Research Article

On the Durability of Nuclear Waste Forms from the Perspective of Long-Term Geologic Repository Performance

Yifeng Wang*, Carlos F. Jove-Colon, Robert J. Finch

Sandia National Laboratories, P. O. Box 5800, Albuquerque, NM 87185, USA

Correspondence: E-mail: ywang@sandia.gov; Tel: +505-844-8271.

Abstract: High solid/water ratios and slow water percolation cause the water in a repository to quickly (on a repository time scale) reach radionuclide solubility controlled by the equilibrium with alteration products; the total release of radionuclides then becomes insensitive to the dissolution rates of primary waste forms. It is therefore suggested that future waste form development be focused on conditioning waste forms or repository environments to minimize radionuclide solubility, rather than on marginally improving the durability of primary waste forms.

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1. Introduction

Durability is commonly considered to be the most important attribute of nuclear waste forms (WF) [1,2,3]. A great deal of effort has been devoted to creating durable waste forms, ranging from borosilicate glasses to crystalline mineral analogues [4,5], with the assumption that a slow waste form dissolution rate is the most effective means of limiting the release of radionuclides (RN) from a repository to the human accessible environment. This assumption is based on an untested premise that the kinetic dissolution of a primary waste form is the rate-limiting step for radionuclide release. In this short communication, we demonstrate that this may not be the case in an actual repository environment. Once in contact with incoming water, a primary waste form in a repository will eventually degrade into various more stable alteration products (or secondary waste forms). We show that the long-term rate at which radionuclides are released from a repository will be controlled by the solubilities of the alteration products rather than by the dissolution rates of the primary waste forms. Therefore, current requirements for waste form development need to be re-evaluated.

2. Results

Long-term performance assessments (PA) of a geologic repository generally model the degradation of a waste form as a kinetic process, whereas alteration products are assumed to be in chemical equilibrium with the contacting water [6]. Such treatment is referred to as the partial

equilibrium approach, which assumes no supersaturation in the system. This approach has been invoked by the IAEA [7] and has been used to assess long-term waste isolation in a geologic repository [8,9]. This approach seems appropriate, if we look at the dissolution and alteration of natural materials in subsurface environments. We have calculated mineral-saturation indices for groundwater samples collected from Columbia Basin [10], which indicate that a majority of water samples are close to equilibrium with calcite and cristobalite, with little or no oversaturation with other low temperature minerals. This is probably due to the presence of a large number of nucleation and growth sites on mineral surfaces in a rock-weathering system, which effectively lowers the saturation degree for secondary mineral precipitation. As shown in Figure 1, calcium release due to basalt weathering can be very well predicted (within one log unit) by assuming calcite to be the solubility-controlling mineral for dissolved calcium. A similar observation can be made on uranium ore deposits. For example, Lu et al. [11] describes the oxidation of uraninite from a uranium ore deposit in China and the formation of secondary solubility-controlling uranyl-bearing solids.
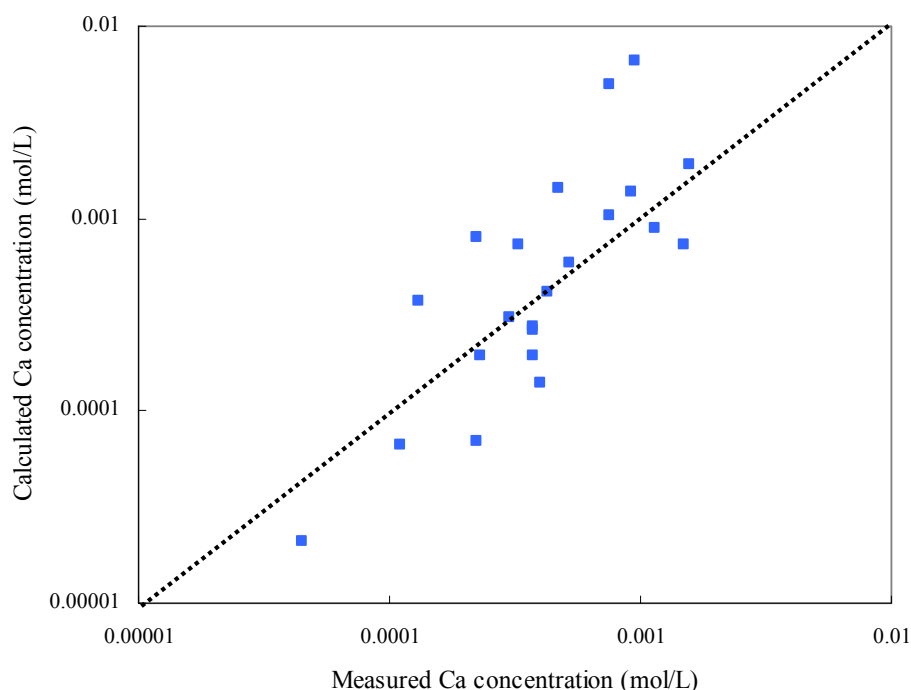
Figure 1. Dissolved calcium concentrations predicted with the assumption that calcium release is controlled by equilibrium with calcite. The good agreement between the calculated and the measured concentrations justifies the partial equilibrium assumption generally used in modeling of waste form degradation in a deep geologic repository.

Based on the assumption of partial equilibrium, in an actual repository environment, waste degradation and radionuclide release can be divided into three stages (Figure 2): Stage I, in which the dissolved concentration of the radionuclide has not reached its solubility limit; Stage II, in which the radionuclide concentration has reached its solubility limit and continues to maintain equilibrium with a solubility-controlling secondary phase; and Stage III, in which the dissolved radionuclide concentration drops rapidly to zero due to the disappearance of both the primary waste form and the solubility-controlling secondary phase. The actual release mode of a radionuclide depends on how

fast the repository system can reach Stage II, which is controlled by three factors: (1) the rate of radionuclide release from the waste form, (2) the rate at which water flows through the repository, and (3) the radionuclide's solubility under repository conditions.
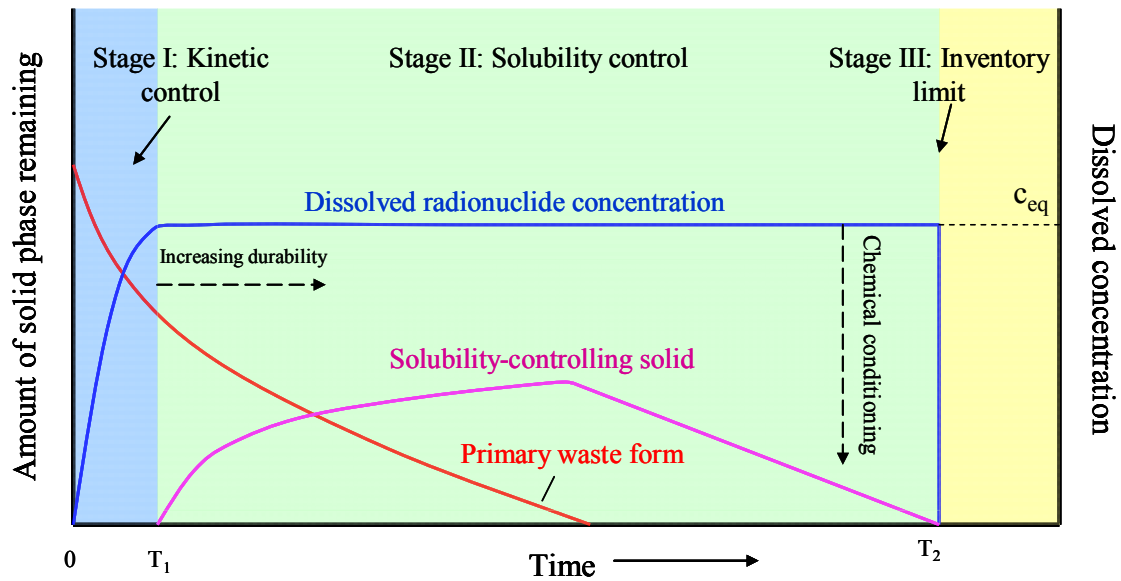
Figure 2. Schematic diagram of waste degradation and radionuclide release in a repository environment under the partial equilibrium assumption. The duration of stage I is generally much shorter than that of stage II. Stage III may never be reached for a radionuclide with a relatively large initial inventory and a slow decay rate. As demonstrated in this paper, chemical conditioning can be more effective in reducing the total radionuclide release than further improving waste form durability.

In Stage I, the concentration of a specific radionuclide in a disposal system can be modeled as follows:

$$V_T \phi \frac{dc}{dt} = -\frac{\alpha}{m_w} \frac{dM}{dt} - vc \qquad \text{for} \quad c < c_{eq} \qquad (1)$$

$$\frac{dM}{dt} = -M \cdot A \cdot R \qquad (2)$$

where V_T is the total volume a disposal system (dm^3); ϕ is the porosity in the disposal system after waste emplacement; c is the dissolved concentration of a radionuclide of interest (mol·L^{-1}); t is the time since disposal (s); α is the waste loading factor (g$_{RN}$·g$_{WF}^{-1}$); m_w is the molecular weight of the radionuclide (g$_{RN}$·mol^{-1}); M is the total mass of a waste form in the disposal system (g$_{WF}$); v is the rate of water flow percolating through the disposal system (L·s^{-1}); c_{eq} is the solubility of the radionuclide (mol/L); A is the specific surface area of waste form (m^2·g$_{WF}^{-1}$); and R is the surface-normalized dissolution rate of the waste form (g$_{WF}$·m^{-2}·s^{-1}). R depends on various factors such as the chemical affinity for waste form dissolution and the coating of alteration products. For simplicity, we assume that the effect of those factors is captured by wide ranges of variability in dissolution rates reported in the literature. In Equation (1), we ignore the concentration change due to radioactive

decay. This simplification does not change the overall conclusion drawn in this paper, especially for long-lived radionuclides in which we are interested. Also here we use term "radionuclide" interchangeably with "radioelement" when we refer to "radionuclide solubility".

Solving Equation (2) and plugging the solution into Equation (1), we obtain:

$$V_T \phi \frac{dc}{dt} = -\frac{\alpha A R M_0}{m_w} e^{-A \cdot R \cdot t} - vc \qquad (3)$$

The initial mass of waste form M_0 is $M_0 = \rho(1-\phi)V_T$, where ρ is the density of waste form ($g_{WF} \cdot m^{-3}$). Equation (3) can be scaled into:

$$\frac{du}{d\tau} = e^{-\beta\tau} - \gamma u \qquad \text{for } u < 1 \qquad (4)$$

with

$$\tau = \frac{t}{T} \qquad T = \frac{c_{eq} m_w \phi}{\alpha A R \rho (1-\phi)} \qquad \beta = \frac{c_{eq} m_w \phi}{\alpha \rho (1-\phi)}$$

$$u = \frac{c}{c_{eq}} \qquad \gamma = \frac{c_{eq} m_w \phi}{\alpha A R \rho (1-\phi)} \frac{1}{T_r} \qquad T_r = \frac{V_T \phi}{v} \qquad (5)$$

Parameter T represents a typical time scale for the variation of dissolved radionuclide concentration, over which $du/d\tau$ is on the order of 1; T_r characterizes the residence time water inside the disposal room. For typical parameter values given in Table 1, $\beta < 10^{-4}$, and thus Equation (4) can be simplified to:

$$\frac{du}{d\tau} \approx 1 - \gamma u \qquad \text{for } u < 1. \qquad (6)$$

The small value of β is a characteristic of subsurface systems with high solid/water ratios [12].

Table 1. Typical model parameter values

Parameter	Values	Comment
Radionuclide solubility (c_{eq})	10^{-5} mol/L	
Molecular weight (m_w)	237 g/mol	Use Np as an example
Porosity (ϕ)	0.4	
Density of waste form	2.7–2.9 g/cm^3	Use high-level waste glass as an example.
Reactive surface area of waste form	0.01 m^2/g	
Pore volume in a WIPP waste panel	10^3–10^4 m^3	[14]

Maximum rate of water flow pore upper boreholes in a WIPP waste panel	0.55 m³/yr	[14]
Volume of a waste container in Yucca Mountain repository	15 m³	[13]
Rate of water flow percolating through a Yucca Mountain waste container	0.1–100 L/yr	[13]
Water flow rates for other repository-relevant formations	Approx. 10^{-5} L/yr for clay (Meuse/Haute-Marne site); 100–10,000 L/yr for granite	[28]

For a solubility control of radionuclide release, it is required that $\gamma < 1$; that is,

$$T_r > \frac{c_{eq} m_w \phi}{\alpha A R \rho (1 - \phi)}.$$ (7)

This ensures that the rate of radionuclide dissolution into the solution exceeds the rate of radionuclide transport away from the system by water advection. By solving Equation (6) and then setting $u = 1$, the time for a dissolved radionuclide to reach its solubility limit (T_l) can be calculated as follows:

$$T_1 = -\frac{T}{\gamma} \ln(1 - \gamma) = -T_r \ln \left[1 - \frac{c_{eq} m_w \phi}{\alpha A R (1 - \phi) \rho T_r} \right]$$ (8)

As indicated in Figure 3, with increasing the residence time of water in the disposal system or increasing dissolution rate of the primary waste form, the concentration of the radionuclide will change from being kinetically controlled to being solubility-controlled. The residence time depends on the actual water flow rate and the total pore volume of the disposal system. An actual disposal system can be a waste container or a waste panel. In the Yucca Mountain repository, radioactive wastes will be container in steel/alloy packages, and each waste package, with a total internal volume of ~15 m³ 9 can be considered as a separate disposal system (note that ignoring the WP and assuming the tunnel immediately surrounding the waste effectively increases the value of pore volume and the corresponding value of T_r). Choosing a typical flow rate in the range 0.1–100 L/year/waste package [13], we estimate the minimum water residence time to be ~60 years. Similarly, for the Waste Isolation Pilot Plant (WIPP), a disposal system can be defined as an individual waste panel, each with the pore volume of 0.3–1.0x10⁴ m³ (Helton et al., 1998). The maximum rate of water flow through boreholes during a human intrusion scenario is estimated to be ~5.5 m³/year [14]. The minimum water residence time in the WIPP is thus estimated to be ~5,000 year. Therefore, as shown in Figure 3, in an actual repository environment, even for the most durable waste forms, the radionuclide release from the near-field of a repository will likely be controlled by the solubility limit of the radionuclide.
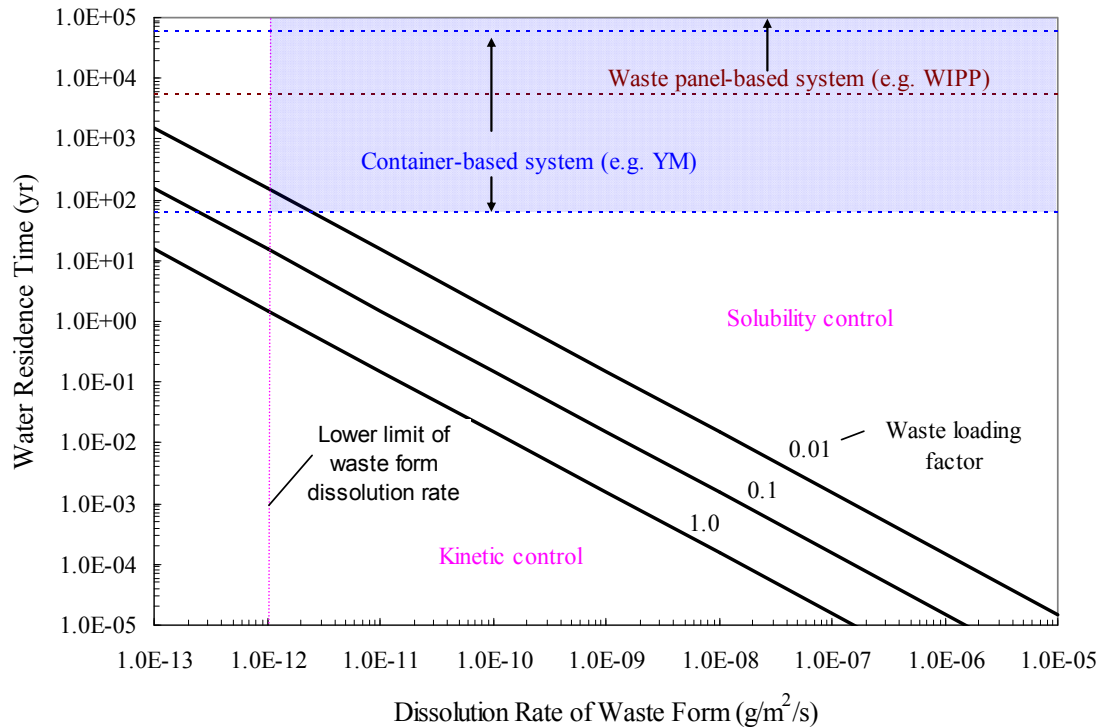
Figure 3. Radionuclide release modes as controlled by waste form dissolution rate and waste loading factor as well as by water residence time. It is apparent that in an actual repository environment radionuclide release is most likely controlled by solubility of alteration phases. The lower limit of waste form dissolution rate is assumed to be the minimum dissolution rate of zirconia (see Figure 4). The parameter values used in constructing this diagram are shown in Table 1.

For a given repository environment, the time for a radionuclide to reach its solubility limit is determined by the dissolution rate of the waste form that hosts the radionuclide. We have compiled dissolution rates for various waste forms. As shown in Figure 4, for all waste forms considered, the time for a radionuclide to reach its solubility limit is generally less than 300 years. Compared with a typical repository regulatory time (T_{reg}) (10^4–10^6 years), this transient time is negligible. Therefore, the accumulative release of a specific radionuclide can be approximated by:

$$\text{Total release} = \int_0^{T_{reg}} c \cdot v\, dt \approx \int_{T_1}^{\min(T_2, T_{reg})} c_{eq}\, v\, dt \ . \tag{9}$$

As indicated in Equation (9), there are two ways to reduce the total radionuclide release. One way is to reduce the water flow rate v with an engineered physical barrier, for example, encapsulate a waste form with a low-permeability clay layer [15] (see Table 1). The problem with an engineered barrier is that it is difficult to demonstrate the long-term integrity of barrier over a regulatory time period. The other way, which we believe will be more effective in reducing radionuclide release, is to chemically condition waste forms or repository environments to minimize radionuclide solubility.
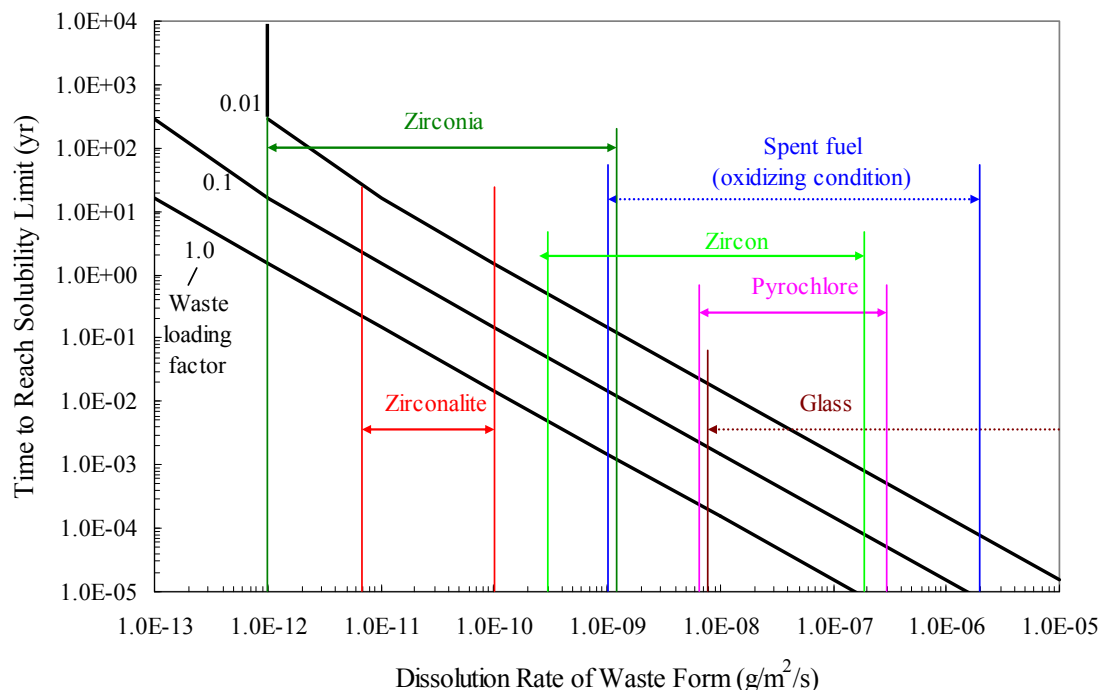
Figure 4. Time for a radionuclide to reach its solubility limit as a function of waste form dissolution rate. The water residence time is assumed to be 200 years. Dissolution rates are taken from [22] for glass, [23] for spent fuel, [24,25] for pyrochlore, [26] for zirconalite, [5] for zirconia, and [2,27] for zircon. The parameter values used in constructing this diagram are shown in Table 1.

The concept of conditioning repository environments can be best demonstrated with the Waste Isolation Pilot Plant (WIPP) [16], which is located in a salt bed in southern New Mexico and designed by U.S. Department of Energy for permanent disposal of defense-related transuranic wastes. WIPP wastes contain a large quantity of organic materials and various nutrients. Thus, there is a concern about the potential impact of microbial CO_2 generation on actinide solubilities. To mitigate this effect, a sufficient amount of MgO will be added to the repository with the backfill. Hydrated MgO will react with CO_2 to form magnesite:

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O. \tag{10}$$

Reaction (10) will buffer CO_2 fugacity at $\sim 10^{-7}$ atm. This low CO_2 fugacity implies that Reaction (10) will remove practically all CO_2 from both gaseous and liquid phases in the repository. A thermodynamic equilibrium calculation using the EQ3/6 code shows that the addition of MgO will buffer pH around 10 for WIPP brines [16]. Under these chemical conditions, actinide solubilities become minimal (Figure 5).

As shown in Figure 5, by appropriately conditioning the near-field environments the dissolved concentration of a radionuclide can be reduced by orders of magnitude. The chemical composition of a waste form can strongly affect the near-field chemistry of a repository, and so an appropriate choice of waste form composition can be an important aspect of overall chemical conditioning. In this sense, amorphous materials may have an advantage over crystalline materials, although the former are generally less "durable" than the latter. Amorphous materials such as glasses have considerable flexibility in incorporating various chemical components. It is known that many

radionuclides, especially actinides, can form sparingly soluble phosphates within the glass corrosion layers [17,18] or as alteration products in uranium deposits [11]. Phosphate has also been used for immobilization of heavy metals in soils and sediments [19,20]. Therefore, it may be desirable to formulate a high-level waste (HLW) glass by adjusting its phosphate content or even to employ a phosphate glass [21] to minimize radionuclide solubility during glass degradation.
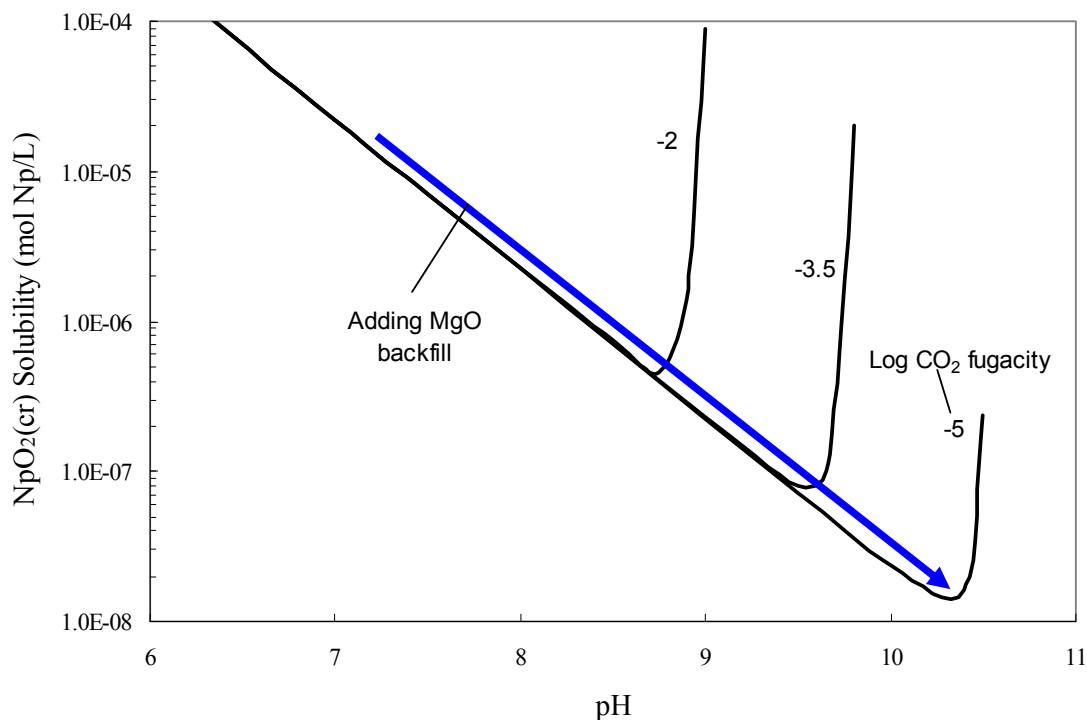
Figure 5. NpO2(cr) solubility as a function of pH and partial pressure of CO₂. Addition of MgO to the repository greatly reduces Np solubility.

For a given repository environment, dissolved concentrations of some radionuclides may never become solubility-limited, and their releases are generally limited by the dissolution rate of the primary waste form. Clearly, long-term durability of a waste form — especially one that contains a substantial inventory of such potentially mobile radionuclides — is a crucial aspect in limiting radionuclide releases; we are not suggesting otherwise. On the other hand, the proposed chemical conditioning concept may allow us to design waste forms or backfill materials that include chemical components that can precipitate low-solubility radionuclide-bearing solids that would otherwise not be stable. For example, iodine-129, which is considered a highly mobile radionuclide in nearly all repository environments, can potentially form insoluble solids in either a reducing or an oxidizing environment, provided that appropriate chemical components (such as Cu^+) are added to the host waste form or backfill materials.

Radiation damage has been a concern for the long-term performance of a waste form [2]. The existing studies in this area have been exclusively focused on primary waste forms [29,30,31]. Our analysis, however, suggests that the future focus of these studies be shifted to evaluating the potential effect of radiation damage on the stabilities of secondary mineral phases that will directly control dissolved radionuclide concentrations.

3. Conclusion

In summary, due to high solid/water ratios and slow groundwater percolation rates, the concentrations of radionuclides dissolved in water flowing through a repository are expected to reach solubility control by radionuclide-bearing alteration products well within typical regulatory timeframes. Consequently, total release of radionuclides will become insensitive to the dissolution rates of primary waste forms. Our analysis suggests that future waste-form development should be increasingly focused on conditioning waste forms or repository environments to minimize radionuclide solubility, rather than on striving for marginal improvements to the durability of primary waste forms.

Acknowledgment

Conflict of Interest

All authors declare no conflicts of interest in this paper.

References

1. Ringwood AE, Kesson SE, Revve KD, et al. (1988) Synroc (for radiowaste solidification), in *Radioactive Waste Forms for the Future*, W. Lutze and R. C. Ewing (eds), North-Holland, Amsterdam, 233-334.
2. Ewing RC (1999) Nuclear waste forms for actinides. *Proc Natl Acad Sci* 96: 3432-3439.
3. Peters MT, Ewing RC (2007) A science-based approach to understanding waste form durability in open and closed nuclear fuel cycles. *J Nucl Mater* 362: 395-401.
4. Grambow B (2006) Nuclear waste glasses – how durable? *Elements* 2: 357-364.
5. Lumpkin GR (2006) Ceramic Waste Forms for Actinides *Elements* 2: 365-372.
6. SNL (Sandia National Laboratories) (2008) Total System Performance Assessment Model/Analysis for the License Application, Sandia National Laboratories, Albuquerque, New Mexico.
7. IAEA (2003) Technical Reports Series No. 4I3, Scientific and Technical Basis for the Geological Disposal of Radioactive Wastes.
8. Murphy WM (2004) Measures of geologic isolation. *Mat Res Soc Symp Proc* 824: cc3.5.1-cc3.5.9.
9. Kienzler B, Metz V, Lutzenkirchen J, et al. (2007) Geochemically based safety assessment. *J Nucl Sci Technol* 44: 470-476.
10. Hearn PP, Steinkampf WC, Bortleson GC, et al. (1985) Geochemical Controls on Dissolved Sodium in Basalt Aquifers of the Columbia Plateau, Washington. Water-Resources Investigations Report 84-4304. Tacoma, Washington: U.S. Geological Survey.
11. Lu L, Chen F, Ewing RC, et al. (2007) Trace element immobilization by uranyl minerals in granite-hosted uranium ores: Evidences from the Xiazhuang ore field of Guangdong province, China. *Radiochim Acta* 95: 25-32.
12. Ortoleva P, Merino E, Moore C, et al. (1987) Geochemical self-organization, I. Feedbacks, quantitative modeling. *Am J Sci* 287: 979–1007.

13. Wang Y, Jove-Colon CF, Mattie PD, et al. (2010), Thermal, hydrodynamic, and chemical constraints on water availability inside breached waste packages in the Yucca mountain repository. *Nucl Technol* 171: 201-219.

14. Helton JC, Bean JE, Berglund JW, et al. (1998) Uncertainty and Sensitivity Analysis Results Obtained in the 1996 Performance Assessment for the Waste Isolation Pilot Plant. Sandia National Laboratories, Albuquerque, New Mexico.

15. ANDRA (2005) Dossier 2005 Argile: Evaluation of the feasibility of a geological repository in an argillaceous formation.

16. Wang Y, Brush LH, Bynum RV (1997) Use of MgO to mitigate the effect of microbial CO_2 production in the Waste Isolation Pilot Plant. WM'97, March 2 - 6, 1997, Tucson, Arizona..

17. Bates JK, Bradley JP, Teetsov A, et al. (1992) Colloid formation during waste form reaction: Implications for nuclear waste disposal. *Science* 256: 649-651.

18. Buck EC, Bates JK (1999) Microanalysis of colloids and suspended particles from nuclear waste glass alteration. *Appl Geochem* 14: 635-653.

19. S. B. Chen, Y. G. Zhu, Y. B. Ma (2006) The effect of grain size of rock phosphate amendment on metal immobilization in contaminated soils. *J. Hazardous Mater* 134: 74-79.

20. Ndiba P, Axe L, Boonfueng T (2008) Heavy Metal immobilization through phosphate and thermal treatment of dredged sediments. *Environ. Sci Technol* 42: 920-926.

21. Kim CW, Day D (2003) Immobilization of Hanford LAW in iron phosphate glasses. *J Non-Crystalline Solids* 331: 20-31.

22. Ojovan MI, Hand RJ, Ojovan NV, et al. (2005) Corrosion of alkali-boro silicate waste glass K-26 in nono-saturated conditions. *J Nucl Mater* 340: 12-24.

23. BSC (Bechtel SAIC Company) (2004) CSNF Waste Form Degradation: Summary Abstraction. ANL-EBS-MD-000015 REV 02. Las Vegas, Nevada: Bechtel SAIC Company.

24. Strachan DM, Scheele RD, Buck EC, et al. (2005) Radiation damage effects in candidate titanates for Pu Pu disposition: Pyrochlore, *J Nucl Mater* 345: 109-135.

25. Begg BD, Hess NJ, Weber WJ, et al. (2001) Heavy-ion irradiation effects on structures and acidic dissolution of pyrochlores. *J Nucl Mater* 288: 208-216.

26. Zhang Y, Hart KP, Bourcier WL, et al. (2001) Kinetics of uranium release from Synroc phases. *J Nucl Mater* 289: 254-262.

27. Ewing RC, Haaker RF, Lutze W (1982) Leachability of zircon as a function of alpha dose, in *Scientific Basis for Nuclear Waste Management V.*, Lutze W (ed), Elsevier, New York, 389-397.

28. ANDRA (2005) Dossier 2005 Argile: Evaluation of the feasibility of a geological repository in an argillaceous formation. December 2005 and Dossier 2005 Granite: Assets of granite formations for deep geological disposal.

29. Lumpkin GR (2001) Alpha-decay damage and aqueous durability of actinide host phases in natural systems. *J Nucl Mater* 289: 136-166.

30. Geisler T, Schaltegger U, Tomaschek F (2007) Re-equilibration of zircon in aqueous fluids and melts. *Elements* 3: 43-50.

31. Tromans J (2006) Solubility of crystalline and metamict zircon: A thermodynamic analysis. *J Nucl Mater* 357: 221-223.