

INFLUENCE OF CARBONATION ON LEACHING OF CEMENTITIOUS WASTEFORMS

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ABSTRACT: The presented work represents a combined experimental and modeling approach to evaluate the role of carbon dioxide in the long-term performance of cementitious wasteforms. Small wasteforms were cast with Portland cement and synthetic wastewater containing known amounts of dissolved metals and nitrate as a tracer. A series of wasteforms was exposed to a control (CO₂-free) and an accelerated environment for carbonation (50% CO₂). The samples were subjected to dynamic leaching tests, and the results were fit to the two-dimensional diffusional release equation. Comparison of results for carbonated and noncarbonated samples indicated that both physical and chemical properties controlling release were altered by carbonation. Carbonation slowed the diffusional release of strontium and increased the release of nitrate, calcium, cadmium, lead, and cobalt. Comparison of the leaching rate of each metal relative to calcium was used to indicate solid solution in calcium hydroxide (cadmium) and calcium carbonate (cadmium and strontium). Leaching of cadmium and strontium appears to be heavily influenced by solid solution in calcium bearing phases.

INTRODUCTION

Solidification and stabilization with cementitious materials is a widely accepted and economically attractive waste management option for disposal of heavy metals and radionuclides; however, the stabilization mechanisms and processes controlling long-term performance are not well understood. Most research on cementitious wasteforms deals with refinements of mixes or 'recipes' to improve the performance relative to standardized tests [Toxicity Characteristic Leaching Procedure (TCLP) and ANSI/ANS-16.1]. Standardized leach tests provide only a limited amount of information and are insufficient for estimation of long-term performance. The accepted test for radioactive wastes is the ANSI/ANS-16.1 leach test (*Measurement* 1986). In this test, a single parameter called the 'leachability index' is determined by fitting the diffusion-based release equation to short-term leaching results. The Toxicity Characteristic Leaching Procedure (TCLP) ("Toxicity" 1986), promoted by the U.S. Environmental Protection Agency (EPA), is based on overnight extraction using acetic acid solution and a crushed wasteform. A major concern for risk assessments is how the short-term leaching results under controlled conditions relate to in situ leach rates. Quantitative interpretation of these tests is hampered by lack of correspondence between test conditions and the service environment.

According to the current regulatory requirements in the United States, stabilized wasteforms must be placed in the vadose or partially water saturated zone above the water table. The vadose zone, in general, provides a much more aggressive long-term environment for cementitious materials by increasing contact with carbon dioxide and oxygen in the soil air and variable contact with water. The standardized performance

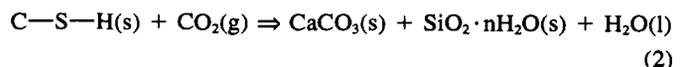
tests of cementitious wasteforms ignore the role of carbonation, a potentially important natural weathering process of cementitious materials. Significant research has been carried out to examine the physical changes (porosity, tortuosity, permeability, etc.) due to carbonation of cementitious material (Reardon and Dewaele 1990; Houst and Wittmann 1994). Chemical changes from carbonation of wasteforms have also been investigated (Mollah et al. 1992; Lange et al. 1996). The role of carbonation on dynamic leaching of nitrate, calcium, and strontium from cementitious wasteforms into pure water has been reported previously (Walton et al. 1997), and it was observed that carbonation resulted in lower leaching of strontium whereas leaching of nitrate and calcium were increased by carbonation. The purpose of this paper is to report work with other metals in a more aggressive leaching environment.

CARBONATION OF CEMENTITIOUS MATERIAL

Soil air is expected to contain increased levels of CO₂ and reduced levels of O₂ (relative to the atmosphere) as a result of microbial activities. The fugacity of CO₂ for equilibrium among water, portlandite, and calcite is sufficiently low (10⁻¹³ bar compared to the atmospheric value of 10^{-3.5} bar) that introduction of CO₂ can have a significant effect on cementitious materials. Over long time periods, cementitious wasteforms react irreversibly with soil gases within the vadose zone in a process known as carbonation. Major mineralogical changes associated with carbonation include conversion of portlandite (Dayal and Reardon 1992):



and calcium silicate hydrate gel to calcite:



Portlandite, as shown in (1), reacts most rapidly with CO₂; however, other cement phases are subject to carbonation.

The conceptual model of carbonation is that CO₂ diffuses into the wasteform, reacts with cementitious material, and surrounds the inner zone of intact wasteform with a growing rind of altered wasteform. The thickness of the carbonated shell can be approximated from a shrinking core model (Smith and Walton 1991). The migration of the front is most rapid at a relative humidity of 50-65% and declines at greater and lower relative humidity (Papadakis et al. 1989). Carbonation changes the physical and chemical characteristics of the wasteform. The conversion of portlandite into calcite leads to a reorga-

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TABLE 1. Synthetic Wastewater Composition

Species (1)	Concentration (mg/l) (2)
Nitrate	3,200
Strontium	1,000
Cadmium	3,000
Cobalt	3,000
Lead	3,000

nization of the microstructure, an increase in weight and bulk density, a decrease in porosity and permeability, and a decrease in total volume (Houst and Wittmann 1994). Augmentation of molar volume and shrinkage during carbonation may lead to microcracking (Houst and Wittmann 1994).

The best known chemical effect of carbonation is the loss of pH from around 13 to 8.3 (Reardon and Dewaele 1990), which changes (usually increases) the solubility of waste metals previously immobilized by the high pH of the wastefrom. Another change in wastefrom behavior is the potential for solid solution of some ions in calcite present in the carbonated zone (Pingitore and Eastman 1996). Initial calculations of the importance of calcite solid solution on contaminant release from cementitious wastefroms suggest that the process is potentially important in limiting the release of some ions (Smith and Walton 1991).

EXPERIMENTAL METHOD

Cylindrical wastefroms of diameter 3.1 cm and height 6.7 cm were used for this experiment. Wastefroms were cast with Portland cement and synthetic wastewater containing dissolved metal ions as illustrated in Table 1. A high water-to-cement ratio (0.6) was employed for casting to get an appreciable amount of contaminant release within the experimental time frame. The wastefroms were cured at 100% relative humidity for seven days at room temperature and then placed into a controlled environment chamber at a temperature of 50° ± 1°C.

In a controlled environment chamber, the experimental wastefroms were exposed to a 50% CO₂ atmosphere at 75–50% relative humidity to enhance the rate of carbonation. An air stream containing 50% CO₂ was maintained by a diffuser tube in the chamber of the experimental samples. The controls were placed in identical environments, except that CO₂-free air was provided by passing the air stream for the controls through sodium hydroxide. The relative humidity of the chamber was maintained by bubbling air through a saturated sodium chloride solution.

After 52 days exposure, the experimental wastefroms were fully carbonated in the accelerated chamber. Five replicates of each of the experimental and control wastefroms were subjected to leaching at room temperature in 150 mL of 0.5 N acetic acid with pH around 5. Acidic water was used to create a more aggressive leaching situation. The choice of mildly acidic solution has some basis in natural systems; landfill leachate may contain acetic acid from partial microbial breakdown of organic wastes and packaging materials. The leachate was changed on each of the samples at intervals of two hours, seven hours, one day, one day, two days, four days, seven days, seven days, 14 days, and 14 days.

The leachates were analyzed by atomic absorption spectrophotometry and ion chromatography following standard methods. Subsequent to leaching, samples were dried at 105° until a constant mass was obtained. Porosity was estimated from weight loss during drying.

DATA ANALYSIS

A common methodology for dealing with diffusion in concrete wastefroms is to define the diffusion coefficient based upon the total concentration of a contaminant in the porous media (Atkinson and Nickerson 1988). The mass balance of a species is written in terms of total concentration in the porous media:

$$\frac{\partial C_t}{\partial t} = \nabla \cdot D_a \nabla C_t \tag{3}$$

where D_a = the apparent diffusion coefficient (cm²/s); C_t = total concentration of metals in the wastefrom (mole/cm³); and t = time (s).

A closed form expression for diffusive fractional release of a chemical substance from a finite size wastefrom proposed by Pescatore (1990) was used for the mathematical model to analyze the experimental data.

RESULTS AND COMMENTARY

The average porosity was 0.48 for the controls and 0.35 for the carbonated wastefroms. The reduction in porosity results from the larger molar volume of calcite relative to the initial portlandite in the cement and from carbonation related shrinkage. The average bulk calcium carbonate concentration for the carbonated wastefrom was 5.8×10^{-3} mol/cm³ and below detection for the controls. Calcium carbonate content was measured by digesting the wastefroms in acid solution and measuring CO₂ given off in the gas phase.

The leaching results for different species are shown in Figs. 1–6. The apparent diffusion coefficients (Table 2) have been calculated based upon the nonlinear best fit diffusion model curve with the experimental data. Release was faster in the

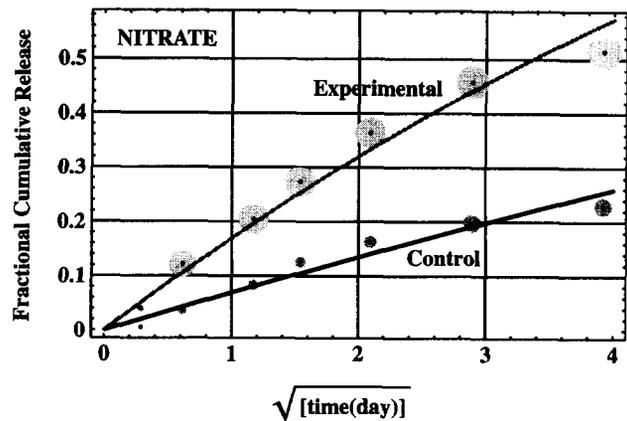


FIG. 1. Fractional Cumulative Release (FCR) of Nitrate

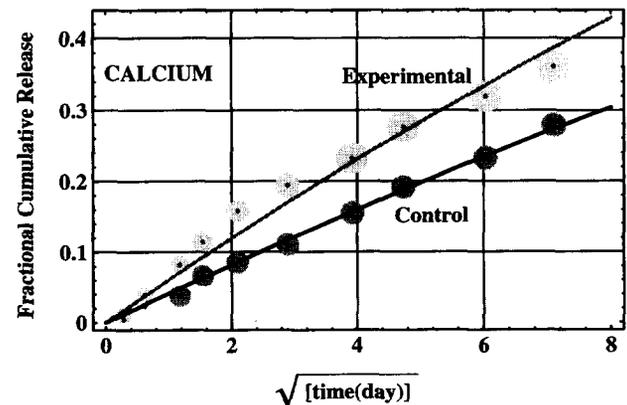


FIG. 2. Fractional Cumulative Release (FCR) of Calcium

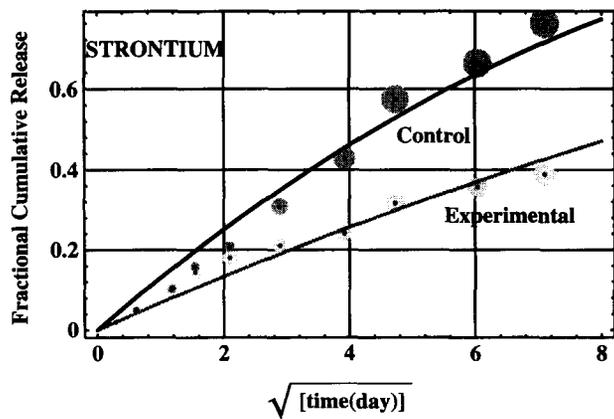


FIG. 3. Fractional Cumulative Release (FCR) of Strontium

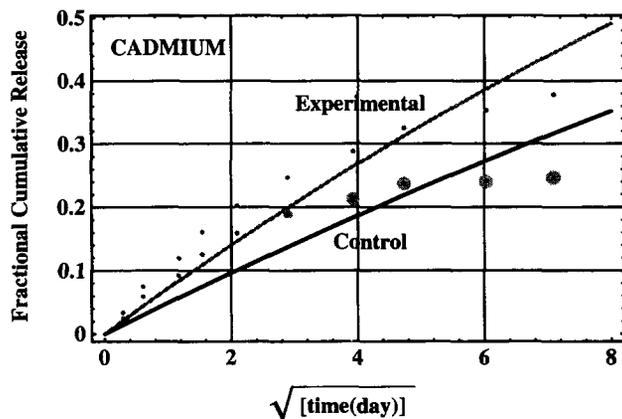


FIG. 4. Fractional Cumulative Release (FCR) of Cadmium

carbonated wasteforms for all the species except strontium. The plotted data points represent the average of five replicates. The gray circle surrounding the plotted data point represents the variability associated with the five replicates. Circles were drawn with a radius of two times the standard deviation. Propagation of error was considered when calculating cumulative release. This causes the uncertainty bands to grow with time.

The nitrate results are indicative of physical changes in the wasteforms from carbonation because of the high solubility and low adsorption of the nitrate anion. Changes in processes controlling chemical properties due to carbonation (solubility and partitioning) should not affect the diffusion rate of nitrate markedly. Theoretically, the lower porosity of the carbonated samples should lead to lower diffusion coefficients—just the opposite of what is observed in Fig. 1. The discrepancy may occur from increased microcracking (Houst 1997) in the carbonated samples as a result of contractive forces generated during carbonation, or perhaps a modification of the pore size distribution toward larger average pore size and/or removal of occluded pores. Because nitrate remains in solution, the tortuosity factor can be estimated by comparing its apparent diffusion coefficient with its molecular diffusion coefficient. The tortuosity factor was 6.0×10^{-3} for the carbonated and 9.3×10^{-4} for the control wasteforms. This indicates, from a physical standpoint, that diffusion is six times faster in the carbonated wasteforms.

A shrinking core model curve was also derived and fit to the experimental data. The shrinking core model assumes that release occurs by diffusion from a "shrinking core" of intact wasteform across an altered (by leaching) outer zone. The shrinking core model gives the same predicted release curve as the two-dimensional diffusion model except that the fit parameter is the species effective solubility rather than the apparent diffusion coefficient, D_a . The equivalence between dif-

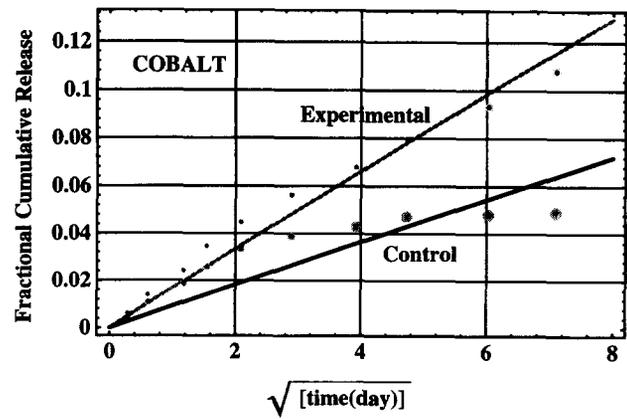


FIG. 5. Fractional Cumulative Release (FCR) of Cobalt

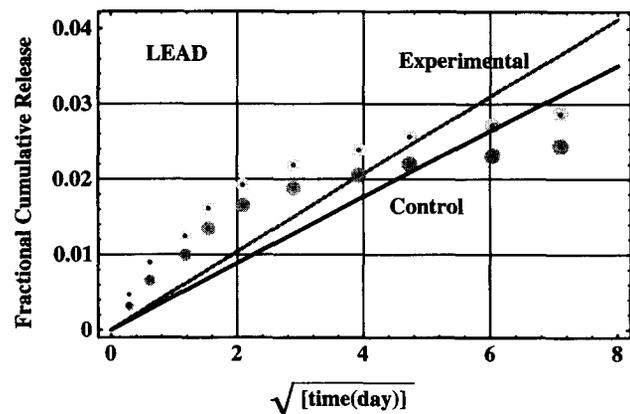


FIG. 6. Fractional Cumulative Release (FCR) of Lead

TABLE 2. Ionic Radii and Apparent Diffusion Coefficients (D_a) of Species

Species (1)	Ionic radius (relative to calcium) (2)	Sample (3)	Apparent diffusion coefficient (cm^2/s) (4)
Nitrate	—	Experimental	1.14E-7
		Control	1.77E-8
Calcium	1.00	Experimental	1.39E-8
		Control	6.33E-9
Strontium	1.16	Experimental	1.74E-8
		Control	6.61E-8
Cadmium	0.95	Experimental	1.92E-8
		Control	8.80E-9
Cobalt	0.74	Experimental	1.03E-9
		Control	3.06E-10
Lead	1.18	Experimental	9.79E-11
		Control	7.08E-11

fusion and shrinking core models has been shown previously (Walton et al. 1997) for the one-dimensional case. Both models predict that release declines with the square root of time during early time periods.

In both the models, consideration of increasing effective or apparent diffusion coefficients (i.e., higher porosity or lower tortuosity) towards the periphery of the circular cross-section of the wasteform gives better agreement with experimental data when compared with the assumption of homogeneous physical properties throughout the domain. This could be caused by small surface cracks, higher concentration of contaminants in outer portions of the wasteforms from "bleed water" at the time of casting with a high water-to-cement ratio (0.6), migration of species toward the outer surface during drying of the wasteforms from 100% to 50-75% relative hu-

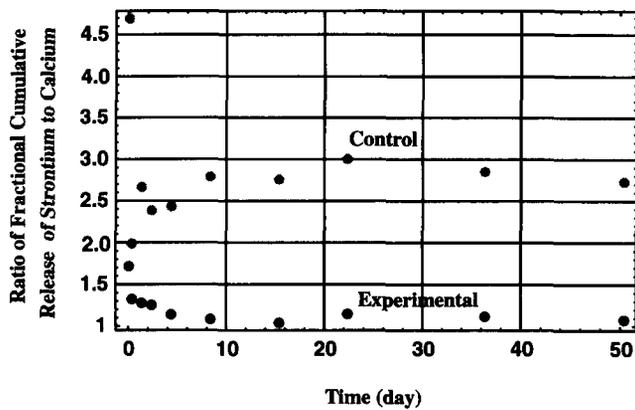


FIG. 7. Ratio of Fractional Cumulative Release of Strontium to Calcium

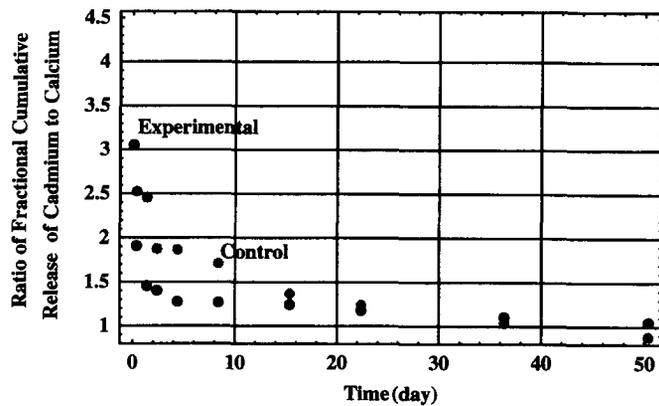


FIG. 8. Ratio of Fractional Cumulative Release of Cadmium to Calcium

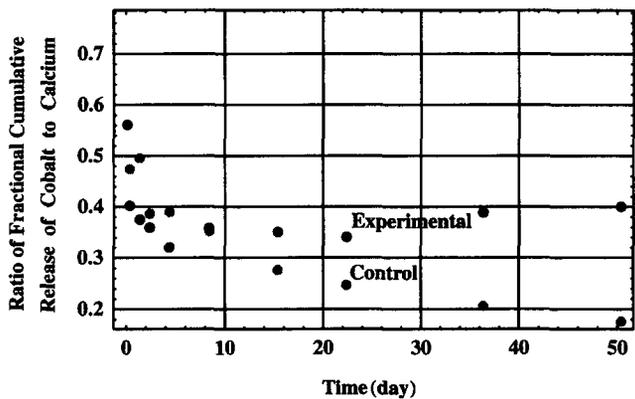


FIG. 9. Ratio of Fractional Cumulative Release of Cobalt to Calcium

midity, and/or from slow chemical reaction kinetics. The data clearly indicate that the simple diffusion model with a constant diffusion coefficient is not adequate to fully describe the leaching results.

Figs. 7–10 give the measured cumulative fractional release of each metal relative to calcium. Several interesting trends emerge from the figures. Strontium is released at the same relative rate as calcium in the carbonated wastefoms but more rapidly than calcium in the controls. Cadmium follows calcium closely in both the carbonated and control wastefoms. Cobalt and lead are released more slowly in experimental and control wastefoms than calcium.

Ratios near one indicate the metal is bound to the calcium phase, predominantly calcium hydroxide in the uncarbonated and calcium carbonate in the carbonated wastefoms. A solid

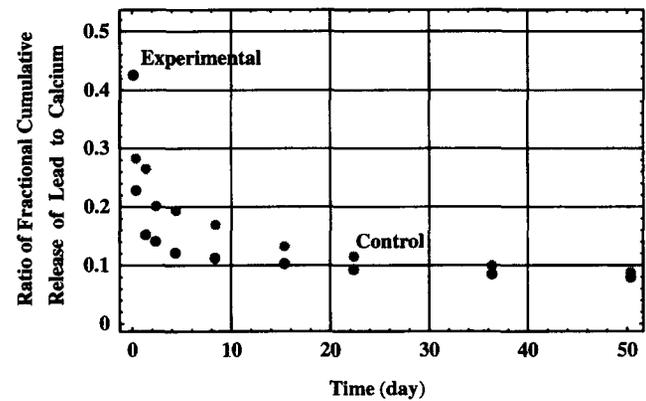


FIG. 10. Ratio of Fractional Cumulative Release of Lead to Calcium

solution can occur when ions of one type substitute ions of another type in a lattice, forming a single crystalline phase. Solid solutions form best when both ions form relatively low solubility solids and have similar ionic radii. Ionic radii of different species are given in Table 2. The ionic radius of cadmium is close to calcium, and cadmium goes readily into solid solution with calcium carbonate (Tesoriere and Pankow 1996). Cadmium has low solubility cadmium hydroxide and carbonate phases and appears to go into solid solution in both calcium phases based upon the near 1:1 leaching ratio (Fig. 8). Mollah et al. (1994) indicated evidence for a $(\text{Cd}, \text{Ca}) (\text{OH})_2$ phase in cementitious wastefoms. Strontium has a low solubility carbonate phase but no low solubility hydroxide phase, indicating that solid solution should be strong in calcium carbonate but not calcium hydroxide. Fig. 7 indicates that strontium goes into solid solution in calcium carbonate (leaching ratio near 1:1) but not in calcium hydroxide in the wastefoms (leaching ratio 2–3:1). Lead and cobalt have leaching ratios below 1:1 in experimental and control wastefoms, suggesting that they are associated with other low solubility phases in the wastefoms.

CONCLUSIONS

The experimental data indicate that carbonation leads to decreased physical retention of contaminants despite the fact that carbonation causes a significant decrease in porosity. The decrease in physical retention may reflect microcracking and/or the rearrangement of pores to remove or decrease occluded areas. The physical changes are evidenced by the more rapid release of NO_3^- from the carbonated wastefoms in relation to the controls. Strontium is more tightly bound in the carbonated wastefoms through solid solution in calcium carbonate, giving a lower apparent diffusion coefficient (D_a) for the carbonated wastefom. Because cadmium has a low solubility phase for both calcium hydroxide and calcium carbonate, it goes into solid solution for both control and carbonated wastefoms. Unlike strontium, the apparent diffusion coefficients (D_a) of cadmium, cobalt, and lead are higher for the carbonated wastefoms. The net result of carbonation may be either to increase or decrease the release rate and depends upon the specific species of concern. The importance of carbonation in determining long-term performance is ignored in current standardized test methodologies and may limit the usefulness of those tests in predicting long-term performance.

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