CaO, S = SiO_2, A = AL_2O_3, F = Fe_2O_3, H = H_2O.

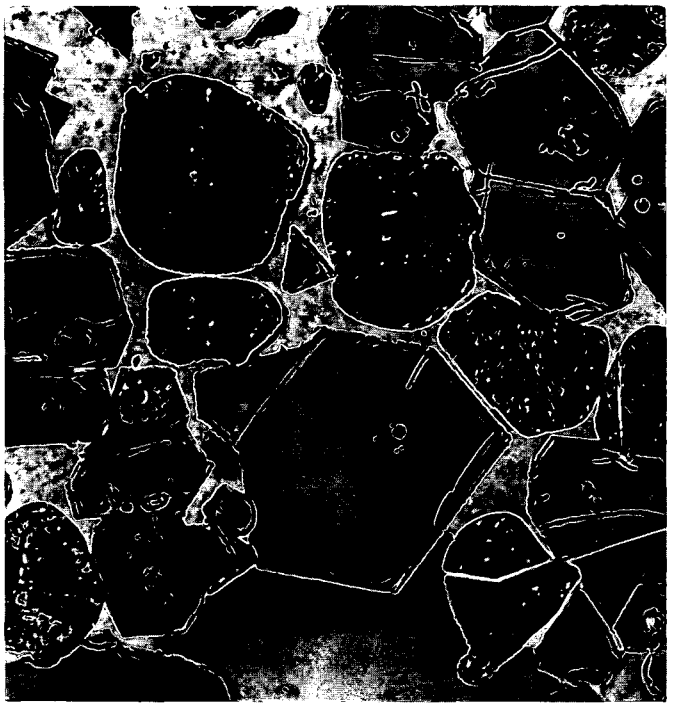


Fig. 6. Polished thin-section examination shows alite C_3S as light, angular gray crystals. The darker, rounded crystals are belite (C_2S). Magnification 400X.

Fig. 7. Scanning electron microscope micrograph of alite (C_3S) crystals. Magnification 3000X.

Cement Hydration

When cement and water are mixed together, a series of chemical reactions begins that results in stiffening, hardening, evolution of heat, and finally development of long-term strength. The overall process is called hydration since water-containing compounds are formed. Without water, cement hydration would not occur. The hydrates that form from the four principal compounds determine most of the characteristics of the hardened cement paste. Understanding how portland cement is used in S/S systems requires some understanding of the cement hydration process. References 14 and 15 provide a basic understanding of the cement hydration process.

The aluminates, C_3A and C_4AF, are the first to react; immediately forming calcium aluminate hydrates, which provide some structure to the system making it stiff. As sulfate from the gypsum enters into solution, it reacts with the aluminates to coat them with a calcium sulfoaluminate hydrate called ettringite. This coating helps slow down the combination of water with the highly reactive aluminates so that the paste can remain plastic and moveable. Within the first few hours, the water reacts with tricalcium silicate, C_3S, to start to produce calcium hydroxide and cement gel. As time goes on, the ettringite reacts with C_3A and water to form a different calcium sulfoaluminate hydrate, and the aluminates begin to hydrate again. C_3A reacts with water and calcium hydroxide to form tetracalcium aluminate hydrate. After several days very little ettringite remains.

During the first few days, dicalcium silicate, C_2S, starts to hydrate. The calcium silicates, C_3S and C_2S, which constitute about 75% of the weight of cement, both hydrate to form calcium hydroxide and cement gel. Hydrated cement contains about 25% calcium hydroxide and 50% cement gel by weight. The strength and other

Table 3. Chemical and Compound Composition and Fineness of Some Typical Cements (Ref. 13)

Type of portland cement	Chemical composition, %						Loss on ignition, %	Insoluble residue, %	Potential compound composition, %*				Blaine fineness, m^2/kg
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3			C_3S	C_2S	C_3A	C_4AF	
Type I	20.9	5.2	2.3	64.4	2.8	2.9	1.0	0.2	55	19	10	7	370
Type II	21.7	4.7	3.6	63.6	2.9	2.4	0.8	0.4	51	24	6	11	370
Type III	21.3	5.1	2.3	64.9	3.0	3.1	0.8	0.2	56	19	10	7	540
Type IV	24.3	4.3	4.1	62.3	1.8	1.9	0.9	0.2	28	49	4	12	380
Type V	25.0	3.4	2.8	64.4	1.9	1.6	0.9	0.2	38	43	4	9	380

*"Potential compound composition" refers to the maximum compound composition allowable by ASTM C 150 calculations using The chemical composition of the cement. The actual compound composition may be less due to incomplete or altered chemical reactions.

properties of hydrated cement are due primarily to cement gel. The cement gel acts as the principal binder and hardener in the portland cement/water system. The primary hydration reactions (compound transformations) are shown in Table 4.

Cement gel, one of the major products of cement hydration, is also referred to as calcium silicate hydrate (CSH) or tobermorite gel. This gel is a nearly amorphous (uncrystallized) material with lime to silica to water ratios close to the 3/2/3 as shown in Table 4. In fact, these ratios are approximate and will vary depending on the amount of water and the particular cement used to make the cementitious solid. Because of the variability of the composition, the notation for calcium silicate hydrate is usually not written as $C_3S_2H_3$ to emphasize that the ratios are not exact.

The chemical reactions between the cement and the water occur at the boundary of the cement particles forming, initially, some ettringite and principally calcium hydroxide and cement gel. Figure 8 shows the progression of the portland cement hydration process. Initially, the cement particles are dispersed in water (Fig. 8a). As the coating or gel on the cement particles is formed (Fig. 8b), the movement of water toward the unhydrated core of the cement grains is impeded causing the hydration of the cement to slow down. After about two hours, however, the hydration product rims from the dispersed particles fill the space between particles and intermesh with rims of adjacent particles (Fig. 8c). A bond begins to develop between the filaments of the gel forming the basis for a rigid gel structure. The reaction continues, resulting in a solidified, hardened mass after several hours (Fig. 8d) (Ref. 15). Once the matrix has hardened and is no longer plastic, destructive expansive reactions can occur. One of these reactions occurs if the cementitious solid is exposed to materials containing sulfate. The calcium aluminate hydrate reacts with sulfate to form secondary ettringite, which can result in severe damage to the solid.

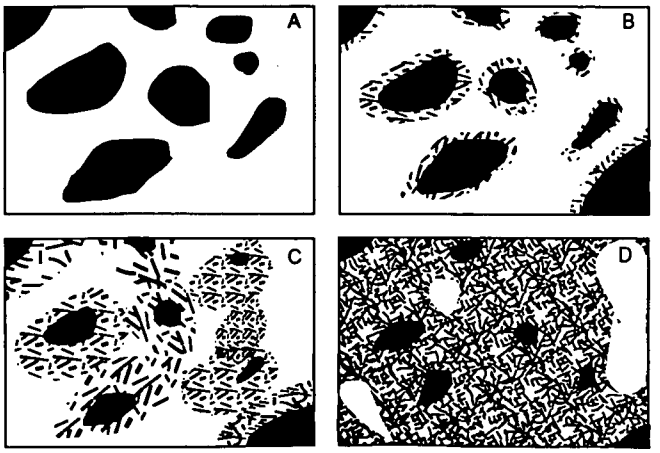


Fig. 8. The phases of cement setting. a) initially cement particles dispersed in water; b) less than 5 minutes later; c) two hours later; d) after several hours. (Ref. 15)

The hydration process of portland cement can be thought of as the filling of the water space with cement gel. It has been estimated that if 1 cu cm (absolute volume) of cement undergoes complete reaction, a cement gel having a volume (solid particles plus gel pores) of about 2.1 cu cm is produced (Ref. 16). Figure 9 shows the development of the paste components at various stages of hydration. The amount of water space and the distance between particles within the cement gel will increase as the water to cement (w/c) ratio increases, and the hydration rims may not intermesh leaving water filled pores through the solid. The consequence of a higher w/c ratio is a more porous and permeable solid that is significantly weaker than one with a lower w/c ratio.

The hydration reactions will continue as long as sufficient (95% relative humidity) moisture is present. Curing is an important element for increasing compressive strength. If our benchmark is concrete moist cured for 28 days, then concrete moist cured 7, 3, and 0 days will attain a compressive strength at 28 days of about 90%, 80%, and 55% respectively of the benchmark strength (Ref. 13).

Table 4. Portland Cement Compound Transformations (Ref. 13)

$2(3CaO{\bullet}SiO_2)$ (Tricalcium silicate)	+ $6H_2O$ (Water)		= $3CaO{\bullet}2SiO_2{\bullet}3H_2O$ (Tobermorite gel)	+ $3Ca(OH)_2$ (Calcium hydroxide)
$2(2CaO{\bullet}SiO_2)$ (Dicalcium silicate)	+ $4H_2O$ (Water)		= $3CaO{\bullet}2SiO_2{\bullet}3H_2O$ (Tobermorite gel)	+ $Ca(OH)_2$ (Calcium hydroxide)
$3CaO{\bullet}Al_2O_3$ (Tricalcium aluminate)	+ $12H_2O$ (Water)	+ $Ca(OH)_2$ (Calcium hydroxide)	= $3CaO{\bullet}Al_2O_3{\bullet}Ca(OH)_2{\bullet}12H_2O$ (Tetracalcium aluminate hydrate)	
$4CaO{\bullet}Al_2O_3{\bullet}Fe_2O_3$ (Tetracalcium aluminoferrite)	+ $10H_2O$ (Water)	+ $2Ca(OH)_2$ (Calcium hydroxide)	= $6CaO{\bullet}Al_2O_3{\bullet}Fe_2O_3{\bullet}12H_2O$ (Calcium aluminoferrite hydrate)	
$3CaO{\bullet}Al_2O_3$ (Tricalcium aluminate)	+ $10H_2O$ (Water)	+ $CaSO_4{\bullet}2H_2O$ (Gypsum)	= $3CaO{\bullet}Al_2O_3{\bullet}CaSO_4{\bullet}12H_2O$ (Calcium monosulfoaluminate hydrate)*	

Note: Table 5 illustrates only primary transformations and not the several minor transformations.
*Ettringite may also develop.

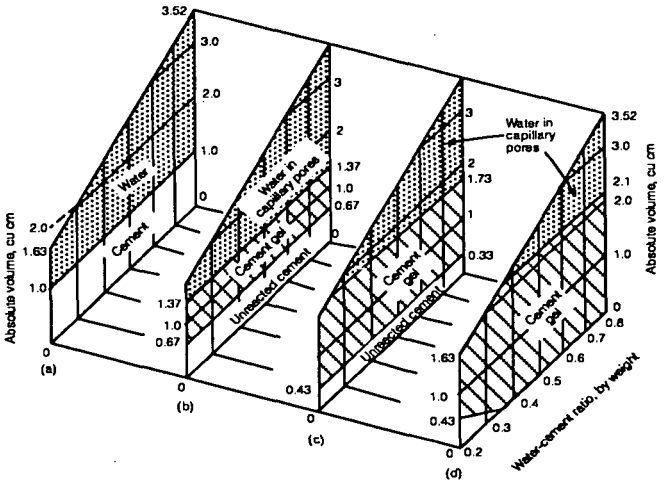


Fig. 9. Space relationships for paste components at various stages of hydration. a) Fresh paste; b) reaction one-third complete; c) reaction two-thirds complete; d) reaction completed. (Ref. 16)

One of the most critical factors for the hydration of cement is the dispersion of the fine grains of cement in the water without significant agglomeration. In concrete technology, historically, a significant excess of water over that required to form the hydrates of cement compounds was employed primarily to obtain good workability. This excess water also helped to disperse the cement particles. Over the last two decades many sophisticated dispersing additives have been introduced and are frequently used in concrete to minimize excess water and maintain a low water to cement (w/c) ratio. The lowest w/c ratio for complete reaction is approximately 0.32; however, most general purpose concrete is made at w/c ratios between 0.4 and 0.6.

It is the presence of calcium hydroxide and alkalies in solution that gives the plastic cement paste its high pH, an important aspect of cement-based S/S technology. Minor constituents, such as heavy metal elements, can greatly affect hydration reactions, in some cases halting the whole process. Some elements find their way into the cement gel and are sequestered there in more or less stable condition. Some new evidence suggests that the actual location of these elements may be more complex than originally envisioned, but nevertheless they can be tied up in some manner in the hydrates (Ref. 10). This ability of the cement gel to sequester certain chemical elements and the contribution of a high pH solution to the system form the basis of stabilization technology using portland cement.

Use of Additives in S/S Systems

Although portland cement has proven to be an effective stabilizing agent by itself, the use of additives often enhances and optimizes portland cement S/S mixtures. Materials such as silica fume, fly ash, clay, and zeolites that adsorb water may also adsorb metals and organics (Ref. 10). The adsorption of water by these substances will reduce excess water and improve (decrease) the net water to cement (w/c) ratio of the cement hydration. In addition, many of the additives are pozzolans, which by themselves possess little or no cementitious value but will, in finely divided form and in the presence of water, chemically react with the calcium hydroxide released by the hydration of portland cement to form additional cementitious compounds. The pozzolanic reactions occur, however, at a much slower rate than cement alone.

Silica fume is a byproduct of silicon and ferrosilicon production that contains 90% or more of non-crystalline silica. Fly ash from coal-fired power plants is a variable byproduct, which usually contains silicate glass containing silica, alumina, iron, calcium, and numerous minor oxides. Clay and zeolites both are silica and alumina materials with the former having a 2-dimensional layered structure and the latter a rigid 3-dimensional structure. All these materials may be considered pozzolans. These materials when mixed with water and cement will be dispersed and intermixed with the grains of cement. In Figure 9, the water space that the gel fills is really water saturated with calcium hydroxide. This saturated solution then can react with the dispersed pozzolanic particles forming rims of reaction product similar to the cement gel. This reaction proceeds more slowly than cement hydration, but it does decrease porosity and permeability while increasing the strength of the solid.

Another common additive used in S/S is soluble silicate usually in the form of concentrated sodium silicate also known as water glass. This is a complex material containing both colloidal and polymeric silicates and does not have a specific formula. It has the ability to gel very rapidly when reacted with the calcium hydroxide of the hydrating cement (Ref. 17). This is very useful when wastes contain substantial amounts of water that are not economically removed. If cement alone or with other admixtures is combined with significant excess water, the solids would settle out before setting. In addition, if wastes contain substances that interfere with cement dispersion or setting, the cement solids may also settle out possibly leaving a separate contaminated watery layer. The rapid gelation of mixtures with sodium silicate stabilizes the dispersion and prevents settling. This allows time for the cement gel to form and set giving the whole mass increased strength. The rapid formation of the gel from soluble silicate by reactions or micro-encapsulation also reduces the mobility of species that may interfere with cement hydration (Ref. 10).

In a mixture of cement and soluble silicate the strength arises not only from the cement and the formation of silicate gel but also from the calcium hydroxide of the cement reacting with the silicate to form calcium silicate hydrate. The solid matrix produced using sodium silicate, however, results in a more porous and weaker material than with cement alone. Low metal ion leachability is often achieved because precipitates block pores and other features that reduce metal diffusion (Ref. 10, 17). Column leaching data is shown in Figure 10 for a plating waste

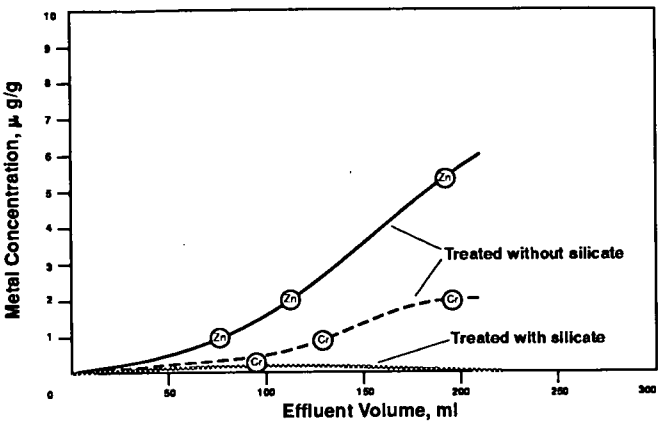


Fig. 10. Leaching of portland cement/flyash treated sludge with citric acid. (Ref. 17)

containing zinc and chromium for a fly ash and cement binder with and without sodium silicate. When sodium silicate is included in the binder, the leaching for both metals is substantially less than for fly ash and cement without the silicate. These systems must be carefully balanced, however, since too much soluble silicate will remove so much calcium ion from the system that cement hydration may virtually stop. Another added benefit to this combination is the alkali (usually as sodium ion) that is present. Moderate amounts of alkali are known accelerators of cement hydration.

The other material frequently used in solidification and stabilization with portland cement is lime or hydrated lime. The lime does not react with cement but can accelerate cement hydration when the waste inhibits hydration. The lime provides calcium hydroxide and supplies a source when the cement hydration is inhibited and not producing it. The other reason for using lime is to neutralize acid wastes and prevent destruction of the cement structure.

Stabilization of Metals

Portland cement and portland cement combinations have been very successful in solidification and stabilization of environmentally regulated metals. When wastes were first regulated, many wastes were dilute solutions that frequently were acidic. These wastes were well suited to treatment with cement systems. Now that environmental regulations promote waste reduction and ban liquid disposal, most wastes are sludges, solids, or pretreated initially to reduce waste volume. This requires a more sophisticated approach to waste treatment. The key to better applications is improved understanding of the wastes and especially the metal species.

Metals in solution are easier to characterize than those in sludges and solids and easier to convert to insoluble species. Generally, when metals are converted to carbonates, hydroxides, silicates, or sulfides, they form low solubility precipitates (Ref. 18). Leachability is further reduced by solidification of the mass. The examples below convert soluble lead chloride to less soluble hydroxide and sulfide compounds:

$$PbCl_2 + 2NaOH \longrightarrow Pb(OH)_2 + 2NaCl \quad \text{and}$$

$$PbCl_2 + Na_2S \longrightarrow PbS + 2NaCl, \text{ where S = sulfide}$$

Two features of metal chemistry may make this difficult, complexation and variable oxidation states. Complexation of metal ions is the formation of species that are very stable in solution under a variety of conditions. Frequently, electroplating wastes contain metal complexes. These complexes usually must be destroyed before successful S/S treatment can be achieved, but these methods are specific for each metal. Variable oxidation is exhibited by chromium, which commonly is found in the 3^+ and 6^+ states. Chromium 3^+ forms an insoluble hydroxide on addition of basic S/S reagents such as cement, but chromium 6^+ does not. Pretreatment by reduction from the 6^+ to the 3^+ state is recommended before S/S treatment of chromium wastes (Ref. 19). Ferrous sulfate is commonly used to convert chromium 6^+ to chromium 3^+, as shown in this example:

$$6FeSO_4 + 2Cr(SO_4)_3 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3$$

Once the chromium 6^+ has been reduced to the chromium 3^+ state, cement can be added to form a less soluble hydroxide compound. Steps should also be taken to assure that no oxidants remain in the solidified system, which would oxidize the chromium back to 6^+ and, therefore, to a more soluble and leachable form.

In general, successful solidification and stabilization of metals will involve the following steps:

1. Control of excess acidity by neutralization.
2. Destruction of metal complexes if necessary.
3. Control of oxidation state as needed.
4. Conversion to insoluble species (stabilization).
5. Formation of a solid with solidification reagents.

Portland cement systems will address steps 1, 4, and 5. Slight acidity can be neutralized by the large calcium reserve of cement. Calcium hydroxide from cement hydration and the silicate hydrates can stabilize metals as hydroxides and silicates and solidify the waste. Properly formulated combinations of cement and additives will stabilize contaminants and solidify the waste, making material at least acceptable at secure landfills.

Sludges and soils often contain the low solubility forms of metals, but in addition may contain other forms and materials that interfere with the S/S process. Contaminated soils are often found at Superfund sites. Wastes such as these must be carefully screened and pretested to optimize the formulation with S/S reagents. A great deal of work

has been done using portland cement with soil to produce soil-cement for pavement bases, slope protection, and low permeable liners (Ref. 2-5). This information can be very useful in developing mix designs, in construction, and in establishing quality control procedures for solidifying contaminated soils.

Role of Calcium Silicate Hydrate in Stabilization of Metals

Calcium silicate hydrate (CSH) is formed from the calcium silicates that make up 70 to 80% of portland cement. The interaction of cadmium, chromium, lead, mercury, and zinc with CSH was investigated, and it was concluded that immobilization probably occurred by one of the following mechanisms (Ref. 20):

- Immobilization by addition reactions where M is the metallic ion can be represented as:

CSH	+	M	—>	MCSH
Calcium silicate hydrate		Metallic ion		Metallic calcium silicate hydrate

- Immobilization may also occur by substitution reaction which may be written:

CSH	+	M	—>	MCSH	+	Ca^{++}
Calcium silicate hydrate		Metallic ion		Metallic calcium silicate hydrate		Calcium ions

- Evidence from X-ray diffraction also indicated new compounds may form, which may immobilize metals.
- Due to the complexity of the system, it is also suggested that multiple mechanisms at any one time may be operating to immobilize the metal ions. For all the metal ions studied, essentially all the metal species were removed from solution and were immobilized in the solid at the level studied.

Individual Metals in Cement-Based S/S Systems

RCRA metals and other regulated metals can often be stabilized by properly formulated solidification using portland cement, cement kiln dust, or combinations of other materials with either one. In any case, small scale experimental evaluation is practically mandatory for successful application. Frequently, satisfactory solidification/stabilization can be achieved without pretreatment even when the metal concentration in the raw waste leachate is several times the regulatory limit. In some cases, pretreatment may be necessary due to oxidation state, complexes, or other interferences such as those discussed previously.

For those cases where pretreatment is needed, the solutions are usually different for different wastes or metal species. In this section some suggestions and examples are discussed for individual metals. These ideas are only a sampling of possible approaches and pretreatments for wastes that are difficult to stabilize usually due to high metal concentrations.

Among the RCRA metals, barium is one of the easiest to handle because relatively insoluble barium sulfate is easily formed, and it is stable in an alkaline environment. Cadmium is also comparatively easy to handle as long as it is not complexed. In portland cement-based S/S systems, cadmium forms hydroxides and silicates that remain relatively stable as long as the pH remains high. The system pH will remain high as long as sufficient cement is used in the formulation.

Selenium and silver apparently are stabilized well in portland cement-based systems; however, there is little information at high concentrations. Silver is valuable enough so almost all waste streams have been pretreated to recover the metal leaving low concentrations in the remaining waste. Addition of chloride to form silver chloride in the S/S binder is usually sufficient to reduce silver leaching to levels below regulatory concern. Selenium is rarely found in significant concentrations in wastes. Selenium behaves like sulfur and forms many very slightly soluble compounds with heavy metals, which may be the reason its level is so low in leachates.

Chromium has been discussed previously where it was pointed out that in the 3^+ oxidation state a very slightly soluble hydroxide is formed, which is stabilized well in cement-based systems. Some evidence suggests (Ref. 20) a stable chromium silicate complex may form. Electroplating wastes often contain chromium complexes, which must be destroyed first (Ref. 18). Chromium leaching from S/S wastes should not be a problem as long as nothing in the solidified waste destabilizes the 3^+ state of the chromium.

Copper, nickel, and zinc are not RCRA metals but are regulated either by other federal regulations or by certain states. These metals all form sulfides that have very low solubility and are stable at high pH such as that found in portland cement solidified wastes. In some instances, the formation of the sulfides may be impractical or too costly. These metals all have low solubility hydroxides, but the minimum occurs in a fairly narrow range of pH.

Lead along with copper, nickel, and zinc has amphoteric hydroxides, which means that the hydroxides are least soluble at a specific pH. These hydroxides are more soluble at both lower pH (more acidic) conditions and at higher pH (more basic) conditions. In order to stabilize these hydroxides, the formulation of the cement-based binder must be carefully tailored to maintain a stable pH at the point of minimum solubility. Solubility of metal species in cement-based solidified waste is not the same as hydroxides only. In solidification systems, the range of pH for low solubility is greater than for the hydroxides alone (Ref. 21) as seen in Figure 11 for lead. Cadmium, copper, nickel, and zinc behave in a similar manner as shown by solubility curves for these metal hydroxides in

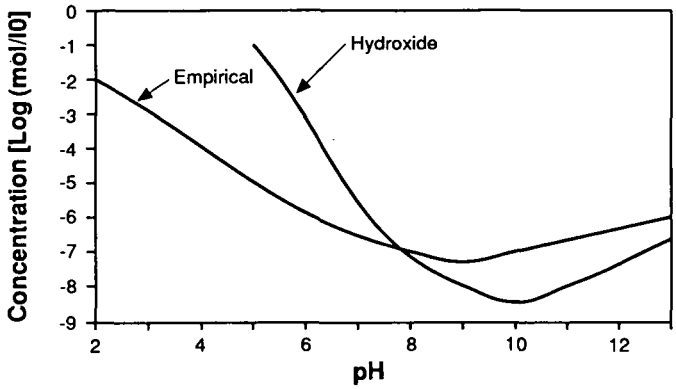


Fig. 11. Solubility of lead vs. pH in a cement/flyash S/S system. (Ref. 21)

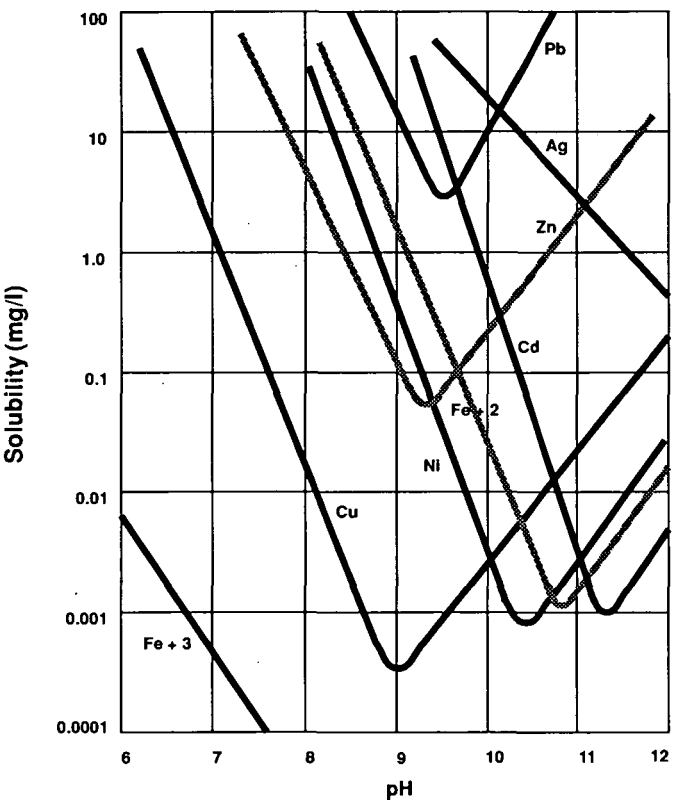


Fig. 12. Solubilities of metal hydroxides as a function of pH. (Ref. 22)

Figure 12. Frequently, the pH of cement solids is higher than the optimum value, and additives must be used to modify the alkalinity and reduce the leachability of these metals. Formulations combining fly ash and portland cement are known to reduce alkalinity and associated deleterious reactions in concrete.

Lead is a frequent contaminant, and often is present in wastes at significant concentrations. Organo-lead compounds, as are found in gasoline, must be converted to inorganic lead compounds before they can be stabilized. Lead also forms carbonates, phosphates, and sulfides with low solubility, and wastes with these compounds can be successfully stabilized in cement-based solidified wastes.

Most mercury compounds have low solubilities so when low levels of mercury are present in wastes, they usually can be successfully stabilized. However, when a significant amount of mercury is present, acceptable stabilization may be difficult due to the extremely low allowable mercury levels set by environmental regulations. An exception would be mercury sulfide, which has a very low solubility and can be effectively stabilized at relatively high concentrations.

Arsenic is classified as a metalloid and not a metal because its behavior is different from most metals. Success has been achieved with some arsenic wastes by stabilizing either the oxide anions or the sulfides. Carefully formulated portland cement-based solidification and stabilization have resulted in treated wastes below RCRA levels. Some arsenic compounds such as arsenic trisulfide and organic arsenic compounds are difficult to stabilize, and pretreatment or special methods are needed for successful stabilization.

Wastes Containing Organic Compounds

For hazardous organic wastes and aqueous wastes with greater than 1% hazardous organics, the landban regulations effectively prohibit treatment by S/S techniques (Ref. 10). For nonhazardous oily wastes, techniques have been developed to solidify these materials when the organic content is below approximately 25% (Ref. 23, 24). There is no concern about leaching standards since these are nonhazardous, and once solidified, these wastes meet the criteria of no free liquid. Some organic wastes with solid organics such as plastics, tars, and resins also are amenable to treatment with portland cement. Many organics are water insoluble and prefer to remain associated with the solid phase. A low permeability matrix may physically retard leaching of some organics, and this may be sufficient for many wastes with low levels of organic compounds. At low levels many organic compounds can be stabilized, but some compounds interfere with the processes of solidification and stabilization.

Interference with portland cement can occur in several ways. Oils and grease can simply coat the cement preventing the reaction between water and cement. Some organics, which are similar to sugars, can be adsorbed on cement surfaces and severely retard cement hydration. Other organics are flocculating agents and will destroy the dispersion of cement grains, which is so vital to successful growth of the hydrated cement structure.

Some approaches can be taken to stabilize organics, but they must be carefully selected for each waste. Sorption by selective reagents may remove interfering compounds. Both activated carbon and organically modified clays (Ref. 25,26) are examples of sorption reagents that have been used with cement stabilization. Organic compounds can also react in several ways under ambient conditions and convert to less hazardous materials. At high pH, several types of organics react with water, and this can easily be accomplished in cement-based systems that already have a high pH. Dechlorination of organochlorine compounds may occur through hydrolysis in the following manner:

$$2\ RCl_5OH + Ca(OH)_2 \longrightarrow 2\ R'HCl_4O_2H + CaCl_2$$

where R and R′ are part of organic molecules

Some calcium salts are less soluble than the organic compounds so salt formation may reduce solubility. For instance, oxalic acid will form the salt, calcium oxalate, which is less soluble. Introduction of oxidants into the S/S system may also be effective in converting organics to new compounds. Some alcohols can be oxidized by hydrogen peroxide to form an organic acid:

$$RCH_2OH + 2H_2O_2 \longrightarrow RCOOH + 3H_2O$$

The acid may then form a calcium salt. In all cases of reactions, these must be carefully selected for undesirable reactions could occur with other components of the waste. The possibility exists that a metal could become more soluble or that a hazardous organic compound could be formed by a side reaction.

Many organics are destroyed by incineration. However, being part of a waste stream, there inevitably will be some ash left as a residue from many wastes. Portland cement-based stabilization and solidification may frequently be the best means of treating these waste residues. These ashes may often be easier to treat by S/S than some of the other wastes previously discussed.

Waste Components Causing Interference

As previously mentioned, waste compounds can interface with cement hydration, structure, or solidification. Individual studies usually examine the effect of one component at a time, and this is the basis of most of the information. Real wastes may have many components that potentially interfere, and predicting those interactions is practically impossible. This overview of some interfering components is, therefore, necessarily a simplified view of a very complex field.

Interferences are often classified by the nature of the effect on the system and include effects well-known in cement and concrete technology such as retarders, accelerators, and dispersants. Other classes are wetting agents, chelating agents, flocculants, and matrix disrupters. Some materials have multiple effects, or the nature of the interference changes with the concentration. A few of the common interactions have been tabulated and are shown in Table 5.

Although most inorganic wastes may be effectively stabilized with cement, some heavy metals such as zinc, tin, and lead are retarders of cement hydration. Additionally, borate compounds can be severe retarders. A few inorganic components such as iron compounds and calcium chloride act as accelerators. Alkalies in low concentrations accelerate hydration, and sulfate compounds can degrade cement solids as explained earlier. In many cases the interference from inorganics is not as troublesome as that from organic components.

Many organic compounds with hydroxyl groups act as retarders and sometimes as dispersants. Sugar and acids such as adipic, citric, and gluconic all retard cement hydration very effectively. Some chlorinated hydrocarbons will decrease the strength of solidified waste. Alcohols and amides, which behave as wetting agents, can help emulsify small amounts of oil and grease that can coat cement particles, and this aids the stabilization/solidification.

A thorough study of both inorganic and organic components and the S/S interference mechanisms has been issued as an EPA project report (Ref. 28). Effects of a variety of interfering components on the unconfined compressive strength (UCS) of cement and cement/ fly ash systems are shown graphically in Figures 13 and 14. It is clear that

Table 5. Effects of Selected Chemicals on Cement-Based Pozzolanic Processes (Ref. 27)

Chemical or Material	Flocculant	Dispersant	Wetting Agent	Chelating Agent	Matrix Disruptor	Retarder	Accelerator	Destroys Reaction
Carboxylic acids		X				X		•
Carbonyls		X				X		•
Amides			X				Allows for better mixing	
Amines	X						X	•
Alcohols			X			X		•
Sulfonates		X				X		
Glucose/sugar				X		X		•
Chlorinated hydrocarbons					X	X		X
Oil								>25-30%§
Calcium chloride					>4%‡		<2%‡	>4%§
Iron†	X				X		X	
Tin					X	X		
Lead					X	X		
Borates					X	X		•
Magnesium	X				X	X		
Gypsum (hydrate)						X		
Gypsum (anhydrate)							X	•
Silica	X					X‡		

• At high concentrations
‡ Only in certain forms
† Ratio of Fe^{+2} to Fe^{+3} important
§ By weight

many factors must be considered to, not only avoid interferences, but also to select the proper ratios of cement, additive, and waste to achieve successful treatment. Conner (Ref. 10) makes one important point, "that there is no one process, product, or system that is best for all waste treatment and disposal scenarios."

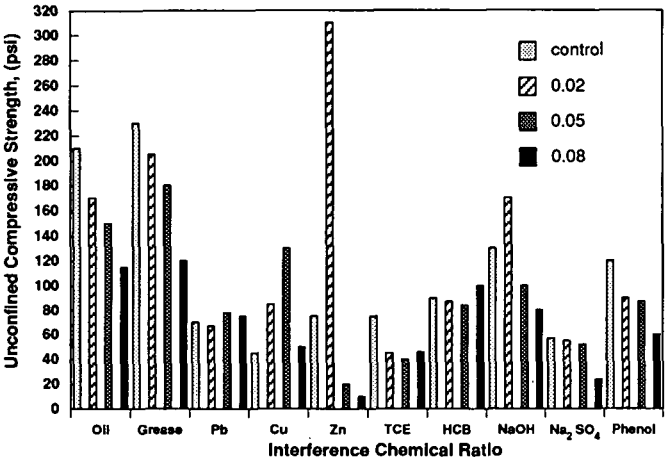


Fig. 13 Effect of interference concentration on 28-day cured UCS for Type I portland cement binder. (Ref. 29)

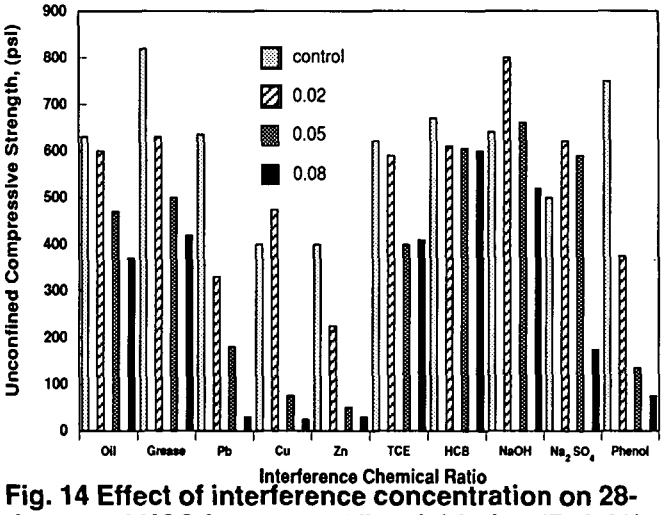


Fig. 14 Effect of interference concentration on 28-day cured UCS for cement/ flyash binder. (Ref. 29)

Treatment Characterization

Waste characterization is required, not only to classify the hazardous nature of the waste, but also to determine the parameters for planning pilot-scale studies. Hazard classification involves a combination of regulatory interpretation and testing as specified by the EPA. Physical testing should include determination of liquid content whether moisture content, organic content, or a combination of the two. Other tests recommended are bulk density, hydraulic conductivity, and some measure of the strength. Compressive strength can be measured on S/S materials through use of cylinders or cores. Information useful for the wetting and mixing behavior may be obtained from measurements of grain size distribution and Atterberg limits. These tests, as well as their usefulness, are summarized well by Cullinane and Jones (Ref. 30).

Chemical characteristics should also be evaluated to determine whether any severe interferences may occur, and this will involve additional testing for components besides the hazardous ones. The specific tests required are largely dependent on the nature of the waste and should be selected with the aid of a materials specialist or a chemist. Pilot-scale testing can be done in a very simple manner to determine water, cement, and additive requirements needed to produce a workable mix that will solidify within a reasonable time. Further refinement may be required if the treated waste must meet some regulatory specifications, and those regulations will guide the additional testing. For many metal-bearing wastes, the requirement will be to produce a stabilized waste whose leachate from the Toxicity Characteristic Leaching Procedure (TCLP) meets a "landban" specified limit.

For nonhazardous wastes and hazardous wastes destined for secure landfills, the principal requirement is to make a product with no free liquid as determined by the paint filter test. Other hazardous wastes will need to meet some regulatory level of contaminant in the leachate as determined by specific leachate tests. In many states the TCLP is the specified regulatory test. In California, however, the regulations require the Waste Extraction Test (WET) procedure. Treated wastes are also usually required to have some minimum strength to insure they can support the weight of other wastes placed on top in a landfill. Minimum unconfined compressive strength from 20 to 50 psi is typically specified. In most cases, cement stabilized wastes far exceed this requirement. These are usually the only tests required by regulations; however, prudent waste managers often require additional tests.

To confirm that stabilization has been achieved beyond the regulatory requirements, additional tests may be advisable. Typical chemical tests include acid neutralization capacity, dynamic leach test, and the multiple extraction procedure. Micromorphological evaluation methods of S/S products consist of X-ray diffraction, scanning electron microscopy, and optical microscopy. References 31 and 32 provide valuable insight into the various test methods. A number of the more common tests for S/S wastes are listed in Table 6.

In determining whether an S/S material is durable, cyclic testing such as freeze-thaw and wet-dry tests are occasionally performed. ASTM D 4842, Freezing and Thawing of Solid Wastes and ASTM D 4843, Wetting and Drying of Solid Wastes were developed based on soil-cement technology. These tests do not simulate actual field conditions, but it is felt that the cyclic tests provide a crude indicator of long-term durability.

Quality control procedures in the field are important to assure that the proper waste-to-binder-to-water ratio is used and adequate mixing is achieved (Fig. 15). Visual observation of the treated waste should be made regularly to check for uniform color and consistency. A treated waste that has a streaked appearance or variable consistency may indicate insufficient mixing.

7355

Fig. 15. Sampling S/S mixture for testing. (Courtesy EPA)

A full scale field demonstration program treating a relatively minor portion of the contaminated waste can be used to document the key variables affecting the treatment process. Equipment reliability, operational procedures, production rates, and QC test methods are parameters that can be documented and evaluated prior to final remediation. The information obtained can confirm the performance after the demonstration is complete and before final remediation. If the demonstration is successful, these parameters can be specified and observed during the remediation as QC indicators. When considering a demonstration program, however, it must be understood that a certain amount of downtime will be necessary between the demonstration and final remediation in order to complete performance tests and develop a meaningful QC program.

Table 6. Test Methods for Solidified Waste Evaluation (Ref. 31, 32)

Test Procedure	Reference	Purpose
Physical Tests:		
Paint Filter Test (PFT)	EPA 9095-SW846	Regulatory requirement to determine the presence of free liquids in a representative sample of bulk or noncontainerized waste.
Liquid Release Test (LRT)	EPA 9096-SW846	To determine presence of liquids under 50 psi pressure.
Moisture Content	ASTM D 2216	To determine the percentage of water in S/S material.
Density	ASTM D 2937, D 1556, D 2922	To determine the in-place density of S/S material.
Hydraulic Conductivity	ASTM D 5084, EPA 9100-SW846	To measure the rate at which a liquid will pass through S/S material.
Unconfined Compressive Strength	ASTM D 1633, D 2166	To measure ability of S/S material to resist vertical loads.
Cone Penetrometer	ASTM D 3441	To determine stability, bearing capacity, and relative density of S/S material in-place.
Freeze-Thaw Durability	ASTM D 4842	To evaluate ability of S/S material to resist repeated freeze-thaw cycles.
Wet-Dry Durability	ASTM D 4843	To evaluate ability of S/S material to resist repeated wet-dry cycles.
Chemical Tests:		
EPA Toxicity Characteristic Leaching Procedure (TCLP)	EPA 1311-SW846	Regulatory requirement to determine the presence of 52 compounds that could cause a waste to be hazardous via toxicity.
Acid Neutralization Capacity	Ref. 31	To determine the buffering capacity of S/S material.
Multiple Extraction Procedure	EPA 1320-SW846	To determine maximum leachate concentrations occurring under acidic conditions. Used in some cases for delisting wastes.
California Waste Extraction Test	Calif. Code, Title 22, Article 11, pp. 1800-75 - 1800.82	Used by state of California to classify waste. May be more stringent leach test than TCLP for some metals.
Equilibrium Leach Test	Ref. 32	To estimate pore water composition of S/S material using distilled water as leaching medium.
Sequential Chemical Extraction	Ref. 31	To evaluate the bonding nature of waste constituents in a stabilized matrix.
Dynamic Leach Test	Adopted from American Nuclear Society Test (ANS)- 16.1	To measure contaminant mobility.
Micromophological Techniques:		
X-Ray Diffraction	Ref. 32	To identify the crystalline phases present in S/S matrix.
Scanning Electron Microscopy	Ref. 32	To create a magnified image up to 10,000 times the original size.
Energy Dispersive X-Ray Analysis	Ref. 32	Used with scanning electron microscopy to determine local composition of crystalline grains.
Optical Microscopy	Ref. 32	To evaluate the gross distribution of different phases.

References

1. Adaska, W.S., and Cavalli, NJ. , "Cement Barriers, " *Proceedings 5th National Conference on Management of Uncontrolled Hazardous Waste Sites*, Washington, D.C. 1984, pp. 126-130.
2. *Soil-Cement for Facing Slopes and Lining Channels, Reservoirs, and Lagoons*, IS126W, Portland Cement Association, 1986.
3. *Soil-Cement Laboratory Handbook*, EB52S,Portland Cement Association, 1971.
4. *Soil-Cement Inspector's Manual,* PA050S, Portland Cement Association, 1980.
5. *Suggested Specifications for Soil-Cement Linings for Lakes, Reservoirs, Lagoons*, IS186W, Portland Cement Association, 1975.
6. Cullinane, M. J., and Jones, L. W., *Stabilization/ Solidification of Hazardous Waste*, U.S. Environmental Protection Agency (U.S. EPA) Hazardous Waste Engineering Research Laboratory (HWERL), EPA/600/D-86/028, Cincinnati, OH, 1986.
7. *Guide to the Disposal of Chemically Stabilized and Solidified Waste*, U.S. EPA SW872, 1982.
8. *Handbook for Stabilization/Solidification of Hazardous Wastes*, U.S. EPA, EPA/540/2-86/001, Cincinnati, OH, 1986.
9. Barth, E. F., "An Overview of the History, Present Status, and Future Direction of Solidification/Stabilization Technologies for Hazardous Waste Treatment," *Proceedings 2nd Annual G.C.H.S.R.C. Symposium, Solidification/Stabilization Mechanisms and Applications*, Beaumont, TX, 1990.
10. Conner, J. R., *Chemical Fixation and Solidification of Hazardous Wastes* , Van Nostrand, Reinhold, NY, 1990.
11. *Annual Book of ASTM Standards,* Volume 04.01, American Society of Testing and Materials, Philadelphia, PA, 1990.
12. *U.S. and Canadian Portland Cement Industry: Plant Information Summary,* Portland Cement Association, 1992.
13. Kosmatka, S. H., and Panarese, W. C., *Design and Control of Concrete Mixtures,* EB001, Portland Cement Association, 1990.
14. Double, D. D., and Hellawell, A., "The Solidification of Cement." *Scientific American*, Vol. 237, No. 1, July 1977, pp. 82-90.
15. Skolny, J., and Daugherty, K. E. , "Everything You Always Wanted to Know About Portland Cement," *ChemTech* , January 1972, pp. 38-45,
16. Troxell, G. E., Davis, H. E., and Kelly, J .W., *Composition and Properties of Concrete*, Second Edition, McGraw-Hill, New York, NY, 1968.
17. Falcone, J. S., Spencer, R. W. , and Katsanes, E. P., *Chemical Interactions of Soluble Silicates in the Management of Hazardous Wastes*, ASTM Special Technical Publication No. 851, 1983.
18. Cherry, K. F., *Plating Waste Treatment*, Ann Arbor Science Publishers, Ann Arbor, MI, 1982.
19. Eary, L. E., and Rai, D., "Chromate Removal From Aqueous Wastes by Chromium Reduction With Ferrous Ion," *Environmental Science Technology,* Vol. 22, No. 8, 1988, pp. 972-977.
20. Bhatty, M. S. Y., "Fixation of Metallic Ions in Portland Cement.," *Proceedings 4th National Conference on Hazardous Wastes and Hazardous Materials*, 1987, pp. 140-145.
21. Cote, P., *Contaminant Leaching from Cement-Based Waste Forms Under Acidic Conditions*, Ph.D. Thesis, McMaster Univ., Hamilton, Ont., Canada, 1986.
22. U.S. EPA, Federal Register, 52(155):29999, August 12, 1987.
23. Delchad, S., "Chemical Treatment: An Inexpensive Alternate to Handling Oily Sludge," *Proceeding's 5th National Conference on Hazardous Wastes and Hazardous Materials*, April 19-21, 1988, pp. 85-88.
24. Suprenant, B. A., Lahrs,, M. C. and Smith, R. L., "Oilcrete," *Civil Engineering* Vol. 60, No. 4, April 1990, pp. 61-63.
25. Alther, G. R., Evans, J. C. , and Pancoski, S. E. , "No Feet of Clay," *Civil Engineering*, Vol. 60, No. 4, August 1990, pp. 60-61.
26. Soundararajan, R., Barth, E. F., Gibbons, J. J., "Using an Organophilic Clay to Chemically Stabilize Waste Containing Organic Compounds," *Hazardous Materials Control*, Vol. 3, No. 1, January/February 1990, pp. 42-45.
27. Freeman, H.M., *Standard Handbook of Hazardous Waste Treatment Disposal,* McGraw-Hill, 1988, p. 7.94.
28. Jones, L. W., *Interference Mechanisms in Waste Stabilization/Solidification Processes*, U.S. EPA HWERL, EPA/600/S2-89/067 Cincinnati, OH, 1990.
29. Cullinane, M.J., Bricka, R. M. , and Francingues, Jr., N. R., "An Assessment of Materials That Interfere With Stabilization/Solidification Processes," *Proceedings 13th Annual Research Symposium*, U.S. EPA, Cincinnati, OH, 1987, pp. 64-71.
30. Cullinane, M. J. and Jones, L. W., "Solidification and Stabilization of Hazardous Wastes," *Hazardous Materials Control*, Vol. 2, No. 1, and Vol. 2, No. 2, 1989.
31. *Stabilization/Solidification of CERCLA and RCRA Wastes, Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities*, U.S. EPA HWERL, EPA/625/6-89/022, Cincinnati, OH, 1989.
32. Stegeman, J.A. and Cote, P.L., *Investigation of Test Methods for Solidified Waste Evaluation - A Cooperative Program*, Report EPS3/HA/8, Ottawa, Ontario, Canada, January 1991.

PORTLAND CEMENT ASSOCIATION MEMBER COMPANIES

United States

Alamo Cement Company
Alaska Basic Industries
Allentown Cement Company, Inc.
Arizona Portland Cement Company
Ash Grove Cement Company
Blue Circle Inc.
Calaveras Cement Company
California Portland Cement Company
Capitol Aggregates, Inc.
Capitol Cement Corporation
CBR Cement Corporation
Coastal Cement Corporation
Continental Cement Company Inc.
CPC Terminals
Dacotah Cement
Dixon-Marquette Cement Company
Dragon Products Company
Eastern Cement Corp.
ESSROC Corp.
ESSROC Materials Inc.
Glens Falls Cement Co., Inc.
Gulf Coast Portland Cement Co.
Hawaiian Cement
Heartland Cement Co.
Hercules Cement Company
Holnam Inc.
Independent Cement Corporation
Kaiser Cement Corporation
Lafarge Corporation
Lehigh Portland Cement Company
Medusa Cement Company
The Monarch Cement Company
National Cement Company of Alabama, Inc.
National Cement Company of California, Inc.
National Portland Cement Company
Phoenix Cement Company
RC Cement Co., Inc.
Rinker Materials Corporation
River Cement Company
Roanoke Cement Company
St. Marys Cement Company
Signal Mountain Cement Company
Southdown, Inc.
Texas-Lehigh Cement Company
Tilbury Cement Company

Canada

Canadian Medusa Cement Limited
Ciment Quebec, Inc.
ESSROC Canada Inc.
Federal White Cement Ltd.
Holnam West Materials Ltd.
Inland Cement Limited
Lafarge Canada Inc.
North Star Cement Limited
St. Lawrence Cement Inc.
St. Marys Cement Corporation
Tilbury Cement Limited

Affiliate Members

California Cement Promotion Council
Cement and Concrete Promotion Council of Texas
Colorado/Wyoming Shippers Association, Inc.
Florida Concrete and Products Association
North Central Cement Promotion Association
Northeast Cement Shippers Association
Northwest Concrete Promotion Group
South Central Cement Promotion Association
Utah Idaho Cement Shippers Association

Associate Members

Allis Mineral Systems
Baker Refractories
BHA Group, Inc.
Cemtech LP
Fuller Company
W. R. Grace and Company
Holderbank Consulting Limited
Magotteaux Slegten Companies
Passamaquoddy Technology
Claudius Peters, Inc.
Polysius Corporation
A B B Raymond
Westvaco Corporation

as of Feburary, 1994

Solidification and Stabilization of Wastes Using Portland Cement

PCA now has a new slide set titled *Solidification and Stabilization of Wastes Using Portland Cement.* This 30-slide set and 12-page script discusses the use of portland cement as a solidifying and stabilizing reagent to treat contaminated waste. The set includes a discussion of the nomenclature, laws, chemistry and tests used for Solidification and Stabilization (S/S) work. The set also includes photos from four environmental clean-up projects utilizing this technology. The set was written to be accompanied by PCA's publication bearing the same title, (EB071).

Price: $40.00 (non-discountable) Code No.: SS403
To order call: Order Processing at 1-800-868-6733

PORTLAND CEMENT PCA ASSOCIATION

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.

5420 Old Orchard Road, Skokie, Illinois 60077-1083

Printed in U.S.A.

EB071.01W