

Leaching boundary in cement-based waste forms

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Abstract

Cement-based fixation systems are among the most commonly employed stabilization/solidification techniques. These cement waste mixtures, however, are vulnerable to acidic leaching solutions. Leaching of cement-based waste forms in acetic acid solutions with different acidic strengths has been investigated in this work. The examination of the pH profile along the acid penetration route by various pH colorimetric indicators is reported. A clear-cut leaching boundary of approximately 100 μm width was observed in every leached sample.

1. Introduction

Stabilization/solidification is a widely practiced, cost-effective means of reducing leachability of hazardous constituents from the disposed waste for landfill disposal. Cement-based immobilization processes generally incorporate portland cement and waste sludge along with certain other additives, such as fly ash or other pozzolanic materials, to form a monolithic, rock-like mass.

Cement-based stabilization/solidification processes have proven successful on many sludges generated by the precipitation of heavy metals [1]. Chemical stabilization and physical encapsulation are the two primary controlling factors in reducing metal mobility in the stabilized/solidified waste forms. The excess calcium hydroxide produced by cement hydration maintains a highly alkaline environment in the waste form. Most of the polyvalent metal ions, which are capable of forming insoluble hydroxides in alkaline aqueous solution, tend to be chemically stabilized in insoluble forms in the cement paste matrix.

For some amphoteric metals (soluble at both low and high pH) and anions (arsenate, selenite, etc.), physical encapsulation could be the major immobi-

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lizing mechanisms at the high pore water pH generally present. Solute transport in the cement-based waste form is a slow process. Cement-based waste forms typically have a permeability value ranging from 10^{-5} to 10^{-9} cm/s [2]. The capillary pores, which serve as a transportation conduit, have a range of pore sizes from $0.01 \mu\text{m}$ to $10 \mu\text{m}$ in the hydrated cement paste [3]. The water/cement ratio is one of the important factors determining the size of the pores. The percentage of the larger pores increases as the water/cement ratio increases, substantially increasing the chance of leaching of the pollutants.

A chemically altered surface layer was observed by some cement researchers in the cement matrix of concrete attacked by natural water and acid solutions. Lea and Desch found that water decomposed cement pastes by dissolving lime and some alumina [4]. Continued leaching eventually left a residue of hydrated silica, iron oxide and alumina, which was a soft and mushy mass. This decomposition reaction can be accelerated by adding acidity in the water. Shively observed that a physically and chemically altered surface layer was formed during the sequential extraction tests of crushed cement-based waste forms [5]. The same phenomenon was also observed during the sequential leach tests of 1" high \times 1" diameter cylindrical cement samples [6]. This surface layer changed color from grey to orange and became soft and friable without a distinct crystal structure. After oven drying the leached sample overnight, this layer on the leached sample could be easily peeled off by hand.

Cement-based fixation systems rely heavily on pH control for stabilization of metal contaminants. The leaching mechanisms of cement-based waste forms in a mild acidic environment are controlled by the penetration of free hydrogen ions from the leachant into the waste form [7]. If this physically and chemically altered surface layer is the consequence of acid attack, the pH distribution within this layer should be distinctly different from the one in the original material. In this paper the evidence that distinguishes the leached surface layer from the remaining unleached waste form is presented. The pH profile along the radius of the leached sample is also discussed.

2. Methods and materials

2.1 Sample preparation

Cement-based waste samples were made in the laboratory by mixing metal sludges with portland cement. The metal sludges were prepared from cadmium nitrate and sodium arsenite by dissolving 0.01 mole of each metal compound per liter of deionized water and then adjusting the pH of the mixture to 8.8 with 6.0 M sodium hydroxide solution. The metal sludges were used as the sole liquid source for the mixing of portland cement. Samples with a 0.6 water/cement weight ratio were cast as 3.7 cm diameter spheres (ping pong balls were used as the molds). A small hole was drilled into the spherical mold, and the cement-based waste mixtures was injected into the mold using a plastic sy-

ringe, and the opening was sealed by a rubber film. The molds were tumbled for a few hours until the cement set and then were stored in a 100% humidity room. Samples were cured for two months before the tests.

2.2 GANC test

Five raw samples were randomly chosen to run the generalized acid neutralization capacity (GANC) test [8]. The GANC test is a single-batch leaching procedure that utilizes a series of dried crushed samples extracted with increasingly acidic leachant. The particle size of the dried sample was reduced to 425 μm , ASTM sieve #40. Approximately 1.00 g dried sample was weighed out into 21 sets of 30 ml bottles. Each set consisted of triplicate specimens for each acid equivalent interval. Acid equivalents were generated by increasing the ratio of acid to water in a total leachant volume of 20 ml. Leachant strength started out at 0 acid equivalents and was increased in proportional intervals until it reached 0.04 acid equivalents. Bottles were rotary agitated to allow full reaction. The pHs of the solutions were measured after 48 h contact time.

2.3 Semi-dynamic leach test

A series of semi-dynamic leach tests were followed. The term "semi-dynamic" means that the leachant is replaced periodically after intervals of static leaching. Four experimental runs were designed to leach the intact samples in 0.2, 0.3, 0.4 and 0.5 N acetic acid solutions, respectively. Each experimental run involved leaching a group of seven samples submerged in seven 1-liter "Nalgene" bottles of the same acid strength. Each bottle contained 870 ml of appropriate acetic acid solution. The solutions were renewed at 1, 8, 15, 22, 29, 36 and 43 days. One sample was removed from each experimental run during each solution renewal period. The leached samples were manually fractured while still damp with a hydraulic splitter. Caution was taken so that the fracture plane passed through the geometric center of the sphere. The fractured sample surface was then observed without delay under an optical microscope equipped with a 35 mm camera.

2.4 Static leach test

A set of seven samples were leached in seven individual acetic acid solutions with 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 N acidic strengths, respectively. This set of samples was identified as the static leached samples. The pH in the solution was measured by a pH meter and recorded with time. The initial pH values of the solutions varied from 2.74 (0.2 N) to 2.37 (0.8 N). The solution in each bottle was not renewed and the leached sample was removed from the bottle when the pH of the solution reached 5.0. The removed samples were fractured and examined following the procedures mentioned above.

TABLE 1

The properties of the pH colorimetric indicators (from [9])

Indicator	Approximate pH range	Color change
Tetrabromophenolphthalein-ethyl ester, K-salt	3.0-4.2	Yellow to Blue
Congo red	3.0-5.0	Blue to Red
Ethyl red	4.0-5.8	Colorless to Red
Alizarin	5.6-7.2	Yellow to Red
Bromothymol blue	6.0-7.6	Yellow to Blue
Phenolphthalein	8.2-10.0	Colorless to Pink
Alizarin yellow R	10.1-12.0	Yellow to Red

2.5 Color indicators

Seven pH colorimetric indicators were applied to the surface of the damp fractured samples in order to identify the pH profile along the radius of the samples. The color indicators are weak acids or bases which change color when changed from neutral to the ionized form. The pH at which the color change takes place depends upon the ionization constant for the particular indicator. For example, Bromothymol blue is yellow in solutions of pH below 6.0 and blue in solutions of pH above 7.6; the color of this indicator is a varying mixture of yellow and blue in the pH range between 6.0 and 7.6. The properties of these indicators are listed in Table 1. The solutions of the indicators were prepared by the methods described in the *CRC Handbook of Chemistry and Physics*, 67th edition [9].

3. Results and discussion

3.1 Fractured sample surface

The exterior surface color of all of the samples changed from grey after curing to pale brown after leaching. On every fractured sample surface, a light grey kernel surrounded by three different color layers were observed. The schematic profile of an acid-leached sample is shown in Fig. 1. Starting from the solid/solution interface of the sample, these layers are the orange layer, the dark grey layer and the medium grey layer.

Semi-dynamically leached samples had broader surface layers compared to those of the static leached samples of the same acidic strength and with similar leaching period. This result is expected and can be explained by the concept of diffusion. The pH difference between bulk liquid and solid surface provides a driving force for the acids to diffuse into the waste form. The pH of the bulk solution increases with time due to the buffering reactions between leached metals and acetic acid. Hence, the rate of acid penetration decreases with time

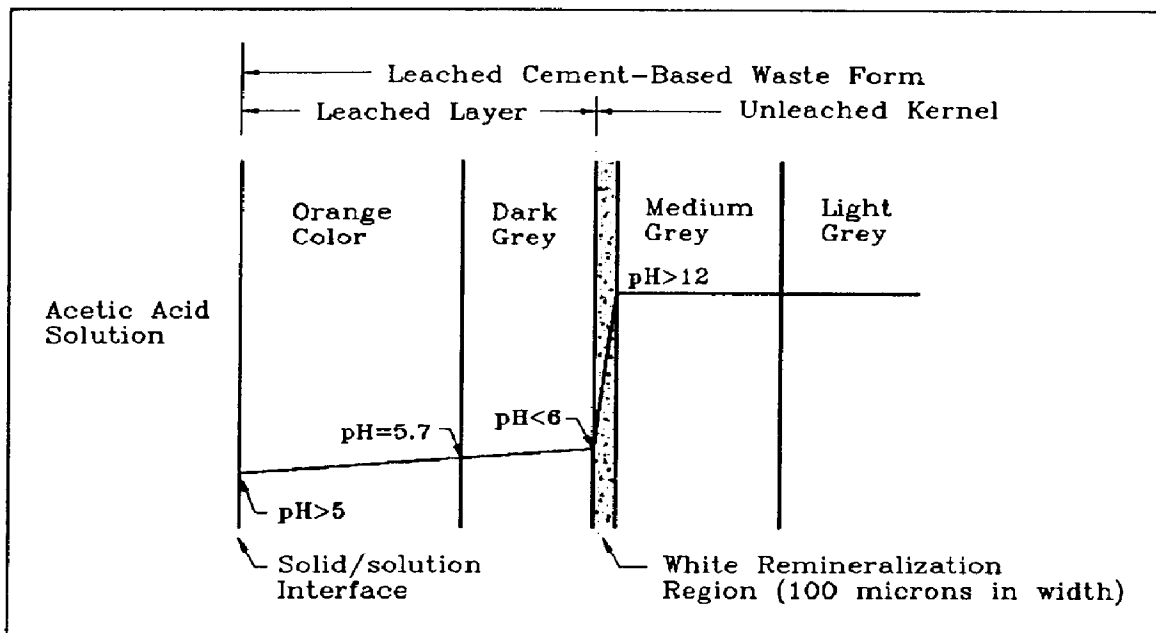


Fig. 1. Schematic profile of an acid-leached sample.

in a static leached condition. In the semi-dynamic leach test, solutions were replaced periodically, which boosted the acid driving force to the maximum level and increased the overall rate of acid penetration.

Most of the raw samples were spherical in shape, except that there was a small dent close to the injection hole due to water segregation. After leaching for a period of time, most of the unleached kernels were still spherical in shape, except for those samples leached at higher acidic strengths and for longer durations. Distortions from sphericity were caused by water segregation during casting which created a more porous area near the dent, and the acid penetration rate near the dent area was faster than the rate for the rest of the waste form. Higher acidic strengths plus longer leaching periods exaggerated this effect and created a deeper and wider depression area on the unleached kernel.

3.2 Application of color indicators

The application of pH color indicators to the surface of the fractured samples to identify the pH profile turned out to be very successful. Different indicators act differently on the surface of the sample. Bromothymol blue, Phenolphthalein and Alizarin yellow R show the best visual results. A summary of the application results is shown in Table 2.

A narrow white line appeared between the dark grey layer and the medium grey layer. This line is difficult to identify before applying the pH indicators. When either the solution of Bromothymol blue, Phenolphthalein, or Alizarin yellow R was applied to the damp sample surface, the narrow white line emerged

TABLE 2

Summary of the application results of the pH color indicators to the fractured surface of acid-leached cement-based waste form

Indicator	Position ^a			
	Zone 1	Zone 2	Zone 3	Zone 4
Tetrabromophenolphthalein-ethyl ester, K-salt	Blue	Blue	Blue	Blue
Congo red	Red	Red	Red	Red
Ethyl red ^b	—	—	—	—
Alizarin ^c	—	—	Red	Red
Bromothymol blue	Yellow	Yellow	Blue	Blue
Phenolphthalein	Colorless	Colorless	Pink	Pink
Alizarin yellow R	Yellow	Yellow	Red	Red

^aZone 1: orange layer; Zone 2: dark grey layer; Zone 3; medium grey layer; Zone 4: light grey kernel (see Fig. 1).

^bThe application was ineffective.

^cThe color changed from yellow to red within the orange layer and the dark grey layer.

with a width of about 100 μm . After the sample was dehydrated in the air for a period of time, the orange layer and the dark grey layer started cracking and peeling along this white line. The peeled materials were friable and of lighter weight than the original waste form.

Phenolphthalein and Alizarin yellow R change the colors along the boundary between the medium grey layer and the white line. This indicated that the pH of the medium grey layer and the light grey kernel was above 12.0. It is believed that the medium grey layer and the light grey kernel are the remaining unleached part of the sample.

Bromothymol blue changes the color at the boundary of the white line and the dark grey layer. Combining this result with the one from Phenolphthalein, it is concluded that the pH value was between 7.6 to 8.0 within the white line and below 6.0 within the dark grey layer and the orange layer. Hence, this white line can be defined as the leaching boundary where the pH changes from 6.0 or below in the leached layer to 12.0 or higher in the unleached kernel. It is believed that this narrow white line is caused by supersaturation and reprecipitation of the dissolved calcium ions in front of the acid. The white color is attributed to calcium hydroxide, which is the dominant alkaline species dissolved by the acetic acid solution.

It is rather difficult to identify the pH distribution within the dark grey layer and the orange layer. Congo red turns out to be red ($\text{pH} > 5$) and tetrabromophenolphthalein ester to be blue ($\text{pH} > 4.2$) on the whole sample surface. This

indicates that the pH within the leached layers is very close to the one in the bulk solution and only varies from about 5.0 on the sample surface to 6.0 in front of the leaching boundary. Alizarin changes the color within the orange layer and the dark grey layer; however, the position where the color changes is difficult to identify. Application of Ethyl red was ineffective. The Ethyl red solution was initially red on the whole sample surface, then the reddish color disappears after the solution is absorbed into the sample.

3.3 Metal reprecipitation

The dissolution of metal ions at the leaching front and reprecipitation of them in front of the leaching boundary can be explained by the concept of concentration gradient. It is well known that molecules diffuse from a region of higher concentration to a region of lower concentration. Within the cement-based form, the concentrations of free calcium ions are quite low since most of the calcium is bound in the calcium hydroxide crystal and calcium silicate hydrate gel. At the leaching boundary, where the pH decreases from 12 to 6, most of the calcium dissolves and forms a concentration peak. The dissolved calcium ions can diffuse either toward the acetic acid solution or toward the kernel of the waste form. The ions diffusing inward, however, may supersaturate in a very narrow region and soon reprecipitate when they encounter the increasing pH in the pore water of the unleached material. The reprecipitated calcium hydroxide fills the pores and makes a denser shell around the unleached kernel of the waste form. This denser shell makes the waste form less permeable to acid penetration, and also blocks the amphoteric metals from leaching out of the waste form.

A similar phenomenon was also found in the case of tooth decay [10]. Teeth are largely made of the mineral hydroxyapatite, commonly described as a non-stoichiometric calcium phosphate. Tooth decay results from bacteria growing in a polysaccharide gel called "plaque" which is attached to the surface of the teeth. These bacteria produce acids which attack the teeth. Near the surface of the tooth, there is a region of remineralization where solid evidently precipitates. Such a combination of dissolution and reprecipitation produces what is clinically called a "white spot", which is believed to be a first step in the formation of dental caries. Cussler successfully demonstrated this phenomenon by solving unsteady-state diffusion equations coupled with a chemical reaction term. It was found that calcium and magnesium precipitated in front of the acid.

3.4 GANC test result

The GANC test result (Fig. 2) is similar to a titration curve for strong bases with weak acid (acetic acid). Instead of continuous titration of titrants into a single containing, the GANC test is designed to add various increments of

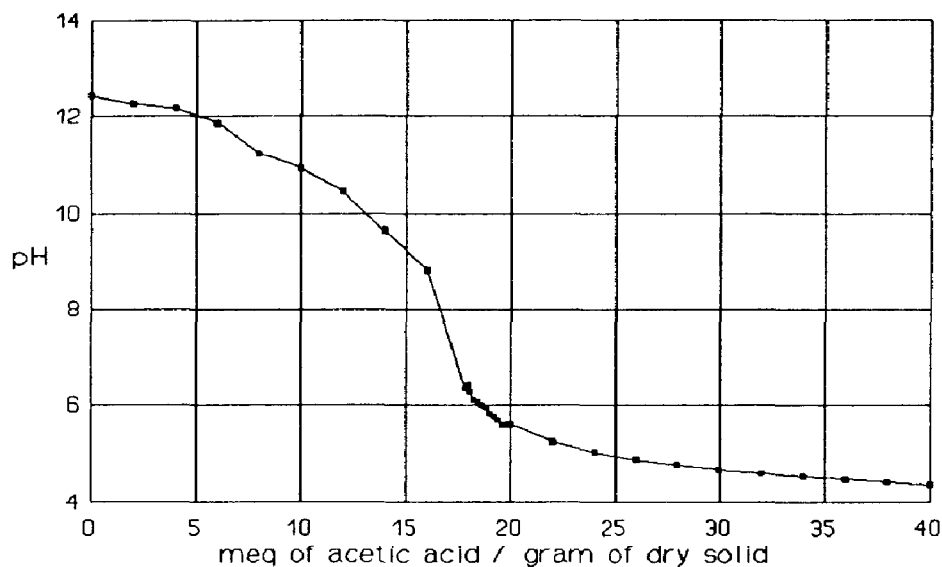


Fig. 2. Generalized acid neutralization capacity (GANC) test for the cement-based waste form.

titrant to separate bottles; the test requires a 48 h contact time in order to allow the solids to equilibrate with the liquid.

Acid neutralization capacity can be defined as the amount of a strong acid required in a titration to reach a preselected equivalence point [11]. The pH of the equivalence point is 7.0 for the titration of strong base with strong acid. For the GANC test, however, the equivalence point should be higher than 7.0 due to the dissociation of the conjugate base of acetic acid. It is estimated that the acid neutralization capacity of the cement-based waste form is 16 meq/g at pH 9.0 (see Fig. 2). It is also found that it requires 18.6 meq/g acetic acid to lower the pH from 12.4 to 6.0 and 24.0 meq/g to 5.0.

The actual pH of the remaining unleached kernel can be found from the GANC test result. The pH value of the first bottle, which contained 1.00 g dried sample in 20 ml of deionized water, can be considered as the pH of the pore water in the unleached portion of sample. The pH of the first bottle was 12.4, which is reasonably close to the equilibrium constant for calcium hydroxide in equilibrium with water, $\log K = -12.85$ [11].

The pH value at the boundary between the dark grey layer and the orange layer can also be found from the GANC test result. During the test, it was noticed that the color of the solutions switched from grey to orange between the 18 meq/g and the 20 meq/g bottles. The pH values were 6.4 in the 18 meq/g bottle and 5.6 in the 20 meq/g bottle. In order to determine the exact pH where the color change takes place, ten more samples were prepared and the same test was run between 18 and 20 meq/g acidic strengths. It was found that the color changed from grey to red in the 19.4 meq/g bottle, which had a pH of

5.7. It is believed that this pH value can be regarded as the pH value at the boundary of the dark grey layer and the orange layer.

3.5 Leach model

Based on the results discussed above, a kinetic leach model can be visualized (Fig. 3). The leaching mechanisms of a cement-based waste form in a mild acid environment are controlled by the acidity in the solution. The concentration differences of acidic species in the aqueous phase and in the solid phase drive the acids from the leachant into the waste form. The acids decompose the cement-based waste form by dissolving lime and other alkaline materials, eventually leaving a silica-rich, porous residue. This residue, called the leached layer, increases with time as the acids progress into the solid. The unleached kernel, surrounded by the leached layer, is the unleached part of cement-based waste form. A leaching boundary can be sharply defined at the interface of the leached layer and the unleached kernel, where the pH changes from below 6 to above 12 within a 100 μm distance.

The acid penetrating process can be idealized as three sequential steps. In the first step, acids diffuse from the bulk solution to the solid surface; in the second, the acids diffuse through the leached layer to the leaching boundary; and in the third, the acids diffuse into the unleached kernel and react with alkaline materials in the pore water.

The first step, mass transfer between the solution/solid interface, usually can be neglected in order to simplify the problem. The second step, diffusion across the leached layer, can be assumed as a steady-state process due to the fact that acids consume most of the alkaline materials and leave a highly po-

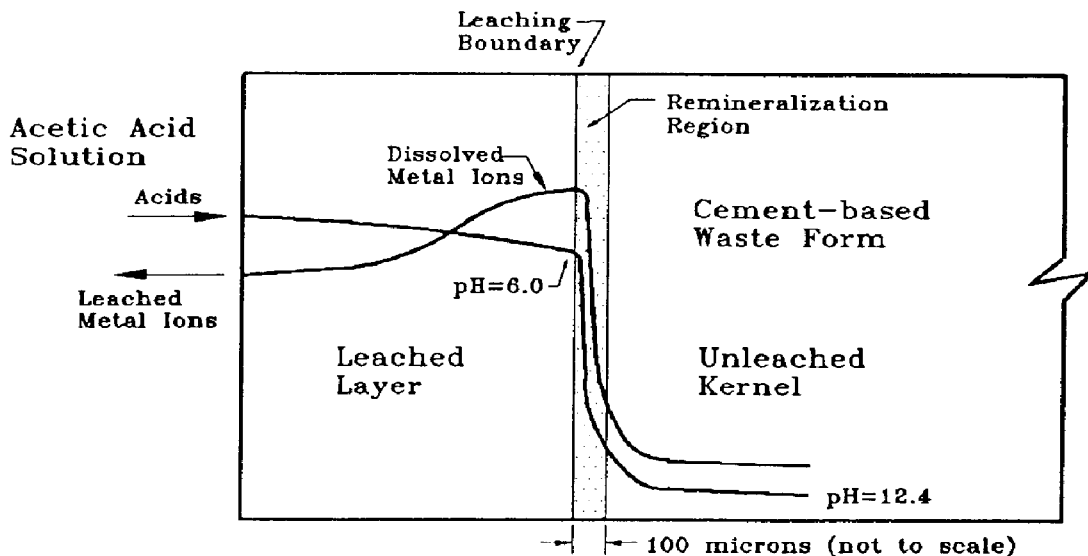


Fig. 3. Kinetic leach model.

rous structure. The steady-state assumption also implies that the diffusion through the leached layer is much faster than the growth of the leached layer.

The third step occurs at the leaching boundary, where diffusion and dissolution reactions occur simultaneously in the pores. Compared with the low permeability of cement-based waste form (10^{-5} – 10^{-7} cm/s [2]) the dissolution reactions are so fast that equilibrium conditions can be assumed. Therefore, the overall process can be idealized as diffusion-controlled fast reactions.

The leaching of metals is the consequence of acid penetration. The leaching rates of metals are controlled by the diffusion rates of the acids into the unleached kernel and the unstabilized metal ions present in the highest concentration near the leaching boundary. From this maximum, they can diffuse out into the bulk solution or further into the porous solid. The calcium ions diffusing inward, however, soon supersaturate and reprecipitate in front of the acids.

4. Conclusions

A demarcation line existed in every leached sample of cement-based waste form. This includes samples leached in 0.2 *N* acetic acid solution for 1 day and in 0.8 *N* acetic acid solution for 56 days. This demarcation line is believed to be the leaching boundary where the pH value changes from 6.0 in the leached layer to 12.4 in the unleached kernel. The demarcation line is white in color and is about 100 μm in width. It is believed that this line is the consequence of metal reprecipitation in front of the acid and the white color can be attributed to calcium hydroxide, which is the dominant alkaline species in the cement-based waste form.

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