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# EFFECTS OF CARBONATION ON THE LONG-TERM LEACHING PERFORMANCE OF CEMENTITIOUS WASTEFORMS

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**ABSTRACT** Cement-based wasteforms are among the most commonly used waste disposal and site remediation options. However, concrete knowledge of the processes controlling long-term performance of the wasteforms is lacking. This research evaluates the effect of carbonation on cementitious wasteforms. Wasteforms were reacted with carbon dioxide for a prolonged period and then subjected to leaching tests. Ions tested were nitrate, strontium, cadmium, cobalt, calcium, and lead. Results indicate that carbonation causes both physical and chemical changes to the concrete. The leaching rate was higher in the carbonated wasteforms for all the ions except strontium. Thus, effects of carbonation can vary depending on the chemical species and other physical and chemical effects.

**KEYWORDS:** cementitious wasteforms, carbonation

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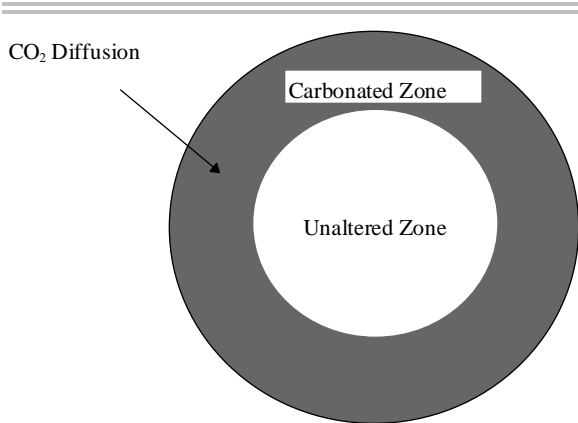
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## INTRODUCTION

The use of cement-based wasteforms for solidification and stabilization of waste has been rapidly increasing in the United States. In fact, it is one of the most commonly used technologies for site remediation and treatment of hazardous wastes. Cement as a binder is an attractive option over others due to its superior performance and economic attractiveness. Examples of its advantages include: readily available materials, low cost, flexibility in tailoring properties for varying wastes, and high strength. In addition, it is a fairly simple material to produce and form, offering a wide range of disposal options.

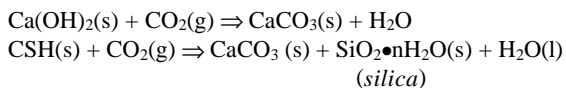
The performance of cement as a solidification and stabilization agent has been evaluated by the U.S. Government. The tests used, however, are short-term laboratory tests which do not mimic the actual service environment of the cementitious wasteforms. These tests such as

the Toxicity Characteristic Leaching Procedure (TCLP) give information on the characteristics of cement wasteforms, but give no indication as to their expected performance in the actual soil environment. One main reason for this is that these tests specify water saturated conditions which are unrepresentative of the actual disposal environment. Because the law requires that wastes be placed in the vadose zone where soil gases are present, it is important to research the extent to which soil gases might affect the physical and chemical properties of the wasteforms. Thus, the reaction of cement with soil gases and its effect on the long-term leaching performance of wasteforms needs to be evaluated. A better understanding of this can aid in the development of standardized leach tests, necessary for making the adequate choices for the proper and safe disposal of wastes.



**FIGURE 1. CARBONATION OF WASTEFORM.**

In terms of long-term performance, the vadose zone offers a very aggressive environment due to the presence of soil gases such as carbon dioxide or CO<sub>2</sub> and oxygen, in addition to variable contact with water. Due to the nature of cement, carbonation is a potentially significant process affecting the leaching behavior of wasteforms. Carbonation can take place when soil or atmospheric carbon dioxide reacts with the cementitious materials resulting in the formation of calcium carbonate. This can lead to physical as well as chemical changes which in turn may affect the leaching rate. The major reactions of Portland cement with carbon dioxide are as follows:



All the calcium-containing phases existent in the cement are subject to carbonation, with calcium hydroxide being the more rapidly reacting compound. These reactions show the formation of calcium carbonate, silica gel, and metallic oxides, which will eventually begin accumulating.

Carbonation can result in physical and chemical changes to cementitious

wasteforms. Permeability and diffusivity will decrease due to the obstruction of pores from calcium carbonate accumulation. CO<sub>2</sub> will also cause a decrease in the pH of the system, which in turn alters the solubility of the waste metals, either increasing or decreasing it. Additionally, carbonation may cause certain ions to go into solid solution in the calcium carbonate, which may limit the release of such ions.

Carbonation occurs through the mechanism of diffusion and proceeds as a reaction front passing through the concrete wasteform. As the gas diffuses through, it alters the concrete. Figure 1 illustrates the conceptual model of this process. The outer ring is the carbonated zone, where the concrete has been altered. This surrounds an inner zone of intact concrete not yet reached by the carbonation front. In addition, the rate of carbonation is dependent on the relative humidity, and has been found to occur more rapidly at a value of 50%. The shrinking core model can be used to approximate the rate of penetration of the reaction front. The equation describing this is as follows:

$$x(t) = \frac{2 \cdot C_{\text{HCO}_3} - D_{\text{HCO}_3} \cdot \phi \cdot \tau \cdot t}{C_{\text{SCa}}}$$

where X represents the thickness of the carbonated shell, C<sub>HCO<sub>3</sub></sub> = aqueous concentration of bicarbonate at the outer edge of the wasteform, D<sub>HCO<sub>3</sub></sub> = aqueous diffusion coefficient of bicarbonate ion in concrete pore fluid, C<sub>SCa</sub> = concentration of calcium in the solid concrete, φ = porosity of the wasteform, τ = tortuosity factor - a ratio of thickness to length of the sinuous path, and t = time.

The leaching of wasteforms can be a complex process to quantify, but is best described through the use of mass transport models. The mechanisms for mass transport

are diffusion and convection. For our purposes, convective transport is neglected due to low permeability of the wasteforms; therefore, diffusion is the controlling factor for describing leachability. Several diffusional models exist ranging from the less complex, such as Fick's First Law, to extensively detailed models which incorporate factors such as porosity and tortuosity of the medium.

One of the most widely used models is that of diffusion through semi-infinite media. In this model, the wasteform is looked at as a semi-infinite domain with a constant diffusion coefficient. This model assumes that the contaminant concentration in the solid remains uniform, that leaching is controlled by diffusion, and that the concentration at the solid-liquid interface is zero. In addition, this model applies to situations where the cumulative fractional release is less than 20%. Using this model, the cumulative fractional release of contaminant can be predicted. The expression is as follows:

$$\frac{\sum a_n}{A_0} \cdot \frac{V}{S} = \sqrt{2 \cdot \frac{D_e t}{\pi}}$$

where  $a_n$  = total amount of material released during time interval  $n$ ;  $A_0$  = initial amount of material in wasteform;  $V$  = volume of wasteform;  $S$  = surface area of the wasteform;  $D_e$  = effective diffusion coefficient; and  $t$  = time period for leaching.

As can be seen from this equation, the fractional cumulative release (FCR) is the first term of the equation, and it has a square root of time dependence. This is important to note because other processes follow the same time dependence. Because this expression is valid only when the cumulative fractional release is less than 20%, other

models must be used in cases where it approaches a value of one. Modeling the release in this case can be done using a more complex model for diffusion through finite media proposed by Pescatore [1].

Another important parameter that needs to be considered in studying leachability is solubility. This is important because, fundamentally, any constituent must first be dissolved in the pore water before it can leach. Solubility of different species varies, and it is related to reaction kinetics and other factors. The solubility product of a reaction can be calculated using the Gibb's Free Energy and the following equation:

$$\Delta G^{\circ}_r = -RT \ln K_{sp}$$

where  $\Delta G^{\circ}_r$  = standard free energy change of the reaction;  $R$  = universal gas constant; and  $T$  = absolute temperature  $K^{\circ}$ .

Another parameter related to solubility is the distribution coefficient,  $K_d$ . This coefficient represents the nature of partitioning of the ion between the solid and liquid phase. It is actually the ratio of ion concentration in the solid phase over the ion concentration in the liquid phase. Whether an ion will partition into the solid or liquid phase is determined partly by this coefficient. The value of  $K_d$  varies with the type of chemical and solid being considered.

The present research examines the role of carbonation in affecting the long-term leaching behavior of cementitious wasteforms. Leaching tests are performed on wasteforms made from Portland cement cured with a highly concentrated waste solution. The research combines the experimental results with modeling programs to evaluate the factors affecting the leaching behavior.

## EXPERIMENTAL METHODS

Portland cement was used to form the wastefoms used in this experiment. The wastefoms are of cylindrical shape with dimensions of 3.1 cm diameter and 6.7 cm height. The wastefoms were cast using a synthetic waste water with high ion concentrations as illustrated in Table 1.

Enough waste water was added to result in a water to cement ratio of 0.6, the ratio found to give optimum results in terms of porosity and strength. The mixture was poured into polyvinylchloride molds and allowed to cure for seven days.

The wastefoms were then reacted with CO<sub>2</sub>. This process was accomplished by placing a number of the wastefoms in stacks in two large beakers. Both sets of beakers were placed in an environmental control chamber to maintain a constant temperature of 50°C. The relative humidity of the system was also maintained at an approximate value of 50% by bubbling of gases through deionized water and into the beakers using diffuser tubes. One of the beakers was bubbled using a gas mixture of 50% CO<sub>2</sub>. These were the carbonated wastefoms and are referred to as the experimental wastefoms. The other set of wastefoms were used as controls and were reacted with CO<sub>2</sub>-removed air by passing of air through sodium hydroxide before bubbling into the deionized water. This reaction stage was continued and

carefully monitored for 26 days.

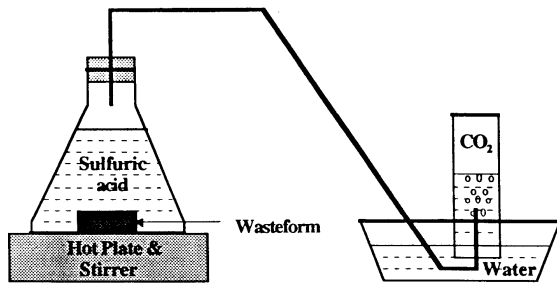
Following the reaction stage, the wastefoms were leached. Two separate leaching tests were conducted. In the first test, wastefoms were leached in 150 ml of deionized water. Five samples each of the experimental and controls were all leached for time intervals of 2, 7, 24, and 48 hours and 4, 7, 14, and 39 days. The leachate water was collected after each of the intervals and replaced with clean water. In the second test a 0.5 Normal acetic acid solution was used as the leachant, but the same time intervals were used except for the last of the series which was leached for 14 days instead of 39. The leachate water was analyzed by atomic absorption spectrophotometry and ion chromatography for presence of the ions introduced in the synthetic waste, following standard methods.

Following the leaching tests, the wastefoms were subjected to re-carbonation tests. In this procedure the wastefoms were digested in a closed Erlenmeyer flask using a 0.5 Normal sulfuric acid solution. This resulted in release of gas from the wastefoms which was collected and measured simply by using an inverted graduated cylinder in water, which was connected to the flask by plastic tubing (Figure 2). The collected gas was then analyzed in a carbon analyzer to determine the CO<sub>2</sub> content. Knowing the CO<sub>2</sub> concentration, the calcite concentration in the wastefoms can be calculated using the gas laws.

To ascertain the extent of carbonation occurring in the cement, the thickness of the carbonated shell was determined by performing a phenolphthalein test. A wasteform from each of the leaching tests was cut in half and topically dosed with a solution of 1% phenolphthalein in 70% ethyl alcohol. Phenolphthalein serves as an indicator; for pH values over 9.2 it turns red

**TABLE 1. SYNTHETIC WASTE WATER.**

Salt	Ion Conc. (mg/l)
CdCl <sub>2</sub>	3,000 (Cd)
Co Cl <sub>2</sub>	3,000 (Co)
Pb(NO <sub>3</sub> ) <sub>2</sub>	3,000 (Pb)
Sr(NO <sub>3</sub> ) <sub>2</sub>	1,000 (Sr)
ZnCl <sub>2</sub>	3,000 (Zn)



**FIGURE 2.** SCHEMATIC OF RE-CARBONATION TEST.

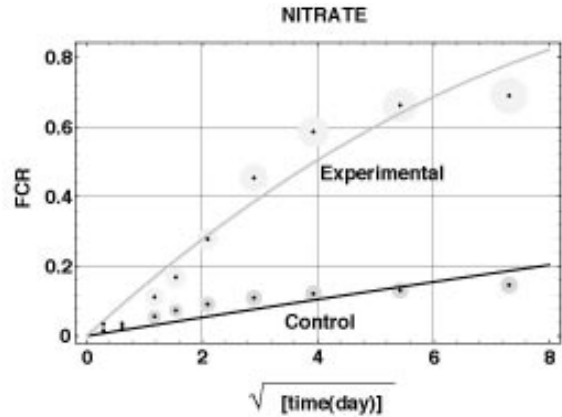
on contact whereas it remains uncolored for low pH values.

## RESULTS AND DISCUSSION

Wasteforms were measured and weighed to determine their physical properties. In the case of the experimental wasteforms, the final porosity was 35.39%, and they were found to be fully carbonated with an average bulk calcium carbonate concentration of  $9 \times 10^{-4} \text{ mol/cm}^3$ . The non-carbonated control samples had a porosity of 48.11%. Thus, it is evident that carbonation results in reduced porosity due to the larger molar volume of calcite ( $\text{CaCO}_3$ ) relative to the initial portlandite ( $\text{Ca(OH)}_2$ ) in the cement.

### *First leaching test*

Leaching results were obtained only for strontium and nitrates. Results for the other ions couldn't be obtained because their concentrations were below detection limits. Graphs of the fractional cumulative release (FCR) vs. square root of time were drawn in order to determine the apparent diffusion coefficient of the different species. The square root of time was used due to the fact that several processes including simple diffusional release lead to a square root of time dependence for total contaminant release. The theoretical model of FCR vs. time is non-linear, but plotting FCR vs. the



**FIGURE 3.** FRACTIONAL CUMULATIVE RELEASE (FCR) OF NITRATE.

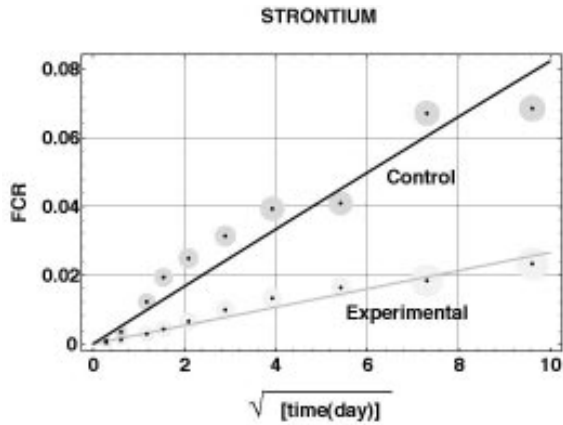
square root of time results in a straight line, indicating that the wasteform acts like a semi-infinite domain during early time periods. The line then curves towards the right as the FCR approaches a value of 1.

Solubility graphs were also constructed. These are, of course, essential in determining the species present at varying pH. Other important parameters in determining the apparent diffusion coefficient are the retardation factor and tortuosity, which are related to the apparent diffusion coefficient by the following [2]:

$$D_a = \frac{\tau D}{R_d}$$

where  $\tau$  = tortuosity;  $D_a$  = apparent diffusion coefficient;  $D$  = diffusion coefficient in water;  $R_d$  = retardation factor of the ion;  $\rho_b$  = bulk density ( $\text{g/cm}^3$ );  $K_d$  = distribution coefficient; and  $\theta$  = volumetric water content.

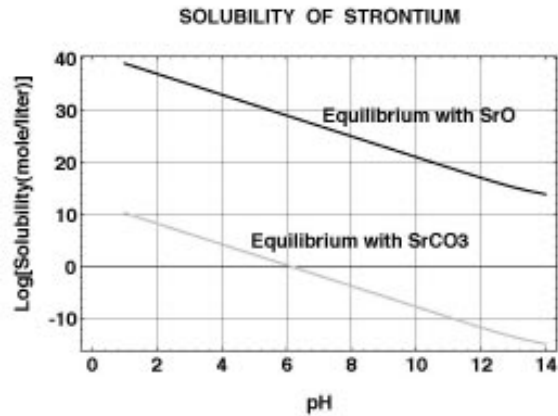
The results of the nitrate analysis are indicated in Figure 3. Each of the points represents an average of five replicates; the line indicates the non-linear fit to the finite domain diffusion equation [1]. The



**FIGURE 4.** FRACTIONAL CUMULATIVE RELEASE (FCR) OF STRONTIUM.

calculated apparent diffusion coefficients for nitrate were  $2.55 \times 10^{-10} \text{ cm}^2/\text{s}$  for the controls and  $2.59 \times 10^{-11} \text{ cm}^2/\text{s}$  for the carbonated wasteforms. The leaching rate of nitrate is rapid. For this reason, nitrate was placed in the wasteforms so as to assess the diffusion rate of a chemical species which would not interact chemically with the wasteforms. This would indicate physical changes taking place in the wasteform. Our results show that the carbonated wasteforms had a higher leaching rate than the controls. This is contrary to what was expected, since the carbonated wasteforms have a lower porosity which should lead to a lower diffusion coefficient. A reason for this discrepancy could be that increased microcracking from the expansive forces generated in the carbonated samples led to higher initial leaching rates or resulted in a modification of the pore distribution favoring a larger average pore size.

The results of the strontium analysis are indicated in Figure 4. Here we see that the leaching of strontium from the carbonated wasteforms is lower than from the controls. The apparent diffusion coefficients are  $2.55 \times 10^{-10} \text{ cm}^2/\text{s}$  for the controls and  $2.59 \times 10^{-11} \text{ cm}^2/\text{s}$  for the experimental. In this case



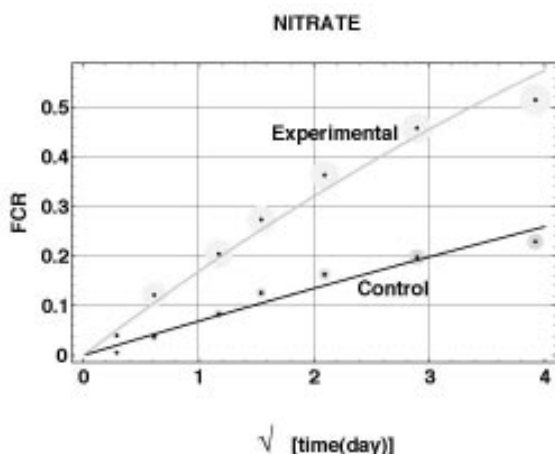
**FIGURE 5.** SOLUBILITY OF STRONTIUM.

results are consistent with other factors such as the retardation factor which had values of 4.32 for the controls and 1,336.07 for the experimental. The distribution coefficient was also consistent with a higher index of leachability of the controls, giving values of 0.84 ml/g for the controls and 375.54 ml/g for the experimental. This indicates a higher concentration of strontium in the pore water than in the solid. Figure 5 shows the equilibrium diagram of strontium, which indicates that strontium is of higher solubility at lower pH. This is consistent with our results.

### *Second leaching test*

The use of acetic acid as the leachant resulted in higher leaching rates for all the species in the second leaching test. In this case, results were obtained for a number of ions including cadmium, calcium, lead, and cobalt.

The results of the nitrate analysis are similar to those in the first test. Figure 6 shows the results for nitrate. As can be seen, the experimental samples leached at a higher rate than the controls. The curves for each set of data are the non-linear best fit model and result in apparent diffusion coefficient

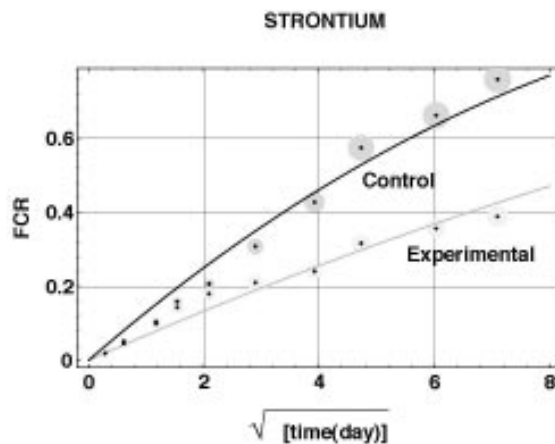


**FIGURE 6.** FRACTIONAL CUMULATIVE RELEASE (FCR) OF NITRATE IN ACETIC ACID.

values of  $1.77 \times 10^{-8}$  for the controls and  $1.14 \times 10^{-7}$  for the carbonated samples.

The strontium results also supported those of the first test. Figure 7 shows that the leaching rate of the controls is higher than that of the carbonated samples. The apparent diffusion coefficients based upon the non-linear best fit model were found to be  $6.61 \times 10^{-8}$  for the controls and  $1.74 \times 10^{-8}$  for the carbonated samples. Again, in this case, the other parameters of the retardation factor and distribution coefficient were consistent with the results. The retardation factors are 0.121 for the controls and 2.38 for the carbonated samples. The distribution coefficients are -0.22 and 0.38 ml/g for the controls and carbonated samples, respectively. The negative value of the distribution coefficient is not theoretically possible and could be due to the fact that the molecular diffusion coefficient of strontium in water instead of acidic water was used to calculate it.

Analyses were also performed for ions of calcium, cadmium, cobalt, and lead. For all of these ions, the leaching rate was higher in the carbonated wastefoms than the controls.



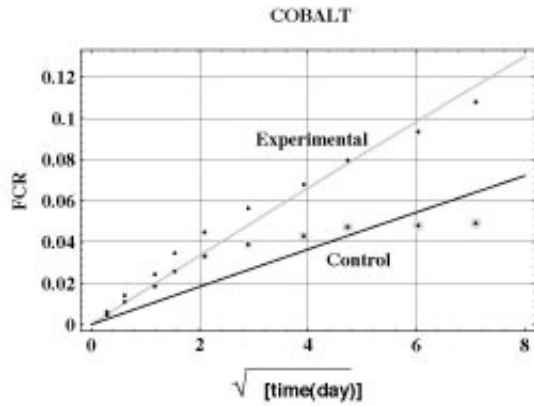
**FIGURE 7.** FRACTIONAL CUMULATIVE RELEASE (FCR) OF STRONTIUM IN ACETIC ACID.

This might indicate that factors other than diffusion are dominating. It follows that the apparent diffusion coefficients calculated for each of these ions is larger in the carbonated wastefoms. The graphs of the FCR and solubility for these ions are contained in Figures 8-13. The calculated porosities, however, are inconsistent with these results, being greater in the controls than the experimental wastefoms.

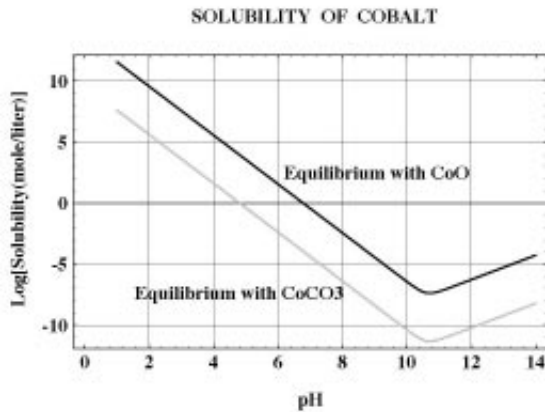
## CONCLUSION

The presented research was done with the goal of reproducing as closely as possible one of the fundamental environmental processes encountered by wastefoms in the vadose zone, carbonation.

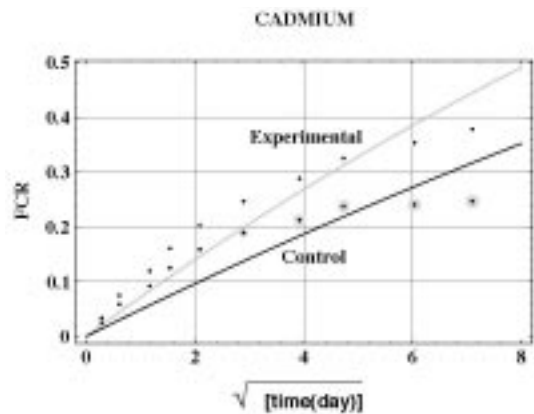
It is clearly evident that carbonation leads to physical and chemical changes in cementitious wastefoms. The results indicate that carbonation indeed does affect the leaching rate, but does not affect it in the same manner all the time. Although it leads to decreased porosity, it also resulted in higher leaching rates for some ions. It is believed this is due to microcracking in the carbonated samples. Microcracks may



**FIGURE 8.** FRACTIONAL CUMULATIVE RELEASE (FCR) OF COBALT.

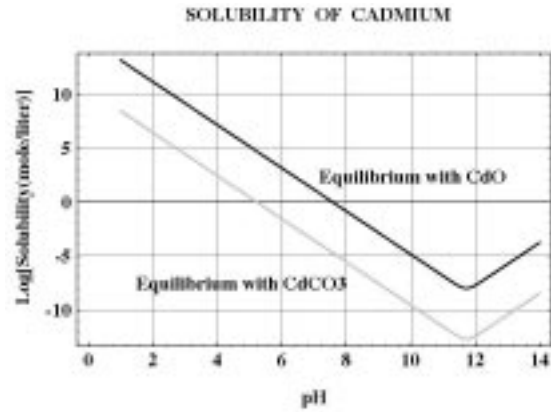


**FIGURE 9.** SOLUBILITY OF COBALT.



**FIGURE 10.** FRACTIONAL CUMULATIVE RELEASE (FCR) OF CADMIUM.

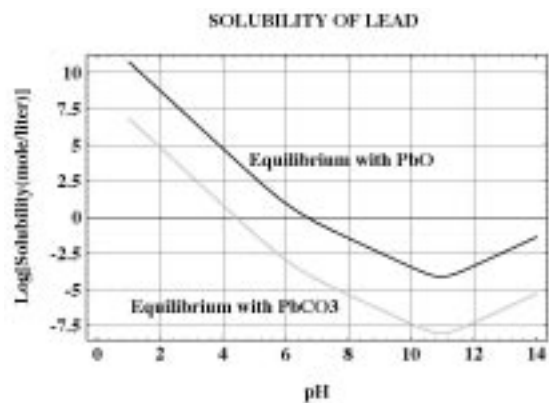
provide a conduit through which the contaminants leach faster.



**FIGURE 11.** SOLUBILITY OF CADMIUM.



**FIGURE 12.** FRACTIONAL CUMULATIVE RELEASE (FCR) OF LEAD.



**FIGURE 13.** SOLUBILITY OF LEAD.

Leaching can be affected by a combination of physical and chemical effects. Strong chemical effects in the carbonated wastefoms are believed to limit the leaching rate. In our research, however, there seems

to be a crossover between physical and chemical effects, leading to increased leaching from carbonation for certain species. What net effect it will have is dependent on the contaminant species itself.

Other than strontium, carbonation resulted in higher leaching rates for all the other chemical species. Thus, for the ions tested, carbonation seems to have a negative effect on the leaching characteristics of cementitious wastefoms.

## **ACKNOWLEDGMENT**

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