Applications of Soil and Cement Chemistry to Stabilization/Solidification

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The main objective of waste stabilization/solidification (S/S) is to add binders to reduce the mobility of toxic contaminants. Immobilization can occur by either physical or chemical means. Physical immobilization occurs when the contaminant is encapsulated in a solid matrix. Chemical immobilization occurs when the contaminant is converted by chemical reaction to a less mobile form. Precipitation and adsorption are examples of chemical processes that can lead to immobilization. Physical processes in soil treatment have received the greatest attention with more data being collected on physical properties of the treated materials. The chemical processes associated with S/S have received less attention, particularly those processes that affect contaminants. Discussed in this paper are applications of cement and soil chemistry to S/S technology. The relative importance of kinetics and equilibrium of chemical immobilization in S/S are also examined.

Equilibrium chemistry is presented as a practical method for describing how reactions between binders and soil produce the chemical environment that determines whether contaminants will exist in mobile or immobile forms. The use of chemical equilibrium models and programs such as SOLTEQ are discussed. SOLTEQ, a modification of an EPA-supported program (MINTEQ), can calculate concentrations of contaminants in both mobile and immobile phases and provides mechanisms to integrate chemical information from a variety of systems, including cementitious-pozzolanic systems such as soils or wastes by S/S. The importance of pozzolanic reactions to developing the chemical environment in wastes and soils treated by S/S is also discussed.

The goal of stabilization/solidification (S/S) technology applied to wastes is to contain contaminants and prevent them from moving into the environment (1). This goal is accomplished through the addition of additives to chemically bind and physically entrap contaminants in a solid. A secondary objective is the production of solids that are more manageable when disposed or used for some beneficial purpose (1–3). The use of S/S technology for soil treatment also has the goal of immobilization by chemical and physical means; however, the final result is often the creation of materials for construction or site remediation (4–6).

Application of S/S technology to soils requires that ample attention is paid to the system chemistry. System chemistry largely determines the ability of materials to resist leaching. Chemical reactions form compounds that determine the physical properties of treated materials. Therefore, it is essential that chemistry be considered. Economic constraints and resource availability will affect binder choice, but not how binders behave in treatment (7).

The most commonly used S/S processes use chemical reactions achieved by mixing cement, lime, fly ash, kiln dust, or combinations of these to effect pozzolanic reactions. These reactions can result in contaminant binding, liquid and sludge conversion into solid waste forms, and the development of engineering properties suitable for construction (2,4). Reviewed in this paper are combinations of cement and pozzolanic materials in soils. However, the results are also applicable to combinations involving fly ash and lime. The paper will include a discussion of the chemistry involved, the ability to model such systems, and preliminary results from applying the technology to the chemical immobilization of contaminated soils.

DEFINITIONS AND TERMINOLOGY

There are no “official” definition sets currently in the S/S area, but agencies such as ASTM and the Environmental Protection Agency (EPA) are either working toward this or have officially promulgated terminology (3). Unfortunately, there has been a tendency to use such words as chemical fixation, stabilization, and solidification interchangeably, although such terms have very distinct meanings when applied to S/S technology (3). Stabilization and solidification have been defined as follows (3,8):

Stabilization refers to those techniques that reduce the hazard potential of a waste by converting the contaminants into a less soluble, mobile, or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization.

Solidification refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. The encapsulation may be of fine waste particles or of a large block or container of waste. Solidification does not necessarily involve chemical interaction between wastes and solidifying reagents, but may mechanically bind the waste into the monolith.

It is important to note the difference in this definition of stabilization and the definition associated with treating soils to improve mechanical properties. To avoid confusion, the term “chemical immobilization” will be used in this paper in place of “stabilization” as previously defined and the term “soil strengthening” in place of “stabilization” as used to denote processes of improving soil mechanical properties.
PHYSICAL IMMOBILIZATION AND PHYSICAL PROPERTIES

Physical processes in S/S have received the greatest attention and thus most of the data available describe physical properties of treated materials. Physical immobilization is accomplished through the encapsulation of toxic materials or waste agglomerates with binders (1). If encapsulation is the only mechanism holding a contaminant, the degree of environmental protection is strongly based on the physical integrity and durability of the treated materials (3).

Common examples of measurements often conducted on samples are plasticity index, unconfined compressive strength, shrinkage/swell potential, freeze/thaw durability, and moisture susceptibility. These types of measurements are typically used to reflect changes in physical properties of treated materials; however, they are not very useful for predicting whether contaminants will leach from treated materials. If a S/S treatment is to be considered successful from an environmental standpoint, data must reflect how much material could leach from the S/S form in the short and long term.

CHEMICAL IMMOBILIZATION

The ability to chemically immobilize material is an important aspect of S/S technology because of its strong impact on the level of contaminant mobility. Furthermore, chemical reactions determine properties of treated materials that are important to their use as construction materials.

Chemical binding requires that some reactions occur before desired pozzolanic or cementitious reactions, or both, take place. In soil systems treated by lime or cement, the reactions that must occur are hydration, cation exchange, flocculation, and agglomeration. Hydration processes provide necessary means to increase soluble ionic concentrations. When cement hydrates or lime ionizes in water, the dissolved concentrations of calcium and hydroxide ions are initially increased because calcium hydroxide is released either from calcium silicates as they hydrate (9,10) or directly from added lime (4). The increase in hydroxide ions produced by hydration also increases the pH of the solution. These initial reactions are typically completed within a few hours.

After initial reactions, pozzolanic or cementitious reactions, or both, can take place. It is important in soil strengthening to differentiate between cementitious and pozzolanic reactions (9). Cementitious reactions refer to the hydration reactions that occur when calcium silicates and calcium aluminate hydrate CSH) and calcium-aluminate-hydrate (CAH) reaction products. Pozzolanic reactions are reactions among alkaline earth elements, such as calcium, and reactive siliceous materials with high surface areas, such as clays. If clay is strengthened by cement hydration, this reaction may simply “cement” grains or clods of clay together without penetrating into the clay and affecting the clay mineralogy. However, if pozzolanic reactions occur, physical properties of the clay are often altered considerably, because the clay is actually “attacked” as it reacts. Changes in clay mineralogy have been well documented as a result of pozzolanic reactivity through scanning electron microscopy and X-ray diffraction (11,12). Both these reactions are time- and temperature-dependent and can continue to affect properties of treated materials years after initial treatment.

Precipitation reactions convert mobile forms of contaminants into immobile solids. High-pH environments in chemically immobilized systems often lead to the formation of metal-hydroxide precipitates (3), but metal-silicate, carbonate, and sulfate precipitates also are formed (3,13).

MODELING OF SYSTEMS

The complexity of modeling leaching of contaminants from materials treated by S/S is the result of the combination of physical and chemical factors that exists. However, simple leach models can be used to demonstrate leaching relationships using these factors, even when they are not useful in predicting leaching.

The simplest leach models assume that treated solids are semi-infinite slabs of rectangular geometry contained within well mixed, infinite baths (14). The material balance equation and its initial and boundary conditions are (14)

\[ \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial X^2} - R \] (1)

Initial Condition: \( C = C_0 \) at \( t = 0 \), all \( X \)

Boundary Conditions: \( C = 0 \), at \( X = 0 \), all \( t \)

\[ C \rightarrow C_0 \text{ as } X \rightarrow \infty \]

where

- \( C = \) mobile component concentration,
- \( C_0 = \) mobile component concentration at time zero,
- \( t = \) time,
- \( D_e = \) effective diffusivity,
- \( X = \) distance into solid, and
- \( R = \) removal rate of mobile component from solution per volume of total solid.

This mass balance is applicable for any system with transport in one direction whether infinite or not.

When the general mass balance is constrained with the assumptions of (a) no reactions, (b) infinite baths, (c) semi-infinite slab, and (d) homogeneous solid, this system can be solved to give the following relationship for the fraction of contaminant leached (14):

\[ \frac{M_t}{M_0} = \left( \frac{4D_e}{\pi L^2} \right)^{0.5} t^{0.5} \] (2)

where

- \( M_t = \) component mass leached at time = \( t \),
- \( M_0 = \) component mass in solid at time = 0, and
- \( L = \) distance from center of slab to surface.

The semi-infinite slab assumption can limit this model when the fraction leached is moderately high (i.e., \( M_t/M_0 > 0.20 \)). Care must therefore be taken when using this equation.

The systems of most interest are those in which chemicals do react. The effect of simple reactions can be described easily
if the reactions are assumed to be in equilibrium (14). This is normally a good assumption because the time required for reaction is generally smaller than that required for transport out of the waste form (14). Leaching equations can be shown to have the same form as Equation 2 for numerous simple reactions, but the equation contains an observed diffusivity rather than an effective diffusivity (14–16).

\[
\frac{M_f}{M_0} = \left(\frac{4D_{obs}}{\pi L^2}\right)^{0.5} t^{0.5}
\]  

(3)

The definition of observed diffusivity depends on the assumed chemical and physical reactions.

\[
D_{obs} = \frac{D_m}{f_c \times f_p}
\]  

(4)

where

\[
D_{obs} = \text{diffusivity observed from the effect of chemical and physical mechanisms}, \\
D_m = \text{molecular diffusivity}, \\
f_c = \text{factor describing chemical immobilization}, \text{ and} \\
f_p = \text{factor describing physical immobilization}.
\]

The physical factor \(f_p\) is the ratio of molecular diffusivity to effective diffusivity and has been defined as the MacMullin number (15,17).

\[
D_{obs} = \frac{D_m}{N_M \times f_c}
\]  

(5)

where \(N_M\) is the MacMullin number.

\(N_M\) can be determined by a technique based on electrical conductivity measurements (15). Transport of ions by either diffusion or electrical field is affected in the same way by the structure of a porous solid; therefore, measurement of solid and pore water conductivity can be used to calculate the effective diffusivity of a compound within the solid (15). \(N_M\) can be calculated as the ratio of pore water conductivity to solid conductivity.

The chemical factor \(f_c\) depends on the type of reactions assumed. If linear sorption is assumed, the observed diffusivity is defined (14,16)

\[
D_{obs} = \frac{D_e}{1 + K_p} = F_m D_e = \frac{D_m}{(N_m)(1 + K_p)}
\]  

(6)

\[
f_c = (1 + K_p)
\]  

(7)

where \(K_p\) is the linear partition coefficient, equal to ratio of sorbed phase concentration to solution phase concentration at equilibrium and \(F_m\) is the contaminant fraction initially mobile.

If a portion of the contaminant is assumed to have reversibly precipitated, the following definition applies (14):

\[
D_{obs} = \frac{\pi[F_m(1 - F_m) + 0.5F_p^2]D_e}{2}
\]

\[
= \frac{D_m\pi[F_m(1 - F_m) + 0.5F_p^2]}{N_M \times 2}
\]  

(8)

\[
f_c = \left(\frac{2}{\pi F_m}\right)
\]

(9)

If the fraction of contaminant in the mobile phase is small, this reduces to the following (14):

\[
D_{obs} = \frac{\pi F_m D_e}{2} = \frac{D_m \pi F_m}{N_M \times 2}
\]  

(10)

These simple leach models demonstrate the importance of observed diffusivity on the ultimate leachability of an S/S material. The equations presented show how observed diffusivity is highly dependent on physical and chemical factors. The relative importance of the chemical factor is dependent on the contaminants involved, and this is reflected in measured values of observed diffusivity. Observed diffusivities for several contaminants are shown in Table 1. The table shows that different contaminants are immobilized to widely different degrees in the same solidified waste (15), and, because the data were obtained from the same waste form, all differences in observed diffusivity can be attributed to chemical factors. A small observed diffusivity (i.e., a large \(-\log D_{obs}\)) represents a high degree of immobilization. Thus, those contaminants that should be relatively nonreactive, such as sodium, have the highest \(D_{obs}\), and more reactive contaminants, such as lead, have the lowest \(D_{obs}\).

The similarity of molecular diffusivity for several substances in a water medium is shown in Table 2. Values of molecular diffusivity have been measured for numerous compounds and can be estimated for numerous others (15,17,18). However,

\begin{table}[h]
\centering
\caption{Reported Values of the Leachability Index (\(-\log D_{obs}\)) for Various Contaminants (15)}
\begin{tabular}{|l|l|}
\hline
Contaminant & \(-\log D_{obs}\) (m\(^2\)/s) \\
\hline
Na & 12.3 \\
Phenol & 13.5 \\
Nitrate & 14.7 \\
As & 15.9 \\
Cr & 17.2 \\
Pb & 19.4 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Reported Values of Molecular Diffusivity in Water (17,18)}
\begin{tabular}{|l|l|}
\hline
Substance & \(-\log D_m\) (m\(^2\)/s) \\
\hline
Ethanol & 8.92 \\
Glucose & 9.16 \\
Acetone & 8.89 \\
Propan-2-ol & 8.96 \\
Chloride & 8.82 \\
CO\(_2\) & 8.70 \\
O\(_2\) & 8.62 \\
N\(_2\) & 8.59 \\
\hline
\end{tabular}
\end{table}
when molecular diffusivity is measured for different substances in a similar medium, there is little difference in the values obtained.

Because molecular diffusivity varies little, the only factors that can influence the fraction of mobile contaminants are chemical and physical. Shown in Table 3 is \( N_m \) for several water/cement (w/c) ratios and for several levels of a silica fume admixture. These data show how \( N_m \) can vary with w/c ratios, curing time (17), and levels of admixtures (19).

The simple leach models are based on assuming simple reactions of one or two components. Chemical reactions in materials treated by S/S are much more complex. Many components are present and they can react in many ways. However, it is reasonable to assume that these reactions react relatively fast when compared with leaching so that chemical equilibrium is achieved. Currently, a chemical equilibrium model (SOLTEQ), which is a modification of an EPA-supported program (MINTEQ), is being used to predict chemical equilibrium that exists in S/S waste forms (14).

SOLTEQ can be used to estimate the fraction of contaminant in the mobile phase, \( F_m \) (14). As shown by Equations 9 and 10, the mobile fraction can be used to calculate observed diffusivity for simple one-component systems (14). However, this approach is quite limited because it ignores multicomponent chemical interactions.

SOLTEQ can also be used to predict the effect of multicomponent chemical interactions on leaching (14). The material balance equation presented for a nonreactive component, Equation 1, must be modified to consider a component that can exist in a number of different forms (14). The accumulation term must consider total concentration, and the transport term only considers mobile phase concentration (14). Because all reactions are conversions among species of the same component, the rate term is irrelevant and the material balance equation becomes the following (14):

\[
\frac{\partial T_i}{\partial t} = D \frac{\partial^2 C_{i,m}}{\partial x^2}
\]  

(12)

<table>
<thead>
<tr>
<th>w/b Ratio</th>
<th>( N_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>207</td>
</tr>
<tr>
<td>0.50</td>
<td>171</td>
</tr>
<tr>
<td>0.60</td>
<td>97</td>
</tr>
<tr>
<td>0.80</td>
<td>54</td>
</tr>
<tr>
<td>1.00</td>
<td>27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>w/b Ratio = 0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>b = Cement + Silica Fume</td>
</tr>
<tr>
<td>Cement to Silica Fume Ratio (Weight % : Weight %)</td>
</tr>
<tr>
<td>95 : 5</td>
</tr>
<tr>
<td>90 : 10</td>
</tr>
<tr>
<td>85 : 15</td>
</tr>
<tr>
<td>80 : 20</td>
</tr>
<tr>
<td>75 : 25</td>
</tr>
</tbody>
</table>

where \( T_i \) is the total concentration of component \( i \), and \( C_{i,m} \) is the concentration of component \( i \) in all its mobile forms. This equation can be solved simultaneously for numerous components by numerical techniques (14,20).

SOLTEQ provides a general multicomponent model to describe equilibrium partitioning of binder and waste components. It contains a thermodynamic data base with data for some compounds and pore water conditions often found in treated waste (14). However, SOLTEQ is limited by insufficient thermodynamic data for solid species not commonly found in cementitious forms, the phase rule for solid formation, and the heterogeneous mineralogy of waste forms encountered (14).

**APPLICATION OF S/S TECHNOLOGY TO CONTAMINATED SOILS**

The focus of soil strengthening has been on benefits achieved in the physical or engineering properties of the treated soil. Common physical properties examined before, during, and years after treatment are of limited importance to ultimate leachability. Therefore, when S/S technology is applied to contaminated soils, the focus should turn to those properties affecting leachability, such as soil pH, diffusivity, and the durability of the solid.

Soil pH is probably the single most important factor in determining the extent of chemical immobilization of contaminants. For applications of soil strengthening, the primary reason for measuring soil pH is to ensure that sufficient lime has been added to drive strength-producing reactions (4). A soil pH of 12.4 is typically used to indicate the presence of excess lime needed to drive pozzolanic reactions. However, reaching this pH does not ensure adequate performance, because it does not establish whether the soil will react with lime to produce a substantial strength gain; therefore, a strength test is necessary to show strength increases. Conventional techniques for measuring soil pH rely on mixing distilled water with a soil sample and measuring the pH of the resulting extract. This procedure is adequate for measuring pH in soil solutions equilibrated with lime, because lime particles can dissolve in the added water to maintain a pH near 12.4. However, this procedure will not likely be suitable when the pH of the soil water is controlled by a set of reactions more complex than the simple dissolution of lime.

Because pore water pH is directly related to the leachability of treated materials, a more accurate procedure is needed to measure the pH. A device has been developed to extract pore water from cured samples so that the hydroxide concentration of the pore water can be measured directly by titration (17,21). Pore water hydroxide concentrations can be used to accurately determine pH by calculation.

**Research Plan**

Because of the importance of soil pH to chemical immobilization, an experimental plan was developed to evaluate a pore water extraction method for measuring pore water hydroxide ion concentration. Experiments were conducted to evaluate effects of mix design and curing time on pore water hydroxide...
concentration and the amount of hydroxide per total amount of mixture. Mix designs used in experimentation were chosen to maintain constant mass ratio of simulated soil to cement. Shown in Table 4 are the percentages of components on the basis of total mass of material mixed. Nine replicate samples were prepared for each series with three replicates analyzed on each sampling. Specimens were cured at room temperature under lime water. The hydroxide ion concentration was determined through acid-base titration of expressed pore water to an endpoint of pH 7.

**Methods**

Samples were prepared by mixing Type I portland cement, sodium bentonite clay, and a 30-mesh sand with appropriate amounts of distilled water so that mixtures set sufficiently to prevent bleeding. Portions were then transferred to plastic concrete molds (50 mm × 100 mm), placed in a tumbler for 24 hr, and then placed in plastic bags under lime water to cure for the specified times. After curing, pore water was expressed from samples by using a pore water expression device (17,21). A schematic of the device is shown in Figure 1.

The pH of the expressed pore water was measured with a pH meter, Fisher 925, and then titrated with a sulfuric acid solution to an endpoint of pH 7.

**Discussion of Results**

Pore water hydroxide ion concentration versus the percentage clay content at different curing times is shown in Figure 2. The hydroxide ion concentration varies slightly with the percentage clay content. However, the curing time and the percentage clay content appear to affect hydroxide concentration, especially between 14 and 28 days of curing. The lack of initial change in pore water hydroxide concentrations has been noted elsewhere (9); however, upward trends exhibited with higher percentages of clay may be atypical of cement curing. These upward trends could be a result of not curing long enough to reach an equilibrium condition.

The amount of hydroxide ions per total mass of mixture versus the percentage clay content varied with time is shown in Figure 3. The results in Figure 3 show a trend similar to that in Figure 2. However, a more pronounced reduction in the amount hydroxide present as clay content is increased when measured after 7 days of curing is shown in Figure 3.

**SUMMARY**

The importance of leachability to the development of an environmentally sound S/S waste form cannot be overstated. Because of its importance, the chemistry of S/S will be very important to the application of S/S technology to contaminated soils. Knowledge and experience gained from dealing with waste S/S can be combined with that of soil strengthening to treat contaminated soils so that they are environmentally and structurally sound for many years. In particular, models for leaching and equilibrium chemistry and characterization techniques for pore water analysis and MacMullin number can be applied to soil treatment.

The application of S/S to contaminated soils will also be beneficial because of the relatively low cost of treatment and the ability to create a more easily workable soil for final disposal or in situ encapsulation at a waste site.

As more data from laboratory experiments and field demonstrations are collected on S/S of contaminated soils, the
chemistry of such systems will be more fully understood, and questions about long-term leachability will be better addressed.

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REFERENCES


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