# INTERFERENCE MECHANISMS IN WASTE STABILIZATION/SOLIDIFICATION PROCESSES

by

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The attached report entitled "Interference Mechanisms in Waste Stabilization/Solidification Processes," was prepared by the Risk Reduction Engineering Laboratory (RREL) of the Office of Environmental Engineering and Technology Demonstration (OEETD). It is being transmitted in fulfillment of our commitment to you in the FY 1988 Hazardous Waste Research Program planning process. This deliverable supports the Agency's effort to identify possible types of interference materials which might be encountered in typical waste/binder systems. With this information it may be possible to avoid undesirable effects.

This study investigated the characteristics of Portland cement and pozzolan, the effects of added constituents on their setting characteristics, and the effects of typical organic waste components on the physical properties of the treated waste product. A glossary of common cement terminology and three bibliographic appendices covering a compilation of references and annotated citations for both Portland cement and asphaltic waste treatment systems is also included.

This report has also been forwarded to Alessi Otte of your staff for review and utilization.

Attachment

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## FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of National environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the research and the user community.

This report describes and details the procedures used in the ultimate development of an "expert system" to evaluate closure options for RCRA permitted waste management facilities. The report identifies a consensus need, the procedures used to select the language and delivery platforms and the actual defining and development of the systems modules.

E. Timothy Oppelt, Acting Director
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*Formerly the Hazardous Waste Engineering Research Laboratory (HWERL)

## ABSTRACT

The stabilization/solidification of hazardous wastes involves a series of chemical treatment procedures. The waste is normally treated so as to complex or bind the contaminants into a stable, insoluble form (stabilization), or to entrap the waste material in a solid and/or crystalline matrix (solidification). Hazardous wastes contain many constituents that could interfere with the binding process. This project is concerned with identifying possible interference mechanisms between particular waste components and commercially available waste-binding systems.

This report presents a literature review and information concerning Portland cement and pozzolan chemistry, the effects of added constituents (admixtures) on their setting characteristics, and the effects of typical organic waste components on the physical and containment properties of the treated waste product. These topics are presented so that conclusions may be drawn as to possible types of interference materials that might be encountered in typical waste/binder systems. Also included are a glossary of common cement terminology and three bibliographic appendices covering a compilation of references and annotated citations for both Portland cement and asphaltic waste treatment systems.

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The study was conducted under the general supervision of Dr. John Harrison, Chief, EL; Dr. Raymond L. Montgomery, Chief, Environmental Engineering Division; and Mr. Norman R. Francingues, Jr., Chief, Water Supply and Waste Treatment Group. Commander and Director of WES was COL Dwayne G. Lee, CE; Technical Director was Dr. Robert W. Whalin.

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## SECTION 1

## INTRODUCTION

Waste treatment processes that are designed to decrease the toxicity or volume of hazardous wastes (e.g., precipitation or incineration) generate persistent residues that must be prepared for safe final or ultimate disposal. In most cases, final disposal of these residuals is by means of secure, shallow-land burial. The disposal problem is most critical in the case of wastes that cannot be destroyed or detoxified, such as heavy metal sludges and brines. Thus, even with improved waste treatment methods, there will continue to be a need for technology related to the safe land disposal of hazardous wastes. Stabilization/solidification (S/S) of hazardous wastes before final disposal has been proposed as a way to prevent release of the hazardous waste constituents to the environment.

According to Title 40 of the Code of Federal Regulations, the U.S. Environmental Protection Agency is responsible for evaluating the suitability of hazardous waste for land disposal and for the examination of hazardous waste delisting petitions. A thorough understanding of the potential behavior of stabilized/solidified wastes is necessary to make judgments as to the long-term effectiveness of their containment. The extent to which various contaminants are securely held in stabilized/solidified wastes must be determined for all S/S processes so that individual processes and delisting petitions can be evaluated. There are several available methods for the S/S of hazardous wastes. These methods have been developed primarily for inorganic wastes. However, organic wastes are increasingly being included as their volume continues to increase and S/S additives and technology improve. Some of the chemical components of the complex wastes may interfere with the proposed S/S process and cause undesired results (e.g., flash set, set retardation, spalling, etc.). This report surveys the literature concerned with the effects of various waste constituents on the most common S/S binder systems: Portland cement, pozzolan, and asphalt. At this time there is a paucity of quantitative data concerning the specific effects of these interfering compounds alone or in concert upon particular S/S processes.

### LITERATURE SEARCH PROCEDURES

The literature search was conducted using facilities available in the U.S. Army Engineer Waterways Experiment Station (WES) Library and the WES Concrete Technology Division Library. The search included American Cement Institute Journals and Indexes, American Society for Testing and Materials (ASTM) Journals and Indexes, "Cement and Concrete Research" Journals, "Chemical Abstracts," available textbooks, personal libraries and files of the Concrete Technology Division staff members, and telephone communication with various experts in the field of S/S of hazardous wastes.

The Technical Information Center at the WES conducted two computer searches using the Compendex Data Base, National Technology Information

Service Data Base, and Technical Research Information Service Data Base using the following key words:

| | |
|---|---|
| additives | organic waste |
| admixture | Portland cement |
| asphalt | set time |
| asphaltic cement | solidification |
| chemical | solidify |
| chemical solidification | stabilization |
| interference | stabilize |
| organic | waste |

Additional computer searches were conducted using the Data Base Index (DBI), Chemical Abstracts Data Base, Engineering Information and Technical Meetings Data Base (EIMET), Environment Abstracts Data Base (ENVIROLINE), Electrical Power Information Abstracts Data Base (EPIA), and Geological References Data Base (GEOREF) of the American Geological Institute. The following key words were used:

| | |
|---|---|
| admixtures | interference |
| cement | Portland cement |
| chemical interference | solidification |
| hazardous waste | stabilization |

Three bibliographies developed through these procedures are included as appendices. Appendix A is an annotated bibliography of references on effects of additives on Portland cement concrete, listed alphabetically by first key word in the title. Appendix B is an annotated bibliography of references on the effects of additives on asphalt materials, arranged similarly to Appendix A. Appendix C is an alphabetical listing of all applicable references, by author's name.

A glossary of cement chemistry terminology is presented as Appendix D.

## EFFECTS OF SPECIFIC MATERIALS ON CEMENT AND POZZOLAN CHEMISTRY

Although chemical stabilization and solidification of hazardous wastes before disposal is increasing in importance, very little work has been done concerning the effects of specific waste components on the physical and containment properties of the final S/S waste product. Many categories of inorganic and organic materials are known to have either beneficial or harmful effects on concrete and asphalt products as used in the construction industry. Such admixtures (materials added to change the physical properties of concrete) are routinely added to concrete formulations to retard set, lower heat production, increase water resistance, and/or increase final product strength. Likewise, care has to be taken to see that aggregates or other components do not contain deleterious materials.

A review of cement literature reveals that the chemistry of the hardening of concrete is not well understood although the basic chemical reactions and their products are fairly well known. Several theories have been proposed and are discussed concerning how additives produce their effects by interfering with cement hydration reactions, but none appears to be entirely satisfactory.

Pozzolan chemistry is less well known, although it is thought to be analogous in some ways to that of Portland cement.

The complexity of the hydration reactions and the effects of slight variations in process formulations or mixing parameters complicate the prediction of the effects of additives on the final S/S waste product. Effects of single-component additions are only poorly understood. Predicting the effects of complex and variable compositions such as those found in a real waste is beyond the current state-of-the-art.

As an example, the use of short-term or accelerated curing tests for compressive strength may give erroneous results as to the long-term stability of the binder-waste mix. Materials that cause the retardation of set often bring about increased long-term strength in both Portland cement and lime/fly ash S/S systems. For mixes containing organic wastes or other known set retarders, a 90-day cure (in addition to 28-day samples) is recommended. This long curing time brings about obvious difficulties in the day-to-day operation of a waste S/S plant. No short-term testing protocols have yet been developed to adequately predict long-term stability, durability, and strength characteristics of S/S waste products.

Nonpolar organic materials of low volatility should not hinder strength development in cement or pozzolan systems. Since chlorinated hydrocarbons comprise a large proportion of the hazardous organic wastes, a study of their effects upon these systems is strongly recommended. Organic wastes that contain hydroxyl (e.g., sugars and alcohols) or carboxylic acid (e.g., citric acid, acetic acid) groups (and perhaps amines) can be expected to delay or stop altogether the pozzolanic reactions. These functional groups are present in wastes such as biological sludges, paint sludges, and many solvents.

The final properties of a waste-cement mixture are highly dependent upon: 1) the constituents of the waste that may interfere with the setting reactions; 2) the water/cement ratio which is the primary determinant of the size configuration of the void space and permeability of the final product; 3) presence of admixtures such as fly ash, surfactants, or others that may modify setting or final strength parameters of the product; and 4) procedures and conditions used for mixing and curing the treated wastes. The strength and durability of concrete products are directly related to the type and number of voids in the final product. Adequate design of the formulation and mixing parameters can change the durability/accessibility of water to waste constituents of the final S/S product by several orders of magnitude.

Asphaltic and polymeric materials used for waste S/S also are affected by low levels of some waste components. Solvents and oils may weaken and liquefy the asphaltic base. Oxidizers and some inorganic materials may cause or promote fies or flash-set of the final mixture. Care should be taken to thoroughly test specific wastes that are candidates for this treatment process.

## STUDIES OF WASTE INTERFERENCE WITH S/S PROCESSES

A great variety in the types of reagents used and testing performed is found in the few published studies which allude to the effects of waste

components on the S/S process. Details of materials and reagents, preparation and mixing procedures, and product testing protocols are often sketchy and incomplete. In this review, all reports which impinge upon effects of different waste constituents on specific S/S processes are discussed in the light of current testing and disposal requirements. No broad generalizations could be gleaned from the studies reviewed, but a list of those materials which should be studied further include heavy metal interferences such as lead, copper, and zinc; organics, such as grease and oils, phenolics, degreasers, and pesticides; and stringent conditions such as high sulfate and strong bases.

There is a clear need for further experimental work to obtain physical and chemical data relative to cementitious and asphaltic S/S treatment systems. Enough basic information should be developed so that valid prediction and modeling of waste-binder interactions are possible. This ability would overcome the current need to test each specific waste-binder combination for possible interferences. However, the variability and complexity of most waste streams, as well as cement and pozzolanic setting reactions, still may preclude broad generalizations.

## SECTION 2

## CONCLUSIONS AND RECOMMENDATIONS

Although chemical stabilization and solidification (S/S) of hazardous wastes before disposal is increasing in importance, very little work has been done concerning the effects of specific waste components on the physical and containment properties of the final S/S waste product. Many categories of inorganic and organic materials are known to have either beneficial or harmful effects on concrete and asphalt products as used in the construction industry. Such admixtures (materials added to change the physical properties of concrete) are routinely added to concrete formulations to retard set, lower heat production, increase water resistance, and/or increase final product strength. Likewise, care has to be taken to see that aggregates or other components do not contain deleterious materials.

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The final properties of waste-cement mixtures are highly dependent upon: 1) the constituents of the waste that may interfere with the setting reactions; 2) the water/cement ratio, which is the primary determinant of the size and configuration of the void space and permeability of the final product; 3) presence of admixtures such as fly ash, surfactants, or others that may modify setting or final strength parameters of the product; and 4) procedures and conditions used for mixing and curing the treated wastes. The strength and durability of concrete products is directly related to the type and number of voids in the final product. Adequate design of the formulation and mixing parameters can change the durability and accessibility of water to waste constituents of the final S/S product by several orders of magnitude.

Asphaltic and polymeric materials used for waste S/S also are affected by low levels of some waste components. Solvents and oils may weaken and liquefy the asphaltic base. Oxidizers and some inorganic materials may cause or promote fires or flash set of the final mixture. Care should be taken to thoroughly test specific wastes that are candidates for this treatment process.

A great variety in the types of reagents used and the testing performed is found in the few published studies which allude to the effects of waste components on the S/S process. Details of materials and reagents, preparation and mixing procedures, and product testing protocols are often sketchy and incomplete. In this review, all reports that impinge upon the effects of different waste constituents on specific S/S processes are discussed in light of current testing and disposal requirements. No broad generalizations could be gleaned from the studies reviewed, but a list of those materials which appear to be appropriate for further study include heavy metals interferences, such as lead, copper and zinc; organics, such as grease and oils, phenolics, degreasers, and pesticides; and stringent conditions such as high sulfate and strong bases.

There is a clear need for further experimental work to obtain physical and chemical data relative to cementitious and asphaltic S/S treatment systems. Enough basic information should be developed using standard mixing and testing protocols so that valid prediction and modeling of waste-binder interactions are possible. The ability to generalize concerning interference effects would overcome the current need to test each specific waste-binder combination for possible interferences. However, the variability and complexity of most waste streams as well as cement and pozzolanic setting reactions may still preclude such generalizations.

## SECTION 3

## CEMENT AND POZZOLAN PROPERTIES THAT MAY AFFECT WASTE CONTAINMENT

### INTRODUCTION

The ability of a stabilized/solidified (S/S) waste product to contain a given hazardous constituent depends primarily upon its resistance to leaching or volatilization of waste constituents and its long-term durability. This section develops the background necessary for an understanding of factors controlling leaching and durability characteristics of cement and pozzolanic systems.

Comparison of the finished S/S waste product with standard construction materials is not entirely appropriate since most hazardous wastes treated by S/S technologies are liquid slurries with relatively low solids content (10 to 40 percent solids by weight). The mixture of a solidification agent such as cement with a slurried waste more closely resembles a hydrated cement paste rather than a typical concrete with a large proportion of aggregate (60 to 80 percent of the final concrete volume). Experimentation with hydrated cement pastes provides a basis for speculation on the effects of various hazardous waste constituents on a S/S waste product.

As noted above, the characteristics of S/S wastes that are most important to waste containment are leachability and durability. However, unconfined compressive strength (UCS) is the commonly specified measure of concrete quality since it is determined easily and inexpensively by a reproducible test. No correlation has been demonstrated between UCS and leachability.

Coté et al. (1984) has based a theoretical model of the leaching of specific, low-to-high solubility material from a solid matrix to a large extent on the rate of internal diffusion of the material in the solid matrix. Internal diffusion of soluble ions or molecules in a solid matrix depends largely upon the relative amount and character of void spaces in the solid, which in turn relates directly to the permeability of the porous solid and its ultimate strength.

Numerous researchers have investigated the chemistry and the physical characteristics of cement and pozzolanic mixtures. These studies serve as an excellent foundation for understanding the similar properties of cement- and pozzolan-based S/S processes. This section presents a brief overview of cement and pozzolan chemistry and terminology. Detailed information on the subject is available in the following primary sources.

1. Bye, G. C. 1983. Portland Cement: Composition, Production and Properties. Pergamon Press, New York. 149 pp.

2. Mehta, P. K. 1987. Concrete Structure, Properties and Materials. Prentice-Hall, Inc., Englewood Cliffs, NJ.

3. Neville, A. M. 1981. Properties of Concrete. Pitman Publishing, Inc., Marshfield, MA.

4. Portland Cement Association. 1968. Design and Control of Concrete Mixtures. 11th ed., Portland Cement Association, Skokie, IL.

5. Powers, T. C. 1958. The Physical Structure and Engineering Properties of Concrete. Bulletin 90, Portland Cement Association, Skokie, IL.

6. U.S. Bureau of Reclamation. 1975. Concrete Manual. Washington, DC.

7. Woods, H. 1968. Durability of Concrete. ACI Monograph 4. American Concrete Institute, Detroit, MI.

## PORTLAND CEMENT

Portland cement is probably the most common cementitious additive for the S/S of hazardous waste. Portland cement is highly uniform, relatively inexpensive, and widely available; it can be worked in normal construction machinery by unskilled labor; and it produces products with highly predictable characteristics. A variety of standard types of Portland cement are available for specific applications, and many admixtures have been developed to modify its setting and final properties.

### The Solids in Hydrated Cement

The hydration of Portland cement is a series of simultaneous and consecutive reactions between water and solid cement constituents which occur in the setting and hardening processes. Anhydrous Portland cement consists of angular particles (usually 1 to 50 μm) with a chemical composition of the primary clinker materials that corresponds approximately to $C_3S$, $C_2S$, $C_3A$, and $C_4AF$, where C = CaO, S = $SiO_2$, A = $Al_2O_3$, F = $Fe_2O_3$, $\bar{S}$ = $SO_3$, and H = $H_2O$. In ordinary Portland cements, the respective amounts range between 45 and 60, 15 and 30, 6 and 12, and 6 and 8 percent (with a small added amount of $C\bar{S}$). Table 1 lists selected characteristics of these materials.

Dispersing Portland cement in water causes the various constituents to go into solution, which rapidly saturates the liquid phase with the various ionic species. The first needle-like crystals of calcium sulfoaluminate hydrate (ettringite) appear within a few minutes of cement hydration (see Equation 2 below). After a few hours, large, prismatic crystals of calcium hydroxide (CH) and very small fibrous crystals of calcium silicate hydrates (C-S-H) begin to fill the empty spaces formerly occupied by water and the dissolving cement particles. The most important reactions in later stages are the hydration of calcium silicates (to produce C-S-H), which continues for many months at decreasing rates (Popovics 1979).

The rapid changes in the solution composition which occur upon initial hydration are followed by a relatively constant composition, depending upon the initial cement material and the water/cement ratio. The solution is

TABLE 1. PRINCIPAL COMPOUNDS OF PORTLAND CEMENT AND THEIR CHARACTERISTICS

| Approximate composition | $3CaO \cdot SiO_2$ | $\beta 2CaO \cdot SiO_2$ | $3CaO \cdot Al_2O_3$ | $4CaO \cdot Al_2O_3Fe_2O_3$ |
|---|---|---|---|---|
| Abbreviated formula | $C_3S$ | $\beta C_2S$ | $C_3A$ | $C_4AF$ |
| Common name | Alite | Belite | --- | Ferrite phase, Fss |
| Principal impurities | $MgO$, $Al_2O_3$, $Fe_2O_3$ | $MgO$, $Al_2O_3$, $Fe_2O_3$ | $SiO_2$, $MgO$, alkalies | $SiO_2$, $MgO$ |
| Common crystalline form | Monoclinic | Monoclinic | Cubic, orthorhombic | Orthorhombic |
| Proportion present (%) | | | | |
| Range | 35-65 | 10-40 | 0-15 | 5-15 |
| Average in ordinary cement | 50 | 25 | 8 | 8 |
| Rate of reaction with water | Medium | Slow | Fast | Medium |
| Contribution to strength | | | | |
| Early age | Good | Low | Good | Good |
| Ultimate | Good | High | Medium | Medium |
| Heat of hydration | Medium | Low | High | Medium |
| Typical (cal/g) | 120 | 60 | 320 | 100 |

supersaturated in calcium hydroxide (CH) and hydrated calcium sulfate ($C\bar{S}H$) until the reaction involving the formation of calcium sulfoaluminate removes most of the calcium sulfate from solution. The CH, however, remains in solution, and solid CH is present at all stages of the cement setting reactions.

Since the hydration of tricalcium silicate ($C_3S$) is the dominating mechanism in the overall hydration process, several distinct stages in its hydration have been identified (Kondo and Daimon 1969; Young 1972, 1976). These stages are shown in the conduction calorimetry curve in Figure 1. During Stage I, the initial hydrolysis of $C_3S$ occurs, with a rapid release of heat and calcium hydroxide into solution. This leaves a $C_3S$ particle with an approximately 10-nm insulating rind of hydrated $C_3S$.

In Stage II the release of CH continues, but at a slower rate limited by the ability of CH to interact with available water through the rind. The

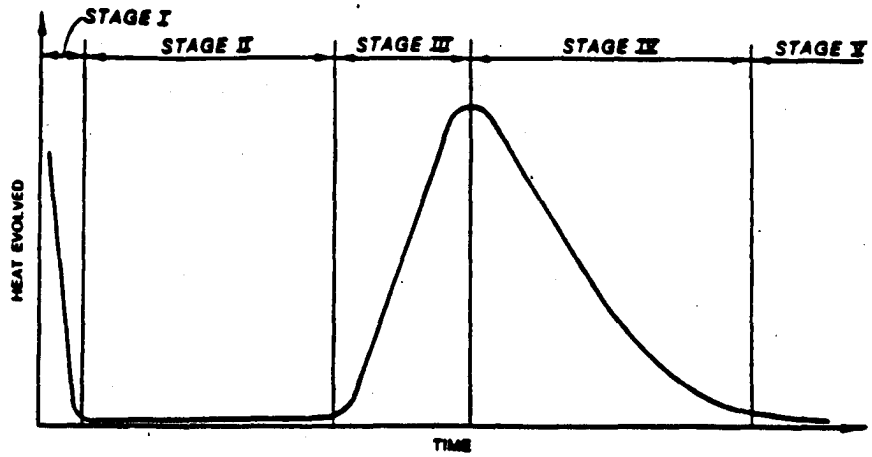


Figure 1. Heat liberation curve by hydrating tricalcium silicate as determined by isothermal calorimetry (Source: Kondo and Daimon 1969).

thin layers of hydrated calcium silicate (C-S-H) that make up the rind are probably a polymerization of the hydrolyzed silicate groups. Stage III is represented by an accelerated $C_3S$ crystallization and the initiation of calcium hydroxide crystallization. Simultaneously, a transformation of the C-S-H gel occurs, exposing additional surface area of the anhydrous particle. Deceleration of these diffusion-controlled reactions typifies Stages IV and V, which continue as slowing exothermic reactions.

Hydration of tricalcium aluminate ($C_3A$), while not being critical to strength development, is crucial in determining cement set time and other Stage I and II characteristics (Hansen 1959). Hydration of $C_3A$ in the absence of sulfate ions can be represented by the following equation:

$$2C_3A + 21\ H \longrightarrow \underset{\text{(metastable hexagonal hydrates)}}{C_4AH_{13} + C_2AH_8} \xrightarrow{\text{slow}} \underset{\text{(stable hydrate)}}{2C_3AH_6} + 9H \qquad (1)$$

The heat liberated in Equation 1 is sufficient to speed up the reaction to the stable form, $C_3AH_6$. Portland cement does, however, contain a small amount of sulfate as calcium sulfate (gypsum). This alters the hydration to the form of

$$C_3A + 3C\bar{S}H_2 + 26H \longrightarrow \underset{\text{(ettringite)}}{C_3A \cdot 3C\bar{S} \cdot H_{32}} \qquad (2)$$

The addition of 26 water molecules during the formation of ettringite brings about a corresponding volume increase. When ettringite forms early in the solidification process, the additional space is not a problem; it even develops binding properties that contribute to the early strength of the product. This phenomenon can actually be used to bind large amounts of sulfate in a solidification product by using clay-rich (alumina) binders. However, if the ettringite forms after solidification, the additional space required loosens the structure and causes an observable increase in permeability with a

concomitant loss in strength (Wiedemann 1982). After a period of time, the length of which depends on the alumina-to-sulfate ratio of the cement, the ettringite crystals may react with $C_2A$ according to

$$4H + 2C_2A + \underset{\text{(ettringite)}}{C_3A \cdot 3C\bar{S} \cdot H_{32}} \longrightarrow \underset{\text{(monosulfoaluminate)}}{3C_3A \cdot C\bar{S} \cdot H_{32}} + 4H \qquad (3)$$

Monosulfoaluminate in Portland cement concrete makes the concrete vulnerable to sulfate attack.

The major constituents of fully hydrated cement paste are discussed below.

1. Calcium silicate hydrate (C-S-H) makes up 50 to 60 percent of the volume of solids in fully hydrated Portland cement paste. Termed a C-S-H gel in older literature, this ill-defined compound forms small, poorly defined crystalline fibers in a reticular network.

2. Calcium hydroxide crystals constitute 20 to 25 percent of the volume of solids in the fully hydrated paste; it tends to form large crystals with distinctive hexagonal-prism morphology. The presence of significant amounts of calcium hydroxide makes the concrete reactive to acidic solutions.

3. Calcium sulfoaluminates make up 15 to 20 percent of the solids volume in the fully hydrated paste but appear to play a minor role in the structure and properties of the final product.

## Voids in Hydrated Cement and Concrete

The several kinds of voids in hydrated cement paste have great influence on its final properties of strength, durability, and permeability. The smallest voids, which occur within the C-S-H gel structure, are 0.5 to 2.5 nm in diameter. They account for about 28 percent of the porosity in solid C-S-H. These small voids have little effect on the strength and permeability of the final product but appear to be important in drying shrinkage and creep.

Capillary voids account for the larger spaces which are not filled by solid components. In well-hydrated, low water/cement ratio mixes, capillary voids range from 10 to 50 nm, but in high-ratio mixes they may be as large as 3,000 to 5,000 nm. It is generally held that pore size distribution, and not simply total capillary porosity, is a better criterion for evaluating the characteristic of a cementitious product. Capillary voids larger than about 50 nm are thought to be detrimental to strength and permeability, while voids smaller than 50 nm are more important to drying shrinkage and creep. Capillary voids limit the strength of concrete by acting as "stress concentrators" (Hirsh et al. 1983).

The third type of voids, usually called "air voids," are generally spherical and usually range from 0.05 to 0.2 mm but may range up to 3 mm. Air voids are usually introduced intentionally into the hydrated cement paste to increase the resistance of the final product to freeze-thaw (frost) damage even though they typically adversely affect its strength and permeability.

Depending on the environmental conditions, the voids are capable of holding large amounts of water. Capillary water (in voids 5 nm or larger) is bulk water that is largely free from attractive surface forces. Water in voids greater than about 50 nm is considered free-water since its loss causes no shrinkage in the final product, while loss of water held by capillary tension in voids from about 5 to 50 nm may cause some shrinkage. Changes in the amount of capillary pore space with degree of hydration are illustrated in Figure 2a for a cement paste with a water/cement ratio of 0.66 and in Figure 2b for fully hydrated pastes of different water/cement ratios.

Absorbed water is close to the surface (probably within 1.5 nm of the surface) and held by hydrogen bonding and Van der Wal forces. Loss of absorbed water, even in air of 30-percent relative humidity, is mainly responsible for the shrinkage and cracking of the solidifying mass. The water more tightly bound in the interlayers of the C-S-H structure will be lost only in air with relative humidities below about 10 percent. The loss of water from the C-S-H structure will cause considerable drying shrinkage.

## POZZOLANIC MATERIALS

By definition, pozzolans are materials that display no cementing actions by themselves but which contain constituents that combine with lime at ordinary temperatures and in the presence of water to form cementitious compounds. At present, the main pozzolans used commercially are fly ash from coal-fired power plants and kiln dust from lime or cement kilns. Fly ash is the fine ash produced by combustion of powdered coal with forced draft. The ash is carried up in the flue gases and collected in special equipment such as electrostatic precipitators or bag houses. Fly ash was first reported in the literature in terms of its pozzolanic properties in 1937 (Davis et al. 1937).

Most traditional literature is concerned with fly ash as an admixture in cement rather than as an independent pozzolanic material. Minnick (1967) investigated eight U.S. fly ashes and their reactions with hydrated lime over reaction periods up to 32 weeks. Minnick has suggested pozzolanic reactions according to the following:

$$CH + S \xrightarrow{H_2O} C_xS_yH_z \qquad (4)$$

(C-S-H of varying stoichiometry)

$$CH + A \xrightarrow{H_2O} C_xA_yH_z \qquad (5)$$

(hexagonal and cubic aluminate hydrates)

$$CH + A + S \xrightarrow{H_2O} C_xA_yS_zH_w \qquad (6)$$

(hydrogarnets)

$$CH + \bar{S} + A \xrightarrow{H_2O} C_xA_y(C\bar{S})_zH_w \qquad (7)$$

(ettringite and derivatives)

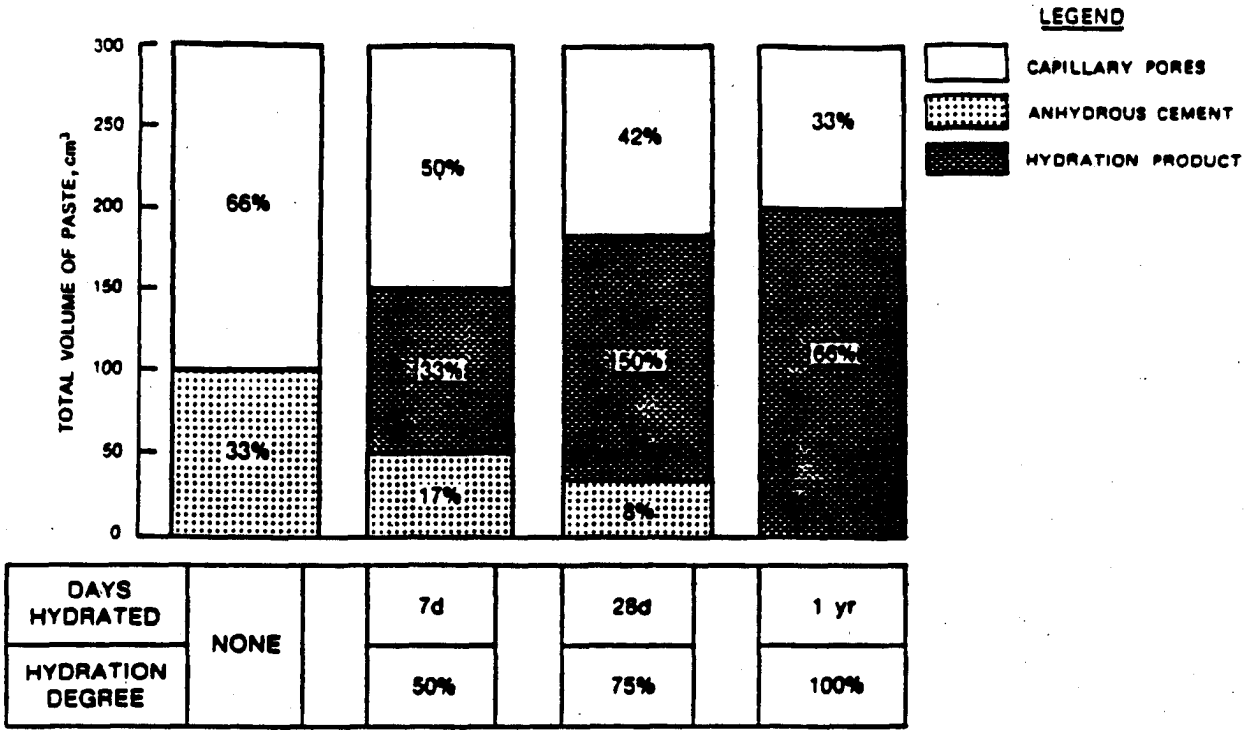


Figure 2a. Change in the amount of capillary pore space with degree of hydration for a cement paste with a 0.66 water/cement ratio (after Mehta 1987)

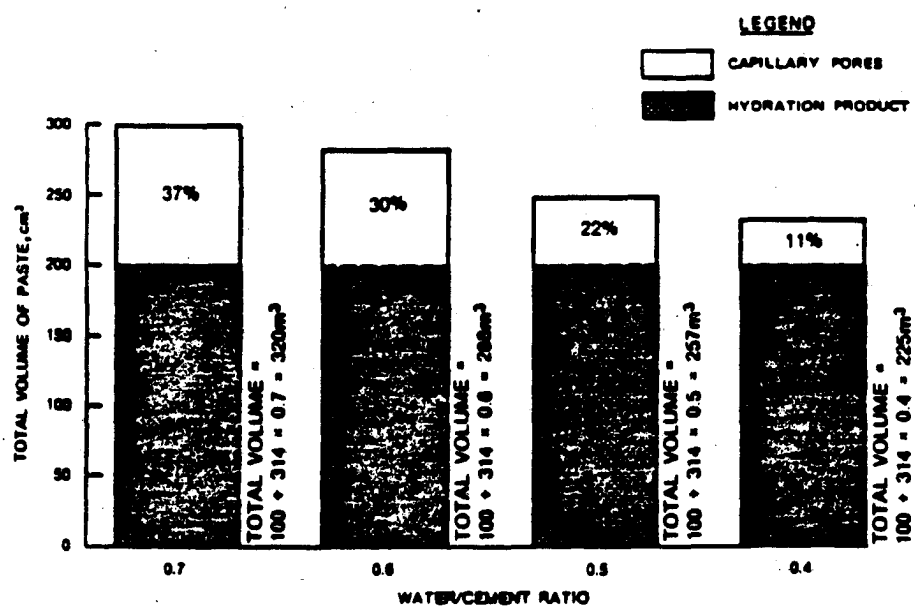


Figure 2b. Change in the amount of capillary pore space for a fully hydrated cement paste with differing water/cement ratios, based on equal amounts of Portland cement (after Mehta 1987)

The above reactions yield products whose properties are similar to the reaction products of Portland cement. One primary difference is that pozzolanic reactions consume lime rather than produce it, as with typical Portland cement hydration. This is an important factor in sulfate corrosion resistance and in differences in the effects of additives on the two S/S materials.

Pozzolanic reactions, while not identical, are similar to Portland cement reactions. The strength of products produced in both processes results from the formation of hydrated calcium silicates (C-S-H); however, pozzolanic reactions are not pure hydration reactions like those of Portland cement. Portland cement involves two or more solid phases plus water. Pozzolanic reactions generally are much slower than cement reactions, and set times are usually measured in days or weeks instead of hours.

## THE STRENGTH-POROSITY RELATIONSHIP

Factors that influence the strength of a cement on pozzolanic mass are listed in Table 2. By far the most important factor is the water/cement ratio-porosity relationship. This is usually explained as the natural consequence of the weakening of the cement matrix caused by increasing porosity with increasing water/cement ratios (as discussed above, see especially Figure 2b). Typical data illustrating this point are shown in Table 3. Figure 2b also illustrates the increase in strength with increasing hydration (time of cure) which corresponds to a decrease in the total pore space.

TABLE 2. PRINCIPAL FACTORS AFFECTING STRENGTH OF CONCRETE AND STABILIZED/SOLIDIFIED WASTE

- Matrix Porosity
  - Water/cement ratio
  - Degree of hydration
    - Curing time
    - Temperature
    - Humidity
  - Mineral admixtures
  - Air content
- Specimen Parameters
  - Geometry
  - Dimensions
  - Moisture
- Chemical Interactions with Waste
  - Waste constituents
  - Cement and waste loading
- Stress Parameters
  - Stress type
  - Rate of application

TABLE 3. INFLUENCE OF WATER/CEMENT RATIO AND DEGREE OF HYDRATION ON CONCRETE STRENGTH

| Water/cement ratios by weight | Unconfined compressive strength (psi) after different lengths of cure | | | |
|---|---|---|---|---|
| | 1 day | 3 days | 7 days | 28 days |
| 0.35 | 1,300 | 2,900 | 4,450 | 6,300 |
| 0.45 | 900 | 2,200 | 3,500 | 5,250 |
| 0.55 | 550 | 1,650 | 2,750 | 4,350 |
| 0.65 | 300 | 1,200 | 2,000 | 3,450 |
| 0.75 | 200 | 950 | 1,550 | 2,800 |

Source: Portland Cement Association 1968.
Notes: Cylinders (6 by 12 in.) (15 by 30 cm) of normal type I cement undergoing moist-cure. To convert pounds (force) per square inch to megapascals, multiply by 0.006894757.

## Water/Cement Ratio and Degree of Hydration

The relationship between porosity and strength is of great importance to the prediction of the ability of a given waste-cement mixture to contain the contaminants when subjected to various environmental conditions. Therefore, compressive strength may be an indicator of the S/S waste's resistance to leaching. This thought is further developed below in the section on durability-permeability.

## Mineral Admixtures

The use of pozzolanic and cementitious by-products such as fly ash, blast furnace slag, or kiln dusts as admixtures is an important issue in waste S/S. When used in addition to, or as a partial replacement for Portland cement, the presence of the mineral generally retards the rate of strength gain. However, the mineral admixture reacts with the excess calcium hydroxide present in the hydrated Portland cement to form additional C-S-H and leads to a significant reduction in porosity and ultimate strength gain in the final product (Marsh et al. 1985). Consequently, considerable improvement in the ultimate strength and impermeability (water tightness) can be achieved by their incorporation.

## Air Entrainment

Additives causing stable air incorporation into the cement paste are universally deleterious to the ultimate strength and impermeability of the concrete, due most likely to the added large-pore space. However, the entrained air increases the resistance of the products to freezing.

## Specimen Parameters

The standard test specimen for the uniaxial compression test in the United States (ASTM C 469) is a right cylinder of 6 in. (15 cm) diameter (d)

and 12 in. (30 cm) height (h) (ratio h/d = 2 ). Measured strengths vary indirectly with h/d ratio, with a h/d ratio of 1 giving 15 to 20 percent higher strength and a ratio of 4 about 10 percent less. Specimens of different sizes, but having a h/d = 2 , have different measured strengths. A 3- by 6-in. (7- by 15-cm) cylinder has about 6 percent higher strength, and a 9- by 18-in. (23- by 46-cm) specimen has about 10 percent lower strength than the standard 6- by 12-in. cylinder.

Strength tests based upon the 6-in. standard test cube, which are common in European countries, generally indicate strengths 10 to 15 percent higher than tests of the same material using 6- by 12-in. cylinder. Similarly, the use of a 2-in. cube for compressive strength testing would be expected to give 15 to 25 percent higher strength values for the same cement mixtures.

Concrete products also perform differently under different stresses, compressive strength being the outstanding feature of structural concrete. Most designs emphasize compressive strength, since the tensile strength of concrete is usually an order of magnitude lower. The rate of stress application is also important, as long-term stress brings on creep strain due to moisture movement in the C-S-H voids and the development of microcracks.

### Chemical Interaction of Waste with the Cement Binder

Wastes most amenable to S/S are usually water-based sludges containing a wide variety of inorganic and organic constituents at different and varying concentrations. Predicting the effect of these poorly defined mixtures on the strength of hydrating cement paste without benefit of bench- or pilot-scale studies is complex at best and probably beyond the state of the art.

## THE DURABILITY-PERMEABILITY RELATIONSHIP

Long-term durability of the S/S waste product is a prime consideration in the design and specification of waste S/S systems. Prediction of long-term integrity of the final waste form requires consideration of all possible modes of failure (Table 4). For cementitious S/S products, water is generally involved in every form of deterioration; in porous solids, permeability of the material to water usually determines the rate of deterioration. Internal movement and changes in the structure of water are known to cause disruptive volume changes of many types. Examples are freezing of water into ice, formation of ordered structure of water inside fine pores, development of osmotic pressures due to different ionic concentrations, and hydrostatic pressure buildup by differential vapor pressures. All of these can lead to large internal stresses within a moist solid and result in its ultimate failure.

In porous solids, water also acts as a vehicle for transport of solutes through the material, both aggressive ions into and waste materials out. A discussion of permeability is therefore of basic interest to an understanding of both durability and leachability. Permeability of concrete products depends primarily on the water/cement ratio (which determines the size, volume, and continuity of capillary voids) and the development of microcracks that occur between the cement paste and the surface of included solids (such as aggregates or waste solids). The suspended particulates in waste sludges (acting as small aggregate) are typically very small. In general, the smaller

TABLE 4. PHYSICAL CAUSES OF DETERIORATION OF CONCRETE PRODUCTS

- Surface Wear
  - Abrasion
  - Erosion
  - Cavitation
- Cracking
  - Volume changes
    - Moisture gradients and humidity
    - Crystallization pressures of salts in pores
  - Exposure to temperature extremes
    - Freeze-thaw action
    - Fire
  - Structural loading
    - Overload or impact
    - Cyclic loading

the suspended particles, the fewer the microcracks at their surface, and the lower the overall permeability of the final product. The primary consideration of permeability of S/S waste sludges of small particle size then, is the water/cement ratio.

Cracking by Crystallization of Salts in Pores

Stabilization/solidification waste products often contain substantial amounts of salts and/or organic molecules with appreciable water solubilities. Concentration of these materials at or below the surface of the solid where evaporation of pore water is occurring can cause the development of supersaturated solutions and the formation of salt crystals in the pores of the S/S product.

Crystallization occurs only when the concentration of the solute (C) exceeds the saturation concentration (Cs) at a given temperature. Generally, the higher the degree of supersaturation (the ratio of $C/Cs$), the greater the crystallization pressure exerted on the solid structure. Table 5 presents crystallization pressures for $C/Cs = 2$ of a series of salts that are common in stone and concrete materials. These values were calculated by Winkler (1975) in an effort to understand the rapid deterioration of stone and concrete monuments by smog and acid (high-sulfate) rain. For example, at $C/Cs = 2$, halite (NaCl) at 25° C produces 605 atm (61 MPa) of pressure, and at $C/Cs = 10$, 2,020 atm (205 MPa). These pressures are strong enough to disrupt the structure of the stone or concrete products which contain these constituents. As seen in Table 5, common salts have a wide range of crystallization pressures. Due to the wide variety of materials found in hazardous wastes, this effect can be appreciable.

Damage typical of this effect is the powdering or spalling of the subsurface of the solid material which progressively deepens into the material as

TABLE 5. CRYSTALLIZATION PRESSURES FOR SALTS

| Salt | Chemical Formula | Pressure (atm)* $C/C_s = 2$ 0° C | 50° C |
|---|---|---|---|
| Anhydrite | $CaSO_4$ | 335 | 398 |
| Bischofite | $MgCl_2 \cdot 6H_2O$ | 119 | 142 |
| Dodekahydrate | $MgSO_4 \cdot 12H_2O$ | 67 | 80 |
| Epsomite | $MgSO_4 \cdot 7H_2O$ | 105 | 125 |
| Gypsum | $CaSO_4 \cdot 2H_2O$ | 282 | 334 |
| Halite | $NaCl$ | 554 | 654 |
| Heptahydrite | $Na_2CO_3 \cdot 7H_2O$ | 100 | 119 |
| Hexahydrite | $MgSO_4 \cdot 6H_2O$ | 118 | 141 |
| Kieserite | $MgSO_4 \cdot H_2O$ | 272 | 324 |
| Mirabilite | $Na_2SO_4 \cdot 10H_2O$ | 72 | 83 |
| Natron | $Na_2CO_3 \cdot 10H_2O$ | 78 | 92 |
| Tachhydrite | $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$ | 50 | 59 |
| Thenardite | $Na_2SO_4$ | 292 | 345 |
| Thermonatrite | $Na_2CO_3 \cdot H_2O$ | 280 | 333 |

Source: Winkler (1975).
* To convert atmospheres (standard) to megapascals, multiply by 0.101325.

its porosity increases. Damage to S/S products due to wet-dry cycles may be to a large extent due to the cyclic dissolution and crystallization of contained salt.

Wet-Dry Cycling

Other than cracking by salt crystallization as described above, wet-dry cycling of normal concrete products does not usually produce significant damage to its structure. However, as the total proportion of cement is reduced or the water/cement ratio is increased, as is common in waste S/S practice, wet-dry cycling may cause rapid deterioration of the S/S waste product. Jones and Malone (1982) reported rapid deterioration of S/S inorganic waste products produced by commercial S/S vendors using ASTM standard test procedure D559-57 for compacted soil-cement mixtures (ASTM 1976).

## Effects of Radiation

Large doses of gamma radiation do not appear to affect setting properties or cause appreciable loss of strength or increased leachability in Portland cement solidified waste products (Neilson et al. 1987). Waste forms produced with 15.6 wt%, fully loaded (with radioactive cesium and strontium) resin beads, 21.7 percent water, and 62.7 percent Portland type I-II cement were subjected to high doses of gamma irradiation (4.0 to 5.7 × $10^8$ rads) and subjected to testing. Results of the tests are presented in Table 7.

TABLE 7. STABILITY OF PORTLAND CEMENT SOLIDIFIED WASTES TO HIGH DOSES OF GAMMA RADIATION

| Attribute | Waste* | Control | Irradiated (5 × $10^8$ rads) |
|---|---|---|---|
| Compressive strength (psi) | | | |
| | PF-7 | 20,200 ± 3,300 | 25,100 ± 9,900 |
| | PF-24 | 25,000 ± 5,000 | 22,800 ± 11,800 |
| Leachability index** for $^{134}Cs$ and $^{137}Cs$ (averaged) | | | |
| Distilled water | PF-7 | 10.3 | 9.35 |
| Distilled water | PF-24 | 10.5 | 10.0 |
| Sea water | PF-7 | 9.6 | 10.0 |
| Sea water | PF-24 | 10.4 | 10.9 |

* Fully loaded resin beads from prefilter no. 7 or no. 24.

** Leachability index is negative log of leaching rate (larger numbers leach less) (see American Nuclear Society (ANS) 1986).

## SECTION 4

## EFFECTS OF STANDARD ADMIXTURES ON PORTLAND CEMENT/POZZOLAN PRODUCTS

### INTRODUCTION

The properties of concrete in both the fresh and hardened state are typically modified by adding specific materials to the concrete mixtures. The additives, generally called admixtures, vary widely in chemical composition and may modify more than one property of the concrete mixture. It has been estimated that 88 percent of concrete placed in Canada and 70 percent placed in the United States includes one or more admixtures (Mehta 1987).

An understanding of the effects of common, well-studied admixtures gives a basis for assessing the possible range of effects of the S/S waste constituents on the concrete or pozzolanic matrix. American Concrete Institute (ACI) Committee 212 report Admixtures for Concrete (1963) contains a thorough report on the various effects of standard admixtures in concrete production, and ASTM Standard C 494-82 covers chemical admixtures for concrete (ASTM 1982). Vivian (1960) has written an excellent review of early work in this field. Rixon (1978), Schutz (1983), and Ramachandran (1984) have written more recently on chemical admixtures.

Admixtures fall broadly into three categories: 1) surface active molecules that work on the cement-water system immediately upon addition by influencing the surface tension of water and by absorbing onto the surface of cement particles; 2) set-controlling materials that ionize and affect the chemical reaction between the cement and the water only after several minutes or hours; and 3) finely ground, insoluble minerals, either natural materials or by-products, which immediately affect the rheological behavior of the fresh concrete, but whose chemical effects take several days or months to manifest themselves. A summary of commonly used concrete admixtures, and the applicable ASTM specifications, is given in Table 8.

Many admixture operations are dependent upon the conditions under which the admixtures are applied. For instance, triethanolamine has been shown to retard the hydration of $C_3S$ but to accelerate the hydration of $C_3A$ (Ramachandran 1976a). Lignosulfonate acts as a set retarder and, in the proper dosages, also increases strength (Young 1972). Admixture dosage is critical if the desired effects are to be attained. Parameters such as water content of the concrete formulation also play an important role. For example, amines and amino acids show accelerating properties at low water content, but become retarders if the water content is sufficiently increased.

### SURFACE-ACTIVE CHEMICALS (SURFACTANTS)

Surface active molecules are those which lower the surface tension of water; examples are soaps and detergents. See Camp et al. (1985) for a general discussion of surfactants. Two major uses of surfactants as concrete

TABLE 8. COMMONLY USED CONCRETE ADMIXTURES

| Primary function | Principal active ingredients/ ASTM specifications | Side effects |
|---|---|---|
| **Water-reducing** | | |
| Normal | Salts, modifications and derivatives of lignosulfonic acid, hydroxylated carboxylic acids, and polyhydroxy compounds. ASTM C 494 (Type A). | Lignosulfonates may cause air entrainment and strength loss; Type A admixes tend to be set-retarding when used in high dosage. |
| High range | Sulfonated naphthalene or melamine formaldehyde condensates. ASTM C 494 (Type F). | Early slump loss; difficulty in controlling void spacing when air entrainment is also required. |
| **Set-controlling** | | |
| Accelerating | Calcium chloride, calcium formate, and triethanolamine. ASTM C 494 (Type C). | Accelerators containing chloride increase the risk of corrosion of the embedded metals. |
| Retarding | Same as in ASTM Type A; compounds such as phosphates may be present. ASTM C 494 (Type B). | |
| **Water-reducing and set-controlling** | | |
| Water-reducing & retarding | Same as used for normal water reduction. ASTM C 494 (Type D). | (See Type A above.) |
| Water-reducing & accelerating | Mixtures of Types A and C. ASTM C 494 (Type E). | (See Type C above.) |
| High-range water-reducing & retarding | Same as used for Type F with lignosulfonates added. ASTM C 494 (Type G). | (See Type F above.) |

(Continued)

TABLE 8. (Concluded)

| Primary function | Principal active ingredients/ ASTM specifications | Side effects |
|---|---|---|
| **Workability-improving** | | |
| Increasing consistency | Water-reducing agents, [e.g., ASTM C 494 (Type A)]. | (See Type A above.) |
| Reducing Segregation | (a) Finely divided minerals (e.g., ASTM C 618). | Loss of early strength when used as cement replacement. |
| | (b) Air-entrainment surfactants (ASTM C 260). | Loss of strength. |
| **Strength-increasing** | | |
| By water-reducing admixtures | Same as listed under ASTM C 494 (Types A, D, F, and G). | (See Types A and F above.) |
| By pozzolanic & cementitious | Same as listed under ASTM C 618 and C 989. | Workability and durability may be improved. |
| **Durability-improving** | | |
| Frost action (air entraining) | Wood resins, proteinaceous materials, and synthetic detergents (ASTM C 260). | Strength loss. |
| Thermal cracking<br>Alkali-aggregate expansion<br>Acidic solutions<br>Sulfate solutions | Fly ashes and raw or calcined natural pozzolans (ASTM C 618); granulated and ground iron blast-furnace slag (ASTM C 989); condensed silica fume; rice husk ash produced by controlled combustion. (High-calcium and high-alumina fly ashes, and slag-Portland cement mixtures containing less than 60% slag may not be sulfate resistant.) | Loss of strength at early ages, except when highly pozzolanic admixtures are used in conjunction with water-reducing agents. |

Adapted from Mehta (1987).

admixtures are for reduction of the proportion of water in concretes (water-reducing admixtures) and for introducing large numbers of small air bubbles into the concrete mix (air-entrainment admixtures).

The materials that have been described and are generally available for use as water-reducing admixtures and set-controlling admixtures fall into five general classes:

1. Lignosulfonic acids and their salts.
2. Modifications and derivatives of lignosulfonic acids and their salts.
3. Hydroxylated carboxylic acids and their salts.
4. Modifications and derivatives of hydroxylated carboxylic acids and their salts.
5. Other materials, which include:
   (a) Inorganic materials, such as zinc salts, borates, phosphates, chlorides.
   (b) Amines and their derivatives.
   (c) Carbohydrates, polysaccharides, and sugar acids.
   (d) Certain polymeric compounds, such as cellulose ethers, melamine derivatives, naphthalene derivatives, silicones, and sulfonated hydrocarbons.

These admixtures can be used either alone or in combination with other organic or inorganic materials.

Water-Reducing Surfactants

When water is added to cement, the mixture does not become well dispersed because of the high surface tension of the water and the tendency of the cement particles to adhere and form flocs due to the attraction of oppositely charged edges of the cement particles. Water-reducing surfactants, or plasticizing surfactants, act by adsorbing to the surface charges of the cement particles so that the surface of the particle becomes hydrophilic and no longer attracted to other cement particles. Typical examples are citric acid, gluconic acid, and lignosulfonic acid. A better dispersed suspension of the cement paste means that 1) at a given water-cement ratio, the cement paste has a higher consistency and pumpability, 2) a lower water/cement ratio can be used to increase strength and lower permeability without a change in consistency, and 3) less cement can be used in the mix at the same water-cement ratio (more aggregate or waste loading).

Superplasticizers, sometimes called high-range water-reducing admixtures, are 3 to 4 times as effective as normal water-reducing admixtures (Malhotra 1979). They are long carbon-chain, high molecular weight anionic surfactants with a large number of polar groups. Adsorbed onto the cement particles, superplasticizers import a strong negative charge to their surface which helps lower the surface tension of surrounding water and greatly increases the fluidity of the system. The better dispersion of the cement particles does tend to cause their more rapid hydration, increasing the rate of set. Set retardants are sometimes added to offset this effect.

Water reducing admixtures may be useful in waste S/S with cement. The 5- to 10-percent water reduction made possible with normal plasticizers, or

the 25- to 30-percent water reduction with superplasticizers, increases the compressive strength and decreases the amount of void space and therefore the permeability of the final product for a given amount of cement. A more leach resistant and durable S/S waste product should result.

Air-Entraining Surfactants

These materials differ from the water-reducing surfactants in that the molecule contains a nonpolar portion along with the anionic, polar group. The surfactants coat the surface of small air bubbles and stabilize them so that they do not coalesce and separate from the concrete during mixing or setting. They also coat the charged surfaces of the cement particles, causing them to become hydrophobic, which can cause a lower rate of hydration (delayed setting) at higher doses. Doses of 0.05 percent by weight of cement are often sufficient to incorporate 0.05- to 1-mm bubbles into the cement. Air contents of 3 to 8 percent of the total mix are recommended for the production of frost-resistant concretes, depending upon the size of aggregates (larger aggregates require less entrained air) and the degree of exposure (more severe exposure requires more air entrainment).

SET-CONTROLLING CHEMICALS

The early events in the setting and hardening of concrete involve the dissolution, ionization, and hydration of sparingly soluble chemical components. Any added soluble chemical that interferes with any of these processes may delay or accelerate the rates of hydration of the various cement components, depending on its relative effect on all of the components present.

Hydrating cement mixtures are composed primarily of acidic anions (silicate and aluminate) and a base cation (calcium). The solubilities of each of these ions is dependent upon the concentrations of the other ions in solution. Since most chemical admixtures which affect the rate of hydration of cement pastes ionize in water solution, their presence is believed to alter the type and concentrations of the ionic constituents in the solution phase, which influences the dissolution and crystallization of the cement compounds. The following guidelines are proposed by Joisel (see Mehta 1987):

1. Accelerators must promote the dissolution of the calcium cations and anions from the cement particles. The most effective accelerator would promote the dissolution of the least soluble constituent (silicate).

2. Retarding admixtures must interfere with the dissolution cations (calcium) and anions, preferably that anion which has the highest rate of dissolution during early hydration (i.e., the aluminate ions).

3. A strong cation (e.g., $K^+$ or $Na^+$) will reduce the solubility of the calcium cation but will accelerate the solubility of the anions (silicate and aluminate). At lower concentrations the former effect is dominant; at the higher concentrations, the latter.

4. A strong anion (e.g., $Cl^-$, $NO_3^-$, or $SO_4^=$) reduces the solubility of the cement anions (silicates and aluminates) but tends to increase the mobility of the calcium cation. At low concentrations the former effect appears dominant; at higher concentrations, the latter.

From these considerations, it can be seen that the net effect of any admixture on the rate of hydration depends on the balance of its effect on the type and concentration of ions contributed by the admixture. For instance, small concentrations of the salt of a weak base and a strong acid (e.g., $CaCl_2$), or a strong base and a weak acid (e.g., $K_2CO_3$), will tend to retard the solubility of the calcium and aluminate ions. At higher concentrations, the accelerating effects of the increased solubilities of silicate and aluminate ions predominate, and the salts become accelerators.

Calcium chloride at 1 to 3 percent the weight of cement is the most common accelerator and has been widely studied (Ramachandran 1976b, 1984). Some of the properties of hydrating cement paste which are influenced by calcium chloride are summarized in Table 9. Other salts that accelerate cement paste hydration are sodium fluoride, aluminum chloride, sodium aluminate, and potassium carbonate. Setting time as short as 15 to 30 seconds can be obtained. Some ready-to-use mixtures have an initial set of 1 to 4 minutes with a final set of 3 to 10 minutes.

Organic acids and their weakly acid soluble salts act as accelerators because they increase the dissolution of calcium. Calcium formate and formic acid are common accelerators. Triethanolamine is an active accelerator because of its ability to accelerate the hydration of $C_3A$ and the formation of ettringite; however, it also retards the hydration of $C_3S$ and reduces the rate of strength development. Comparison of the development of strength and of setting times for some common accelerators is illustrated in Table 10.

Set retarders also work by other mechanisms. Surfactants such as gluconates and lignosulfonates delay bond formation among the hydration products, delaying crystallization (Hansen 1959, Young 1976). Other retarders such as sodium salts of phosphoric, boric, oxalic, and hydrofluoric acid form insoluble calcium salts which precipitate out and form insoluble and impermeable barriers around the cement particles. This slows hydration considerably and retards set and strength development.

Early strengths are lower in specimens with retarders than those in reference specimens, as would be expected. However, at longer periods the specimens containing retarders generally have higher compressive strength and comparable flexural strength (see Tables 11 and 12). The drying-shrinkages of specimens containing retarders are also comparable to those reference specimens without admixtures. Soluble calcium salts which may provide anions that adsorb onto the calcium hydroxide crystal surfaces cause a retarding effect (e.g., calcium nitrate).

Scholer (1975) studied the effects of 65 different chemical compounds and three ASTM Type D admixtures on the fresh and hydrated condition of cement pastes. Setting time, molecular configuration related to the effectiveness of the retarders, oven-dry shrinkage, nonevaporable water, and specific surface area were determined for each admixture. Long-term shrinkage of concrete was

TABLE 9. SOME OF THE PROPERTIES INFLUENCED BY THE USE OF CALCIUM CHLORIDE ADMIXTURE IN CONCRETE

| Property | General effect | Remarks |
|---|---|---|
| Setting | Reduces both initial and final setting | ASTM standard requires that initial and final setting times should occur at least 1 hour earlier with respect to reference concrete. |
| Compressive strength | Increases significantly the compressive strength in the first 3 days of curing (gain may be about 30-100%). | ASTM requires an increase of at least 125% over control concrete at 3 days. At 6-12 months, requirement is only 90% of control specimen. |
| Tensile strength | A slight decrease at 28 days. | |
| Flexural strength | A decrease of about 10% at 7 days. | This figure may vary depending on the starting materials and method of curing. The decrease may be more at 28 days. |
| Heat of hydration | An increase of about 30% in 24 hours. | Total amount of heat at longer times is almost the same as that evolved by reference concrete. |
| Resistance to sulfate attack | Reduced | Can be overcome by use of Type V cement with adequate air entrainment. |
| Alkali-aggregate reaction | Aggravated | Can be controlled by use of low-alkali cement or pozzolana. |
| Corrosion | Causes no problems in normal reinforced concrete if adequate precautions taken. Dosage should not exceed 1.5% $CaCl_2$, and adequate cover to be given. Should not be used in concrete containing a combination of dissimilar metals or where there is a possibility of stray currents. | Calcium chloride admixture should not be used in prestressed concrete or in a concrete containing a combination of dissimilar metals. Some specifications do not allow use of $CaCl_2$ in reinforced concretes. |

(Continued)

TABLE 9. (Concluded)

| Property | General effect | Remarks |
|---|---|---|
| Shrinkage and creep | Increased | |
| Volume change | Increase of 0-15% reported. | |
| Resistance to damage by freezing and thawing | Early resistance improved. | At later ages may be less resistant to freezing and thawing. |
| Watertightness | Improved at early ages. | |
| Modulus of elasticity | Increased at early ages. | At longer periods almost same with respect to reference concrete. |
| Bleeding | Reduced | |

Adapted from Mehta 1986, p 263.

TABLE 10. EFFECT OF ACCELERATORS TRIETHANOLAMINE, CALCIUM FORMATE, AND CALCIUM CHLORIDE ON THE RATE OF HARDENING AND COMPRESSIVE STRENGTH OF CONCRETE

| Admixture | Rate of use (wt % of cement) | Compressive strength (psi)* | | Time of final setting (hr) |
|---|---|---|---|---|
| | | 7-day | 28-day | |
| None | -- | 4,810 | 6,710 | 12.0 |
| Triethanolamine | 0.025 | 5,160 | 6,670 | 9.7 |
| None | -- | 4,430 | 6,130 | 12.4 |
| $CaCl_2$ | 2.00 | 4,490 | 5,615 | 4.0 |
| Calcium formate | 0.05 | 4,630 | 6,275 | 8.9 |
| Calcium formate | 1.00 | 4,910 | 6,485 | 8.4 |
| Calcium formate | 1.50 | 5,200 | 6,585 | 7.6 |
| Calcium formate | 2.00 | 5,330 | 6,610 | 6.7 |

Source: Rosskopf, Linton, and Peppler 1975.
* To convert pounds (force) per square inch to megapascals, multiply by 0.006894757.

TABLE 11. COMPRESSIVE STRENGTH (CS) OF MORTARS CONTAINING RETARDERS

| Retarder | Admixture (wt % of cement) | 1 day CS | 2 days CS | 7 days CS | 28 days CS | 90 days CS |
|---|---|---|---|---|---|---|
| None | --- | 11.8 | 21.6 | 37.8 | 45.3 | 53.9 |
| Sucrose | 0.5 | 10.0 | 21.6 | 47.1 | 59.8 | 62.8 |
| Sucrose | 1.0 | 1.3 | 11.8 | 43.2 | 53.9 | 60.3 |
| Glucose | 1.0 | 7.1 | 23.7 | 36.8 | 53.4 | 58.8 |
| Glucose | 2.0 | 1.0 | 8.3 | 27.9 | 45.6 | 51.5 |
| Phosphoric acid | 0.5 | 7.1 | 18.1 | 48.1 | 60.8 | 71.1 |
| Phosphoric acid | 1.0 | 2.2 | 14.7 | 45.1 | 64.7 | 74.0 |
| Phosphoric acid | 2.0 | 1.2 | 12.3 | 44.1 | 60.3 | 69.6 |

Note: All values given in megapascals (1 MPa = 145 psi).

TABLE 12. FLEXURAL STRENGTH (FS) OF MORTARS CONTAINING RETARDERS

| Retarder | Admixture (wt % of cement) | 1 day FS | 2 days FS | 7 days FS | 28 days FS | 90 days FS |
|---|---|---|---|---|---|---|
| None | --- | 3.5 | 4.8 | 7.6 | 8.6 | 8.8 |
| Sucrose | 0.5 | 2.9 | 5.0 | 7.8 | 8.1 | 8.2 |
| Sucrose | 1.0 | 0.4 | 2.8 | 7.6 | 7.9 | 9.4 |
| Glucose | 1.0 | 2.0 | 4.9 | 6.7 | 7.5 | 7.9 |
| Glucose | 2.0 | 0.1 | 2.5 | 5.5 | 7.4 | 7.9 |
| Phosphoric acid | 0.5 | 1.8 | 4.2 | 7.6 | 8.3 | 8.1 |
| Phosphoric acid | 1.0 | 0.5 | 3.3 | 7.6 | 8.5 | 8.6 |
| Phosphoric acid | 2.0 | 0.2 | 3.2 | 7.7 | 7.5 | 8.0 |

Note: All values given in megapascals (1 MPa = 145 psi).

not appreciably affected. He concluded that strong retarders have a molecular composition that includes many oxygen atoms that are constrained to approach each other closely. Hydroxyl, carboxyl, and carbonyl are all affective, but carbonyl is especially strong in its influence on set time. These groups are presumed to exert a polarizing influence that contributes to the strong adsorption on the solid surfaces. More weakly electronegative atoms on the molecule do not have the same effect as oxygens.

The retarding effects of sugars on cement hydration were studied in detail by Thomas and Birchall (1983). They compared different sugars using solution analysis, colorimetry, calcium binding ability, and alkaline stability. The best retarders were sucrose and raffinose, which also have a remarkable ability to solubilize cement constituents and give rise to dramatic increases (10 to 20 times) in the amount of silica present in solution. However, no evidence for sucrose-silicate complexes was found using $^{13}C$ and $^{29}Si$ nuclear magnetic resonance (NMR) analysis. The authors relate the retarding action of sugars in terms of adsorption onto and the poisoning of hydrating surfaces.

## MACRO-DEFECT-FREE (MDF) CEMENT PASTES

A new class of high-strength cement materials, called macro-defect-free (MDF) cements, achieves higher strengths by the absence of the relatively large voids or defects which are usually present in conventionally mixed cement pastes (Roy 1987). In this process, 4 to 7 percent of one of several water-soluble polymers, such as hydroxypropylmethyl cellulose, polyacrylamide, or hydrolyzed polyvinylacetate, is added as a rheological aid to permit cement to be mixed with very low water-cement ratios. Coupled with high-shear mixing, the method produces a plastic, cohesive mixture that can be shaped by extrusion or other forming techniques. Set times range from minutes to hours. The polymers also appear to be a significant structural component. Where ordinary cement mixtures have compressive strengths of around 40 MPa (5,800 psi), MDF cements can have a compressive strength as high as 100 to 300 MPa (14,500 to 43,500 psi).

## MINERAL ADMIXTURES

Mineral admixtures are usually siliceous materials that are added to the cement mixtures in relatively high proportions, for example 15 to 100 percent of the weight of cement. Typical admixtures are pozzolanic (e.g., volcanic glass, silica fume, rice husk ash, and Class F fly ash), cementitious (granulated iron blast-furnace slag, hydraulic limes, and slag cements), or both (high-calcium Class C fly ash). Other non-setting mineral admixtures are finely divided quartz; siliceous sands; dolomitic and calcitic limestones; marble, granite, and other rock dusts; and hydrated dolomitic or high-calcium lime. Of these, fly ash, kiln dusts, and blast-furnace slags are by far the most commonly used mineral admixtures.

### Pozzolanic Admixtures

Proposed minimum standards for fly ash used as a cement admixture are given by Idorn and Thaulow (1985). For Class F fly ashes, the major constituent, $SiO_2$, should comprise a minimum of 50 percent of the material by weight; $Al_2O_3$ should comprise 20 to 35 percent; and CaO, 2 to 8 percent. Between 60 and 85 percent of the volume of the fly ash should be noncrystalline or glass. Pozzolanic materials, by definition, react with hydrated calcium hydroxide to form C-S-H,

$$\text{Pozzolan} + CH + H_2O \xrightarrow{\text{slow}} 2\text{C-S-H}$$

while in Portland cement the reaction is

$$C_3S + 3H_2O \xrightarrow{\text{fast}} \text{C-S-H} + 2CH$$

The addition of pozzolan to Portland cement then slows the overall hydration rate of the mixture as the pozzolan reacts with the free lime (CH), which is liberated from the Portland cement hydration reaction. In consuming the free lime, the pozzolan has been shown to fill the large capillary spaces in which the calcium hydroxide crystals normally form, thus improving the strength and impermeability of the system. Reductions in permeability of up to 3 orders of magnitude are common (Marsh et al. 1985). The reduction in permeability

resulting from pozzolan addition is thought to be the reason for lower leaching losses, although a certain amount of additional binding of heavy metals by the active silica (thus preventing their leaching) may be responsible for some of the effect (Coté and Webster 1987, Van der Sloot et al. 1987).

The setting and strength characteristics of Portland cement products containing Class C (high lime) fly ash were studied by Baker and Laguros (1985). Class C fly ash from western coal has not been studied to such an extent as Class F low-lime, eastern fly ash. They found that setting time and development of compressive strength were delayed, but after 1 week, the compressive strength of all mixtures containing Class C fly ash (at 20 to 50 percent replacement of cement) surpassed the cement-only controls. A decrease in the level of calcium hydroxide was not seen (as is typical for mixes with Class F fly ash). They suggested that the retardation mechanism may be associated with the high levels of ettringite formed early in the hydration process and its subsequent conversion to monsulfoaluminate. A simple heat of hydration test was presented to help explain the observed strength gains. High- and low-calcium fly ash-cement mixtures were also compared by Grutzeck et al. (1985), who found similar results, with high-calcium mixtures retarding early strength development to a larger extent.

The primary commercial advantage of mineral admixtures is to lower the amount of cement required to attain a given strength in the final structure. Adding a mineral admixture to a given cement mixture produces multiple effects: improved workability, retardation of set and reduced thermal cracking, increased ultimate strength, increased impermeability, and better durability to chemical attack such as by sulfate (Berry and Malhotra 1982).

The use of mineral additives has been studied as a method of reducing the general permeability of cured cement matrices containing low-level nuclear waste (Carlson 1987). Improved admixtures have exhibited markedly superior leach resistance, even for very mobile, radioactive cesium.

## Soluble Silicate Admixtures

Soluble silicates have been added to waste S/S systems and were a part of an early patented process (Jones and Malone 1982). Recent studies (Davis et al. 1987) have confirmed the benefit of soluble silicate addition. These studies showed that added silicate levels up to 5 percent of the weight of the waste resulted in a 25- to 90-percent reduction in the metal ion concentration of an acid (pH 5) leachate. In S/S waste products including aggregates, the larger the aggregate, the larger the effect of added silicate.

Effects of soluble silicates have traditionally been credited to the formation of metal silicates that are more stable and less soluble than metal hydroxides (Falcone et al. 1984). However, data of Davis et al. (1987) using a simple penetration model suggested that the primary influence of the soluble silicate is due to a reduction in permeability and improved waste integrity. The soluble silicate apparently reacts with the free lime produced in the normal cement hydration process, decreasing the porosity and thus the permeability in a manner similar to the effects of added reactive silicates in fly ash or blast furnace slags, as discussed above.

POSSIBLE MECHANISMS OF THE EFFECTS OF
ORGANIC COMPOUNDS ON PORTLAND CEMENT PRODUCTS

The variables associated with the use of admixtures in concrete production are numerous. These variables are magnified when a toxic waste is being considered for S/S. The variable and complex composition of a typical hazardous waste increases the complexity of evaluating the S/S process. The potential mechanisms for chemical influence of organic materials on Portland cement must be studied and understood. However, even then, the prediction of the effects of specific levels of individual waste constituents on final product characteristics will be difficult at best (Hansen 1959).

An example of the complexity surrounding the interaction of organics with cement matrices has been reported by Cartledge et al. (1987). Several phenols with different substituents on the aromatic ring were solidified with types I and III Portland cement at several concentrations up to 20 percent by weight of cement. At various times of cure, the products were extensively investigated using water and solvent extraction, optical and scanning electron microscopy, X-ray diffraction, and NMR spectroscopy. Although all phenol derivatives were readily leached from all specimens, significant differences in physical characteristics (such as setting times and compressive strengths), the morphology of the cement matrix, and the nature of the crystalline phases were observed. The authors state that even subtle differences in the structure of the organic may result in major differences in the nature of the cement-organic interaction.

Several conceptual models of the interference mechanisms of organics on cementitious and pozzolanic are addressed below. These potential mechanisms include interference via adsorption, complexation, precipitation, and nucleation (Young 1972, 1976).

Adsorption

One possible interfering mechanism is adsorption of added molecules onto the surface of the cement particles, thus blocking the normal hydration reactions. Studies by Young (1972) have shown that the retarding effect of organic compounds is related to the strength of their adsorption on metastable, hexagonal, calcium aluminate hydrates. In this way the organic compound is thought to inhibit crystal growth and conversion to $C_3AH_6$. The inhibiting effect roughly correlates with the number of hydroxyl (e.g., alcohols, glycerol, or sugars), carboxylic (e.g., acids, acetic acid, citric acid), and carbonyl (e.g., ketones, dimethyl ketone, methyl ethyl ketone) groups in the organic molecule. Hansen (1952, 1959) noted the effect of two particular families of organic compounds (lignosulfonic acid derivatives and hydroxylated carboxylic acids) on setting reactions. Lignosulfonates are strongly adsorbed onto $C_3A$ (Kawoda and Nishiyama 1960, Blank et al. 1963). The adsorption of calcium lignosulfonate onto $C_3A$ results in a relatively thick film or layer, which is indicative of a chemical reaction involving the organic and $C_3A$ hydration production. Adsorption of the hydroxylated carboxylic acids, such as gluconate or oxalates, involves simultaneous $Ca^{+2}$ ion adsorption to the carboxyl groups and adsorption of silicate ions by the hydroxyl groups (Figure 3a). Taplin (1962) found retarding effects from

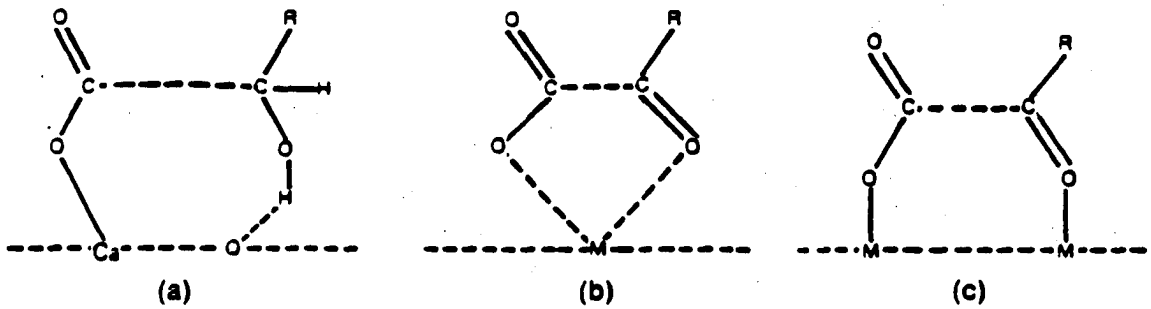


Figure 3. Possible adsorption mechanisms of organic admixtures onto surfaces. (Note: C, H, O, M, R = carbon, hydrogen and oxygen atoms, metal, ions, and rest of the molecule, respectively.) (Source: Hansen 1952.)

aliphatic and aromatic dicarboxylic acids (e.g., maleic acid). In alkaline solutions where maleic acid has no hydroxyl group for hydrogen bond adsorption, chelation may be the mechanism of set retardation (Figures 3b and 3c).

The overall retardation of hydration can be the result of an initial acceleration followed by retardation. This effect has been observed with $C_3A$ in the presence of sugars and also for $C_3S$ hydration in the presence of lignosulfonates (Seligmann and Greening 1964, Chatterji 1967, Daugherty and Kowalewski 1968). The organic compound, when adsorbed onto the cement clinker, first assists in hydration, and later retards hydration by adsorption onto the hydration product. These effects are altered by the presence of sulfate ions, which increases the formation of ettringite and lowers that of $C_3AH_6$ because the adsorption of calcium lignosulfonate or sugar onto $C_3A$ is reduced. The morphology of ettringite can also be modified by the presence of sugars (Daugherty and Kowalewski 1968).

The adsorption of organic retarders by $C_3S$ and $C_2S$ in an aqueous solution is much weaker than adsorption by $C_3A$. However, the amount adsorbed (3 to 5 mg/g on $C_3S$ and 1 to 2 mg/g on $C_2S$) is sufficient to form a multilayer film on the $C_3S$ and $C_2S$. The occurrence of calcium ion concentrations in the aqueous solution (Figure 4) soon after the addition of retarders indicates that the retarding reaction is not with $C_3S$ or $C_2S$, but rather with other hydration products. Strong retarders can extend indefinitely the hydration of $C_3S$. Addition of hydrated $C_3S$ or calcium hydroxide can curtail the retarder effect and permit hydration.

Although data indicate the stronger adsorption of organic compounds by $C_3S$, the organic retarders act primarily by retarding the $C_3S$ hydration. Therefore, most of the retarder is adsorbed by $C_3A$, but sufficient amounts must be present to be adsorbed by $C_3S$ to actually retard the set. In some instances, differential adsorptive properties and hydration dynamics make it advantageous to delay addition of the retarding agent (Bruere 1963, 1966). When addition of the retarder is delayed, the adsorption of $C_3A$ is reduced, and adsorption on $C_3S$ in increased. The initial set is not hindered; however, the retardation effect on the final set is increased.

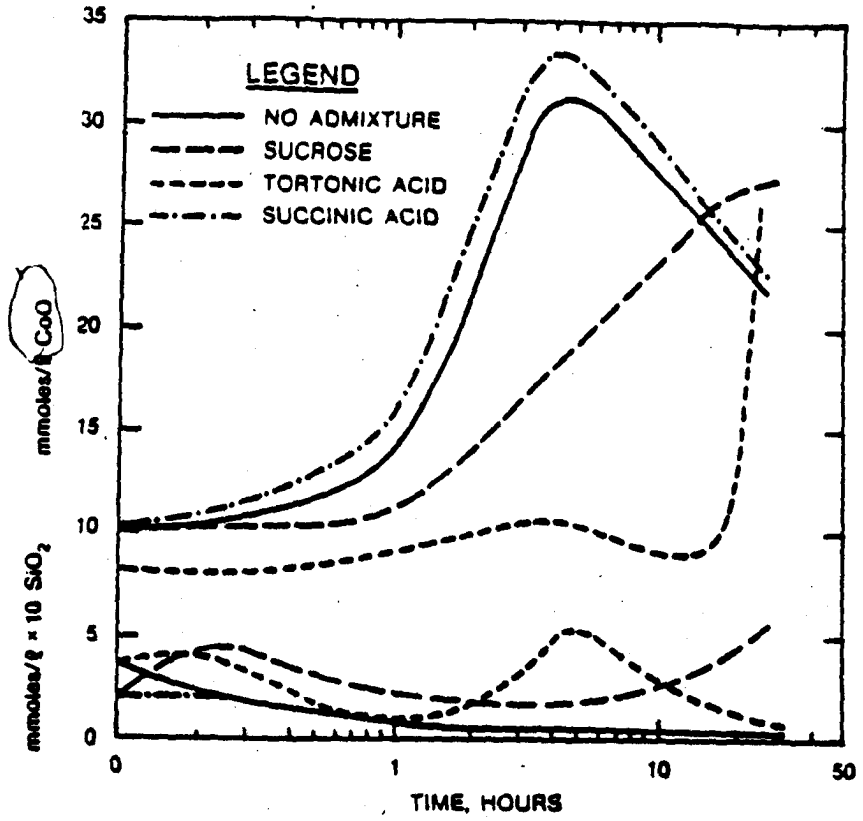


Figure 4. Influence of some organic admixtures on soluble CaO and $SiO_2$ during early hydration of tricalcium silicate. (1 wt % additions) (Source: Young 1972.)

Although adsorption of organic retarders is primarily on $C_3A$, retardation is due to adsorption on $C_3S$. There is no evidence of adsorption on $C_3S$. Nor is there evidence of adsorption onto anhydrous surfaces. Organic additives can have an important bearing on reaction rates during cement hydration. However, adsorption is not the only conceptual model that can account for set retardation.

## Complexation

Taplin (1962) related the retarding activity of the organic compounds he studied to the proximity of oxygen atoms to carbon atoms. He observed that compounds with oxy-functional groups in proximity to each other were more effective as retarders. He theorized that chelation to metal ions was an important factor in set retardation. Calcium ions can chelate with various hydroxyl or carboxylic acids, but the retarder or accelerators (respectively) are so dilute that complexation of the calcium could not be an important factor (Young 1972).

The effects of complexing calcium are more significant when the additive to affected-ion ratio is large, and when the effected ion is important to the setting system. Such would be the case for the aluminate and ferrite ions.

Several workers (Kalousek et al. 1943, Suzuki and Nishi 1959, Roberts 1967) have shown that the addition of sucrose increases the concentration of alumina and calcium ions to above-normal levels. Experiments (Young 1972) with $C_3A$ indicate that 1 wt % additions of sucrose, succinic acid, or tartaric acid increase the amounts of calcium and alumina in solution at first, but concentrations later decrease to normal or below normal. Silica concentrations are also increased when additives that affect alumina concentrations are used. Apparently, conditions in a cement paste are favorable for aluminate, ferrite, and silicate ion complexation. It is possible that complexation delays the formation of hydration products. When cement crystal-forming ions are kept in solution by complexation, hydration barriers are established that retard the set.

## Precipitation

The formation of insoluble hydration products by additives reacting with cement compounds has been reported conceptually not to be a realistic mechanism of admixture interference (Young 1972). Certainly, the formation of insoluble compounds could impede water transport, solubility, and subsequent hydration reactions. However, if retardation is due to precipitation, then the process should be nonselective. In this case, $C_3S$ and $C_3A$ should both release calcium ions, and the resulting effect on setting should be equally weighted in regard to $C_3S$ and $C_3A$ activity. Regardless, the retardation is known to be related primarily to $C_3A$ content (Young 1972).

However, if the precipitation reaction involves the hydration product itself, the precipitated product would preferentially be produced at the surface of the hydrating material. This is thought to be the mechanism of action of phosphates, borates, and oxalates (Mehta 1987).

## Nucleation

The inhibition of nucleation of crystalline calcium hydroxide by soluble silica, which is present in small quantity, is believed to be the self-retarding set feature of $C_3S$ hydration. Growth of a crystalline matrix is retarded by the adsorbed silica ions when a C-S-H layer results in a diffusion barrier to calcium hydroxide. Eventually, crystal growth results in the adsorbed silica being trapped in the crystalline matrix as the hydration process continues. Prismatic growth of calcium hydroxide results from differential adsorption of silica on calcium hydroxide crystal faces (Young 1972).

It is postulated that organic retarders act much the same as silica ions in being adsorbed onto the calcium hydroxide nuclei. However, as the name implies, organic retarders are much more effective in being adsorbed and more completely cover the crystal growth surfaces. This results in part from more retarders being solubilized. The resulting retardation of crystal growth results in more crystallite nuclei forming in the saturated solution. The net effect of crystal growth on these many nuclei is responsible for the acceleration of hydration following the retardation period (Young 1976). With about 1 percent of a strong retarding agent, $C_3S$ hydration is completely inhibited. Additions of prehydrated $C_3S$ can overcome the effect of the organic retarder, lending support to an adsorption/nucleation model.

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## SECTION 5

## EFFECTS OF WASTES ON CEMENT/POZZOLAN PROCESSES

### INTRODUCTION

Acids, salts, bases, and organic materials may be present in hazardous wastes singly and in combinations. As such, predicting their single and collective effect on the durability and containment of the typical cement and pozzolan S/S processes presents a difficult problem for process designers and regulatory agencies. Long-term effects are especially difficult to estimate because subtle differences in environmental parameters can have significant long-term consequences on the integrity of the S/S waste.

Early concerns about the effects of industrial wastes in the environment on concrete corrosion are described by Biczok (1967). He lists industrial wastes that are harmless to concrete and mortar products:

1. Brines containing bases but no sulfates.
2. Potassium permanganate, occurring at fermenting and purification installations.
3. Sodium carbonate (soda) and potassium carbonate (potash).
4. Bases (caustic lyes of potash and soda, lime and ammonia), provided their concentration is not excessively high.
5. Oxalic acid occurring at tanneries.
6. Mineral oils and petroleum products (benzene, kerosene, cut-back oil, naphtha, paraffin, tar), as long as these contain no acids that can continue to remain in the products after chemical treatment.

Industrial wastes deemed to be aggressive and detrimental to concrete and mortar products are

1. Water containing gypsum, e.g., that used for quenching coal slag.
2. Ammonia salts.
3. Hydrochloric acid, nitric acid, and sulfuric acid.
4. Chlorine and bromine.
5. Acetic acid.
6. Pure alcohol (in certain cases only, e.g., absolute alcohol, owing to the dehydrating effect).
7. All sulfur and magnesium salts.
8. Hydrogen sulfide and sulfur dioxide gas.
9. Animal fats.
10. Salts of strong acids, formed with magnesium, zinc, copper, iron, aluminum, and other metals, the hydroxides of which are poorly soluble in water.
11. Vegetable, animal, and some acidic.

Biczok (1967) also suggests that besides the wide variety of salts listed above, the salts formed by weak bases and strong acids, such as $ZnSO_4$, $ZnCl_2$,

$Zn(NO_3)_2$, $FeSO_4$, $FeCl_2$, $Fe(NO_3)_3$, $CuSO_4$, $CuCl_2$, $Cu(NO_3)_2$, $Al_2(SO_4)_3$, $AlCl_3$, and $Al(NO_3)_3$, may be regarded as potentially aggressive. Furthermore, chlorine, bromine, and iodine are considered to be aggressive. If sugar, molasses, spirit, ammoniac, salt, strong acids or animal fats are present, expert opinion based on literature information, practical experience, or previous analyses should be obtained.

ORGANIC WASTES

A few studies have been directed toward the effects of typical organic waste components upon cement and pozzolan S/S processes. However, most of these studies did not include extensive testing of the resultant S/S waste products. Strength and leaching tests are complicated by the fact that the setting waste/binder matrix is a dynamic system whose properties will vary considerably over the first few weeks or months after they are produced. For instance, many of the materials that retard the initial setting of cement and pozzolan products will result in higher ultimate strength and containment properties of the solid (see Roberts 1978 and Smith 1979). A further complication is that interference effects can vary with cement- or pozzolan-to-water ratio, interactions with other waste components, and even with order, type, and timing of mixing.

Portland Cement Mixtures

The mechanisms by which organic constituents interact with cement matrices is important to predicting the long-term effects of S/S waste technologies. Ideally, long-term stability could be assayed using short-term testing techniques. Several testing techniques such as X-ray diffraction and electron and optical microscopy are necessary to assess the effects of waste constituents on the complex chemistry of cement setting reactions (Tittlebaum et al. 1986). There is also some information that the chemical matrix of inorganic binders can increase the solubility and reactivity of organic waste components (Wiedemann 1982). Some organics have greater water solubility and reactivity in a strong acid environment, while others are more reactive under strong alkaline conditions. Phenols, for example, are transformed to more reactive phenolates in basic pHs. The water solubilities of some compounds like kepone also vary with pH.

Clark et al. (1982a,b) studied selected cement media to determine interference and retention capacities of an oil and a synthetic organic liquid mixture (see Table 13). Media used in the study included Portland type I cement, vermiculite plus Portland type I cement, Nutek 380-cement process (Nuclear Technology Corporation), Portland type I cement with sodium silicate and an oil emulsifier, Delaware Custom Materials' (DCM) cement process, and U.S. Gypsum's Envirostone Process. All of the processes were applied to stabilization of oil (Inland Vacuum Industries No. 19 Vacuum Pump Oil), but only the Nutek and Envirostone processes were applied to the synthetic organic liquid. The solidified waste forms were evaluated only in terms of being free-standing, monolithic solids and having no free liquids following solidification. Other preliminary testing was conducted only on selected specimens--immersion testing (72 hours soak to check for loss of integrity), vibratory shock testing, and flame testing. Approximately 100 subjectively determined formulations were prepared and examined.

TABLE 13. COMPOSITION OF SIMULATED ORGANIC LIQUID WASTE USED BY CLARK ET AL. (1982)

| Component | Volume % | Component formula |
|---|---|---|
| Methanol | 22 | $CH_3OH$ |
| Ethanol | 22 | $C_2H_5OH$ |
| Acetone | 9 | $CH_3COCH_3$ |
| Isopropanol | 5 | $CH_3CHOHCH_3$ |
| Diethyl ether | 9 | $C_2H_5OC_2H_5$ |
| Ethyl acetate | 4 | $C_2H_5COOCH_3$ |
| n-Hexane | 9 | $CH_3(CH_2)_4CH_3$ |
| Benzene | 4 | $C_6H_6$ |
| Toluene | 4 | $C_6H_5CH_3$ |
| Acetonitrile | 4 | $CH_3CN$ |
| 1,2-Ethylene dichloride | 4 | $C_2H_4Cl_2$ |
| Chloroform | 4 | $CHCl_3$ |

In general, loadings of the oil up to 30 percent of the volume of final product yielded free-standing solids that passed the immersion test. However, loadings of over about 10 percent of the organic liquid waste cause loss of physical integrity and the formation of free liquid from the solidified product. The 10 formulations judged by Clark et al. (1982) to have the highest loadings and which gave satisfactory monoliths using their criteria (given only as "reasonable physical integrity") are given in Table 14.

Telles et al. (1984) presented a review of available treatment processes used in the S/S of organic wastes. Table 15 summarizes the organic contaminants reported and the S/S materials covered in their review. Telles et al. (1983) presented some unpublished results from studies involving fixation of synthetic sludges containing chromium, cadmium, lead, and nitrocellulose. The fixatives were polysilicates and amine-cured epoxides. Inorganic dry sludge containing Pb, Cr, and Cd was treated with polysilicates and with polysilicates in combination with Portland cement and fly ash. An organic wet sludge containing nitrocellulose was also treated with polysilicates. The fixing agents were mixed in five compositions that included variable amounts of the following: sodium silicate, Portland cement, fly ash, $CaCl_2$, $HNO_3$, and NaOH. The mixtures of the various compositions were allowed to cure from 3 to 4 days and then were subjected to extraction procedure (EP) toxicity testing to determine the effectiveness of the fixation mechanism in regard to leaching of contaminants.

TABLE 15. ORGANIC CONTAMINANTS AND FIXATIVES USED IN EXPERIMENTAL STUDIES

| Contaminants | Fixatives |
|---|---|
| PCBs | Cement-based processes/silicates, polyesters, limes, polymer-cements |
| Kepone | Cement-based/silicates, sulfur, epoxide |
| Various chlorinated aliphatic and aromatic hydrocarbons | Cement-based/proprietary organic polymers, gypsum |
| Phenol, toluene | Cement-based/silicates |
| Ion-exchange resins | Cement-based/silicates, polymer-cements, epoxides, polyester, asphalt, polyethylene gypsum, ureas |
| Various pesticides | Polymer-cements, polybutadiene/polyethylene (surface encapsulation) |
| Oils | Cement-based/silicates, polymer cements, proprietary polymers, ureas |
| Mixed solvents* | Gypsum, polymer-cements, cement/silicates |
| Nitrocellulose | Cement/silicate, epoxide |
| Dioxin | Calcium oxide, asphalt, Portland cement, asphalt/sulfur |

Source: Telles et al. 1984.
* A mixture comprised of the following: alcohols, ketones, aldehydes, esters, ethers, alkanes, acetonitrite, and chlorinated cleaning solvents.

Acceptable leaching performance for calcium-polysilicate fixed contaminants was only obtained in these tests at or below the 0.2-percent weight (2,000 ppm) loading of Pb. Mixtures with Cd, Cr, and Pb were also managed at the 0.2-percent weight loading. Results of tests on contaminants fixed with sodium silicate and Portland cement indicated that samples with contaminant loadings as high as 24,000 ppm (2.4 percent) were able to meet EPA toxicity criteria. Organic sludges containing nitrocellulose were not acceptably stabilized using polysilicates and Portland cement.

Buchler (1987) studied the adsorption of water-soluble organic molecules onto a tetramethyl ammonium chloride (TAC) derivative of Wyoming bentonite clay as a possible S/S pretreatment method. The hydrophobic nature of the TAC compared with the normal sodium cation makes the clay more receptive to organic molecules, especially polar organics. The strength of the adsorption was inversely proportional to the temperature so that higher leaching losses would be expected in the summer months. Treatment of 1,000-ppm phenol wastes at 20° C produced an effluent containing 150 ppm phenol; effectiveness decreased at lower phenol concentrations and higher temperatures. Glucose, glycine, and dextran were also tested but showed a lower adsorption pattern.

In a similar study, Sheriff et al. (1987) used activated charcoal as well as tetra-alkylammonium substituted bentonite clays as prestabilization adsorbents before incorporating them in a number of cementitious matrices. They found a clear trend between the degree of polarity of substituted phenols and their ability to be absorbed by the substituted clays. Activated charcoal effectively adsorbed up to a 1,000-ppm concentration of the phenols and chlorinated phenols. Leachability and physical strength measurements are to be carried out on the S/S products.

Newton (1987) described an organic S/S system in which a fast sorption interaction occurs between a sodium magnesium fluorolithosilicate and/or sodium bentonite that has been reacted with a quaternary ammonium compound. Other admixtures are also added to decrease the permeability of the final product and to improve mixing and leaching characteristics. The formulation is being sold as a proprietary S/S agent that is claimed to have been successful in treating a variety of organic-bearing wastes.

An amorphous silicate glass foam of 8 to 200 mesh spheres with numerous cells has been suggested to be the universal sorbent material (Temple et al. 1978). The material is free-flowing granules with a loose bulk density of 2 lb/cu ft (32 kg/cu m). The material is said to be an excellent absorbent for acid, alkalies, alcohols, aldehydes, arsenates, ketones, petroleum products, and chlorinated solvents. It absorbs more than 10 times as much liquid as expanded clays, and its sorbent capacity ranges from 0.77 gal/lb (6.4 cu dm/kg) for perchloroethylene to 1.82 gal/lb (15 cu dm/kg) for phosphoric acid. The loaded material has safely been solidified using Portland cement and sodium silicate, but no testing results were available.

Roberts (1978) and Smith (1979) report results of an extensive study of the effects of selected organics upon the strength and leaching characteristics of a typical lime/fly ash S/S formulation. Organic compounds included methanol, xylene, benzene, adipic acid, and an oil and grease mixture.

The effects of ethylene glycol on cement-based solidification processes have been documented (Chalasani et al. 1986, Walsh et al. 1986). These investigators used a combination of techniques including extraction with solvents of varying polarity, scanning electron microscopy, and X-ray powder diffraction. The ethylene glycol appears to occupy three different sites in the solidified product as ascertained by their different extractability. No visible gross alteration in morphology of the cement matrix is apparent until the ethylene glycol reaches around 10 percent of the cement by weight. Levels above 10 percent clearly weaken the structure and cause higher leachability of the compound. Some evidence from X-ray diffraction indicates that the ethylene glycol moves into the 0.5- to 2.5-nm voids in the C-S-H gel phase and alters its structure. A major effect of the organic addition is the retardation of setting reactions so that significant changes in the matrix occur for up to at least 1 year of curing time.

Conner (1984) describes the successful solidification of 4 million gallons of waste containing 6.6 percent ethylene glycol, 2.5 percent sodium terephthalate, 8.3 percent sodium chloride, and 234 mg/ℓ antimony. The final product had a UCS of 55 to 70 psi (0.38 to 0.48 MPa) and leached 0.1 mg/ℓ

antimony, 5 mg/ℓ sulfate, 160 mg/ℓ chloride, and 350 mg/ℓ chemical oxygen demand. No details on the type of reagents or leaching tests used were given.

Gilliam et al. (1986) studied the immobilization of four waste streams in simple cement grout. One of the wastes contained 2,230 ppm PCBs and 17,400 ppm each of lindane (hexachlorocyclohexane), pentachlorophenol, and 9,9'-dichlorofluorene (PNA) dissolved in a typical pump oil. The waste was solidified using 19 wt percent Portland cement (type I), 17.5 percent fly ash (class F), 37.7 percent water, 3 percent attagel 150, 1.7 percent microcel E, 0.1 percent Sparr 80 emulsifier, and 0.02 percent Tributyl $PO_4$ antifoam so that a total waste loading was 20 percent by weight. Leaching of the solid after 90-day cure in 100-percent humidity using the MCC-1 static leaching procedure (Materials Characterization Center 1981) gave saturation values after 28 days of leaching of <1.5 ppb PCBs, <0.76 ppb lindane, less than 10 ppm pentachlorophenol, and 0.607 ppm dichlorofluorene. The authors state that by tailoring and adjusting the mixture, satisfactory solidification of organic wastes in these categories (PCBs, chlorinated cyclohexane, chlorinated phenol, and PNAs) should be possible.

## Pozzolanic Systems

Limited information is available on the effects of organics in pozzolanic systems. Researchers have suggested that unpyrolized organics reduce the cementing ability of fly ash by taking up reactive surface sites of the ash and preventing cementing-type contact of the various constituents (Davidson et al. 1958, Leonard and Davidson 1959, Thorne and Watt 1965, Thornton et al. 1975). Thornton et al. (1975), however, did show that pozzolans could be used to solidify clay soil with an organic content of 11.4 percent. The addition of a 5-percent lignite fly ash to the soil increased the UCS approximately 40 percent.

The compounds were added up to 8.5 percent of the dry weight of the reagents; the formulations used are shown in Table 16. The organics range in water solubility from very high to virtual insolubility and cover a structural range from simple single carbon alcohol to linear organic acids, to simple and substituted aromatic ring, to long unsaturated hydrocarbon chains.

Unconfined compressive strengths were made on 40-gram minicylinders (1 in. diameter by 2 in. height) that were prepared on a Carver hydraulic press (500 psi (3.4 MPa) for 20 sec). During compaction, all 8.5-percent organic mixes exuded some of the organic material. Only the adipic acid at both 1- and 8.5-percent formulations appreciably affected the compressive strength after 2 or 3 months. Adipic acid is a 6-carbon, dicarboxylic acid that must neutralize the added lime (producing calcium adipate) and therefore interfere with the pozzolanic reaction. Also evident is the action of methanol as a retarder of the pozzolan reaction. But typical of most retarders, the ultimate strength of the mixture eventually equals that attained by the control. Such a delay in setting time is not generally considered to be important in most waste S/S processes. Smaller delays in setting time are also evident for xylene and benzene at 8.5 percent, the effect of benzene still evident (but not significant) after 90 days of cure.

TABLE 16. EFFECTS OF SELECTED ORGANICS ON UCS AND LEACHING CHARACTERISTICS OF A LIME/FLY ASH FORMULATION

| Formulations* % dry weight | | | Unconfined compressive strength† (days curing @ 23° C) | | | | | Leaching test results‡ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | 28-day cure | | | | 90-day cure | | | |
| Fly ash | Lime | Additives | 7 | 14 | 28 | 62 | 92 | pH | Ca | TDS | TOC | pH | Ca | TDS | TOC |
| 95.2 | 4.8 | None | 190 | 315 | 454 | 579 | 664 | 11.65 | 225 | 890 | 29 | 11.40 | 81 | 728 | 8 |
| 95.1 | 4.8 | 0.1 Methanol | 223 | 305 | 371 | 495 | 570 | 11.70 | 215 | 836 | 40 | 11.15 | 71 | 714 | 10 |
| 94.2 | 4.8 | 1.0 Methanol | 219 | 301 | 435 | 542 | 618 | 11.55 | 140 | 564 | 173 | 11.35 | 63 | 712 | 87 |
| 87.1 | 4.4 | 8.5 Methanol | 37 | 41 | 200 | 510 | 648 | 11.90 | 480 | 1046 | 1538 | 11.40 | 100 | 762 | 734 |
| 95.1 | 4.8 | 0.1 Xylene | 257 | 310 | 446 | 557 | 666 | 11.70 | 210 | 746 | 40 | 11.40 | 71 | 724 | 10 |
| 94.2 | 4.8 | 1.0 Xylene | 247 | 308 | 421 | 535 | 655 | 11.70 | 205 | 726 | 44 | 11.45 | 63 | 652 | 27 |
| 87.1 | 4.4 | 8.5 Xylene | 201 | 297 | 362 | 497 | 640 | 11.85 | 355 | 900 | 62 | ND | ND | ND | ND |
| 95.1 | 4.8 | 0.1 Benzene | 246 | 313 | 435 | 525 | 637 | 11.65 | 150 | 606 | 29 | 11.40 | 63 | 706 | 10 |
| 94.2 | 4.8 | 1.0 Benzene | 245 | 301 | 452 | 540 | 621 | 11.70 | 205 | 768 | 39 | 11.40 | 81 | 626 | 9 |
| 87.1 | 4.4 | 8.5 Benzene | 196 | 267 | 317 | 415 | 553 | 11.90 | 410 | 1030 | 41 | ND | ND | ND | ND |
| 95.2 | 4.8 | None | 185 | 279 | 290 | 426 | 401 | ND | ND | ND | ND | 12.30 | ND | ND | ND |
| 94.2 | 4.8 | 1.0 Adipic acid | 62 | 95 | 117 | 218 | 187 | ND | ND | ND | ND | 12.10 | ND | ND | ND |
| 87.1 | 4.4 | 8.5 Adipic acid | 57 | 69 | 66 | 70 | 77 | ND | ND | ND | ND | 10.20 | ND | ND | ND |
| 94.3 | 4.8 | 1.0 Oil & grease | 165 | 271 | 351 | 515 | 485 | ND | ND | ND | ND | 12.10 | ND | ND | ND |
| 87.1 | 4.4 | 8.5 Oil & grease | 161 | 314 | 388 | 466 | 488 | ND | ND | ND | ND | 12.10 | ND | ND | ND |

Source: Roberts 1978, Smith 1979.

Note: ND = no data; TDS = total dissolved solids; and TOC = total organic carbon.

* All mixes prepared at 82-percent solids (including organics).

† All values given in pounds (force) per square inch and are an average of three determinations. (To convert values to megapascals, multiply by 0.00089457.)

‡ All values (except pH) are in milligrams per litre of leachate (from ASTM 48-hour leaching test).

Selected leaching results upon the minicylinders after 28 and 90 days are also shown in Table 16. The pH, total dissolved solids (TDS), calcium (Ca) and total organic carbon (TOC) content of the leachates increased in the 8.5-percent mixes of methanol, xylene, and benzene in the 28-day cure test. Although not shown in Table 16, the loss of methanol is quite high from the 8.5 percent mixes and remains so after 90 days of curing; these losses represent about 20 percent of the added methanol in 48 hours of leaching from the samples cured 28 days and about 10 percent after 90 days of curing. The general tendency toward reduced loss for all constituents is evident for all parameters analyzed.

No significant effect of the addition of methanol, xylene, or benzene is seen for either arsenic or chromium (data not shown). In all cases, arsenic averaged around 0.01 mg/ℓ in the leachates from both the 28- and 90-day cured samples. Chromium averaged around 0.06 mg/ℓ in the 28-day cure samples and 0.10 mg/ℓ after 90 days cure.

The X-ray diffraction analysis of all of the formulations gave little information except that no new crystalline compounds were formed in detectable amounts. Scanning electron micrographs indicated that the presence of the organic compounds altered the morphological structure of the lime/fly ash reaction products, even at the 0.1-percent level and even though compressive strength and leaching character were not affected appreciably.

Smith (1979) concluded that a good correlation exists between his findings for the effects of organic compounds on lime/fly ash pozzolanic systems and reported effects on the hydration of Portland cement; therefore, the large amount of information concerning additives and inferences on Portland cement should also be applicable to systems using pozzolanic reactions. Some organic wastes appear to be compatible with these systems, such as rolling mill sludges, electroplating wastes, or oily sludges from petroleum refineries. However, organic wastes containing hydroxyl or carboxylic acid functional groups, such as biological wastes, paint sludges, and some solvents, can be expected to delay or completely inhibit the pozzolanic reactions responsible for solidification.

## Summary of Organic Effects

In a recent study, Spooner et al. (1984) reviewed existing information about the capability of S/S binders with different classes of organic chemicals. Material for this study was obtained through a literature review and through contacts with representatives from universities, industry, trade associations and government agencies. From the gathered information, matrices were developed which summarized and defined the compatibilities of various S/S binder systems with particular chemical groups.

The binder categories chosen for Spooner's study include: Portland cement types I, II, and V; clay (bentonite); clay-cement; and silicates. The chemical categories chosen were divided into 16 groups that represented the types of organic compounds most likely to be found in hazardous wastes and in leachate from a hazardous waste disposal site. Table 17 (Spooner et al. 1984) was developed from the data gathered. It presents a matrix of information