FOR PRESENTATION AT THE NUCLEAR ENERGY AGENCY SORPTION WORKSHOP

THERMODYNAMIC SORPTION MODELS IN SAFETY ASSESSMENTS

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INTRODUCTION: Sorption is a key process in delaying the transport of certain radionuclides from an underground nuclear waste repository to the accessible environment. Any key feature, event, or process (FEP) that either significantly contributes to the performance of the repository system or detracts from it will be of significant interest during evaluation of the safety case developed by the implementer.

The regulations applicable to the potential geologic repository at Yucca Mountain in Nevada, USA, are specified in Title 10, Part 63 of the Code of Federal Regulations (10 CFR Part 63). The regulations require that a repository system consist of diverse multiple barriers (specifically at least one engineered and one natural) where a barrier is defined as (10 CFR 63.2), "...any material, structure, or feature that, for a period to be determined by NRC, prevents or substantially reduces the rate of movement of water or radionuclides from the Yucca Mountain repository to the accessible environment, or prevents the release or substantially reduces the release rate of radionuclides from the waste."

The potential geologic repository at Yucca Mountain, Nevada, will be located in the middle of a 700 m [2,300 ft] thick unsaturated volcanic rock sequence about 350 m [1,150 ft] below ground surface and approximately an equal distance above the water table. The region surrounding and including Yucca Mountain is characterized by a sequence of gently dipping silica-rich volcanic rocks that are underlain by sedimentary rocks (CRWMS M&O, 2002; 2000). The mountain is cut by a subparallel series of near-vertical north-trending faults. The volcanic sequence consists of welded and nonwelded tuffs. Flow and transport in the unsaturated zone can be complex, but generally, fractures are the pathways in the welded tuff, while flow and transport occur in the rock matrix in the nonwelded tuff. The saturated zone down gradient of the repository consists of a fractured tuff aquifer and an alluvial valley fill aquifer.

The location for determining regulatory compliance (dose to a reasonably maximally exposed individual) is specified as any point outside the controlled area, which works out to be at about 18 km [11 mi] due south of the repository in the Amargosa valley. The maximally exposed individual is defined as an individual who has a diet and living style representative of the people who now reside in the town of Amargosa valley, Nevada. Current performance assessments suggest that a major contributor to dose may be via the ground-water pathway. This pathway involves dissolution of radioactive waste from breached waste packages, transport through the unsaturated zone down to the water table, and then transport horizontally in the saturated zone to the accessible environment in the direction of ambient flow. The hydrologically unsaturated geologic layers below the repository and the saturated zone from the repository to the compliance point are identified by the U.S. Department of Energy (USDOE), as natural barriers because of the relatively low flow velocities and favorable sorption characteristics.

NATURE OF REGULATORY REVIEWS: The regulations in 10 CFR Part 63 are "risk informed and performance based." In practical terms, this means that the FEPs that either significantly contribute to or reduce the estimated risk to the environment and the public are to be given correspondingly greater attention during regulatory reviews. In addition, the standard of "reasonable expectation" is incorporated into regulations. The four attributes of reasonable expectation are defined in 10 CFR 63.304 as (i) requires less than absolute proof, (ii) accounts for uncertainty, (iii) does not exclude important parameters that may be hard to quantify to high degree of confidence, and (iv) focuses on full range of defensible and reasonable rather than extreme physical situations and parameters.

One objective of the licensing review by the U.S. Nuclear Regulatory Commission (USNRC) will be to determine whether the USDOE safety demonstration complies with the regulations in 10 CFR Part 63. Guidance for review methods and acceptance criteria to be used in the regulatory review are described in the Yucca Mountain Review Plan (YMRP) (USNRC, 2003), which was finalized following public comment. The YMRP allows flexibility in tailoring the extent of the regulatory review of a FEP in proportion to its risk significance or importance. USDOE is expected to include an assessment of the risk significance for each FEP in its license application and safety case. The guidance in the YMRP will be followed to review the USDOE analyses, previous published analyses, international experience, and independent analyses to determine the risk significance of various FEPs and tailor its review accordingly.

As a specific example of the flexibility in the YMRP, thermodynamic modeling of sorption processes is not explicitly mentioned as something that is required or necessary for demonstrating compliance. However, one of the acceptance criteria, with respect to sorption process applied to saturated zone transport, is stated as, "For those radionuclides where the total system performance assessment abstraction indicates that transport in fractures and matrix in the saturated zone is important to waste isolation (i) estimated flow and transport parameters are appropriate and valid, based on techniques that may include laboratory experiments, field measurements, natural analog research, and process-level modeling studies conducted under conditions relevant to the saturated zone at Yucca Mountain; and (ii) models are demonstrated to adequately predict field transport test results. For example, if a sorption coefficient approach is used, the assumptions implicit in that approach are validated." Therefore, for some radionuclides that are main contributors to individual dose, detailed process-level modeling using thermodynamic principles may be appropriate and necessary to adequately justify sorption values used in safety analyses.

RISK SIGNIFICANCE OF SORPTION: It is up to the licensee to decide on appropriate techniques for incorporating the sorption process in its safety assessments. It is also up to the licensee to select an appropriate combination of laboratory experiments, field measurements, natural analog research, and process-level modeling to develop a technical basis for the adequacy of its selected technique(s) and corresponding parameters. From a regulatory perspective, the effort needed to demonstrate the adequacy of the technical basis depends primarily on the credit that the licensee takes for sorption in its safety case and secondarily on alternate hypotheses that may have been proposed by other stakeholders and the independent analyses conducted by the regulator. Based on available information, the USNRC (2005) concluded that sorption in the saturated alluvium aquifer has high-risk significance, while sorption in the tuff aquifer has medium significance.

During this workshop, Dr. David Turner will present a companion paper explaining some of the independent process-level analyses and laboratory experiments [conducted by the Center for Nuclear Waste Regulatory Analyses (CNWRA) on behalf of the USNRC] related to sorption. Consequently, these topics are not discussed in my brief talk. However, the use of this information in performance assessment is discussed below.

INDEPENDENT ANALYSES BY THE REGULATOR: CNWRA and the USNRC have developed the TPA computer software as a confirmatory review tool for evaluating performance during licensing reviews. Through iterative performance assessments and detailed auxiliary analyses, 20 radionuclides (Table 1) were identified as important to performance. Sorption on colloidal particles and subsequent transport is modeled separate from sorption and transport of dissolved species. Colloidal transport is not discussed in this paper.

The complexity of natural systems, the scarcity of relevant thermodynamic data, and slow reaction kinetics make it impractical to directly implement a thermodynamic sorption model in the TPA code, and maintain computational efficiency. Such models are used in auxiliary analyses to develop the choice of K_d values to be used in the simpler sorption model incorporated in the TPA code. The K_d approach assumes that the linear relationship $K_d \times C = S$ holds at all times, where C (g/mL) and S (g/g) are the masses of a radionuclide in solution and sorbed on solid substrate, respectively. The simplest sorption models assume the K_d for each radionuclide to be constant, thus neglecting the influence of any variations (in space and time) of groundwater chemistry and properties of the solid substrate. Despite its simplicity, K_d is a powerful concept that has led to acceptable solutions to many practical problems related to the transport of species in flowing groundwater. Nevertheless, for long-term projections extending to many thousands of years (as is needed for a nuclear waste repository) the use of a constant K_d may not be considered realistic.

A first-level improvement over the constant K_d approach is to incorporate variations in K_d through assigning a probability distribution to it. Such an approach assumes that the variation in K_d from all causes is encompassed in its probability distribution. Thus, the variation is accounted for once the K_d probability distribution is propagated through a performance assessment model, either explicitly through a Monte Carlo approach, or implicitly through the sensitivity analyses of deterministic models. A second level of improvement is to develop functional relationships between water chemistry and K_d in various geologic units through the use of thermodynamic models. A possible third level of improvement is to incorporate uncertainties in the thermodynamic models to obtain stochastic functional relations, which can then be used in the performance models. Of course, one has to be careful that the sophistication of the model does not exceed the support provided to it by data.

The first and second level improvements described in the previous paragraph are adopted for incorporating sorption in the TPA code. The following steps describe the approach.

Table 1. Radionuclides (Default Set) for Which Transport in Groundwater is Modeled			
Element	**Radionuclide**	**Half-life (yr)**	**Inventory *(Ci/MTU)**
Americium	Am–241	4.322E+02	3.76E+03
	Am–243	7.380E+03	3.21E+01
Carbon	C–14	5.729E+03	7.60E−01
Chlorine	Cl–36	3.010E+05	1.72E−02
Curium	Cm–245	8.499E+03	6.00E−01
	Cm–246	4.731E+03	2.05E−01
Cesium	Cs–135	2.300E+06	8.63E−01
Iodine	I–129	1.570E+07	3.88E−02
Niobium	Nb–94	2.030E+04	1.46E+00
Nickel	Ni–59	8.000E+04	4.52E+00
Neptunium	Np–237	2.140E+06	4.17E−01
Lead	Pb–210	2.230E+01	0.00E+00
Plutonium	Pu–239	2.406E+04	3.39E+02
	Pu–240	6.537E+03	5.91E+02
Radium	Ra–226	1.600E+03	0.00E+00
Selenium	Se–79	6.496E+04	1.08E−01
Technetium	Tc–99	2.130E+05	1.62E+01
Thorium	Th–230	7.700E+04	4.74E−04
Uranium	U–234	2.445E+05	1.42E+00
	U–238	4.468E+09	3.32E−01
* 1 Ci = 37 GBq			

1. Using surface complexation models, an empirical relation (a response surface) is developed between a normalized distribution coefficient (K_a) and two geochemical parameters, pH and P_{CO2}, where $K_a = K_d/A$, A being the effective surface area of the substrate. pH and P_{CO2} are basic stochastic input variables for the TPA code. Variations of pH and P_{CO2} for the Yucca Mountain area are shown in Figure 1. An empirical probability distribution is fitted to these variables as shown in Figure 2. An example of a computed response surface [coded as a 5^{th} order polynomial (6 coefficients) in the TPA code] is provided in Figure 3.

2. The values of A for a substrate are obtained either from measurements or from a geometric relation given by Arthur (1996); $A = 3\ \theta/\rho r$, where θ is porosity, ρ is bulk density, and r is the average pore radius. A is also a stochastic input variable.

3. A sample is drawn from the probability distributions for pH and P_{CO2}. Using the response surface developed in the first step, a value for K_a is determined. Using the sampled value of A, K_a is then converted to K_d.

The above procedure is followed for actinides (i.e., Americium, Neptunium, Plutonium, Thorium, and Uranium). Four of the elements in Table 1 (i.e., iodine, chlorine, technetium, and carbon) are considered to be nonsorbing, and the remaining (i.e., curium, radium, cesium, nickel, lead, selenium, and niobium) are assigned constant K_d values for sorption in rock matrix and a zero value for sorption in the fractures. The later radionuclides were assigned constant K_d values in contrast to probability distributions because the calculated dose was found to be insensitive to the uncertainty in them.

CONCLUSIONS: Independent analysis conducted on behalf of the regulator, such as described above, is not meant to suggest that this is the only or even the preferred way to model sorption in a system-level analysis. The implementer is expected to develop its safety case based on available information and use techniques that provide sufficient confidence to reach the "reasonable expectation" standard of proof. In a risk-informed framework, the level of expected information and rigor of analysis are dependent upon the influence a FEP is projected to have on the system performance. As a part of its review, one is able to select certain topics based on their risk ranking to conduct more in-depth detailed reviews, which may include independent analyses. Ultimately, however, the implementer is responsible for the safety case and its defense during the licensing process.

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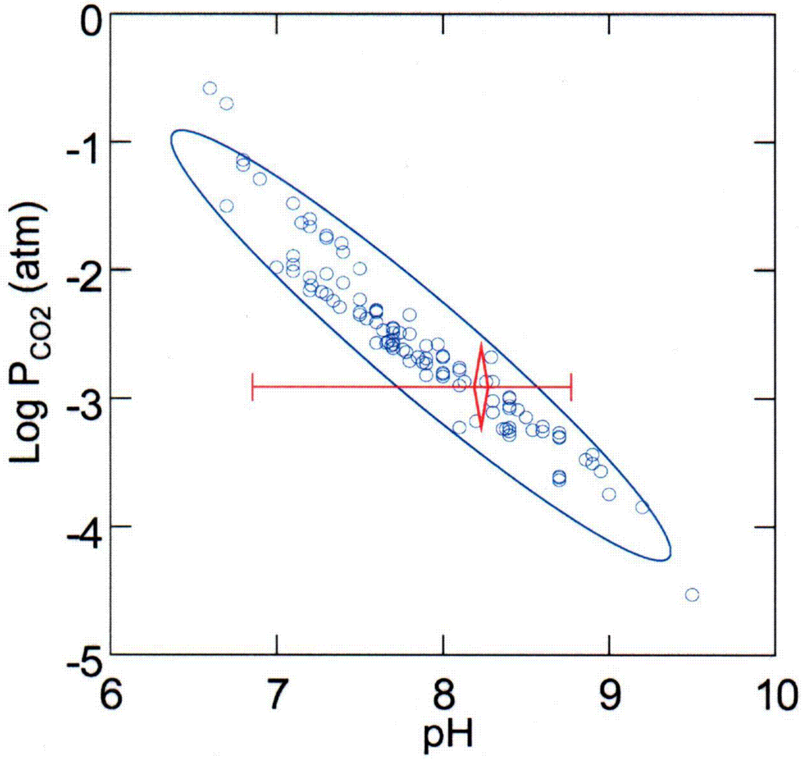


(1 atm = 1 x 10^5 Pa)

Figure 1. Plot of Water Chemistry Data from Wells Located Within the Site-Scale Model Area (Bechtel SAIC Company, LLC, 2003) in the Yucca Mountain Vicinity. The 95% Confidence Ellipse (Blue Line) is Shown for the pH and CO_2 Data. The Red Bar Approximately Indicates the Range of pH Values from an Analysis of Unsaturated Zone Waters (103 Samples) from Yucca Mountain (Browning and Murphy, 2002), While the Red Diamond Approximately Indicates the Median pH Value from the Same Study (McMurry and Bertetti, 2005).

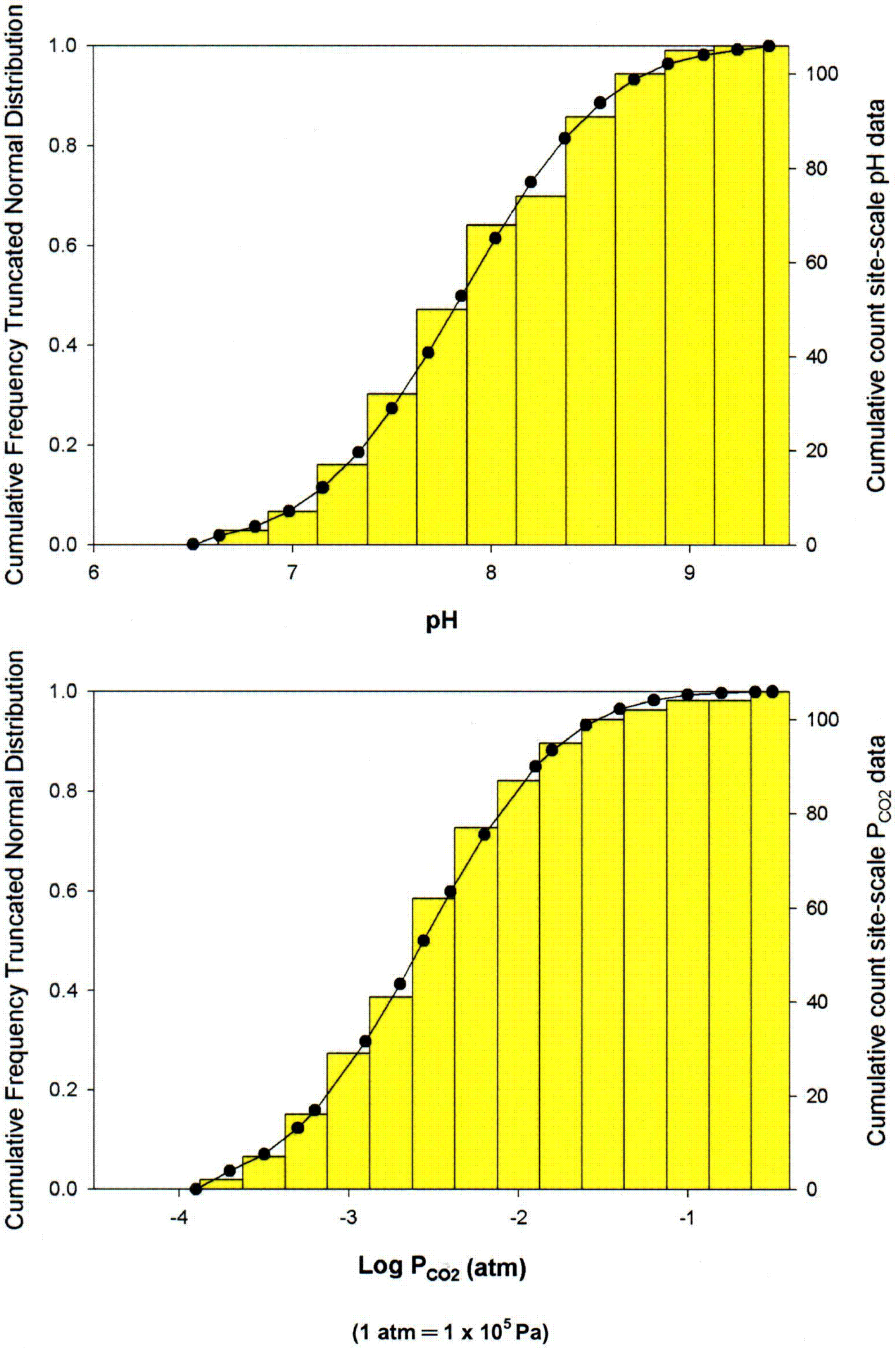
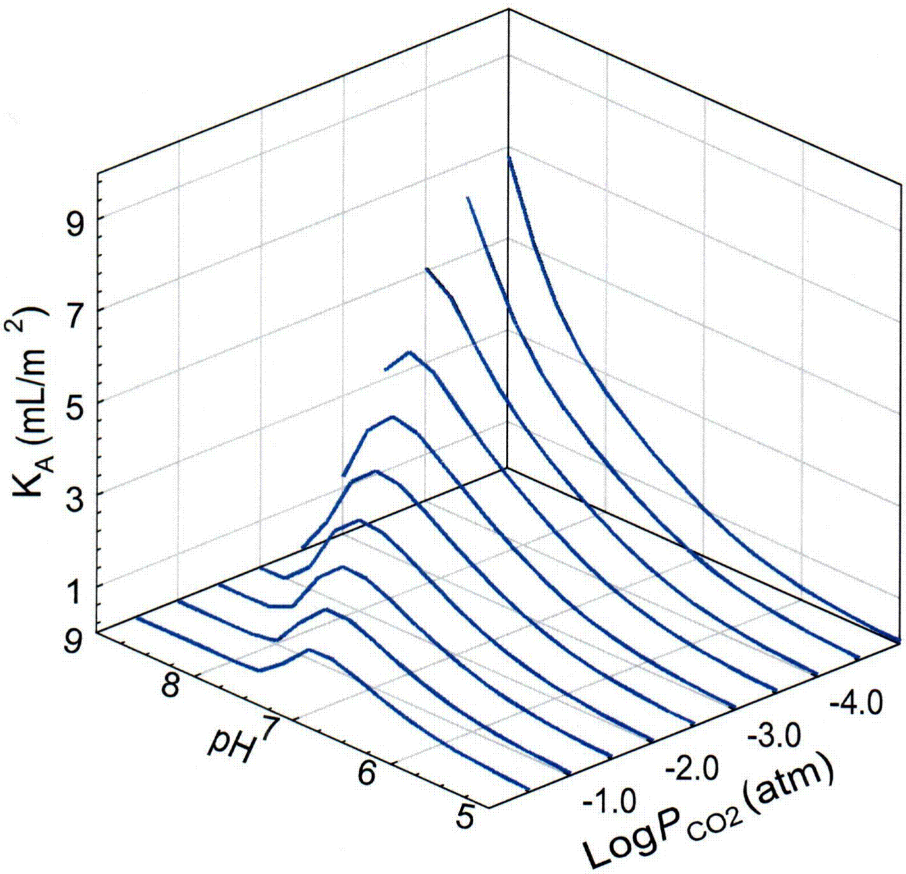


Figure 2. Table of Values for the User-Specified Piecewise Distributions Used for pH and P_{CO2} in TPA Version 5.0.1. Plots Compare the Distributions (Lines) with pH and P_{CO2} Site-Scale Data (atm) (McMurry and Bertetti, 2005).



(1 atm = 1 x 10^5 Pa)   (1 mL/m^2 = 3.28 ft^3/ft^2)

Figure 3. Sorption Response Surface For Neptinium Plotted in Terms of Effective Surface Area Normalized Distribution Coefficient (K_a) at Discrete Values of P_{CO2} Concentrations and Over a Range of pH Values (McMurry and Bertetti, 2005)

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