WSRC-TR-2003-00417
Rev. 0

Key Words:
Performance Assessment
Decommissioning

Retention: Permanent

SPECIAL ANALYSIS:

Revised ^{14}C Disposal Limits for the Saltstone Disposal Facility

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September 12, 2003

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**Prepared for the U.S. Department of Energy Under
Contract Number DE-AC09-96SR18500**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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Introduction

The Saltstone Special Analysis (Cook et al., 2002) calculated a limit for ^{14}C based on the atmospheric pathway of 52 pCi/mL using some very conservative assumptions. This was compared to the estimated Low Curie Salt concentration of 0.45 pCi/mL and since the limit was two orders of magnitude greater than the estimated concentration, the decision was made that no further analysis was needed.

The ^{14}C concentration in Tank 41 has been found to be much greater than the estimated concentration and to exceed the limit derived in the Special Analysis. A more rigorous analysis is now warranted.

Assessment

The assumption made in the Special Analysis was that the entire inventory of ^{14}C was released to the atmosphere and transported to a receptor in one year. This is the assumption used in the performance assessment for the E-Area Low-Level Waste Facility for near surface disposal.

Within the Saltstone waste form, an alkaline chemical system will exist for thousands of years. In a high pH environment the chemical equilibrium of the carbon-containing phases will greatly restrict the amount of ^{14}C available for release to the atmosphere.

Unlike many other radionuclides (e.g., ^{137}Cs, ^{230}Th), ^{14}C (e.g., as carbon dioxide or the bicarbonate ion) can be highly mobile in many geological environments. Consequently, the ability of the Saltstone Disposal Facility to isolate ^{14}C from the surrounding geologic environment is of particular importance. The cement-based waste form, concrete vaults and the RCRA-like cover act as an effective physical barrier to the migration of ^{14}C from the waste package to the surrounding environment.

Statement of Problem:

Over time, the ability of the cement-based waste form, concrete vaults and the underlying cement pad to isolate ^{14}C in the waste materials from the environment will change. Carbonation of the cementitous material with environmental CO_2 from outside the waste package will ultimately result in the transformation of the hydroxide-rich cementitous vault materials (e.g., portlandite – ($Ca(OH)_2$) into carbonate phases (e.g., $CaCO_3$). The volume change associated with this transformation may cause degradation of the structural integrity of the concrete vault due to cracking. Owing to this and other natural weathering and erosion processes, the length of time that the physical and structural integrity of the concrete vaults could fail is less than 500 years. Consequently, it is of concern as to whether the physical transformation of this waste containment package will eventually result in the release of unacceptably high levels of ^{14}C activity (e.g., release by diffusion of $^{14}CO_2$ at a rate that could result in harm to human health or the environment). In the sections below the implications of experimental and modeling studies of cementitous waste as well as an investigation of a natural analogue for a waste package environment are reviewed and discussed relative to ^{14}C mobility.

Experimental and Modeling Investigations:

Experimental investigations of the impacts of the chemical and mineralogical changes to cementitous materials suggest that carbonization of these materials will actually decrease the permeability of the vault walls thereby decreasing the potential rates of $^{14}CO_2$ diffusion out of the waste package. Dayal (1995) evaluated the potential mobility of ^{14}C associated with a bicarbonate/carbonate mixed bed resin contaminated with ^{14}C that had been stabilized by a carbonated cementitous grout. In such a high pH environment, the great majority of any dissolved inorganic carbon present (including ^{14}C) should be present in the form of the carbonate ion. Dayal (1995) reported that the bicarbonate/carbonate from the resin 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 cementitous waste package would be 0.07 mg/L. 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. The findings of Dayal (1995) suggest 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. This 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.

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, cementitous, 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 TDS 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 (see above). These natural waters probably represent a more realistic chemical analogue for water that could evolve in a cementitous 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.

Dissolved Carbonate Limits and Equilibrated CO_2 in the Waste Pore Space

Although pH is a master variable that largely controls the speciation and mobility of carbon in aqueous environments, the general major element chemistry of a pore solution will also be an important control on ^{14}C mobility within the waste package. In high pH solutions with a low TDS and that are not chemically complex, calculations suggest that dissolved carbonate concentrations as low as 0.07 mg/L 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 cementitous 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 cementitous waste package (Khoury et. al. 1985). In either case, the amount of carbon present in the system as CO_2 will be miniscule at a pH of 10.5 (<< 1%). Consequently, the amount of ^{14}C that will be released will be largely dependent on the flow regime in which the wastes reside. The activity of ^{14}C released from a waste package in a very low flow saturated system or an unsaturated system will be minimal.

The approach adopted to calculate the $^{14}CO_2$ released from the saltstone 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 = 2.7×10^{-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 °C and a pH of 10.5. In equilibrium the following reaction occurs:

$$CO_2(\text{gas}) + H_2O = H_2CO_3 \qquad (1)$$

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_2CO_3 and H_2O by

$$[H_2CO_3]/P(CO_2) \cdot [H_2O] = K_o = 10^{-1.26} \qquad (2)$$

where [ ] indicates concentration. Because there is always excess water, $[H_2O] = 1$ and this equation simplifies to

$$[H_2CO_3]/P(CO_2) = K_o = 10^{-1.26} \qquad (3)$$

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

$$H_2CO_3 = H^+ + HCO_3^- \qquad (4)$$

$$K_1 = [(H^+) \cdot (HCO_3^-)]/[H_2CO_3] = 10^{-6.47} \qquad (5)$$

and

$$HCO_3^- = H^+ + CO_3^{2-} \qquad (6)$$

$$K_2 = [(H^+) \cdot (CO_3^{2-})]/[HCO_3^-] = 10^{-10.49}. \qquad (7)$$

Combining Equations (4) and (6), one obtains

$$H_2CO_3 = 2H^+ + CO_3^{2-}. \qquad (8)$$

Rearranging Equations (5) and (7), one obtains

$$[H_2CO_3] = [(H^+) \cdot (HCO_3^-)]/K_1, \qquad (9)$$

$$[HCO_3^-] = [(H^+) \cdot (CO_3^{2-})]/K_2. \qquad (10)$$

Combining Equations (8), (9), and (10)

$$[H_2CO_3] = [(H^+)^2 \cdot (CO_3^{2-})]/K_1K_2, \qquad (11)$$

such that

$$P(CO_2) = [H_2CO_3]/K_o = [(H^+)^2 \cdot (CO_3^{2-})]/K_oK_1K_2. \qquad (12)$$

Substituting $10^{-10.5}$ *M* for (H^+) and $10^{-2.57}$ *M* for $[CO_3^{2-}]$ into Equation (12),

$$P(CO_2) = 10^{-5.35}\text{ atm} = 4.5 \times 10^{-6}\text{ atm.} \qquad (13)$$

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

$$N = P(CO_2)/RT = 1.9 \times 10^{-4}\text{ mole/m}^3 = 8.4 \times 10^{-3}\text{ g/m}^3 \qquad (14)$$

where $P(CO_2) = 4.5 \times 10^{-6}$ atm, R is 0.0821×10^{-3} atm·m^3/mol·K, and T is 288 degrees Kelvin (K).

Assuming that the atmospheric $^{12}CO_2(g)$ does not dilute the $^{14}CO_2(g)$ emanating from the saltstone (i.e., all the ^{12}C originates from the salt solution in the saltstone), then:

$$(^{14}CO_2)/(^{12}CO_2) = (1.43 \times 10^{-10}\text{ mol/L})^{(1)}/(0.164\text{ mol/L})^{(2)} = 8.7 \times 10^{-10} \qquad (15)$$

The concentration of $^{14}CO_2$ in the waste pore space is therefore (8.4×10^{-3} g/m^3) * (8.7×10^{-10}), or 7.3×10^{-12} g/m^3 (or 3.3×10^{-11} Ci/m^3).

This result can be normalized on a per curie per 12 cell vault basis by dividing by the inventory of ^{14}C in a twelve cell vault. MMES, 1992, states on page 2-63 that the entire facility will have 174 cells, and on page 2-66 give the entire inventory of ^{14}C to be disposed as 6.5 Ci. This means that there will be an average of 0.45 Ci/12 cell vault. Therefore, the concentration of 3.3×10^{-11} Ci/m^3 can be expressed as 7.3×10^{-11} Ci/m^3 per Ci of ^{14}C in a 12 cell vault.

To convert concentration into a flux with units of Ci/m^2·yr, conceptually, CO_2 was permitted to diffuse from the air in contact with the saltstone surface to the overlying aboveground air. To do this, it was assumed that the air had no $CO_2(g)$, a conservative assumption that will create a greater concentration gradient, which is the driving force behind diffusion. Fick's First Law of Diffusion can be written as

$$J = D\left(\frac{C_0}{L_{depth} \times f}\right) \times L_{length} \times L_{width} \qquad (16)$$

where,

J = annual flux at the soil surface, Ci/Ci ·yr,
D = diffusion coefficient in air, 440 m^2/yr [3]
C_0 = source concentration in the vapor phase, 7.3×10^{-11} Ci/m^3
L_{depth} = cover thickness over vault, 3.6 m
L_{length} = vault length, 180 m
L_{width} = vault width, 60 m
f = porosity, 0.44 m^3/m^3

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[1] MMES, 1992; Table 2.6-2, page 2-66, for nominal blend
[2] MMES, 1992; Table 2.6-1, page 2-65, for nominal blend
[3] CRC, 1985; page F-45.

Using Equation (16), the annual flux at the soil surface is 2.2 x 10^{-4} Ci /yr $^{14}CO_2(g)$ per Ci in a 12 cell vault.

Two points and times of exposure were used in the analysis. For the first 100 years, the minimum time per USDOE Order 435.1 for which institutional control will be maintained, the point of maximum exposure will be at the SRS boundary, about 11 km north of E-Area. Doses were also calculated at a point 100 m from the E-Area Disposal Facility at 100 years after closure.

The air pathway analysis using the MAXIGASP computer program, 1 Ci/yr as a release term and the parameters shown in Table 1 resulted in the dose factors, in mrem/Ci given in Table 2.

The dose limit used in the air pathway analysis is 10 mrem/yr, effective dose equivalent, as required by DOE Order 435.1. The inventory limit for ^{14}C is that number of curies in the Saltstone waste form that would give a dose of 10 mrem/yr. This limiting inventory can be calculated for each of the exposure locations using the relationship:

Inventory Limit (Ci) = Dose Limit (mrem/yr) / Release Rate (Ci/yr-Ci) * Dose Factor (mrem/yr-Ci)

The resulting inventory limits based on each of the exposure points are given in Table 3. The limit based on exposure at the 100 meter location is more restrictive, and is therefore used for the air pathway-based inventory limit.

The overall disposal limit is based on analyses of the intruder and groundwater exposure scenarios, as well as the air pathway. Tables 4 and 5 compare the limits derived in the Special Analysis (Cook et al., 2002) for the groundwater and intruder analyses with the air pathway results for the 10,000 and 1,000 year time of compliance cases, respectively. The results for the air pathway are independent of the time of compliance choice because it is assumed the release begins at a time much earlier than 1,000 years. Table 6 gives the ^{14}C limit expressed in units of Ci/L of salt solution, while Table 7 gives the limit as pCi/mL of salt solution.

Conclusion

A rigorous analysis of the release of ^{14}C via the air pathway that considers the chemical effects of the Saltstone system has shown that the flux of ^{14}C is significantly less than that assumed in the Special Analysis (Cook et al., 2002). The net result is an inventory limit for ^{14}C that is significantly higher than that derived in the Special Analysis that will also meet the performance objectives of DOE Order 435.1.

Table 1. Parameters Used in Air Dose Calculations

Relative Concentration (X/Q):	1.70E-04 (sec/m^3)
Decayed X/Q:	1.70E-04 (sec/m^3)
Depleted X/Q:	1.70E-04 (sec/m^3)
Relative Deposition (D/Q):	5.20E-07 (1/m^2)
Distance to Receptor:	100 (m)
Vegetable Consumption:	276 (kg/yr)
Leafy Vegetable Consumption:	43 (kg/yr)
Milk Consumption:	230 (L/yr)
Meat Consumption:	81 (kg/yr)
Origin of Milk:	cow
Deposition Buildup Time:	25 (yr)
Breathing Rate:	8,000 (m^3/yr)
Elemental Iodine Fraction:	1
Absolute Humidity:	0.0114 (kg/m^3)
Tritium Plant-to-Air Ratio:	0.5
Shielding Factor:	0.23
Fraction of Year C-14 Released:	1
Retained Fraction (iodine):	1
Retained Fraction (particulates):	0.2
Weathering Rate Constant:	18.1 (1/yr)
Crop Exposure Time:	0.164 (yr)
Pasture Grass Exposure Time:	0.0822 (yr)
Pasture Grass Productivity:	1.8(kg/m^2)
Produce Productivity:	0.7(kg/m^2)
Surface Soil Density (15 cm):	240(kg/m^2)
Pasture Grass Holdup Time:	0(yrs)
Stored Feed Holdup Time:	0.247(yrs)
Leafy Vegetable Holdup Time:	0.00274(yrs)
Produce Holdup Time:	0.164(yrs)
Milk Cattle Feed Consumption:	44(kg/day)
Beef Cattle Feed Consumption:	44(kg/day)
Feed-Milk-Man Transport Time:	0.00548 (yr)
Fraction of Year on Pasture (beef):	1
Fraction of Year on Pasture (milk):	1
Fraction Intake from Pasture (beef):	0.75
Fraction Intake from Pasture (milk):	0.56
Slaughter to Consumption Time:	0.0164(yr)
Fraction of Produce from Garden:	0.76
Fraction of Leafy Vegetables from Garden:	1

Table 2. Dose factors for the air pathway

Nuclide	100 m Location (mrem/Ci Released)	Site Boundary Location (mrem/Ci Released)
C-14	3.8	1.0×10^{-3}

Table 3. Inventory limits for the air pathway

Nuclide	100 m Location Ci/vault	Site Boundary Location Ci/vault
C-14	1.2×10^{4}	4.6×10^{7}

Table 4. Radionuclide limits for a 10,000-year assessment period, in Ci/vault

Nuclide	Intruder Limit, Ci/Vault	Groundwater Limit, Total Ci	Air Limit, Ci/Vault	Radon Limit, Ci/Vault
C-14	No limit	1.7×10^{8}	1.2×10^{4}	—

Table 5. Radionuclide limits for a 1,000-year assessment period, in Ci/vault

Nuclide	Intruder Limit, Ci/Vault	Groundwater Limit, Total Ci	Air Limit, Ci/Vault	Radon Limit, Ci/Vault
C-14	No limit	No limit	1.2×10^{4}	—

Table 6. Radionuclide limits for C-14, in Ci/L of Salt Solution

Radionuclide	Limiting Pathway	Limit, Ci/L in Salt Solution
C-14	Air	2.4×10^{-4}

Table 7. Saltstone Waste Acceptance Criteria derived from this Special Analysis

Radionuclide	WAC, pCi/mL, in Salt Solution
C-14	2.4×10^{5}

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