



## ORIGINAL CONTRIBUTION

# GEOCHEMICAL ENGINEERING OF LOW LEVEL RADIOACTIVE WASTE IN CEMENTITIOUS ENVIRONMENTS

Patrick V. Brady and Matthew W. Kozak\*

Sandia National Laboratory (MS 750), Albuquerque, NM 87185, U.S.A.

**ABSTRACT.** Significantly reduced releases of radionuclides from low level radioactive waste disposal facilities may be achieved by passively engineering the geochemical environment in and immediately adjacent to shallow land burial sites. Mineral growth and adsorption onto cementitious waste forms, casks, and backfills is calculated to minimize the transport of  $^{234,238}\text{U}$ ,  $^{241}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{232}\text{Th}$ ,  $^{59,63}\text{Ni}$  and  $^{14}\text{C}$ . Reductive adsorption of Tc to Fe(II)-rich minerals may be engineered by emplacing a fine-grained mafic (basalt, serpentinite, scrap iron) blanket of aggregate below and around the LLRW repository.  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  transport into the biosphere may also be retarded due to adsorption on cementitious material, through scavenging by the Fe-oxyhydroxide weathering products of the mafic blanket, and by dilution.

## 1. INTRODUCTION

Low-level radioactive waste (LLRW) is disposed of in near-surface facilities. Traditionally, the latter have consisted of simple shallow trenches. However, in recent years, progressively greater emphasis has been placed on disposal in engineered structures. This shift in emphasis has been produced by the perception that trench isolation does not adequately reduce releases to the environment, and by a desire of public groups for facilities that produce no releases whatsoever.

While the latter goal is clearly unattainable for any real disposal system, engineered disposal designs may indeed minimize groundwater flow into the waste, thus reducing releases relative to those that are expected from trench burial. Absolute release rates ultimately depend on the performance of the disposal facility and the geosphere as a whole. For the disposal facility to be licensed, there must be reasonable assurance that the maximally exposed member of the facility will not receive 25 mrem/year

committed effective dose equivalent, or 75 mrem/year to the thyroid, or 25 mrem/year to any critical organ. The analysis that is used for this demonstration, performance assessment, synthesizes knowledge and data about all components of the system behavior. Performance assessment is a site-specific exercise that allows practical decisions to be made about the behavior of the site relative to performance standards. Because of the nature of the analysis, confidence in the results is best produced by demonstrating that the analysis is conservative, or pessimistic, rather than attempting to accurately represent in detail the future behavior of the facility.

Since the performance assessment models the overall behavior of the system, information is needed describing the behavior of each component of the analysis. Kozak *et al.*<sup>1</sup> evaluated each component of information of low-level waste performance assessment, including the behavior of vaults. They concluded that the uncertainty in the flow through vaults, projected into the future, was sufficiently great that one cannot take much credit for the functional capability of the vault. This uncertainty has led to an unsatisfactory state, in which most analysts believe that vaults will reduce doses, but in which the performance assessment treats a vault very similarly to a trench. Kozak *et al.*<sup>1</sup> have suggested that the chemistry of the source term may provide a resolution to this dilemma. Specifically, concrete and grout strongly influence the chemistry of the vault;

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\*Present address: Intera Information Technologies Inc., 3609 South Wadsworth Blv. No. 550, Denver, CO 80235, U.S.A.

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as a consequence, the potential exists to reduce the uncertainty in chemical limitations to release and transport from the vault.

The purpose of this paper is to provide an initial analysis of the influence of concrete on low-level waste. The intent is to develop an upper bound to solubilities and a somewhat lower bound to sorption capabilities. In this way, we attempt to produce a generically applicable and generically conservative analysis of concrete-stabilized waste.

Two factors can be brought to play in reducing releases from the source. First, one can physically contain the waste by reducing contact with infiltrating water. Performance assessment practitioners believe that this can be accomplished with good success through the use of concrete vaults, engineered covers, overpacks and steel or polyethylene containers. This success will, however, probably be short-lived.<sup>1</sup> Each of these structures are known to degrade over time, in the process losing their advantageous hydraulic characteristics. There is considerable uncertainty in the manner, rate, and timing of degradation. This uncertainty is so great that little credit can be taken for hydraulic isolation in performance assessments. An alternative approach is to engineer the chemical environment of the disposal facility. The chemical environment of the facility is expected to be more stable over long periods of time than is the ability of the facility to exclude water. Engineering the chemistry of the source term therefore has the potential to limit release rates in a more demonstrably effective manner as it is relatively insensitive to degradation phenomena that are poorly understood.

Taking the most obvious example of such an approach, cement-based waste forms can be expected through their slow degradation to cause the disposal facility environment to become alkaline for long periods of time. Under these conditions many (but not all) radionuclides have very low solubilities. Using cement-based material as a waste form or backfill material may potentially lead to a simpler, more defensible performance assessment for a number of reasons. Mineral solubilities and radionuclide adsorption depend largely on the concentration of  $H^+$  in soil solutions, which can vary by orders of magnitude from soil to soil. Hydrogeochemical modeling of radionuclide mobility in the near field is much more straightforward if the pH is known to be "fixed" by hydrolysis of cement. The radionuclides likely to drop out of solution as adsorbates, or as components of new minerals, can then be estimated. Methods for engineering the retention of those soluble radionuclides which will not adsorb can then be specifically examined. Engineering the chemistry of the near field of a disposal facility is also attractive because it may avoid the collection of some site-specific geologic data. Once release rates used in the

performance assessment have been justifiably reduced, less effort need be expended on evaluating the geosphere. Instead research efforts would be focused on a "one size fits all" generic design which would require less site-specific adjustment.

Note that use of a generic cement-based design depends on the degree to which it can be demonstrated to immobilize radionuclide transport in the near field. We outline what materials (organic and inorganic) are likely to exist in LLRW and examine radionuclide mobility in hyperalkaline fluids, concentrating on the solubilities of radionuclide containing solids, and then radionuclide adsorption to soil and aggregate surfaces. We then examine the behavior of those radionuclides which neither sorb nor precipitate and propose engineered reaction paths to limit their long-term transport. We will neglect the physical controls on concrete degradation (stress cracking, freeze-thaw, etc.) as the chemical effects of concrete-water interaction are expected to last for time spans on the order of tens of thousands of years, that is, far longer than the disposal facility is expected to remain structurally sound (e.g. Ref. 3). Ideally, we would like to be able to demonstrate that regulatory performance objectives (see below) can be met using concentrations leaching from the disposal facility. If such a demonstration can be made, there will be more confidence in the results of the performance assessment as a whole. Even if this ideal goal is not met, confidence will be produced by; (1) reducing the number of radionuclides which must be considered, (2) providing a justifiable conservative technical basis for source-term analyses, and (3) focussing attention on radionuclides that are problems.

## 2. RADIONUCLIDE INVENTORIES FOR LLRW SITES

Relative concentrations of the respective radionuclides will vary from site to site, depending on the waste stream. Source term variation will also arise from the associated non-radioactive material, much of which will be organic. LLRW inventories from waste sites at Barnwell (S Carolina), Beatty (NV) and Richland (WA) include resins, filter media, evaporator bottoms, activated reactor hardware and equipment.<sup>4</sup> Organic leachates from LLRW waste sites at Maxey Flats (KY) and West Valley (NY) contained a large number of different compounds derived from cellulose, solvents, scintillation liquids, etc.<sup>5</sup> Important functional groups included aliphatic and aromatic acids, alcohols, aldehydes, ketones, aromatic hydrocarbons, esters, ethers, and phenols.<sup>5</sup> Organic material may affect radionuclide transport by stabilizing reducing conditions and by providing ligands (e.g. carboxylates and phenolates) which may potentially enhance the aqueous transport of



TABLE 1  
Important radionuclides in Low Level Radioactive Waste and Their Half Lives (in Years)

$^3\text{H}$	12.33
$^{59}\text{Ni}$	8E4
$^{63}\text{Ni}$	100
$^{90}\text{Sr}$	29
$^{99}\text{Tc}$	2.1E5
$^{129}\text{I}$	1.6E6
$^{137}\text{Cs}$	30.17
$^{226}\text{Ra}$	1600
$^{232}\text{Th}$	1.4E10
$^{234}\text{U}$	2.4E5
$^{238}\text{U}$	4.5E9
$^{241}\text{Am}$	432
$^{241}\text{Pu}$	14.7
$^{14}\text{C}$	5400

Source: Weast.<sup>7</sup>

radionuclides. In the analysis below we do not specifically consider transport of radionuclides by organic ligands for two reasons: (1) reducing conditions generally favor radionuclide retention (see below); and (2) even in organic-rich soils organic ligand levels are seldom high enough to transport metals over distances of tens of meters due, in large part, to the rapid turnover in organic ligand populations caused by microbial degradation in soils.

We assume that no leakage of radionuclides will occur in the first century after burial, as current regulations call for at least 100 years of institutional control, during which time any releases can be mitigated directly.<sup>6</sup> Those isotopes with half lives of 10 years or less will, after 100 years, have decayed to insignificant levels and can be neglected in subsequent transport modeling. In Table 1 are listed all of the radionuclides with half lives of ten years or greater which are present in existing disposal facilities at Barnwell, Beatty and Richland<sup>4</sup> at activity levels greater than 1 part in 100,000 relative to the total.<sup>7</sup> The latter cutoff was used to specifically focus on those radionuclides which make up the overwhelming bulk of LLRW. The lesser isotopes ( $^{243,248,244}\text{Cm}$ ,  $^{237}\text{Np}$ ,  $^{231}\text{Pa}$ ,  $^{227}\text{Ac}$ ,  $^{207}\text{Bi}$ ,  $^{193}\text{Pt}$ ,  $^{158,157}\text{Tb}$ ,  $^{152}\text{Eu}$ ,  $^{151}\text{Sm}$ ,  $^{148}\text{Gd}$ ,  $^{145}\text{Pm}$ ,  $^{36}\text{Cl}$ ,  $^{133}\text{Ba}$ ,  $^{123}\text{Te}$ ,  $^{113}\text{Cd}$ ,  $^{94,96}\text{Nb}$ ,  $^{93}\text{Mo}$ ,  $^{210}\text{Pb}$ ,  $^{108}\text{Ag}$ ,  $^{40}\text{K}$ ,  $^{32}\text{Si}$ ,  $^{26}\text{Al}$ ) consist to an appreciable extent of rare earths. Because of their scarcity in surface and ground waters there is limited thermodynamic data (e.g. solubilities and adsorption isotherms) for the latter elements which can be used to assess transport behavior. These will be useful areas of future research if these isotopes are ever deemed to produce a non-trivial dose. Of the remainder, Si and Al are, respectively, the second and third most abundant elements in the Earth's crust after oxygen, and certain to be diluted in the near field of a disposal facility. (The same is likely to

be true for potassium.) For the initial analysis we ignore daughter products.

### 2.1. Dose-based Limits for Transport

A critical question is how insoluble (or strongly sorbed) must an element be before the dose that may result from its release can be neglected as being insignificant. In other words, what level must radionuclide concentrations be engineered to? Obviously this limiting concentration will vary from isotope to isotope and depend upon the likely ingestion pathway, the allowable exposure, as well as the normalized dose risk, which will account for radiation type, as well as the mass and sensitivity of the likely target organ. Dose-based limiting concentrations (DBLCs) were calculated for each of the isotopes in Table 1 by assuming that the drinking of water contaminated by a LLRW facility produced the dominant dose. Assuming a water consumption rate of 2 l/day (730 l/year), a maximum annual allowable dose of 25 mrem/year<sup>8</sup> and using limiting dose conversion factors for radionuclide ingestion<sup>9</sup> DBLCs were calculated as follows.

$$\begin{aligned} \text{Allowable Dose:} \\ (25 \text{ mrem/year})(1 \text{ Sv}/10^5 \text{ mrem})/(730 \text{ l/year}) = \\ 10^{-6.46} \text{ Sv/l} \quad [i]_{\text{DBLC}} = (\tau_{1/2} / 6 \times 10^{23} \times \ln 2) \\ (10^{-6.46} \text{ Sv/l})/\text{DEC}. \end{aligned}$$

$[i]_{\text{DBLC}}$  is the dose based limiting concentration (mol/l) of a given isotope  $i$ . DEC is the limiting dose conversion factor for ingestion (Sv/Bq).  $\tau_{1/2}$  is the half life of the given radionuclide (s). Note that the DEC values were chosen to maximize the dose, i.e. maximal values were used. In the same vein it was also assumed that the whole dose came from each of the respective isotopes. Calculated values of  $[i]_{\text{DBLC}}$  are shown in Table 2.

TABLE 2  
Calculated Dose-based Limiting Concentrations

Isotope	DEC(Sv/Bq) <sup>a</sup>	$[i]_{\text{DBLC}}$ (mol/l)
$^3\text{H}$	1.73E-11	1.9E-11
$^{14}\text{C}$	5.64E-10	1.9E-6
$^{59}\text{Ni}$	5.67E-11	3.7E-08
$^{63}\text{Ni}$	1.56E-10	1.7E-11
$^{90}\text{Sr}$	4.19E-07	1.8E-15
$^{99}\text{Tc}$	3.95E-10	1.4E-08
$^{129}\text{I}$	2.48E-06	<sup>b</sup> 5.1E-10
$^{137}\text{Cs}$	1.35E-08	5.9E-14
$^{226}\text{Ra}$	6.83E-06	6.2E-15
$^{232}\text{Th}$	1.85E-05	2.0E-08
$^{234}\text{U}$	1.13E-06	5.7E-12
$^{238}\text{U}$	1.01E-06	1.2E-07
$^{241}\text{Am}$	1.81E-05	6.3E-16
$^{241}\text{Pu}$	3.48E-07	1.1E-15

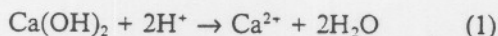
<sup>a</sup>Taken from Eckerman *et al.*<sup>9</sup>

<sup>b</sup>Calculated for a 75 mrem/year thyroid dose.

If chemical processes (mineral growth and sorption) in the facility can be engineered to limit ambient concentrations to levels less than those shown in Table 2, little effort will be required to further evaluate potential off-site pathways. If, on the other hand, source-term concentrations are predicted to significantly exceed the values above, regulatory compliance will be somewhat more difficult to demonstrate. For these reasons reasonable radionuclide concentrations in concrete-water systems must first be determined. Note, though, that all of the calculated limiting concentrations are extremely low and, with a few exceptions, less than the detection limit of the respective elements in water.

### 3. CONCRETE HYDROLYSIS

The solubilities of a number of the elements in Table 1 can vary by several orders of magnitude as a function of pH. As a result their potential movement will depend critically on the amount of acid consumed by the dissolution of cement-based waste forms, structures and backfills. By the same token the predominant dissolved form of nuclides also depends on near-field pH, as does the surface charge, hence the adsorptive potential of soil and aggregate minerals. Cement is, broadly speaking, a mixture of lime (CaO), its hydrated equivalent portlandite [ $\text{Ca}(\text{OH})_2$ ], calcium-silicate-hydrate (CSH) gel, water, and alkali oxides ( $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ ). When exposed to ground or soil water, alkalis and  $\text{Ca}^{2+}$  are exchanged from the cement for  $\text{H}^+$  from solution, causing a rise in solution pH through reactions such as



Dissolution of CSH-gel likewise causes pH and calcium levels to rise. At some point calcium salts may begin to grow; gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), fluorite ( $\text{CaF}_2$ ), and calcite ( $\text{CaCO}_3$ ). These reactions depend on the initial makeup of the reacting solution, the amount of the respective salts leached from the cement itself, and the degree of communication with the atmosphere. Once all of the base cations are leached from the cement, pH will fall, and the structure will fall apart. However, examination of Roman ruins indicate that this process will not progress to completion even given several thousands of years (e.g. Ref. 10).

To simulate the near-field environment a geochemical reaction path code, REACT<sup>11</sup> was used. REACT is a standard reaction-path code which calculates the geochemical evolution of the concrete-water system by tracking the dissolution of portlandite and wollastonite ( $\text{CaSiO}_3$ ) into a dilute sulfate-containing solution. At each point in the reaction REACT calculates the distribution of aqueous species using tabulated thermodynamic data from the literature and mass balance constraints.

Wollastonite was used in the calculation as a chemically-similar substitute for CSH-gel. Two limiting cases were examined to establish the effect of soil redox state on contaminant movement. In the first, the "oxygenated LLRW site", the cement-water system was assumed to remain in communication with  $\text{O}_2$  and  $\text{CO}_2$  in the atmosphere. The second scenario modeled was the "non-oxygenated LLRW site" in which no exchange of  $\text{O}_2$  and  $\text{CO}_2$  occurred between the concrete-water system and the atmosphere. The oxygenated state is intended to represent common current near-surface disposal designs, which almost universally are in good connection with the atmosphere. The non-oxygenated state would be more typical of disposal below the water table<sup>12</sup> and possibly of concrete monoliths, which will tend to be saturated under most field conditions. Another situation that may potentially lead to a non-oxygenated state may be produced by inadequate vault drain design. If the vault drain were to become clogged during the postclosure period (as is commonly the case in sanitary landfills), then the vault can potentially form a "bathtub". Under these conditions the chemical state of the system would be best represented by the non-oxygenated state. To model the chemical dynamics of a non-oxygenated site, the partial pressure of methane was set to one atmosphere. This accounts for the consumption of  $\text{O}_2$  through aerobic degradation and subsequent fermentive production of methane. The long term partial pressure of oxygen would be much less than atmospheric and a number of redox-sensitive radionuclides (e.g. Tc, U) would be found in their lower valence states.

For the non-oxygenated state two scenarios were examined; one where no  $\text{CO}_2$  exchange between the facility and the surrounding atmosphere occurred (see above), and the second where the partial pressure of  $\text{CO}_2$  was set to  $10^{-1.5}$  atm, 100 times atmo-

TABLE 3  
Limiting Radionuclide Solubilities

Element	Concentration (Mol/l)			
	Oxygenated	Non-Oxygen. no $\text{CO}_2$ exchange	Non-Oxygen. $p \text{ CO}_2 = 10^{-1.5}$ atm	<sup>a</sup> [i]DBLC
Pu	1.7E-7	1.3E-10	1.5E-6	1.1E-15
Am	1.1E-9	4.0E-9	1.5E-8	6.3E-16
Th	3.4E-7	3.4E-7	3.5E-7	2.0E-8
Ni	4.4E-4	7.6E-13	1.4E-16	1.7E-11
Ra	3.0E-7	*	*	6.2E-15
Sr	2.1E-5	2.1E-5	4.0E-5	2.4E-13
U	1.2E-8	2.1E-9	1.7E-13	5.7E-12
Tc	*	1.6E-38	3.6E-22	1.4E-8
Cs	*	*	*	5.9E-14
I	*	*	*	1.7E-10
C	6.1E-4	1.5E-3	7.7E-3	1.9E-6

\*Solubility >  $10^{-3}$  M.



spheric levels. In the first case pH is high ( $>12$ ). Calculated radionuclide concentrations for both scenarios are shown in Table 3. The no- $\text{CO}_2$  exchange results are discussed in detail in the following section. The second case corresponds to what might occur in a facility below the water table where  $\text{CO}_2$  produced by respiration and fermentation would tend to accumulate. In terms of dose-based limits the primary difference between the two non-oxygenated cases is that in the second ( $\text{CO}_2$  exchange) case plutonium is roughly four orders of magnitude more soluble relative to the no- $\text{CO}_2$  exchange case. A number of the other radionuclides (e.g. Ni) are less soluble. Tc and Am are more soluble, but only in a relative sense. They are both so insoluble (and strongly sorbed in the case of Am) in an absolute sense that the difference in solubility between the two cases has little effect on their dose (see below). Accurate prediction of the  $\text{CO}_2$  exchange and long-term  $E_d$  evolution of the system is impossible because of the difficulties in quantifying rates of organic degradation over long periods of time. Once all organic material has been degraded conditions should approximate the mildly oxidizing conditions of normal unsaturated soils.

In Table 3 are listed calculated solubilities of each of the radionuclides listed in Table 1 for the oxygenated case and for the two non-oxygenated cases. Also shown are dose-based limits. Where two isotopes exist (e.g. Ni) the lower dose-based limit is shown. Each of the limiting solubilities was calculated by using REACT to simulate the reaction of the portlandite-CSH mixture with a dilute solution initially containing  $1 \mu\text{M Ca}^{2+}$ ,  $1 \text{ mM sulfate}$ ,  $1 \mu\text{M SiO}_{2\text{aq}}$ , and high concentrations of the given radionuclide. Plutonium, uranium, americium and thorium are calculated to be relatively insoluble in both the oxygenated and non-oxygenated LLRW site. In the oxygenated waste site formation of the hydrated solid  $\text{PuO}_2(\text{OH})_2$  would maintain  $[\text{Pu}]_{\text{total}}$  levels near  $1.7 \times 10^{-7} \text{ M}$ . In the non-oxygenated aquifer  $\text{Pu}(\text{OH})_4$  would keep  $[\text{Pu}]_{\text{total}}$  levels near  $1.3 \times 10^{-10} \text{ M}$ . The primary aqueous form of Pu in the oxidizing environment would be the hydroxycarbonate species,  $\text{PuO}_2(\text{OH})_2\text{HCO}_3^-$ . In the non-oxygenated, non- $\text{CO}_2$  exchanged environment the most abundant species would be  $\text{Pu}(\text{OH})_5^-$ . Dehydration and increasing crystallinity of the solid would cause  $[\text{Pu}]_{\text{total}}$  to drop by several orders of magnitude. Uranium forms strong carbonate complexes, and will exist in the aqueous phase in the oxygenated site primarily as  $\text{UO}_2(\text{CO}_3)_2^{2-}$ . The solubility controlling solid is calculated to be Haiweeite, a calcium-uranium-silicate-hydroxide, observed to form at low temperatures. In the non-oxygenated case the primary uranium complex is calculated to be  $\text{U}(\text{OH})_4$ , and the solubility limiting solid uraninite. Americium solubility will be controlled by  $\text{AmOHCO}_3$  in the oxygenated facility,

and by  $\text{Am}(\text{OH})_3$  in the non-oxygenated environment. The primary dissolved forms will be  $\text{AmCO}_3^+$  and  $\text{Am}(\text{OH})_{3\text{aq}}$  for the two respective end-member cases. For the oxygenated and non-oxygenated LLRW site  $[\text{Am}]_{\text{total}}$  is calculated to be  $1.1 \times 10^{-9}$  and  $4 \times 10^{-9} \text{ M}$ , respectively. The most stable Th-containing phase is thorianite ( $\text{ThO}_2$ ).  $\text{Th}(\text{OH})_4$  is less stable, but probably more likely to form rapidly due to its hydrated state and control levels of dissolved thorium. Taking a more conservative approach and using the latter to calculate maximal Th levels in solution gives  $[\text{Th}]_{\text{total}} = 3.4 \times 10^{-7} \text{ M}$  for both the oxygenated and non-oxygenated waste site. Note that, if through aging or dissolution-precipitation processes  $\text{Th}(\text{OH})_4$  converts to  $\text{ThO}_2$ , this value could drop as low as  $10^{-14} \text{ M}$ .

In the oxygenated site, formation of the solid  $\text{Ni}(\text{OH})_2$  would limit  $[\text{Ni}]_{\text{total}}$  to  $4 \times 10^{-4} \text{ M}$ . It was assumed for the sake of conservatism that neither of the insoluble Ni-containing solids  $\text{Ni}_2\text{SiO}_4$  and  $\text{NiO}$  would form rapidly. In the non-oxygenated waste site  $[\text{Ni}]_{\text{total}}$  would be much lower at  $[\text{Ni}]_{\text{total}} < 10^{-12} \text{ M}$  due to the growth and solubility control by the insoluble metal sulfide  $\text{Ni}_3\text{S}_2$ . If the lower solubility oxide phases were to grow and control aqueous levels of Ni, U, Th and Am the latter values will approximate dose-based limiting concentrations, particularly for Th and Ni (under oxidizing conditions). But the growth of the lower solubility phases cannot be relied upon as dehydroxylated mineral phases are, in general, observed to grow only over very long periods of time.

Technetium is calculated to be highly soluble in the oxygenated LLRW site; i.e.  $[\text{Tc}]_{\text{total}} > 10^{-3} \text{ M}$ . On the other hand Tc will be highly insoluble in a non-oxygenated LLRW. Radium concentrations will be limited by formation of the solid  $\text{RaSO}_4$  in the oxygenated environment. In the non-oxygenated case much of the sulfate is reduced and no insoluble Ra-containing salts are predicted to form. Strontium is predicted to form strontianite,  $\text{SrCO}_3$ , under both oxygenated and non-oxygenated conditions.

Commonly, the Impacts Analysis Methodology<sup>13</sup> is used to model release rates from disposal facilities. The Impacts database relies largely on a partition coefficient which is the ratio of measured trench-water radionuclide concentrations from the Maxey Flats low level waste sites to the estimated concentration in the total inventory. Obvious drawbacks to application of the Impacts database are the uncertainties in the methodology used in developing the database,<sup>14</sup> the non-physical nature of the models,<sup>15</sup> and the questionable relevance of the Maxey Flats data to other sites. For example, the Impacts database contains a remarkably low value for the partition coefficient for uranium, characteristic of the non-oxygenated conditions which predominate

at Maxey Flats. The same coefficient applied to current facility designs, which will probably be oxygenated, would greatly underestimate releases. In general, reliance on the Impacts database makes it more likely that releases of some radionuclides will be markedly overestimated, whereas others are likely to be greatly underestimated.

Carbon and tritium may be released from an LLRW facility in the gas phase resulting in substantial reduction in aqueous phase releases. We will focus here on their transport in the aqueous phase, keeping in mind that a substantial portion of the activity from each isotope is likely to be diluted into the atmosphere beforehand. Carbon will be somewhat soluble ( $[f] \sim 10^{-3}$  M) in the interior of the LLRW facility under both oxygenated and non-oxygenated conditions. Note though that in and immediately adjacent to the facility the interaction of soil (or atmospheric)  $\text{CO}_2$  with Ca leached from the cement will result in the formation of  $\text{CaCO}_3$ , a sink for  $^{14}\text{C}$ . The amount of C remaining in solution (primarily as  $\text{HCO}_3^-$  in the oxygenated case, and  $\text{CO}_3^{2-}$  in the non-oxygenated case) will depend on the amount of Ca in solution and soil  $\text{P}_{\text{CO}_2}$ , which are hard to predict. Chemical analyses of groundwater  $\text{HCO}_3^-$  in carbonate aquifers generally range from 1.6 to 4.9 mM;<sup>16</sup> here we use 4.9 mM.

Tritium will go into the aqueous phase with no appreciable incorporation into solids. No retardation of  $^3\text{H}$  arises from concrete-water interaction.<sup>17</sup> Isotope dilution will therefore be a far more important factor for tritium attenuation than for any of the other radionuclides. One must therefore rely on physical confinement, decay, and dilution in the environment to meet performance objectives for tritium.

### 3.1. Adsorption and Radionuclide Attenuation

While mineral growth reactions will limit the levels of a number of isotopes to less than their dose-based limit (e.g. Ni under reducing conditions, and possibly thorium), for many levels will remain appreciably higher (see Tables 2 and 3). Therefore the potential for radionuclide sorption must be explicitly considered. To do this, adsorption partition coefficients,  $K_d$ s for each of the elements have been taken from the literature and are shown in Table 4.<sup>18-23</sup>  $K_d$  (ml/gm) monitor adsorption and are the measured ratio of the amount of an element adsorbed (mol/g of rock) to the amount remaining in solution (mol/ml).  $K_d$  values are large for strongly sorbed ions (e.g. Pu and Am) and low for ions which sorb only slightly (e.g. Tc).  $K_d$ s lump together a large number of complex chemical factors which are not completely understood. For this reason  $K_d$ s are not completely portable (see Ref. 24) and are therefore used here only as a rough yardstick of sorptive potential. The values in Ref. 4 were taken from the

TABLE 4  
 $K_d$ s in and Adjacent to the Facility\*

Element	$K_{d,\text{cement}}$	$K_{d,\text{soil}}$	Sources
Ni	1500	127	18
Sr	56	41	18
Tc	0	0	19
I	100	0	19,20
Cs	37	300	19,21
Ra	4000	1000	22
C	2000	3	23
U	1000	4	20,19
Th	5000	500	20,19
Am	10000	50	20,19
Pu	2000	500	20,19

\*All numbers are very approximate and represent rough values taken uncritically from the literature.

literature and give a semi-quantitative idea of the relative affinity of ions for cement and soil surfaces. Table 4 is not a critical compilation — the numbers are probably not accurate within an order of magnitude. This is enough to highlight the factors which control transport though.  $K_d$ s are listed for both cement-water systems and for soils, the latter to model the near-field environment.

The  $K_d$ s for Tc were set to 0 because of its anionic, non-sorbing behavior (e.g. Ref. 25). The values in Table 4 can be used to calculate the partitioning of nuclides onto the cement matrix, as well as onto soils in the immediate vicinity of the facility as per

$$[f]_{\text{adsorbed}}/[f] = \frac{\theta}{\rho} K_d \quad (2)$$

$\theta$  is porosity and  $\rho$  is rock density. Note first of all that by using equation (2) we are assuming the most conservative case of saturated flow. We also assume that the porosity and density of the cement and soil\* are each 20% and 2 g/cm<sup>3</sup> respectively. We then modify the value of  $[f]$  calculated from thermodynamics (Table 2), using equation (2) to account for sorption onto the cement, and subsequently onto the soil adjacent to the facility. Calculated values of  $[f]$  after mineral growth and sorption are listed in Table 5.

One of the first conclusions that follows from Table 5 is that cement-water interactions (solubility control + sorption) alone will largely assure minimal releases of isotopes of Am, Th, C, U, Ra (oxidizing conditions) and Ni (non-oxidizing conditions). For the oxygenated case, after mineral growth and adsorption there is still roughly 10 times as much plutonium and nickel in solution as allowable, which means that at least a 10-fold dilution would have to occur in the near and far-field. In the scenario of reducing,  $\text{CO}_2$ -exchanged conditions Pu levels would



TABLE 5  
Calculated Concentrations After Sorption on Cement and Soil  
(See Text)

Isotope	$[i]_{\text{oxygen}}$	$[i]_{\text{non-ox}}$	$[i]_{\text{DBLC}}$
$^{59}\text{Ni}$	2.3E-10	4.0E-19	3.7E-08
$^{63}\text{Ni}$	2.3E-10	4.0E-19	1.7E-11
$^{90}\text{Sr}$	9.1E-10	1.0E-9	1.8E-15
$^{99}\text{Tc}$	*	1.6E-38	1.4E-08
$^{129}\text{I}$	*	*	1.7E-10
$^{137}\text{Cs}$	*	*	5.9E-14
$^{14}\text{C}$	1.0E-8	2.5E-8	1.9E-6
$^{226}\text{Ra}$	7.5E-15	*	6.2E-15
$^{232}\text{Th}$	1.3E-14	1.4E-14	2.0E-08
$^{234}\text{U}$	3.0E-13	5.3E-14	5.7E-12
$^{238}\text{U}$	3.0E-13	5.3E-14	1.2E-07
$^{241}\text{Am}$	2.2E-15	8.0E-15	6.3E-16
$^{241}\text{Pu}$	1.7E-14	1.3E-17	1.1E-15

The isotopes marked with an asterisk are those whose solubilities are  $>10^{-3}\text{M}$ .

be  $1.7 \times 10^{-13}\text{M}$ , after mineral growth and sorption, hence a  $10^2$ -fold dilution would be required.

We now focus on those isotopes whose calculated levels greatly exceed the  $[i]_{\text{DBLC}}$ :  $^{99}\text{Tc}$  (oxidizing conditions),  $^{137}\text{Cs}$ ,  $^{129}\text{I}$ ,  $^{90}\text{Sr}$  and  $^{226}\text{Ra}$  (non-oxidizing conditions), whose releases must be considered most important in the performance assessment. Recall that  $^{99}\text{Tc}$  is only soluble in an oxidizing environment, being insoluble under reducing conditions, and that most current disposal facilities are being designed to be oxygenated. Furthermore, technetium will be anionic in solution and unlikely to be retarded on mineral surfaces in the concrete-water system. However, recent work has shown that  $\text{TcO}_4^-$  adsorbs to Fe(II)-rich minerals, in the process being reduced to the insoluble +4 valence state.<sup>26</sup> This occurs even when the initial solution is mildly oxidizing. Hence, Fe(II)-rich mineral surfaces potentially constitute a previously unaccounted for sink for Tc. The ability of mafic rock components to reductively adsorb electron acceptors from solution is fairly common (see Ref. 27) and may potentially be taken advantage of to reduce Tc releases. An add-on design feature which would maximize the reductive retardation of Tc would be to line the exterior of the LLRW site with mafic (basalt, serpenbnite, etc.) fill. This is shown in Fig. 1.<sup>28</sup> We are presently examining the specific controls on Tc retardation by basalt fills at the bench scale.

The added fill would perform another function in addition to potentially immobilizing Tc, namely acting as a secondary back-up sink for any metals which make it past the immediate disposal facility-soil environment. Fe-rich mafic rocks alter over long periods of time to form high surface area iron hydroxides which are highly effective, high surface

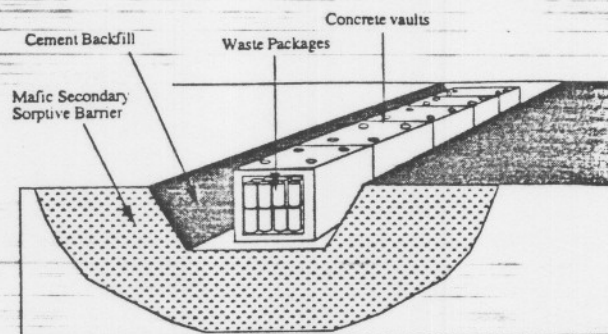


FIGURE 1. Schematic of shallow burial of LLRW (after Ref. 28).

area sorbers of such elements as uranium, strontium, lead, cadmium, etc. (e.g. Refs 29, 30).

Despite its anionic state iodine is observed to be appreciably retarded in cement-water systems, presumably by adsorption to Ca-Al-sulfate phases in the concrete.<sup>31</sup> To our knowledge the only other minerals known to adsorb iodine are cinnabar ( $\text{HgS}$ ) and imogolite, a fibrous mineral which forms in andesols, the weathering residuum of silicic volcanic ash. Even at high pH, where all other mineral surfaces are anionic imogolite may be able to sorb anions from solution (e.g. Ref. 32). Assuming this to be the case, one alternative for retarding iodine movement would be to use imogolite as an additive to the interior fill of the LLRW site or to the mafic blanket. Alternatively andesol could be used as an outer blanket to surround the mafic blanket. Note that to do either ultimately requires that the iodine sorbing capacity and long-term durability of imogolite be more fully demonstrated. We are presently examining I sorption to imogolite in the laboratory. In the meantime, the most reasonable approach to  $^{129}\text{I}$  transport may be to salt the waste with non-radioactive isotopes of iodine and rely on isotopic dilution to mitigate the dose arising from any  $^{129}\text{I}$  not sorbed in the disposal facility environment.

Dilutions on the order of  $10^6$  are needed after sorption and mineral growth to reduce the levels of Sr to its dose-based limit. A significant fraction of this dilution is certainly achievable as between  $10^3$  and  $10^4$  volumes of water will be required to completely degrade the cement.<sup>33</sup> That is, releases can be expected to be spread out over a long period of time. Because there are no insoluble Cs compounds, Cs levels in the leachate will be determined by the steady-state rate of Cs release from the entombed waste and by the extent of dilution. A steady-state Cs concentration of  $6\text{ }\mu\text{M}$  in the waste facility, followed by sorption and a  $10^4$ -fold dilution in the near field would reduce  $^{137}\text{Cs}$  levels below the dose-based limits. No dilution would require Cs levels less than  $6 \times 10^{-3}\text{ }\mu\text{M}$ . For  $^{90}\text{Sr}$ , decay can be expected to drastically reduce doses ( $\tau_{1/2} = 29$  years). The same is true for

$^{137}\text{Cs}$ , with a half life of 30 years. The activity of each isotope will therefore decrease by roughly an order of magnitude every hundred years. Largely for this reason, these isotopes are not expected to be important in performance assessment. In the non-oxygenated case there are no insoluble Ra-containing solids. As a result sorption, dilution and the actual leach rate from the waste must be relied on to limit doses from  $^{226}\text{Ra}$ . Micromolar concentrations of Ra in the facility, followed by sorption and at least a  $10^4$ -fold dilution in the near-field, would drop  $^{226}\text{Ra}$  below its dose-based limiting concentration.

#### 4 SUMMARY

Concrete-based designs are being proposed for almost all new disposal facilities worldwide. Consequently, there is a need to establish a defensible basis for conservative modeling of releases from such disposal facilities. The current contribution is a first step toward developing that defensible basis. Pessimistic estimates have been generated for solubilities of radionuclides of concern in low-level waste. The analysis suggests that release rates of most of the radionuclides are reduced to very low levels by interaction with concrete, to the extent that even consumption of the leachate would produce minimal doses. Of particular interest is the reduction in  $^{14}\text{C}$  releases since  $^{14}\text{C}$  is commonly a concern in low-level waste performance assessments. We have suggested a design modification that may reduce  $^{99}\text{Tc}$  releases to insignificant levels in the event that Tc produces excessive doses in the analysis. However, the chemistry of concrete does not, by itself, render  $^3\text{H}$ ,  $^{90}\text{Sr}$ ,  $^{129}\text{I}$ ,  $^{137}\text{Cs}$  (and to some extent  $^{226}\text{Ra}$ ) concentrations low enough to meet the performance objectives. Consequently, other portions of the performance assessment must be relied on to meet performance objectives.

Note that the conclusions reached in this paper are not site specific. Those geochemical features of soils which are advantageous to LLRW storage (high sorptive potential, low actinide solubilities, etc.) have been explicitly included in the design. Such a site operated in an arid region would evolve very similarly to one in a humid region. The concrete and mafic blanket would weather faster in the latter case due to increased organic activity and water availability. Note though that complete degradation of a concrete-based disposal facility is expected to require several thousand volumes of water (e.g. Ref. 3), which, depending on the hydrogeologic makeup of the site, will require very long periods of time, in either case. At the same time numerous old exposures of mafic rocks in humid climates argue for the persistence of the mafic blanket over at least tens of thousands of years.

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