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Estimate of Gaseous $^{14}$Carbon Concentrations Emanating from the Intermediate-Level Vault Disposal Facility (U)

Daniel I. Kaplan

August 31, 2005
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Abstract

$^{14}$Carbon-bearing resin waste will be disposed in the Low-Activity Waste (LAW) Intermediate Level Vaults (ILV) located in E-Area on the Savannah River Site (SRS). This waste will be buried in a cementitious environment in the vadose zone, i.e., the subsurface zone above the aquifer. As the resin ages, and equilibrates with slowly infiltrating water, it is expected that the $^{14}$C will partition to the solid, liquid, and gaseous phases. The objective of this task was to estimate the concentration of gaseous $^{14}$C in the waste pore space that is in contact with the resin leachate. The approach used to estimate this value was built largely around data generated from lysimeter studies that were conducted for 9 years. These lysimeters contained the same type of used resins (mixed-bed deionizer resins used in the purification of the heavy water moderator of SRS reactors) as are being disposed in the ILV. During the 9 year period, pore water $^{14}$C leaching concentrations were monitored to provide an excellent estimate of the long-term behavior of $^{14}$C release rates from the resins. Thermodynamic calculations were conducted to calculate $^{14}$CO$_2$(g) concentrations. These calculations included the $^{14}$C pore water data from the lysimeter study, and data from a field study that was a natural analogue to a long-term cementitious environment (Khoury et al. 1992). The calculations predicted an extremely low $^{14}$CO$_2$(g) concentration of $1.9 \times 10^{-7}$ Ci/m$^3$ $^{14}$CO$_2$(g) in the air spaces above the resin leachate. This low concentrations is not surprising in light of both laboratory and field observations that concrete acts as a strong sorbent of CO$_2$(g). This calculated $^{14}$CO$_2$(g) concentration will now be included in future risk calculations.

1.0 INTRODUCTION

1.1 Objectives, Approach

The Intermediate Level Vault (ILV) disposal facility located in the E-Area on the Savannah River Site contains Low-Level Waste. Included in this waste are $^{14}$C-bearing resins that were used in deionizers used in the purification of the heavy water moderator of SRS reactors. As these resins age, it is anticipated that the $^{14}$C will partition into three physical states, solid, liquid and gas. The objective of this task is to calculate the release rate of gaseous $^{14}$C from the ILV. This data will then be used in a reactive transport code as part of a Special Analysis.

The general approach taken in this task was to develop a $^{14}$C gaseous release rate based on a conceptual model from a natural analogue study conducted in a region in northern Jordon where pH levels are naturally 12.5, and incorporates experimental results into thermodynamic calculations made relevant to ILV conditions. More specifically, there are four primary processes that were included in these calculations:

1. desorption of $^{14}$C, as $^{14}$CO$_3^{2-}$(aq), from the resin,
2. degradation of resin resulting in the release of $^{12}$CO$_3^{2-}$(aq) and $^{14}$CO$_3^{2-}$(aq),
3. equilibration of $^{12}$CO$_3^{2-}$(aq) and $^{14}$CO$_3^{2-}$(aq) with cementitious pore water, and,
4. volatilization of $^{12}$CO$_2$(g) and $^{14}$CO$_2$(g) from the cement-equilibrated $^{12}$CO$_3^{2-}$(aq) and $^{14}$CO$_3^{2-}$(aq).
1.2 Background

All hydrated cement components of concrete, and grouts are unstable in the presence of carbon dioxide, converting ultimately to an assemblage of calcium carbonate, silica gel, etc. The principal mineralogical changes associated with carbonation of hydrated cement in concretes (CHS(s) calcium-silicate-hydrate gel; the reactive agent in cement) are:

$$\text{CSH}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{silica}(s) + \text{H}_2\text{O}(l) \quad (1)$$

$$\text{Ca(OH)}_2(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(l) \quad (2)$$

where and calcium hydroxide are the principal binding agents of hydrated cement. The calcium carbonate that forms as a result of carbonation reactions is typically in the form of calcite (CaCO$_3$), aragonite (CaCO$_3$), or sometimes vaterite ($\alpha$-CaCO$_3$). The silica product shown in the carbonation reaction (Equation 1) is in the form of a pure gel. The rate of carbonation of cementitious materials is affected by the cement type, porosity, permeability water/cement ratio, partial pressure of CO$_2(g)$, temperature, and relative humidity.

Experimental investigations of the impacts of the chemical and mineralogical changes to cementitious materials suggest that carbonization of these materials will clearly decrease the permeability of concrete thereby decreasing the potential rates of $^{14}$CO$_2$ diffusion out of the waste package (Dayal 1995). Dayal (1995) evaluated the potential mobility of $^{14}$C associated with a bicarbonate/carbonate mixed-bed resin containing $^{14}$C that had been stabilized by a carbonated cementitious grout. In such a high pH environment, the vast majority of any dissolved inorganic carbon present (including $^{14}$C) is present in the form of the carbonate ion. Dayal (1995) reported that the bicarbonate/carbonate from the resin$^1$ reacted with the high pH grout and precipitated as calcium carbonate at the resin/grout interface. After making the reasonable assumption that the resulting pore water of this waste package would be in equilibrium with both calcite and portlandite, Dayal calculated that the total dissolved carbonate concentration in the pore water of the carbonated cementitious waste package would be $6E-6$ M. Consequently the mobility of carbon (and therefore the mobility of $^{14}$C) would be limited by the low solubility of calcium carbonate in a calcium-rich system under high pH conditions (Equation 2). Dayal (1995) showed that under low flow (or unsaturated) conditions, the high pH of this system will be maintained and will act as an effective geochemical barrier to release of $^{14}$C. According to Dayal (1995), solubility models used to predict the chemical evolution of waste repositories containing about 185 kg/m$^3$ cement and interacting with groundwater under very low flow conditions (i.e., $10^{-10}$ m/s) suggest that the pH of these systems could remain above 10.5 for more than 1 million years. Similarly, Using quite conservative assumptions regarding flow and concrete physical integrity, Kaplan and Myers (2001) estimated that the vaults in SRS’s E-Area would maintain a pH of $>11$ for more than 11,000 years. Importantly, the geochemical barrier to $^{14}$C transport will be effective long after the mineralogical changes are well advanced and the structural integrity of the original physical barrier has been diminished.

$^1$ The resin used by Dayal (1995) was a mixed cation and anion (IRN 77/78) resin from Amersham Biosciences, LTD., New Haven, CT.
1.3 Natural Analogue

High pH, alkaline pore waters in the Maqarin area of Northern Jordan have been evaluated as a natural analogue of high pH cement pore waters that would be associated with cementitious radioactive waste repositories (Khoury et. al. 1985; Khoury et. al. 1992; Alexander et. al. 1992; Linklater, et. al., 1996). Geochemical modeling of pore waters and spring water sampled from this area indicates that these hyperalkaline waters (pH 12.5) are in equilibrium with portlandite, ettringite, and other cement-like minerals (Khoury et. al. 1992). The interaction of these high pH waters with carbonate-rich sediments represents a good natural analogue for the reactions that should occur over time in a carbonated, cementitious, waste package.

Khoury et. al. (1985) determined the major elements governing the chemistry of seven water samples collected from different sources in the study area. The pH of all these waters was above 12 and the total dissolved solids of these solutions generally ranged between 1500 and 2000 mg/L (Table 1 in Khoury et. al. 1985). Calcium concentrations averaged between 700-800 mg/L and sulfate concentrations were commonly between 200 to 300 mg/L. Despite the equilibration of these waters with calcium carbonate – bearing sediments and their high pH, analysis of these seven waters yielded a carbonate content ranging from 18.31 to 162 mg/L (average about 65 mg/L). These waters are much more chemically complex than the experimental solutions and modeled solutions discussed by Dayal (1995). These natural waters probably represent a more realistic chemical analogue for water that could evolve in a cementitious waste repository over time. The relatively high sulfate and other anion levels in these natural waters has probably lowered the activity of Ca$^{2+}$ in these waters (by forming the aqueous CaSO$_4$ and other complexes) resulting in a higher solubility for calcite than would otherwise occur.

2.0 EQUATIONS AND ASSUMPTIONS USED TO ESTIMATE GASEOUS $^{14}$C RELEASES FROM THE ILV

There are four primary processes included in these calculations:

1. desorption of $^{14}$C, as $^{14}$CO$_3^{2-}$($aq$), from the resin,
2. degradation of resin resulting in the release of $^{12}$CO$_3^{2-}$($aq$) and $^{14}$CO$_3^{2-}$($aq$),
3. equilibration of $^{12}$CO$_3^{2-}$($aq$) and $^{14}$CO$_3^{2-}$($aq$) with cementitious pore water, and,
4. volatilization of $^{12}$CO$_2(g)$ and $^{14}$CO$_2(g)$ from the cement-equilibrated $^{12}$CO$_3^{2-}$($aq$) and $^{14}$CO$_3^{2-}$($aq$).

Modeling of the first process, desorption, relies upon a long-term SRS field study in which $^{14}$C-bearing moderator resin was buried in a lysimeter for 9-years and the amount of $^{14}$C that leached out from the resin was monitored over time (McIntyre 1987). The leach rate generated from this data was used in these calculations. Modeling resin degradation rate, another process that may contribute to the introduction of $^{14}$C into the environment, was based on long-term laboratory studies conducted (Powell et al. 2002). The third process, equilibrating $^{12}$CO$_3^{2-}$($aq$) and $^{14}$CO$_3^{2-}$($aq$) with cementitious pore water, was based on setting aqueous carbonate concentrations in subsequent calculations to those measured in pore waters collected from a natural analogue site, a site where the pH is naturally 12.5 (Khoury et. al 1985). Finally, thermodynamic calculations
were conducted to determine the concentrations of gaseous CO₂ in contact with pore water in equilibrium with concrete.

2.1 Desorption of 14C:

A series of lysimeters were installed at SRS during the 1970’s, four of which contained moderator deionizer resin. Approximately 1-ft³ of resin, containing 0.35 Ci 14C was placed in each lysimeter and the leachate chemistry was periodically monitored for 9 years. Leachate 14C concentrations ranged from 0.06 to 0.89 µCi/L (McIntyre 1987; Table 5). This value accounts for desorption from resin and resorption to soil or to resin. Based on McIntyre’s data (1987), Cook (1989) estimated 14C fractional release rates ranging from 4 x 10⁻⁵ to 7 x 10⁻⁴ yr⁻¹. The leachate 14C concentration of 0.89 µCi/L 14C value will be used below. It is important to recognize that the resin was simply placed in the sediment and was not enclosed in a stainless steel contained, which in turn was not entombed within concrete. As such, these pore water values represent greater 14C values than would expect from the ILV.²

2.2 Degradation of Resin Resulting in the release of 12CO₃²⁻(aq) and 14CO₃²⁻(aq)

Long-term resin degradation rates have been performed on a number of resins by Powell et al. (2002). Powell et al. (2002) evaluated several materials, including an anion resin, Dowex 21K. The degradation rate for the anion resin was 9.08 x 10⁻¹³ sec⁻¹ (or 2.8 x 10⁻⁵ yr⁻¹; Powell et al. 2002; Table 2). Stated differently, the resin would be expected to totally decompose in 280,000 years. This degradation rate is so slow that it would decrease the effective K_d by ~7 millionth of one percent (calculations presented by Powell et al. 2002). This is well within the uncertainty of the original K_d value. Consequently, there is no need to conduct additional calculations to account for the small effect of resin degradation on enhanced 14C release.

2.3 Equilibration of 12CO₃²⁻(aq) and 14CO₃²⁻(aq) with Cementitious Pore Water and the Subsequent Volatilization of 12CO₂(g)

Although pH is a master variable that largely controls the speciation and mobility of carbon in aqueous environments, the major elemental chemistry of a pore solution will also be an important control on 14C mobility within the waste package. In high pH solutions with a low total dissolved solids and that are not chemically complex, calculations suggest that dissolved carbonate concentrations as low as 6 x 10⁻⁶ M may be present (Dayal 1995). This probably represents a reasonable estimate of the lower limit of the amount of dissolved carbonate present in a carbonated cementitious waste pore solution. Conversely, the carbonate concentrations (18.31 to 162 mg/L) in the sulfate-rich, high pH natural waters from Jordan probably serve as a reasonable upper limit for the concentrations of carbonate that would develop in calcite and portlandite-equilibrated pore water of a cementitious waste package (Khoury et. al 1985). The amount of carbon present in the system as CO₂ will be miniscule at a pH of 10.5 (<< 1%).

² Extending these calculations further, K_d values for these resins were calculated (13,100 mL/g; Appendix A). The values were not used in these calculations, but are often needed by modelers.
Consequently, the amount of \(^{14}\)C that will be released will be largely dependent on the flow regime in which the wastes reside.

The approach adopted to calculate the \(^{14}\)CO\(_2\) released from the Moderator Deionizers within the ILV was first put forth by Doug Gonzales (Bechtel Jacobs Company, LLC, Oak Ridge, TN). To estimate the amount of CO\(_2\) in equilibrium with the estimated upper limit of dissolved carbonate as measured by Khoury et al. (1985; CO\(_3^{2-}\) concentration of 162 mg/L = 2.7 x 10\(^{-3}\) M = 10\(^{-2.57}\) M), it was assumed that the carbonate in solution was in equilibrium with its associated carbonic acid and carbon dioxide reaction products, the activity coefficient for carbonate ions was 1, and the system was at 15 \(^\circ\)C and a pH of 10.5. In equilibrium the following reaction occurs:

\[
\text{CO}_2(g) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3
\]  

The partial pressure of CO\(_2\), P(CO\(_2\)), in the air overlying the liquid containing the dissolved carbonate is expressed in terms of the activities of H\(_2\)CO\(_3\) and H\(_2\)O by

\[
\frac{[\text{H}_2\text{CO}_3]}{P(\text{CO}_2)} \cdot [\text{H}_2\text{O}] = K_\alpha = 10^{-1.26}
\]  

where [ ] indicates concentration. Because there is always excess water, [H\(_2\)O] = 1 and this equation simplifies to

\[
\frac{[\text{H}_2\text{CO}_3]}{P(\text{CO}_2)} = K_\alpha = 10^{-1.26}
\]  

In addition, there are two simultaneously occurring reactions, each with the following mass action constants:

\[
\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- \quad (6)
\]

\[
K_1 = [(\text{H}^+) \cdot (\text{HCO}_3^-)]/[\text{H}_2\text{CO}_3] = 10^{-6.47} \quad (7)
\]

and

\[
\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \quad (8)
\]

\[
K_2 = [(\text{H}^+) \cdot (\text{CO}_3^{2-})]/[\text{HCO}_3^-] = 10^{-10.49} \quad (9)
\]

Combining Equations (6) and (8), one obtains

\[
\text{H}_2\text{CO}_3 = 2\text{H}^+ + \text{CO}_3^{2-}. \quad (10)
\]
Rearranging Equations (7) and (9), one obtains

$$[\text{H}_2\text{CO}_3] = \frac{(\text{H}^+) \cdot (\text{HCO}_3^-)}{K_1}, \quad (11)$$

$$[\text{HCO}_3^-] = \frac{(\text{H}^+) \cdot (\text{CO}_3^{2-})}{K_2}. \quad (12)$$

Combining Equations (11) and (12)

$$[\text{H}_2\text{CO}_3] = \frac{(\text{H}^+)^2 \cdot (\text{CO}_3^{2-})}{K_1K_2}, \quad (13)$$

and then combining equations (5) and (13)

$$P(\text{CO}_2) = \frac{[\text{H}_2\text{CO}_3]}{K_o} = \frac{(\text{H}^+)^2 \cdot (\text{CO}_3^{2-})}{K_oK_1K_2}. \quad (14)$$

Substituting $10^{-10.5} \text{ M}$ for $(\text{H}^+; \text{pH} = 10.5)$ and $10^{-2.57} \text{ M}$ for $[\text{CO}_3^{2-}]$ (based on Khoury et al. 1985; $\text{CO}_3^{2-} = 162 \text{ mg/L} = 2.7 \text{E-3 M}$) into Equation (14),

$$P(\text{CO}_2) = 10^{-5.35} \text{ atm} = 4.5 \times 10^{-6} \text{ atm.} \quad (15)$$

Partial pressure expressed in units of atmospheres can be converted into volumetric concentrations ($N; \text{ moles/m}^3$) through the Ideal Gas Law:

$$N = \frac{P(\text{CO}_2)}{RT} = 1.9 \times 10^{-4} \text{ mole/m}^3 = 8.4 \times 10^{-3} \text{ g/m}^3 \text{ of } ^{12/14}\text{CO}_2(\text{g}) \quad (16)$$

where $P(\text{CO}_2) = 4.5 \times 10^{-6} \text{ atm}$, $R$ is $0.0821 \times 10^{-3} \text{ atm-}\text{m}^3/\text{mol-K}$, and $T$ is 288 degrees Kelvin (K). Therefore, there will be $8.4 \times 10^{-3} \text{ g/m}^3$ of $^{12/14}\text{CO}_2(\text{g})$ total in the pore air in contact with the ILV concrete pore water.

Assuming that the atmospheric $^{12}\text{CO}_2(\text{g})$ does not dilute the $^{14}\text{CO}_2(\text{g})$ emanating from the ILV (i.e., all the $^{14}\text{C}$ originates from the resin) and steady-state conditions exist:

$$\frac{(^{14}\text{C})}{(^{12}\text{C})} = \frac{(1.4 \times 10^{-8} \text{ mol/L } ^{14}\text{CO}_3^{2-})}{(2.7 \times 10^{-3} \text{ mol/L } ^{12}\text{CO}_3^{2-})} = 5.2 \times 10^{-6} \quad (17)$$

where the $^{14}\text{CO}_3^{2-}$ concentration value was taken from Section 2.1 (McIntyre 1987; the 9-year lysimeter study of $^{14}\text{C}$ leaching from Moderator Deionizer resins; $[0.89 \mu\text{Ci/L}] \times [1/10^6 \text{ Ci/µCi}] \times [0.22445 \text{ g/Ci}] \times [1/14 \text{ mol/g}] = 1.4 \times 10^{-8}$) and the $^{12}\text{CO}_3^{2-}$ value is based upon the high pH Jordan analogue site (Khoury et al. 1992). Using the results from Equations 16 and 17, the concentration of $^{14}\text{CO}_2(\text{g})$ in the ILV pore space is therefore:

$$(8.4 \times 10^{-3} \text{ g/m}^3 12/14\text{CO}_2(\text{g})) \ast (5.2 \times 10^{-6} \text{ } ^{14}\text{C}/^{12}\text{C}) = 4.4 \times 10^{-8} \text{ g/m}^3 14\text{CO}_2(\text{g}) \quad \text{or } 1.9 \times 10^{-7} \text{ Ci/m}^3 14\text{CO}_2(\text{g}). \quad (18)$$

---

$^3$ When $^{14}\text{C} \ll ^{12}\text{C}$, as in this scenario, the assumed concentration of $^{14}\text{CO}_3^{2-}$ does not greatly influence the outcome of these calculations; i.e., the result in equation 18.
3.0 CONCLUSION

An estimate of the concentration of $^{14}$CO$_2$(g) released from resins used as moderator deionizers was evaluated. These moderator deionizers will be disposed in the ILV and in a cementitious environment. The concrete will provide a very strong sorbent for the $^{14}$CO$_2$(g). In fact, industries that generate 1000’s of times greater amounts of $^{14}$C than that disposed in the ILV, such as the Ontario Hydro’s Reactors (Dayal et al. 1989; Dayal and Reardon 1992), dispose of $^{14}$C-bearing resins along with concrete slabs; the concrete slabs are referred to as “$^{14}$C-getters.” Consequently, little $^{14}$CO$_2$(g) is expected to be released from the site. Thermodynamic calculations were conducted to calculate $^{14}$CO$_2$(g) concentrations. These calculations included the $^{14}$C pore water data from the lysimeter study, and data from a field study that was a natural analogue to a long-term cementitious environment (Khoury et al. 1992). The calculations predicted an extremely low $^{14}$CO$_2$(g) concentration of 1.9 x 10$^{-7}$ Ci/m$^3$ $^{14}$CO$_2$(g) in the air spaces above the resin leachate. This low concentration is not surprising in light of both laboratory and field observations that concrete acts as a strong sorbent to CO$_2$(g). This calculated $^{14}$CO$_2$(g) concentration will now be included in future risk calculations.

4.0 REFERENCES


5.0 APPENDIX A: DEIONIZER RESIN $K_D$ VALUE CALCULATIONS
Appendix A: Deionizer Resin $K_d$ Value Calculations

$$K_d = \frac{^{14}C_{\text{resin}}}{^{14}C_{\text{pore space}}} = \left( \frac{0.35 \text{ Ci}}{\text{ft}^3} \right) \left( \frac{1 \text{ ft}^3}{28316 \text{ cm}^3} \right) \left( \frac{1 \text{ cm}^3}{1.06 \text{ g}} \right) = \frac{13.1 \text{ L}}{\text{g}} = 13,100 \text{ mL/g}$$

Where 1.06 g/cm$^3$ is the assumed bulk density value for the Amberlite IR-120 and IRA-400 resins.
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