

# CALCITE SOLID SOLUTION FORMATION AND CARBONATION EFFECTS ON THE RADIONUCLIDE RELEASE FROM CONCRETE WASTE FORMS

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## ABSTRACT

The weathering of exposed concrete surfaces by reaction with carbon dioxide causes the formation of an outer layer of carbonated material on the concrete. The carbonated concrete layer is important because some divalent radionuclides will form solid solutions with calcite present in the carbonated layer. The solid solutions result in retardation of radionuclide migration through the weathered concrete thereby leading to improved performance of portland cement based waste forms. Example calculations for  $^{90}\text{Sr}$  and  $^{60}\text{Co}$  indicate that release rates from carbonated concrete waste forms are significantly lower than for intact, unweathered concrete waste forms and that the thin carbonated zone is a significant sink for these radionuclides.

## INTRODUCTION

In the United States and other countries, the design and construction of low-level radioactive waste disposal facilities will involve the use of concrete components. Although concrete is used primarily for its structural (e.g., high compressive strength) and physical properties (e.g., low permeability), the effect of cementitious materials in concrete on the geochemical environment in the immediate vicinity of the concrete is pronounced. The geochemistry of pore fluids in contact with hydrated cementitious materials is characterized by persistent alkaline pH values buffered by the presence of hydrated calcium silicates [C-S-H] and portlandite [ $\text{Ca}(\text{OH})_2$ ] in the cement. Because the  $\text{CO}_2$  fugacity for equilibrium among water-portlandite-calcite is so low ( $10^{-13}$  compared to the atmospheric value of  $10^{-3.5}$ ), the introduction of even small amounts of  $\text{CO}_2$  into concrete pore fluids by either gaseous diffusion or aqueous transport (as bicarbonate) results in the precipitation of calcite [ $\text{CaCO}_3$ ]. This chemical interaction, a major form of weathering for concrete, is called carbonation.

The precipitation of calcite can significantly affect the mass transport of radionuclides that may coprecipitate with the calcite formed by carbonation. Calcite is capable of forming solid solutions with a large number of cations. Solid solution formation with the cationic species  $^{90}\text{Sr}$  and  $^{60}\text{Co}$  is considered herein.

## SOLID SOLUTION MODEL

The thermodynamic behavior of carbonate solid solutions has received considerable recent attention [1-9]. The results of these previous studies indicate that the solid solution behavior of calcite is complicated. The enthalpy of mixing ( $H^{\text{mix}}$ ) can be either negative or positive depending on the substituting ion. In addition, the excess entropy of mixing ( $S^{\text{ex}}$ ) is often not zero, resulting in a temperature dependence of the excess free energy of mixing ( $G^{\text{ex}}$ ).

Experimentally determined values of  $G^{\text{ex}}$  for magnesium-calcite (4) and aragonite-strontianite (3) have been described using a two-term Margules expression. However,

the availability of Margules parameters for other substituting ions (Sr and Co in calcite) appropriate to a low-level radioactive waste disposal facility is limited. Although methods to estimate these parameters at elevated temperatures (typically greater than 300 to 400°C) based on the volumetric properties of the solids have been proposed (10), equivalent methods for temperatures relevant to low-level disposal sites are not available. Therefore, a simple model with predictive capabilities (referred to as the modified Lippmann model) was developed to calculate  $G^{\text{ex}}$  for multi-component solid solutions.

Lippmann (11) proposed a model to describe  $H^{\text{mix}}$  for binary solid solutions of rhombohedral carbonates. This model is based on the difference between calculated electrostatic lattice energies for the two end-member carbonates and the intermediate composition solid solutions. Lippmann justifies this method because of the similarities of the rhombohedral carbonates structure to the rock-salt structure type. Smith and Jenne (12,13) found that Lippmann's model overestimates  $G^{\text{ex}}$  for calcite solid solutions and revised the model in order to provide better agreement between predicted values and experimentally determined values of mixing properties. Values of  $G^{\text{ex}}$  for binary rhombohedral carbonates solid solutions can be estimated from (12):

$$\frac{\Delta G^{\text{ex}}}{RT} = -M \left( \frac{1}{r_1 + \chi_2(r_2 - r_1)} - \frac{\chi_2}{r_2} - \frac{1 - \chi_2}{r_1} \right) \quad (\text{Eq. 1})$$

where  $R$  is the ideal gas constant,  $T$  is the temperature in Kelvin,  $M$  is a fit parameter that is a function of temperature but independent of substituting ions with a value of 2100 Å at 298.15 K, and  $\chi_2$  is the mole fraction of component 2 in the solid solution. The cation-anion distances,  $r_1$  and  $r_2$ , are calculated from:

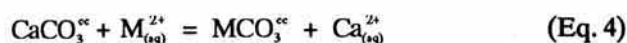
$$r_i = \sqrt{\frac{c_i^2}{144} + \frac{a_i^2}{3}} \quad (\text{Eq. 2})$$

where  $c_i$  and  $a_i$  are the unit cell dimensions of the subscripted pure rhombohedral carbonate. The values of  $r_i$  for  $\text{CaCO}_3$ ,  $\text{CoCO}_3$ , and  $\text{SrCO}_3$  are 3.212, 2.964, and 3.349 Å, respectively (13).

Activity coefficients ( $\lambda_i$ ) for the end-member solids of the solid solution can be calculated from:

$$\ln \lambda_i = -M \left( \frac{2}{r_i + \chi_2(r_2 - r_i)} - \frac{r_i}{(r_i + \chi_2(r_2 - r_i))^2} - \frac{1}{r_i} \right) \quad (\text{Eq. 3})$$

For solid solutions in which only trace substitution occurs ( $\chi_2 \ll 1$ ), compositional calculations can be simplified by use of an equilibrium distribution coefficient. The equilibrium distribution coefficient,  $D_{\text{Ca-M}}$ , for cation  $\text{M}^{2+}$  in calcite (denoted with a cc superscript) is given by (14):



$$D_{\text{Ca-M}} = \frac{\chi_{\text{MCO}_3} / \chi_{\text{CaCO}_3}}{m_{\text{M}^{2+}} / m_{\text{Ca}^{2+}}} \quad (\text{Eq. 5})$$

where  $m_{\text{t},i}$  is the total molal concentration of the subscripted ion. At equilibrium, the distribution coefficient is related to the equilibrium constant,  $K_{\text{Ca-M}}$ , of reaction (4) by:

$$\ln(D_{\text{Ca-M}}) = \ln(K_{\text{Ca-M}}) - \ln \left( \frac{\lambda_{\text{MCO}_3} \gamma_{\text{Ca}^{2+}}}{\lambda_{\text{CaCO}_3} \gamma_{\text{M}^{2+}}} \right) \quad (\text{Eq. 6})$$

where  $\gamma_i$  is the stoichiometric individual ion activity coefficient of the subscripted species (15) defined by  $\gamma_i$  equal to  $a_i/m_{\text{t},i}$ , and incorporates both the ion activity coefficient and ion complexation. Values of  $\gamma_i$ , calculated using an aqueous speciation code such as EQ3NR (16), can be coupled with values of  $\lambda_i$  calculated from Eq. 3 and values of  $K_{\text{Ca-M}}$  derived from tabulated thermodynamic data to estimate equilibrium values of  $D_{\text{Ca-M}}$  as a function of aqueous composition.

The first term inside the parentheses of Eqs. 1 and 3 is the reciprocal of the average cation-anion distance for the intermediate composition solid solution and is assumed to be a linear function of composition. The suitability of this assumption for calculating average cation-anion distances in rhombohedral carbonate solid solutions has been evaluated for numerous binary rhombohedral solid solutions. The results for strontium are shown in Fig. 1. The deviation between cation-anion distance determined from measured cell parameters for rhombohedral solid solutions (symbols, Fig. 1) and values calculated assuming a linear mixing of end-members (curves, Fig. 1) is on the order of 0.01 or less except for  $\text{PbCO}_3$  and  $\text{BaCO}_3$  (not shown). The much larger

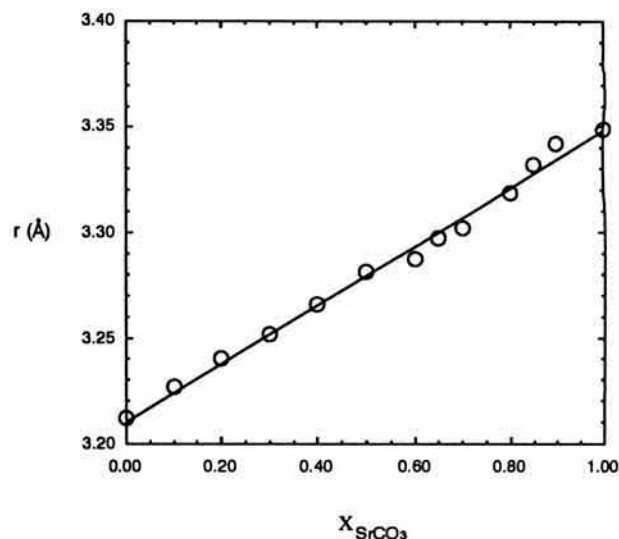


Fig. 1. Comparison between cation-anion distance determined from measured cell parameters for rhombohedral solid solution (symbols) and values calculated assuming linear mixing of end-members (curve) for  $\text{Sr}_x\text{Ca}_{(1-x)}\text{CO}_3$ . Measured data are from Chang (19).

size of  $\text{Pb}^{2+}$  (1.18, (17)) and  $\text{Ba}^{2+}$  (1.36, (17)) than the  $\text{Ca}^{2+}$  ion (1.00, (17)) accounts for the observed difference. In addition, neither rhombohedral  $\text{PbCO}_3$  nor  $\text{BaCO}_3$  are stable at low temperatures or pressures.

The value of  $M$  used in Eqs. 1 and 3 can be estimated from solubility and phase equilibrium experiments on rhombohedral carbonate solid solutions. Three types of experimental results have been evaluated:

- Solubility measurements of carbonate solid solutions at low temperatures.
- Solvi determinations for binary solid solutions from phase equilibrium studies.
- Measurement of the decomposition of carbonate solid solutions as a function of temperature and  $\text{CO}_2$  fugacity.

The sources for the experimental equilibrium data used in this study and a detailed description of the computational methods to estimate  $M$  are presented in Smith and Jenne (13). Smith and Jenne (13) and Smith and Walton (20) give comparisons between measured data and values calculated using the modified Lippmann model.

## CONCRETE CARBONATION

Carbon dioxide reacts with the hydrated cement in concrete to form calcite by the process of carbonation. As an example, consider the reaction of portlandite



The equilibrium  $\text{CO}_2$  fugacity for reaction (7) at 25°C is  $10^{-12.8}$ . This fugacity value compares to a value of  $10^{-3.5}$  for the atmosphere and higher values for soil waters. The introduction of even small amounts of  $\text{CO}_2$  results in the complete conversion of portlandite to calcite. In addition to portlandite, hydrated cement also contains C-S-H gel. Reaction simulations conducted with the EQ6 computer code suggest that C-S-H will also react with  $\text{CO}_2$  to yield calcite and silica. Therefore, as a first approximation, all the calcium in cement can be assumed to be available to react with  $\text{CO}_2$ .

The depth of carbonation is roughly proportional to the square-root of time, doubling between 1 and 4 years, then doubling again between 4 and 10 years. The rate of carbonation depends upon the moisture content of the concrete and the relative humidity of the ambient medium. As relative humidity increases from 0 to 100%, the rate of carbonation passes through a maximum. The maximum rate of carbonation occurs near 50 - 60% relative humidity because an aqueous solution is required for the kinetics of the reaction of  $\text{CO}_2$  and  $\text{Ca(OH)}_2$  to form calcite, but increasing water contents slow the diffusion rate of  $\text{CO}_2$  through the concrete. These offsetting factors result in maximum rates of carbonation at intermediate relative humidity.

For the case of a concrete waste form, a fully saturated concrete is assumed. Below ground environments only very rarely have a relative humidity below 95%, even at arid locations. Because of the small pore sizes characteristic of concrete, the concrete will remain saturated with water at high relative humidity, even when surrounding soil materials are quite dry. Unlike other concrete weathering or degradation processes, carbonation is not inconsistent with long-term durability of concrete. Many of the concretes surviving from Roman times are fully carbonated.

The diffusion of  $\text{CO}_2$  (or bicarbonate) into the concrete results in the formation of a carbonated shell on the concrete. The thickness (X) of this shell increases with increased diffusion (time) and can be described using a shrinking core model [21]:

$$X(t) = \sqrt{\frac{2C_{\text{HCO}_3} D_{\text{HCO}_3} \tau \phi t}{C_{s,\text{Ca}}}} \quad (\text{Eq. 8})$$

where  $C_{\text{HCO}_3}$  is the aqueous concentration of the bicarbonate ion at the outer edge of the concrete barrier,  $D_{\text{HCO}_3}$  is the aqueous diffusion coefficient of the bicarbonate ion in the concrete pore fluid,  $\tau$  is the tortuosity/porosity factor,  $\phi$  is the porosity of the concrete,  $t$  is time, and  $C_{s,\text{Ca}}$  is the concentration of calcium in the solid con-

crete. The calcium may be present as either  $\text{Ca(OH)}_2$  or C-S-H gel.

Carbonation alters the chemical properties of concrete by the formation of a different solid assemblage with modified sorptive properties and pore water chemistries than intact concrete. From the model presented previously for concrete carbonation and calcite solid solution formation, a bulk distribution coefficient,  $K_d$ , for the sorption of radionuclide, M, in carbonated concrete can be estimated from:

$$K_d = \frac{C_{s,\text{Ca}} D_{\text{Ca-M}}}{\rho_b C_{\text{Ca}}} \quad (\text{Eq. 9})$$

where  $\rho_b$  is the bulk density of the carbonated concrete and  $C_{\text{Ca}}$  is the aqueous concentration of calcium in the pore fluid of the carbonated concrete. Values of  $K_d$  calculated from Eq. (9) represent equilibrium conditions (i.e., uniform distribution of the radionuclide in the calcite) and will differ from values measured in short-term experiments for which only surface equilibrium has occurred.

#### RELEASE RATE FROM CONCRETE WASTE FORMS

The potential importance of increased attenuation of some radionuclides in carbonated concrete on waste isolation performance can be evaluated by coupling the carbonation process to diffusional release of radionuclides from a portland cement concrete waste form. Once the waste form is placed into the environment, radionuclides will begin to migrate from the waste form by diffusion. At the same time that radionuclides are migrating from the waste form, carbonation of the concrete will occur as  $\text{CO}_2$  (or carbonate) from the soil environment moves into the concrete. Initially, none of the concrete is carbonated. As  $\text{CO}_2$  from the soil environment moves into the concrete, an outside layer or shell of carbonated concrete develops. Over time the thickness of the carbonated layer increases. As radionuclides pass through the carbonated layer they may be incorporated as solid solutions in the calcite present in the carbonated concrete. The potential importance of this process is shown with two example calculations.

From a mass transport perspective, the problem can be envisioned as diffusion of radionuclides through a two layer system (Fig. 2). The inner layer represents the intact concrete and the outer layer represents carbonated concrete. The boundary between the two layers continually migrates as carbonation progresses, creating a moving boundary problem. Solid/liquid partitioning of the radionuclides in the intact concrete is described assuming linear sorption described with a bulk distribution coefficient ( $K_d$ ). Solid solution theory in the carbonated concrete predicts a linear partitioning between liquid and solid phases at low radionuclide concentrations (Eqs. 6 and 9). Thus the solid



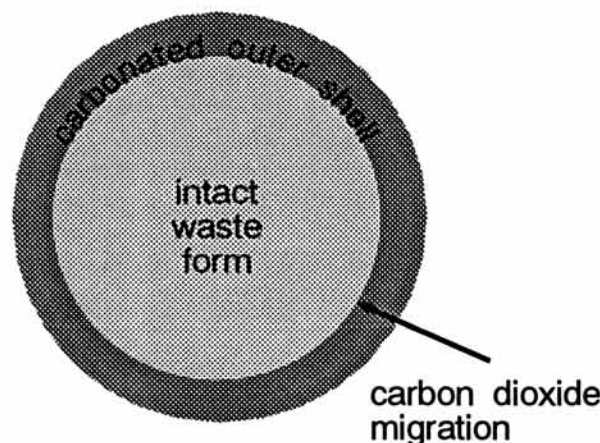


Fig. 2. Schematic diagram of the carbonation process in a concrete slab. Solid solution with calcite in the carbonated concrete serves as a sink for radionuclides present as divalent cations.

solution calculations can be represented mathematically as a bulk  $K_d$  as used in most radionuclide transport models. The effective distribution coefficient for the carbonated concrete represents the results of theoretical calculations rather than empirical measurements.

The rate of migration through concrete with a bulk density of  $\rho_b$  is estimated with the diffusion equation incorporating radioactive decay and linear partitioning between liquid and solid phases:

$$\frac{\partial C_i}{\partial t} = \frac{D_i \tau}{R_{di}} \frac{\partial^2 C_i}{\partial x^2} - \lambda_i C_i \quad (\text{Eq. 10})$$

$$R_{di} = 1 + \frac{\rho_b}{\phi} K_{di} \quad (\text{Eq. 11})$$

where  $C_i$ ,  $D_i$ ,  $R_{di}$ ,  $\lambda_i$ , and  $K_{di}$  are the concentration, diffusion coefficient, retardation factor, decay constant, and bulk distribution coefficient, respectively, for the radionuclide of interest. Boundary conditions are no flux in the middle of the waste form and zero concentration on the outside of the waste form. This assumes that the rate limiting step will be diffusion out of the waste form (i.e., external transport rates are more rapid than release from the waste form).

The equations are solved by finite difference with variable grid spacing and a moving boundary between the two zones. Very fine refinement of the grid is required in the section that becomes carbonated because the carbonation process is slow and the contrast in radionuclide attenuation between the two zones is sharp. The boundary between the two material types is handled by averaging the sorption properties over the interfacial node.

The calculations presented here are for concrete composed of 80% non reactive solids and 20% cement. Based on densities for added solids and hydrated cement (water : cement ratio of 0.42) of  $2.6 \text{ g cm}^{-3}$  and  $2.1 \text{ g cm}^{-3}$  (22), respectively, the bulk density ( $\rho_b$ ) of the concrete is calculated as  $2.5 \text{ g cm}^{-3}$ . The product of the diffusion coefficient and the tortuosity/ constrictivity factor ( $D_i \tau$ ) is assumed to be the same for all aqueous species and has a value of  $5 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ . The porosity of the waste form is fixed at 0.1. The concentration of calcium in the solid is  $0.005 \text{ mol cm}^{-3}$  and corresponds to 65% CaO in the hydrated cement. All calcium is assumed to be available for carbonation. Except for values of  $K_{di}$ , the transport properties are assumed to be the same in intact and carbonated concrete. Depending upon conditions, concrete may have reduced porosity and permeability subsequent to carbonation. Additionally, shrinkage during carbonation may lead to microcracking. Because the net impact of these material property changes on transport properties is currently unknown, the transport properties of both sections are assumed to be identical (a zero order approximation). Additionally the authors wish to focus on the chemical aspects of carbonation rather than changes in physical properties in this paper.

The concrete waste form is assumed to be located in the unsaturated zone. Because of the small pore sizes characteristic of concrete, this is expected to lead to a situation where the concrete pores are water-saturated while surrounding soil materials are partially saturated. The concentration of a pore fluid in equilibrium with carbonated concrete (calcite and silica) and representative  $\text{CO}_2$  partial pressure of  $10^{-2.5}$  bars was calculated using EQ3NR. The resulting boundary concentrations are  $2 \times 10^{-6} \text{ mol cm}^{-3}$  aqueous carbonate,  $1 \times 10^{-6} \text{ mol cm}^{-3}$  aqueous calcium, and a pH of 7.6.

## RESULTS

The example calculations consider two radionuclides,  $^{60}\text{Co}$  and  $^{90}\text{Sr}$ . The radionuclides are assumed to be present at unit concentration in the waste form at time zero. The surface of the waste form is planar and infinitely deep. Because the calculations are for a 20 year period, the waste form thickness which is influenced by diffusion and carbonation at the outer surface constitutes only a few millimeters. Thus waste form thickness is unimportant in the simulations shown herein. The release rate is directly proportional to the initial concentration of radionuclide in each case (i.e., all the governing equations are linear in radionuclide concentration). For this reason, release rates are expressed as a function of  $C_0$ , the initial radionuclide concentration in the solution. The initial unit concentration of radionuclide refers to concentration in the aqueous phase. Total radionuclide concentration in the porous medium (solids + pore fluid) is given by:  $C_0 \phi R_d$ . The release rate from the vault was calculated for concrete undergoing carbonation and

compared with the case where no carbonation occurs. The  $K_d$  values assumed for intact concrete are  $3 \text{ ml g}^{-1}$  [23] and  $2 \text{ ml g}^{-1}$  [24, 25] for  $^{60}\text{Co}$  and  $^{90}\text{Sr}$ , respectively. Calculated values of  $K_d$  [Eqs. (6) and (9)] for carbonated concrete are  $1000 \text{ ml g}^{-1}$  and  $340 \text{ ml g}^{-1}$  for  $^{60}\text{Co}$  and  $^{90}\text{Sr}$ , respectively. Over the 20-year release period, only 0.159 cm of the slab becomes carbonated. Although the thickness of the carbonated shell is small, the incorporation of the radionuclides in calcite solid solution in the carbonated shell of the concrete serves as a very effective sink for  $^{60}\text{Co}$  and  $^{90}\text{Sr}$ , as is shown in Figs. 3-6.

The calculated release rates of radionuclides for both intact and carbonated concrete are presented in Figs. 3 and 4. Because the method used to express release rates eliminates the effects of differences in radionuclide solubility at the waste form, the differences between Figs. 3 and 4 are due to radioactive decay and sorption in the concrete. Fig-

ures 5 and 6 give the cumulative release of radionuclides from carbonated and uncarbonated waste forms.

The significance of assuming that all of the calcium in the concrete waste form is available for carbonation and reacts to form calcite can be examined in light of the governing equations. If only a portion of the calcium reacts, the distribution coefficient for the carbonated section will be reduced. However, if only part of the calcium reacts, the carbonated shell will grow at a more rapid rate. For the time periods of interest, this creates an offsetting effect, reducing the importance of the assumption.

The example calculations presented here consider only  $^{90}\text{Sr}$  and  $^{60}\text{Co}$ . In addition, similar calculations could be performed for any divalent cation (including hexavalent actinides,  $\text{AnO}_2^{2+}$ ) provided values of  $r_i$  and  $K_{\text{Ca-M}}$  (Eq. 4) can be determined or estimated. However, for radionuclides that are strongly sorbed to intact concrete and less strongly sorbed to carbonated concrete, a performance

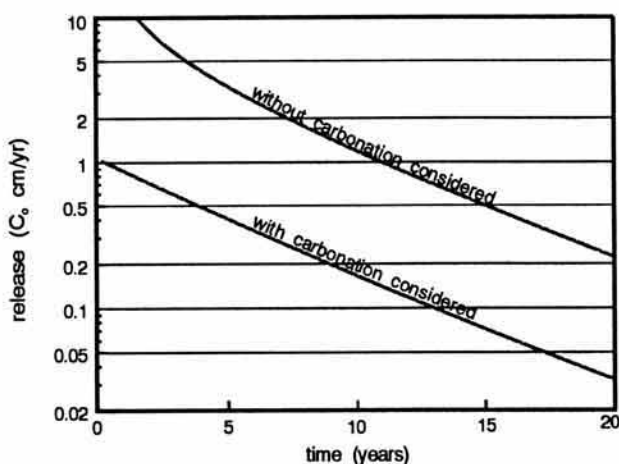


Fig. 3. Comparison of calculated release rate of Cobalt from a concrete waste form with and without consideration of carbonation.

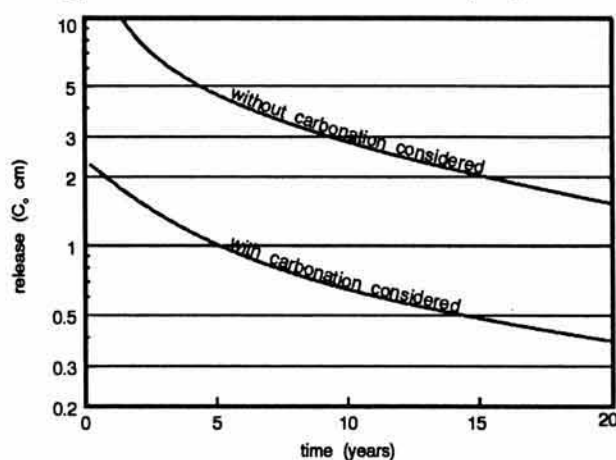


Fig. 4. Comparison of calculated release rate of Strontium from a concrete waste form with and without consideration of carbonation.

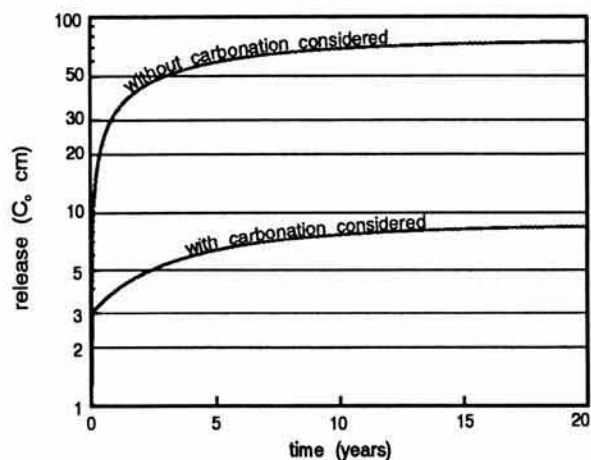


Fig. 5. Cumulative release of Cobalt from a concrete waste form with and without carbonation.

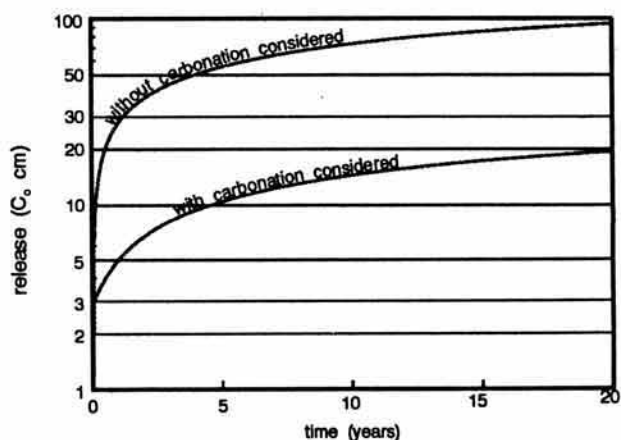


Fig. 6. Cumulative release of Strontium from a concrete waste form with and without consideration of carbonation.

improvement would not be realized. The release rate would be dominated by the properties of a shrinking thickness of intact concrete. However, the calculations presented here indicate that only a 0.159-cm shell of concrete is lost to carbonation during 20 years. Thus carbonation will have only a small impact upon radionuclides which would be released more rapidly from carbonated concrete.

### CONCLUSIONS

Most models and analyses of concrete barriers and their role in radioactive waste disposal focus on the properties of fresh intact concrete. The model and calculations presented here represent an initial attempt to estimate some of the potential impacts of weathered concrete on radionuclide release rates. The weathering or degradation process considered is carbonation of the concrete, which results in precipitation of calcite. Some radionuclides that pass through the carbonated zone may become incorporated into the carbonate phase through solid solution reactions. Incorporation into the carbonate phase results in a predicted reduction in radionuclide release rates for some radionuclides.

The theory of solid solution of radionuclides in carbonated concrete was presented along with example calculations of the impacts of solid solution formation upon release rates. These calculations suggest that the process may be important for  $^{60}\text{Co}$  and  $^{90}\text{Sr}$ . Although this work only considers carbonate phases formed through carbonation of portland cement concrete, solid solution of radionuclides in calcite in concrete may be enhanced by the use of limestone aggregate. In such a case, the favorable impacts of solid solution formation could be obtained throughout the concrete barrier or waste form without reliance on the slower process of carbonation.

The calculations include a number of simplifying assumptions that have not been experimentally validated. The two most important simplifying assumptions are 1) that the transport properties of the carbonated and intact portions of the concrete are identical and 2) that the formation of the carbonate solid solution is governed by equilibrium thermodynamics. Further experimental work is required to determine both the physical and chemical implications of the carbonated shell on radionuclide release. The work presented here is intended to illustrate that solid solution of carbonates is a potentially significant process worthy of further investigation.

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