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2014:38

Detailed assessment of radionuclide Kd-values for the geosphere

Main Review Phase

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SSM perspektiv

Bakgrund

Strålsäkerhetsmyndigheten (SSM) granskar Svensk Kärnbränslehantering AB:s (SKB) ansökningar enligt lagen (1984:3) om kärnteknisk verksamhet om uppförande, innehav och drift av ett slutförvar för använt kärnbränsle och av en inkapslingsanläggning. Som en del i granskningen ger SSM konsulter uppdrag för att inhämta information i avgränsade frågor. I SSM:s Technical note-serie rapporteras resultaten från dessa konsultuppdrag.

Projektets syfte

Syftet med detta uppdrag är att göra en detaljerad utvärdering av den vetenskapliga grunden för SKB:s val av de Kd-värden som används för geosfärstransportmodellering för ett urval av radionuklider.

Författarens sammanfattning

Strålsäkerhetsmyndigheten (SSM) granskar en ansökan från Svensk Kärnbränslehantering AB (SKB) inlämnad under 2011 för att bygga och driva ett djupt geologiskt slutförvar för använt kärnbränsle i Forsmark i Östhammars kommun i Sverige. SKB har presenterat den långsiktiga säkerhetsanalysen, SR-Site, i en huvudrapport (SKB, 2011, TR-11-01) med stöd av tekniska dokument som citeras av huvudrapporten. Vid utvecklingen av säkerhetsanalysen SR-Site, har SKB identifierat geosfärens förmåga till gynnsamma radionuklidtransportförhållanden som en viktig säkerhetsfunktion som bidrar till en optimal prestanda för det föreslagna förvarssystemet. En sådan gynnsam förutsättning är den betydande retardationen av radionuklider via sorption som karaktäriseras av en hög sorptionskoefficient (Kd- värde) för berget. SKB har valt att modellera radionuklidretardation med hjälp av linjära Kd-värden och har baserat framtagandet av Kd-värden med platsspecifika laboratorieexperiment och data från den öppna litteraturen.

Som en del av granskning under SSM:s initiala granskningsfas för SKB:s Forsmarksansökan, gjordes en genomgång av SKB:s val av Kd-värden som använts i SR-Site modellering med hjälp av ett annat gransknings-uppdrag till externa experter (bl.a. Randall 2012, SSM Technical note 2012:63). Dessa granskare identifierade vissa potentiella problemområden inom utvecklingen av Kd-värden och rekommenderade ytterligare insatser såsom (i) att utföra en detaljerad genomgång av hur sorptionsdata från experimentella försök har överförts genom en Kd härledningsprocess, (ii) att genomföra en detaljerad genomgång av experimentell metodik för sorptionsbestämning och utveckling av ursprungliga Kd-värden, och (iii) utvärdera fördelningsfunktioner för Kd-värden som används i säkerhetsanalysmodellering. Föreliggande granskning är en del av SSM:s huvudgranskningsfas och genomfördes för att hantera kommentarer från tidigare granskningar och för att ge en heltäckande bedömning av SKB:s metoder för utveckling av Kd-värden, inklusive metoder och resultat från sorptionsexperiment samt relevansen av data som kommer från denna typ av experiment. Dessutom genomfördes inom ramen för denna granskning en bedömning av överföringsfaktorer som används för att korrigera sorptionsdata för yta, mekaniska skador, katjonbyteskapacitet, och variabilitet för grundvattenkemin. I denna granskning betraktas data från ett urval av radioelement (Cs, Ra, Np, Pu och U) som spänner över en rad olika egenskaper, inklusive datakällor, primära mekanismer för sorption samt betydelser för slutförvarets långsiktiga säkerhet.

SKB har utvecklat Kd-värden som används i säkerhetsanalysmodellering inom SR-Site med hjälp av två huvudprocesser. Först genomförde SKB ett omfattande laboratoriebaserat experimentellt program för att mäta Kd-värden med tillhörande sorptionsparametrar på Forsmark-platsspecifika material med hjälp av vattenkemi som är representativ för den föreslagna platsen. För det andra var laboratorieprogramet med inriktning mot experimentella data kombinerat med data från den öppna vetenskapliga litteraturen som bearbetas för att generera en uppsättning rekommenderade K-värden för varje radioelement av intresse.

Denna granskning visade att SKB:s experimentella program för att karaktärisera radionuklidtransport använde allmänt accepterade tekniska metoder för att mäta grundläggande parametrarna för mineralyta, katjonbyteskapacitet, och sorption. Granskningen visade att SKB har genomfört en noggrant planerad och omfattande experimentellt program för att stödja utvecklingen av Kd-värden och har integrerat en del data från det programmet i en rigorös och väl dokumenterad teknisk rapport som beskriver utvecklingen av de rekommenderade Kd-värden för säkerhetsanalysen SR-Site. Totalt sett har programmet producerat ett antal försvarbara fördelningskoefficienter (Kd-värden) som sannolikt är konservativa. Programmet bedöms dock innehålla flera områden inom vilka förbättringar kan göras. Dessutom finns det dataluckor som bör åtgärdas vart eftersom tillståndsprocessen går framåt. Granskningen visade att det experimentella programmet trots ansträngningar ändå hade flera brister som resulterade i mycket få uppgifter har samlats in under förhållanden som är relevanta för förvarsplatsen. Några exempel på det experimentella programmets brister är en bristande kontroll av viktiga variabler som påverkar sorption, såsom redoxtillstånd av lösningar, lösningarnas pH samt karbonatkoncentration. Dessa brister fördunklar ett misslyckande att uppnå reducerande förhållanden i experimenten. Den resulterande bristen på relevanta sorptionsdata medförde att användning av litteraturdata för att härleda Kd-värdena krävdes för alla aktinidelement samt teknetium.

Granskningen visar att de metoder som används av SKB för att bearbeta experimentella data från platsspecifika material och den öppna litteraturen är rimliga och tekniskt försvarbara. Granskningen visar att de slutliga rekommenderade Kd-värdena troligen är pessimistiska som ett resultat av flera konservativa val som görs under databearbetningsfasen. Ett exempel är att korrigeringar för mineralyta är större än vad som krävs baserat på uppmätta mineralytor hos prover från Forsmark. Ett särskilt problem är att det finns uppenbara räknefel i rapporterna som stöder utvecklingen av Kd-värden. Dessa fel, om de verkligen är fel, påverkar inte signifikant de rekommenderade Kd-värdena, men de tenderar att urholka förtroendet för SKB:s mer detaljerade beräkningar och totala kvalitetssäkring. Slutligen har bristen på experimentella data från försök med material från Forsmark resulterat i ett beroende av icke-platsspecifika data och användning av analogier för att utveckla Kd-värden för flera viktiga radioelement. Även om användningen av icke-platsspecifika data kan vara tillräckligt för hantering i säkerhetsanalysen, så skulle framtagande av ytterligare platsspecifik sorptionsdata bidra till att minska osäkerheter i samband med användning av analoger.

Sammanfattningsvis är SKB:s utvecklingsarbete kopplat till Kd-värden tillräckligt för säkerhetsanalysen SR-Site, men fortfarande finns det väsentliga dataluckor som bör åtgärdas. En sådan datalucka är bristen på platsspecifika data med platsspecifika relevanta förutsättningar för reducerade aktinider och teknetium, som är viktiga för slutförvarets funktion. Denna fråga skulle kunna åtgärdas genom att utföra ytterligare fokuserade experiment och genom ytterligare arbete med geokemisk modellering av sorptionsprocesser för att bestämma de möjliga effekterna av dataluckor.

Projektinformation
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Diarienummer ramavtal: SSM2011-4243
Diarienummer avrop: SSM2013-3217
Aktivitetsnummer: 3030012-4052

SSM perspective

Background

The Swedish Radiation Safety Authority (SSM) reviews the Swedish Nuclear Fuel Company's (SKB) applications under the Act on Nuclear Activities (SFS 1984:3) for the construction and operation of a repository for spent nuclear fuel and for an encapsulation facility. As part of the review, SSM commissions consultants to carry out work in order to obtain information on specific issues. The results from the consultants' tasks are reported in SSM's Technical Note series.

Objectives of the project

The objective of this assignment is to make a detailed evaluation of the scientific basis for SKB's selection of a few radionuclide Kd-values used for geosphere transport modelling.

Summary by the author

The Swedish Radiation Safety Authority (SSM) is reviewing an application submitted by the Swedish Nuclear Fuel and Waste Management Company (SKB) in 2011 to construct and operate a deep geologic repository for spent nuclear fuel at the Forsmark site in the municipality of Östhammar, Sweden. SKB has presented details of its long-term safety assessment, SR-Site, in a main report (SKB, 2011, TR-11-01) and in multiple supporting technical documents that are cited by the main report. In developing the safety case for SR-Site, SKB identified the geosphere's capability to provide favourable radionuclide transport conditions as an important safety function that contributes to the optimum performance of the disposal system. One such favourable condition is the substantial retention of radionuclides owing to high sorption coefficient (Kd) values for the host rock. SKB has chosen to model radionuclide retention using a linear Kd approach and has supported the development of Kd values with site-specific laboratory experiments and data from the open literature.

As part of its initial review phase activities related to SKB's Forsmark application, SSM reviewed SKB's selection of Kd values used in SR-Site performance assessment modelling (e.g., Randall, 2012, SSM Technical Note 2012:63). Those reviews identified some potential concerns regarding the development of Kd values and recommended additional work such as (i) conducting a detailed examination of how sorption experimental data have been transferred through the Kd derivation process, (ii) conducting a detailed review of the sorption experimental methodology and development of original Kd-data, and (iii) evaluating the span of probability distribution functions used in performance assessment models. The present review is part of SSM's main review phase and was undertaken to address comments of the previous reviews and to provide a comprehensive assessment of SKB's approach to Kd value development, including the methods and results of sorption experiments and the relevance of data derived from those experiments. Also examined in this review were the transfer factors used to correct sorption data for surface area, mechanical damage, cation exchange capacity, and groundwater chemistry variations. In the present review, data were considered from a select number of radioelements (Cs, Ra, Np, Pu, and U) that span a range of characteristics including sources of data, primary mechanisms of sorption, and importance to performance.

SKB developed the Kd values used in performance assessment modelling of SR-Site using two main processes. First, SKB conducted an extensive laboratory-based experimental program to measure Kd values and associated sorption parameters on Forsmark-site specific materials using water chemistries representative of the proposed site. Second, the laboratory experimental program data were combined with data from the open scientific literature and processed to generate a set of recommended Kd values for each radioelement of interest.

This review found that SKB's radionuclide transport experimental program employed widely accepted technical methods to measure basic parameters of surface area, cation exchange capacity, and sorption. The review found that SKB has conducted a carefully planned and extensive experimental program to support Kd value development and has integrated some data from that program into a rigorous and well documented technical report describing the development of the recommended Kd values for SR-Site performance assessment. Overall, the program has produced a set of technically defensible distribution coefficients that are likely to be conservative. However, the program as reviewed appears to have several areas in which improvements can be made. Additionally, there are data gaps that should be addressed as the licensing process moves forward. The review found that despite efforts, the experimental program nevertheless had several protocol deficiencies that resulted in very few data collected under conditions relevant to the repository site. Some examples of the experimental program deficiencies include a lack of monitoring of important variables influencing sorption, such as the redox state of solutions and the solution pH and carbonate concentration. These deficiencies obscured the failure to achieve reducing conditions in the experiments. The resulting lack of relevant sorption data required the use of literature derived data to develop Kd values for all of the actinide elements, as well as technetium.

The review found that the methodologies used by SKB to process experimental data from the site-specific work and the open literature were reasonable and technically defensible. The review found that the final recommended Kd values were likely pessimistic as a result of several conservative choices made during the data processing phase. One example is that corrections for surface area were larger than is required based on measured surface areas from the Forsmark site. A particular concern is that there are numerous apparent calculation errors in the reports supporting the Kd value development. These errors, if they indeed are errors, do not significantly impact the recommended Kd values, but they do tend to erode confidence in SKB's more detailed calculations and overall quality assurance. Finally, the lack of experimental data collected under relevant Forsmark site conditions has resulted in a dependence on non-site-specific data and the use of analogues to develop Kd values for several important radioelements. While use of non-site-specific data may be adequate for stabling a safety case, generating additional sorption data that are site-specific can help to reduce uncertainties associated with the use of analogues.

In summary, SKB's development of Kd values is adequate for the SR-Site assessment but still contains substantive data gaps that should be addressed. One such gap is the lack of site-specific data at site-relevant conditions for reduced actinide elements and technetium—radioelements that are important to repository performance. This issue could be addressed by conducting additional focused experiments and by investing effort in geochemical modeling of sorption processes to determine the potential impacts of the data gaps.

Project information
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Content

1. Introduction

The Swedish Radiation Safety Authority (SSM) is tasked, under the Act on Nuclear Activities, to review applications submitted by the Swedish Nuclear Fuel and Waste Management Company (SKB) for the construction and operation of a repository for spent nuclear fuel and for an encapsulation factory. SSM is reviewing an application submitted by SKB in 2011 to construct and operate a deep geologic repository for spent nuclear fuel at the Forsmark site in the municipality of Östhammar, Sweden. SKB has presented details of its long-term safety assessment, SR-Site, in a main report (SKB, 2011) and in multiple supporting technical documents that are cited by the main report. In developing the safety case for SR-Site, SKB identified the geosphere's capability to provide favourable radionuclide transport conditions as an important safety function that contributes to the optimum performance of the disposal system (SKB, 2011, Figure 8-3). One such favourable condition is the substantial retention of radionuclides owing to high sorption coefficient (K_d) values for the host rock.

1.1. Relevance of Distribution Coefficients (K_ds) to Repository Safety

SKB notes that a key safety function of the geosphere surrounding a nuclear waste repository is to provide favourable hydrologic and transport conditions (SKB, 2011). One of the more important favourable conditions is the ability to delay and diminish transport to the environment of radionuclides potentially released from the repository's engineered barriers. The conceptual model for radionuclide transport is that radionuclides that escape the waste packages and near field buffer systems will be transported in groundwater through fractured plutonic rocks via pathways that may provide access for exposure of the public to the radionuclides (SKB, 2010a). The conceptual model is assessed through hydrologic and geochemical modelling and is supported by field and laboratory tests to measure important parameters (e.g., SKB, 2010a; 2010c).

The rate at which radionuclides migrate through the geosphere is sensitive to a number of factors, including the water flow rate, the nature of the geologic materials through which the water travels, the water chemistry, and the chemistry of the radionuclides themselves. Along the transport pathway, dissolved radionuclides may disperse, decay, diffuse in the groundwater, and interact with the rocks—where they may undergo sorption onto minerals exposed along fracture surfaces, or diffuse into the rock matrix and sorb onto matrix minerals exposed to groundwater. The main geosphere-related retardation mechanisms considered in performance assessment models, including SKB models of SR-Site performance, are diffusion of radionuclides into the rock matrix and sorption of radionuclides onto rock and mineral surfaces (SKB, 2010b; Crawford, 2010).

1.1.1. Factors impacting sorption and K_d values

Sorption is a generalized term used to describe the transfer of radionuclides from the solution phase to a solid surface. Sorption can incorporate a number of mechanistic processes, but in performance assessment models, sorption mainly consists of ion exchange (electrostatic interaction) and surface complexation (covalent bonding of aqueous species with surface groups) (SKB, 2010a). For the purposes of SKB's development of K_d values and performance assessment modelling for SR-Site, sorption includes both surface complexation and ion exchange processes (SKB 2010a; 2010b). Surface interactions, such as sorption, between dissolved constituents and solid phases can be complex, particularly in heterogeneous natural systems, and are sensitive to changes in the chemical and physical environment. Both the host rock (sorptive phase) and the aqueous phase of the geosphere have particularly important components that influence sorption. Key rock characteristics include mineralogy, surface area, and sorption site density, while key aqueous phase characteristics include chemical factors such as redox, pH, partial pressure of carbon dioxide (pCO_2), and ionic strength.

The types of minerals that are encountered along potential flow paths in the geosphere are important in assessing the possible sorption of radionuclides. SKB has conducted extensive site geological characterisation to assess the occurrence and predominance of rock types and their associated mineralogies (SKB, 2010a). Reasonable estimates of surface reactivity are often provided by measurements of surface area and cation exchange capacity (CEC). Phyllosilicate minerals, such as micas (e.g., biotite) and clays, have structures that facilitate the ion-exchange of cations. The potential for ion exchange is often quantified by conducting experiments to measure the CEC of rocks and minerals. SKB has conducted a number of tests to evaluate the CEC of rock types at both Forsmark and Laxemar (Selnert et al., 2008; 2009). Minerals with larger specific surface areas typically have greater numbers of available sorption sites. Phyllosilicates (especially clay minerals) and iron oxides are examples of minerals that commonly have large measured specific surface areas, and thus, larger numbers of sorption sites. One accepted method of assessing the surface area of rocks and minerals is BET gas adsorption (Brunauer et al., 1938). SKB has measured the N_2-BET specific surface areas of a number of rock samples from the Forsmark and Laxemar sites (Selnert et al., 2008; 2009). SKB acknowledges the importance of clay minerals on sorption (e.g., Crawford, 2010). At Forsmark, clay minerals mostly are associated with fractures or with rock alteration products (SKB, 2010a). SKB's derived sorption coefficient distributions purposely ignore the presence of these minerals in the subsurface, choosing instead to focus on relatively unaltered rock (Crawford, 2010). This may be seen as an overly conservative approach (e.g., Randall, 2012). In some respects, SKB may account for this uncertainty with a wider range of values in the K_d probability distributions. However, because it is extremely difficult to correlate the expected predominance of fractures contributing to flow paths with the number of fractures that are lined with sorption-enhancing minerals, SKB has chosen to pessimistically exclude them from the analyses (Sandström et al., 2008; SKB, 2010b).

Mineralogy and CEC are important for ion exchange, but may not be as important for surface complexation. In fact, for actinides, sorption onto silicates, aluminosilicates, and oxides has been observed to occur when solution chemical characteristics were appropriate (i.e., conditions that favoured formation of hydroxyl species), somewhat irrespective of the mineral surface (e.g., Bertetti et al., 1998; 2011). On the other hand, the magnitude of sorption is controlled by the number of available sorption sites on the mineral (e.g., Bertetti et al., 2011). Aqueous phase or groundwater characteristics are also important because they influence the speciation and valence state of radioelements. Varying groundwater redox conditions can alter valence states for some elements. In turn, these altered valence states can have a significant influence on sorption magnitude. Several radionuclides important to repository safety assessments are redox sensitive, including neptunium (Np), plutonium (Pu), selenium (Se), technetium (Tc), and uranium (U). Generally, lower redox potential (i.e., lower Eh) results in valence states that increase the magnitude of sorption for these redox-sensitive elements. As such, SKB identified that one safety function of the geosphere in the SKB repository concept is the presence of chemically favourable reducing conditions (low Eh) and limited variation in Eh over the lifetime of the repository (SKB, 2011). SKB includes the effects of redox conditions in the analyses and development of radioelement K_d probability distribution functions (pdfs) (Crawford, 2010). SSM has conducted specific, detailed reviews of SKB technical bases for estimating redox conditions at Forsmark (e.g., McMurry and Bertetti, 2014), and a detailed review of this feature is not included here. In general, McMurry and Bertetti (2014) concluded that SKB appropriately considered and applied the effects of redox when developing sorption parameters for SR-Site.

Solution pH is another key parameter influencing sorption. The pH of the solution influences radioelement speciation, and in particular, the radioelement's hydrolysis and complexation behaviour. With actinides, for example, the solution pH at which the radioelement hydrolyses is typically the same as that of the start of observed sorption (e.g., Bertetti et al, 2011). Another important groundwater chemical parameter is the concentration of inorganic carbon (typically expressed as bicarbonate/carbonate concentration or as pCO_2). Some radioelements, such as U, readily form carbonate complexes (Turner et al., 2002; 2006). Although carbonate complexes can sorb onto mineral surfaces (Crawford, 2010), in general, the formation of carbonate complexes competes with surface adsorption causing a reduction in observed sorption as pH increases (e.g., Turner et al., 2002; 2006; Pabalan et al., 1998). SKB notes that pH and carbonate concentration are of primary relevance to radionuclide sorption, particularly those that sorb via surface complexation (Crawford, 2010). Ion exchange processes are less influenced by changes in pH and redox, so the sorption of radioelements such as caesium (Cs), strontium (Sr), and radium (Ra) are relatively insensitive to those parameters (SKB, 2010b). Ion-exchange is significantly affected by the solution ionic strength (i.e., concentration of ions). Typically, greater ionic strength results in less sorption via ion-exchange because of competition for ion-exchange sorption sites. SKB has conducted a careful and rigorous characterisation of groundwater geochemical conditions at the Forsmark site including quantification of redox, pH, ionic strength, and pCO_2 conditions for various expected water types (Laaksoharju et al., 2008a; 2008b; Salas et al., 2010; SKB, 2010a; McMurry and Bertetti, 2012). This information is used to inform the construction of pdfs for sorption (Crawford 2010).

1.1.2. SKB K_d model

Information about the host rock and the groundwater geochemistry is used to guide the development of values to represent the sorption of radionuclides in the geosphere. The K_d values used in performance assessment may be developed in several ways. The specific methodology used to develop K_d values often depends on the data available and the modelling approach selected for the performance assessment code. Most national spent nuclear fuel repository programs, including the Swedish program, have used experiments on site-specific materials to measure K_ds for important radioelements (e.g., DOE, 2008; Andra, 2005; Bradbury and Baeyens, 2003; SKB, 2011). The experiments may include several types (i.e., batch, column, or *in situ*) and may be both laboratory and field-based (e.g., SKB, 2010a; 2010b). Once the K_d data are collected, empirical or thermodynamic modelling approaches are used to interpret the data and establish appropriate pdfs to represent sorption of radioelements at the repository site. Expert opinion or judgment may be used to estimate K_d values, ranges, and pdfs where data are lacking. Often, expert judgment is used as a supplement to measured sorption data to account for differences in the environmental and geological conditions associated with data collection and those conditions associated with the repository site. The ranges and types of pdfs are developed to represent reasonable estimates of sorption while incorporating spatial and temporal environmental uncertainties.

The specific modelling approach used to interpret measured K_d data and develop K_d pdfs is a matter of choice that is often partly dictated by the transport model utilized for the performance assessment. There is no current “best” approach, and SKB provides a thorough discussion of available methods (Crawford, 2010). SKB has chosen to use a linear K_d model in their performance assessment (SKB 2010b; 2011). The approach of assuming linear, empirically determined equilibrium distribution coefficients to model sorption of radionuclides to mineral surfaces is a well-documented and generally accepted approach for approximating the effects of sorption on delaying radionuclide transport in groundwater and is used in most national repository programs (e.g., DOE, 2008; Andra, 2005; Bradbury and Baeyens, 2003; Painter et al., 2001).

The linear K_d approach used in SR-Site assumes that the sorption process is reversible, has reached equilibrium, and is independent of variations in water chemistry or mineralogy (SKB, 2010c). These assumptions may only be partially met because sorption may vary in response to changes in groundwater chemistry, temperature, properties of the solid substrate on which sorption occurs, or starting concentration of the radionuclide (Chapman and McKinley, 1987). Groundwater and mineral substrates are assumed to maintain their present chemical and mineralogical compositions over time (SKB, 2010a; 2010b; 2010c). In particular, the linear approach assumes that there is no set of conditions that produces a maximum value for sorption and site saturation (SKB, 2010b). This implicit assumption appears reasonable for the geosphere at Forsmark because solubility limits and dilution effects suggest that radionuclide concentrations will be low relative to the number of available mineral sorption sites (SKB, 2010a; 2010b). The approach neglects effects such as slow sorption kinetics and geochemical heterogeneity along the flow path, and thus distribution coefficients and retardation parameters need to be selected prudently. Moreover, an appropriate range of uncertainty needs to be considered to ensure the benefit of radionuclide sorption to total system performance is not overstated. These limitations and assumptions are acknowledged and well-documented in the reports supporting SKB’s Forsmark application (SKB 2010a; 2010b; 2011; Crawford, 2010).

In recognition of the uncertainty and variability associated with the simple empirical K_d approach, performance assessment calculations typically sample K_d values from a range of values that are appropriate to sorption for the expected variation in conditions (i.e., the pdfs). Over the multiple realizations (typically hundreds or more) of a performance assessment analysis, the results cover a broad range of possible sorption outcomes to provide confidence that the uncertainty is bounded by the estimates (SKB, 2010b).

1.2. Previous Reviews of K_d Value Development

SSM conducted an external peer review of various aspects of SKB's performance assessment models in support of SSM's review of SR-Can (Stenhouse et al., 2008). One of the components of that report included a review of geosphere transport parameters, including K_d values and the development of K_d pdfs. The reviewers, using information from Crawford et al. (2006), noted that care must be taken to ensure experiments investigating K_d values be conducted under conditions relevant to the site of interest (Stenhouse et al., 2008). The reviewers were complimentary regarding SKB's systematic approach to surface area corrections, but noted that the Finnish rocks from which a substantial amount of sorption data were derived appeared to have higher surface areas than Swedish rock types under consideration at the time (Stenhouse et al., 2008). The reviewers also suggested that the range of recommended K_d values be kept as broad as possible to guard against bias from small laboratory-based sorption data sets and suggested using a range equivalent to the mean $\log_{10}K_d \pm 2\sigma$ (Stenhouse et al., 2008).

As part of its initial review phase activities related to SKB's Forsmark application, SSM reviewed SKB's selection of K_d values used in SR-Site performance assessment modelling. Some of the findings of that review are summarized in a technical note reviewing radionuclide sorption on bentonite and bedrock (Randall, 2012, SSM Technical Note 2012:63) and an associated technical note reviewing radionuclide transport methodologies (Little et al., 2012, Technical Note 2012:55). Issues brought forward as a result of those reviews included concerns regarding (i) the magnitude of K_d values and span of the K_d probability distribution functions (pdfs) established for certain radioelements (namely, that the magnitudes may be too low and the spans may be too large), (ii) potential deficiencies in the laboratory sorption experiments conducted by SKB, (iii) whether spatial and temporal uncertainties were appropriately incorporated into the pdfs, and (iv) whether the use of certain chemical analogues to establish K_d values for elements where data were lacking was appropriate. The reviews included several recommendations for further work such as (i) conducting a detailed examination of how sorption experimental data have been transferred through the K_d derivation process, (ii) conducting a detailed review of the sorption experimental methodology and development of original K_d data, and (iii) evaluating the span of pdfs used in performance assessment models and whether the pdfs appropriately capture site uncertainties.

1.3. Scope of This Technical Evaluation

The objectives of this technical review are to supplement the initial review findings and evaluate in detail whether (i) the scientific bases for SKB's selection of K_d values for the geosphere surrounding a deep geologic repository at the Forsmark site are defensible and (ii) the data and methodologies employed to establish the probability distribution functions (pdfs) used in transport modelling adequately account for site characteristics and uncertainties.

The review examines SKB's approach to the assessment and modelling of radionuclide K_d values, including the methods and results of sorption experiments and the relevance of data derived from those experiments. The detailed review also examines the methods used to translate experimental data from SKB's program, as well as data derived from literature sources, into the set of K_d values recommended for certain radioelements of interest to performance assessment. This examination includes the transfer factors used to correct for surface area, mechanical damage, cation exchange capacity, and groundwater chemistry variations in the acquired K_d data. Finally, the review considers the methods used to develop K_d pdfs for certain radioelements of interest. Key considerations include the potential for risk dilution and whether the pdfs appropriately capture the expected range of K_d values associated with spatial and temporal uncertainties at the Forsmark site. To facilitate a detailed analysis, a limited number of radioelements are considered in the review. The selected radioelements include Cs, Ra, Np, Pu, and U. The selected radioelements span a range of characteristics including sources of data, primary mechanisms of sorption, and importance to performance. A summary of the factors associated with each radioelement is provided in Table 1.3-1. This technical note concludes with a summary of key findings and recommendations to support SSM's continued review of SKB's licensing case.

Table 1.3-1. Summary of factors associated with selection of radioelements for detailed review

Radioelement	Factors
Cesium (Cs)	Mechanism: Ion-exchange Data source: Internal Other: Sensitive to ionic strength
Radium (Ra)	Mechanism: Ion-exchange Data source: Internal Other: Important nuclide for performance, specified in SSM assignment tasking, sensitive to ionic strength
Neptunium (Np)	Mechanism: Surface complexation Data Source: Internal (not used), K_d from analogue Other: Sensitive to redox, pH, and pCO_2 variations, important nuclide for performance
Plutonium (Pu)	Mechanism: Surface complexation Data Source: External (used for other actinides), K_d from analogue Other: Sensitive to redox, pH, and pCO_2 variations
Uranium (U)	Mechanism: Surface complexation Data source: Internal and External (both used) Other: Sensitive to redox, pH, and pCO_2 variations

2. SKB's Approach to K_d Value Development

SKB developed the K_d values and pdfs used in performance assessment modelling of SR-Site using two main processes. First, SKB conducted an extensive laboratory-based experimental program to measure K_d values and associated sorption parameters, such as surface area and CEC, on Forsmark site-specific materials using water chemistries representative of the proposed site (Selnert et al., 2008; SKB, 2010c). The experimental program also included similar measurements made on materials from Laxemar as part of its parallel site assessment and characterisation (Selnert et al., 2009a; 2009b; SKB, 2010c). Field-based and long-term experiments also generated data, which are available for comparison but were not directly used in the development of the K_d data or the K_d pdfs (Crawford, 2010; Widestrand et al., 2010; SKB, 2010c). Second, the laboratory experimental program data were combined with data from the open scientific literature and processed to generate a set of recommended K_d pdfs for each radioelement of interest (Crawford, 2010; SKB, 2010b; 2010c).

2.1. Experimental Program and Data

SKB conducted an extensive experimental program to support radionuclide transport data development and site characterisation needs at Forsmark (SKB, 2011; 2010a; 2010b; 2010c). Three main components of the transport experimental program were: (1) field measurements to obtain site-specific transport parameters, (2) laboratory experiments on site-specific rock material, and (3) modelling of transport properties (Selnert et al., 2008). In this review, the focus is on the laboratory experiments and, in particular, the experiments and measurements associated with geosphere non-flow related data. Moreover, the review primarily analyzes results from the experiments associated with the Forsmark site (i.e., Selnert et al., 2008). Results from the Laxemar studies (i.e., Selnert et al., 2009a; 2009b) are included only as supporting information when needed.

Although SKB has been investigating radionuclide transport for many years, an updated experimental program plan was developed to support work for site-specific characterization (Widestrand et al., 2003). The primary objectives of the laboratory measurements were to "determine site-specific retardation parameters for solutes (sorbing and nonsorbing) and rock materials of importance for safety assessment" and "to obtain a scientific understanding of the retardation properties of the Forsmark site" (Widestrand et al., 2003).

Designed as a guide rather than a strict instructional manual, Widestrand et al. (2003) provide descriptions of the experimental plans and the technical bases supporting the plan's scope and purpose. Included in the plan were strategies for use of radioelement tracers, strategies for the interpretation of experimental results, and guidance for the prioritization and the expected number of experiments (Widestrand et al., 2003). Importantly, Widestrand et al. (2003) note the general conditions desired for the laboratory experiments. These conditions included (i) establishment of reducing, O_2-free conditions that resembled the prevailing site conditions, (ii) use of synthetic groundwaters that were compositionally equivalent to site groundwaters, and (iii) selection of an appropriate concentration range for the radioelement tracers.

As designed, the laboratory program generated data for several transport-related parameters (Selnert et al., 2008; 2009a). These parameters were porosity, porosity distribution, matrix diffusivity, specific surface area, cation exchange capacity, and sorption coefficients (Selnert et al., 2008; 2009a). The data, methods and results for the latter three parameters are of primary concern since they support the development of K_d values, which is the focus of this review. Transport parameter laboratory experiments were also conducted for rock and groundwater types associated with the Laxemar site (Selnert et al., 2009a). The methods and approaches used to develop the Laxemar data were the same as used for the work at Forsmark (Widestrand et al, 2003; Selnert et al., 2008; 2009a).

2.1.1. Experimental Program Methods

SKB's radionuclide transport experimental program employed widely accepted technical methods to measure basic parameters of surface area, cation exchange capacity, and sorption (Selnert et al., 2008; 2009a). As mentioned previously, surface area measurements were conducted using the BET N_2-gas adsorption method (Brunauer et al., 1938). Both crushed rock samples and whole rock core samples were analysed (Selnert et al., 2008; 2009a). Cation exchange capacity (CEC) measurements were made following ISO method 13536, in which samples are saturated with Ba^{2+} ions and then exposed to an $MgSO_4$ solution (ISO, 1995; Selnert et al., 2008). The quantitative exchange of Mg^{2+} for Ba^{2+} is used to calculate the CEC. Sorption data were measured using a batch sorption technique. Because the batch sorption results are critical to the development of the K_d values and pdfs, they are described in detail in the following section.

2.1.2. Batch Sorption Experiments

Batch sorption experiments were conducted to quantitatively measure radioelement sorption onto site-specific rock samples (Selnert et al., 2008; 2009a). In general, batch sorption experiments involve exposing a rock sample to a solution spiked with one or a mixture of radioelement(s) of interest. Typically, the initial solution concentration of the radioelement is known, and after some period of contact time, the solution is sampled and the radioelement concentration measured. The change in concentration of the radioelement is used to determine the amount of radioelement that has sorbed on the rock sample. Batch sorption experiments conducted by SKB employed this basic approach (Selnert et al., 2008; 2009a).

It is difficult to extrapolate experimentally derived batch sorption data collected under one set of environmental conditions to a different set of environmental conditions encountered in the geosphere. In recognition of this fact, SKB's batch sorption experimental program was designed to incorporate not only site-specific rock materials but also solution chemistries that were equivalent to and/or bounded the groundwater chemistries expected at the site (Widestrand et al., 2003; Selnert et al., 2008; 2009a).

Within the repository target volume [i.e., the northwestern part of the candidate area for the Forsmark site investigation and its extension to depth (Follin, 2008)], the lithology is relatively homogeneous and is dominated by metagranites. The site-specific rock assumed as a reference material for transport calculations is Forsmark metagranite (rock domain RFM029, rock type 101057) (SKB, 2010b; 2011). SKB notes that there are no significant differences in sorption properties for the other main rock domains (SKB, 2011; 2010a). Most of the sorption experimental data generated in the Forsmark site investigation program are focused on this rock type (Selnert et al., 2008).

Based on site hydrogeochemical data, SKB described several distinctive groundwater types in the present-day system at Forsmark, several of which are mixtures with one or more other water types (Laaksoharju et al., 2008a; 2008b). SKB reported that except in the upper few meters to tens of meters of bedrock, redox measurements in groundwater at the Forsmark site gave negative Eh values ranging from −143 to −281 mV (Gimeno et al., 2008; Sidborn et al., 2010). The solutions used in the sorption experiments were based on the chemistries of these water types (Widestrand et al., 2003; Selnert et al., 2008). For the Forsmark experiments, four different groundwater types were selected for use. These represented end-member compositions consistent with those found at the site (Laaksoharju et al., 2008a; 2008b; Salas et al., 2010). The water types were: (1) a fresh dilute Ca-HCO_3 water [Fresh, F], (2) a groundwater with marine character and 5,000 mg/L Cl [Marine, M], (3) a saline groundwater of Na-Ca-Cl type, 5,400 mg/L Cl [Saline-Forsmark, SaF], and (4) a brine type water of very high salinity with a Cl content of 45,000 mg/L [Brine, B] (Selnert et al., 2008).

The sorption experiments included a number of combinations of rock materials, radionuclides, and groundwater compositions. For the Forsmark site, approximately 300 rock samples were collected from 14 boreholes drilled during site characterization activities (SKB, 2010c). Although the samples are predominantly associated with the first six boreholes, SKB indicates that the rock sample collection was found to be representative of the various rock types within the target volume at the Forsmark site (SKB, 2010c; Selnert et al., 2008). Batch sorption experiments for the Laxemar site has a similar focus on and accommodation of site-specific conditions (Selnert et al., 2009a).

Based on information provided in Selnert et al. (2008; 2009a) and Widestrand et al. (2003), the following specific methods were used in the batch sorption experiments. To provide the solid substrate, rock sample materials were crushed and sieved to isolate three size fractions: 0.063–0.125, 0.25–0.5, and 1–2 mm. Some fracture and deformation zone materials were also tested in addition to the reference rock samples. All batch sorption experiments were conducted in a glove box using an N_2 atmosphere without O_2. Experimental solutions (as described previously) were prepared to simulate various groundwater compositions associated with the site. Precautions were taken to ensure the addition of redox-sensitive chemicals (for example, salts of Fe^{+2}, Mn^{+2} and S^{-2} as well as potentially volatile chemicals such as salts of HCO_3^{-}) was completed inside the glove box and only after N_2 gas had been thoroughly bubbled through the water. Two groups of tracers were used in the experiments. One group (Level A) was limited to Cs, Sr, and Am [or an equivalent lanthanide (Ln) of +3 valence] while the other group (Level B) included

Cs, Sr, Ni, Am (or Ln^{+3}), Np, Ra, and U.[1] The tracer and simulated groundwater solutions were added to experimental containers so that the solid mass to liquid volume ratio used in the experiments was 1 g to 4 mL.

Samples were collected to assess sorption at different contact times over the course of the experiments. Samples were taken at 1, 7, 30, 90, and 180 days (although some minor variations in the actual number of days at longer times varied slightly). Typically, three experimental replicates for each size fraction and water type combination were used. The experimental solution volumes decreased over time as samples were withdrawn, but the total volume decreases were limited to less than 10%. Sorption was quantified by comparing the mass of the radionuclide in the experimental solution to the mass of radionuclide in a "blank" experiment (i.e., an experimental container with tracer added but without a rock sample added). Selnert et al. (2008) indicate that in some cases (such as for Am), there was significant sorption of the radionuclide on the blank experimental container walls. As a result, initial concentration values were determined using acidified blank solutions. Selnert et al. (2008) note that the magnitude of sorption on container walls is reduced in the presence of a competing substrate.

2.1.3. Experiment Results

Results from the Forsmark related transport parameter experiments are reported in Selnert et al. (2008) and were, in part, utilized to develop K_d values and pdfs in Crawford (2010). Results for surface area, CEC, and batch sorption measurements are summarized in the following paragraphs.

Specific surface area measurements were made on crushed rock samples (2–4 and 0.063–0.125 mm size fractions), samples of fracture coatings, and intact core samples. Selnert et al. (2008) summarize the results from the BET surface area analyses by noting: (i) the smallest size fraction (0.063–0.125 mm) of crushed rock had measured surface areas greater than the largest size fractions (2–4 mm), (ii) there were no observed differences in measured surface areas for non-altered rocks, but there were significant differences between non-altered rocks (lower) and altered rocks (higher), (iii) rock material sampled from fractures had the highest measured surface areas, and (iv) measurements of non-crushed drill cores gave results in good agreement with their corresponding 2–4 mm size fraction. Selnert et al. (2008) also report that the observed BET surface area increases with decreasing particle size in all samples supports the hypothesis that the crushing process creates surfaces not representative of intact rock. The authors state that the relatively large spread (standard deviation) in measured surface areas for the crushed rock samples may be a result of heterogeneous distribution of small amounts of altered materials in the rock samples (Selnert et al., 2008). Examples of the N_2-BET specific surface area results are shown in Table 2.1.3-1, which displays results for all samples of the reference rock type (101057) and those used in the Level B tracer experiments (Selnert et al., 2008). The inverse relationship between grain size and measured specific surface area has been previously described and used to interpret and extrapolate "inner" and "outer" surface areas of the rock samples (Widestrand et al.,

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[1] Widestrand et al. (2003) and Selnert et al. (2008, p. 19) mention Th(IV) as a component in the Level B tracer mix, but there are no results reported for Th, nor are there explanations or indications as to why it was not included in the experiments.

2003; Byegård et al., 1998), and Selnert et al. (2008) planned a similar application of the technique. However, large uncertainties in the resulting calculations prevented this sort of extrapolation for surface area, and later, the sorption data as well.

CEC measurements were made on crushed rock samples (1–2 mm and 0.063–0.125 mm size fractions) and some fracture mineral samples. Unfortunately, the method chosen to measure CEC was relatively insensitive to the low CEC values characteristic of the Forsmark metagranites (Selnert et al., 2008). Moreover, the measurements of Mg^{2+} were associated with higher than anticipated uncertainties (Selnert et al., 2008). The CEC measurement difficulties were recognized early in the experimental program, and the goals of the analyses and number of samples targeted for measurement were adjusted accordingly (Selnert et al., 2008). The final CEC data have a high degree of uncertainty (Selnert et al., 2008; Crawford, 2010). The CEC value selected by Crawford (2010) for the reference rock type was 1.0 ± 0.5 cmol/kg.

Table 2.1.3-1. N_2-BET measured specific surface area (SA) for relevant rock samples. Drill core samples for rock type 101057 measured 0.024±0.012 m^2/g (Selnert et al., 2008).

Rock Sample Depth (m)	**2-4 mm measured SA (m^2/g)**	**0.063-0.125 mm measured SA (m^2/g)**	**SA ratio**	**Ratio (f_A) used in Crawford (2010)**	**f_A exceeds measured ratio by factor of:**
KFM01A (487.10–487.50)	0.05	0.198	3.96	32	8.08
	0.044	0.129	2.93	32	10.9
Average	***0.047***	***0.1635***	***3.48***	***32***	***9.2***
KFM01B (47.72–47.82)	1.937	3.550	1.83	32	17.5
	2.020	3.695	1.83	32	17.5
Average	***1.979***	***3.623***	***1.83***	***32***	***17.5***
KFM07A (387.47–387.87)	0.026	0.212	8.15	32	3.93
	0.038	0.215	5.66	32	5.66
Average	***0.032***	***0.2135***	***6.67***	***32***	***4.8***
All measured rock type 101057 samples	**0.025 ± 0.015 (27 samples)**	**0.19 ± 0.06 (27 samples)**	**7.6**	**N/A**	**N/A**

Sorption measurements were conducted using crushed rock samples from various boreholes and the four different water types representative of those found at the Forsmark site (Selnert et al., 2008). The actual number of experiments and sorption data accumulated for each radioelement varied depending on whether the radioelement was included in the Level A series, Level B series, or both tracer mixes (Selnert et al., 2008). For example, including replicate analyses, there are over 1300 sorption data points for Cs, while there are on the order of 200 data points each for Ra, Np, and U (Selnert et al., 2008). Some general observations of the sorption results include:

- A strong inverse relationship between experimental solution ionic strength and sorption magnitude (e.g., Figure 2.1.3-1).
- Stronger sorption for smaller grain size fractions (e.g., Figure 2.1.3-2).
- An increase in sorption with time for most experiments (e.g., Figure 2.1.3-3).

- Relatively low sorption for redox sensitive tracers such as Np and U, indicating that reducing conditions were not fully established in the experimental solutions (Selnert et al., 2008).

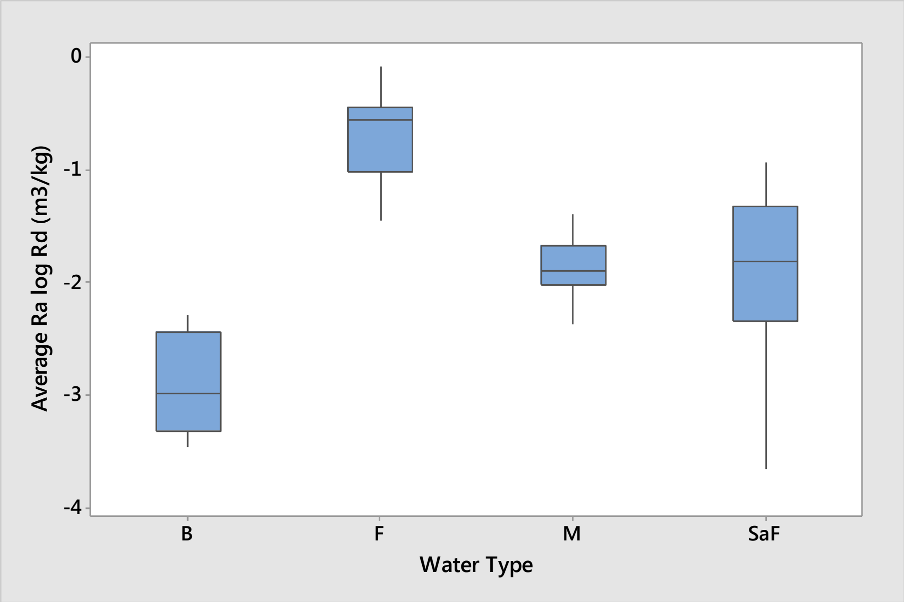

Figure 2.1.3-1. Results of Ra sorption on Forsmark site rocks as a function of water type (Selnert et al., 2008). The magnitude of sorption is inversely related to ionic strength of the waters (ionic strength B>M=SaF>F). Each box indicates the median (centre line) and 1st and 3rd quartiles (ends of the box) of the data. The whiskers are extended to data within ±1.5×IQR (interquartile range, 3Q−1Q) and data beyond ±1.5×IQR are represented as stars.

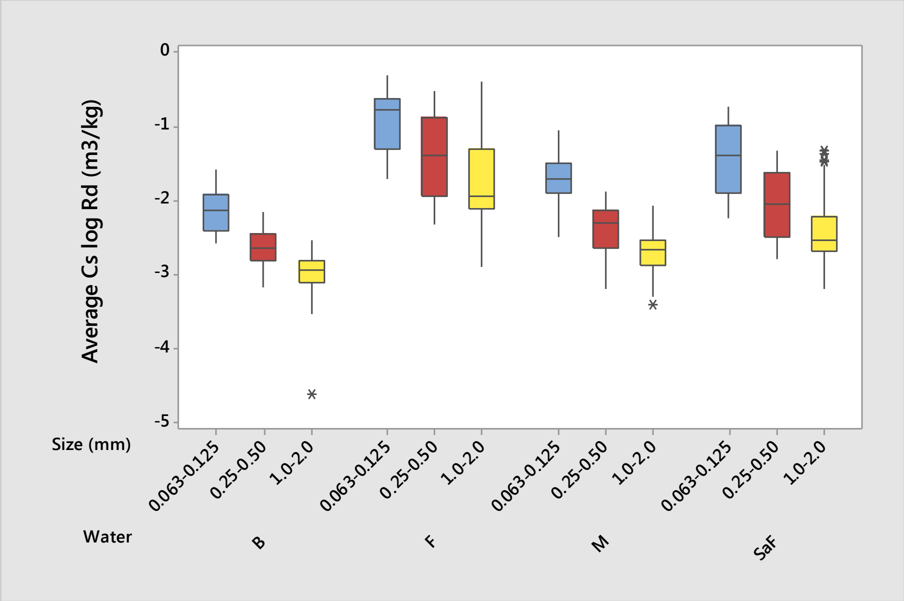

Figure 2.1.3-2. Results of Cs sorption on Forsmark reference rock type (101057) as a function of grain size and water type. Sorption is greater for the smaller size fractions. Each box indicates the median (centre line) and 1st and 3rd quartiles (ends of the box) of the data. The whiskers are extended to data within ±1.5×IQR (interquartile range, 3Q−1Q) and data beyond ±1.5×IQR are represented as stars.

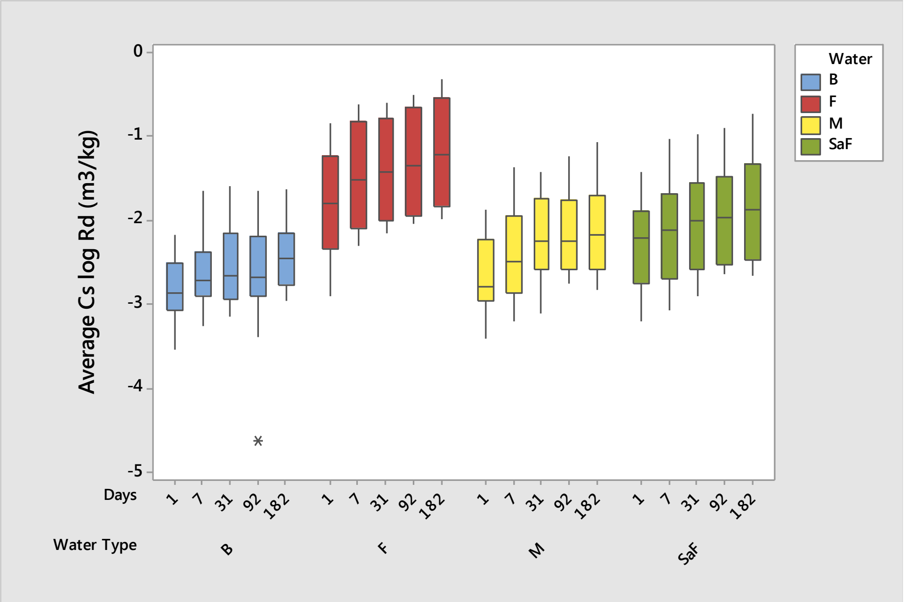

Figure 2.1.3-3. Results of Cs sorption experiments for the Forsmark site (Selnert et al. 2008). As is observed for other radioelements, sorption magnitude tends to increase over time. Each box indicates the median (centre line) and 1st and 3rd quartiles (ends of the box) of the data. The whiskers are extended to data within ±1.5×IQR (interquartile range, 3Q−1Q) and data beyond ±1.5×IQR are represented as stars.

Like the findings associated with the surface area results, Selnert et al. (2008) found that uncertainties and other factors limited the utility of applying the inverse relationship between grain size and sorption magnitude to interpret sorption data as “inner” versus “outer” sorption. This model was not carried forward by Crawford (2010) in the development of K_d values and pdfs. Selnert et al. (2008) attempted to interpret the observed changes in sorption with time using a diffusion model. This approach and similar efforts by Crawford (2010) were not successful in explaining the data. Selnert et al. (2008) concluded that the experiments likely did not reach equilibrium with respect to diffusive processes.

Another issue identified by Selnert et al. (2008) was the rather large amount of sorption observed in the blank experiments. This was attributed to sorption onto experimental container walls, and additional investigations were conducted to understand this behavior further (Selnert et al., 2008). Selnert et al. (2008) found that in the presence of a competing substrate, sorption onto container walls was minimal; as a result, acidified blank solutions were used to determine initial tracer concentrations for some radioelements.

2.2. Technical Review of Experimental Program and Data

The reviewer found that SKB designed and conducted an extensive and carefully planned experimental program in an effort to produce site-specific data for use in developing important transport parameters such as K_d values (Selnert et al., 2008; 2009a; Widestrand et al., 2003). SKB adequately considered relevant site characteristics and made efforts to employ experimental conditions that were representative of the Forsmark site (Selnert et al, 2008; Widestrand et al., 2003). SKB used credible and generally accepted methods to measure specific surface area, CEC, and sorption (Selnert et al., 2008). In the case of CEC, however, the selected method was inadequate for accurate quantitation of CEC given the properties of the rock samples. The Forsmark site-specific experimental program produced a substantial amount of data to support the development of K_d values and pdfs for use in performance assessment (Selnert et al., 2008). Unfortunately, because of several experimental artefacts and uncertainties, the applicability of some of the data is questionable.

2.2.1. Surface area and cation exchange capacity measurements

The N_2-BET analyses to determine specific surface area of cores and crushed rock samples produced data of reasonable quality for a variety of rock types (Selnert et al., 2008). As Selnert et al. (2008) note, the variance observed in the sample measurement results is likely due to the natural variation in mineralogy and texture of the rock samples, and this variability is carried forward by Crawford (2010) in his uncertainty propagation approach to development of final K_d values.

Selnert et al. (2008, p. 42) argue that the observation of increasing measured specific surface area with decreasing grain size supports “the hypothesis that the crushing process creates surfaces not representative of intact rock.” The reviewer strongly disagrees with this statement. The argument that crushed rock surfaces are not representative of the rock as a whole is not supported by the larger measured surface areas of (or greater sorption by) the smaller grain sizes. The change in measured surface area is an expected trend resulting from an increase in surface area to volume ratio associated with sequentially smaller grain sizes. In fact, Selnert et al. (2008) implicitly acknowledge this fact, using assumptions of surface area change based on particle sphericity and grain size to develop their inner and outer surface area model. It would be also expected that additional surface area would have a direct correlation to magnitude of sorption, especially for those radionuclides sorbing through a surface complexation mechanism. Even for ion-exchangers, higher surface area implies additional available exchange sites. However, the basic premise that crushed rock is not representative simply because of surface area changes is incorrect. The differences in surface areas are correctable through surface area normalization or use of a correction ration as is done in Crawford (2010).

Concerns regarding the non-representative nature of crushed versus whole rock are more appropriately related to the creation of fresh, non-weathered or non-equilibrated (non-aged) mineral surfaces or creation of surfaces with different mineral proportions than that of the intact rock. Depending on rock mineralogy, the crushing of samples may be biased as a result of weak grain boundaries or preferential cleavage associated with certain minerals. This could result in increased exposure of specific minerals not associated with surfaces of the intact rock on the crushed sample surfaces. If those minerals have notably different specific surface areas or sorption characteristics, they may bias results. Selnert et al. (2008) acknowledge this possibility in their discussion of surface area results and it is explicitly addressed by Crawford (2010) in discussions of sorption data. Fresh surfaces previously not exposed to groundwater may exhibit different chemical reactivity and kinetic behavior with respect to dissolution/weathering rates (e.g., White et al., 2001). Often, sorption experiments are designed to include a period of equilibration between the rock samples and experimental solutions to account for these effects (e.g., BSC, 2005). The kinetics of sorption were considered in the SKB experimental planning document, and this included the concern that the potential weathering of fresh rock surfaces after crushing and might impact results (Widestrand et al., 2003). How this concern might be/was addressed in the experiments was not described in Widestrand et al. (2003) or in Selnert et al. (2008). Review of Crawford (2013), however, indicates that extensive equilibration was conducted during the sorption experiments. Why this important detail is not presented or discussed in Selnert et al. (2008; 2009a) is unclear. In fact, as is discussed in the sorption review section, there are numerous experimental details impacting the outcome and interpretation of the results that are not presented or discussed in Selnert et al. (2008; 2009a). This seems to be a critical oversight that impedes detailed review of the experiments.

As noted in Selnert et al. (2008), the CEC analyses were severely limited by selection and use of a method unsuited for examination of the Forsmark metagranites. The results are associated with uncertainties that are large enough for Selnert et al. (2008) to declare the data “for comparative use” rather than the detailed quantitative characterisation resource envisioned at the start of the experimental program. In the end, however, even with large uncertainties, the CEC data were used by Crawford (2010) primarily as a means of K_d value correction and comparison to external data, both of which had a relatively minor influence on the K_d pdfs eventually used in performance assessment. Thus, the limited CEC data is not a significant concern unless SKB’s transport modelling approach changes to require more accurate and detailed information regarding the ion exchange characteristics of the host rock.

2.2.2. Batch sorption measurements

Conducting sorption experiments under the particular conditions relevant to the Forsmark site is extremely challenging from both a logistical and technical perspective. The low Eh values measured in Forsmark groundwater indicate that sorption experiments must be conducted using solutions with extremely low concentrations of O_2 (e.g., Gimeno et al., 2008; Sidborn et al., 2010). Establishment of very low O_2 environments typically requires use of an atmosphere-controlled glove box and careful preparation of solutions to strip O_2 before adding tracers. Likewise, low Eh conditions may require the presence of adequate redox pairs to maintain stability. Selnert et al. (2008) took considerable precautions to minimize the potential exposure of experiments to O_2. The experiments were conducted in a glove box, and solutions were prepared in a controlled N_2-atmosphere to prevent exposure to O_2 (Selnert et al., 2008). Additionally, it is time-consuming and costly to conduct sorption experiments that cover the entire range of rock types, groundwater compositions, and variability (Crawford, 2010). Selnert et al. (2008) prioritized their experimental design to include major groundwater compositions that bound groundwater types expected in the vicinity of the repository.

In this review sorption data for various radioelements of interest (Cs, Np, Ra, and U) were extracted from Selnert et al. (2008) for detailed analyses. The results of the sorption experiments and some of the data trends observed are summarized in Figures 2.1.3-1 to 2.1.3-3. The inverse relationship between ionic strength and sorption can be seen in Figure 2.1.3-1, which depicts the results of the Ra sorption experiments on the reference rock type grouped by water type. The mean value of measured Ra sorption in fresh water is about two orders of magnitude greater than that observed in the brine water, while the waters of intermediate composition have intermediate sorption values. When all rock sample types are considered, as in the Cs sorption data, the trend still holds, but the variance is larger with significant data overlap (Figure 2.2.2-1).

Figure 2.1.3-2 depicts the differences in sorption with respect to the grain size of the rock samples. A simple analysis of variance between the size fractions indicates the differences in $\log_{10}R_d$[2] are significant ($p=0.000$, $\alpha=0.05$). An example of the trend of increasing measured R_d values over time is shown in Figure 2.1.3-3 for Cs sorption on the reference rock type in various groundwaters. Although the increase in R_d over time is apparent, in several instances, including this example, the relative differences for the longer experiments times (30–180 days) are small. An analysis of variance for the results shown in Figure 2.1.3-3 indicates that there are no significant differences between the values measured at 30, 90, and 180 days ($p>0.448$, $\alpha=0.05$). This similarity of R_d values with respect to time (for Cs and other radioelements) supports the decision of Crawford (2010) to group all available data for use in the K_d pdf development without filtering for time variance.

As previously discussed, it is expected that sorption will increase with decreasing grain size of the substrate because of an increase in the surface area to volume ratio of the particles. One method of accounting for the measured sorption differences is to normalize results with respect to measured specific surface area. Figures 2.2.2-2 and 2.2.2-3 depict the sorption of U on various grain size fractions used in the experiments. In Figure 2.2.2-2 the mean value of sorption for the 1.0–2.0 mm grain size fraction is significantly different ($p=0.000$, $\alpha=0.05$) than the mean sorption values for the smaller grain size fractions. After surface area normalization, as shown in Figure 2.2.2-3, the mean sorption values are not statistically different from one another ($p=0.258$, $\alpha=0.05$). Interestingly, sorption on some fracture fill materials (Figure 2.2.2-4) is not significantly different than the 0.063–0.125 mm size fraction. Perhaps this is fortuitous, and the variance included in the pdfs indeed represents fracture material sorption as well.

An analysis of the experimental results from Selnert et al. (2008) indicates that the data produced are useful for the conditions explored in the experiments. Unfortunately, the analysis also reveals several shortcomings in the batch experimental program. Taken independently, each issue is relatively minor, but as a group these shortcomings have resulted in the production of a large amount of data that is of good quality, but that is not particularly applicable to conditions at the Forsmark site or useful in developing K_d pdfs for several important radioelements. The resulting lack of applicable data produces a significant gap in the safety analyses with respect to confidence in site sorption characteristics, especially for redox sensitive elements.

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[2] For experimental data that have not been corrected, Selnert et al. (2008) and Crawford (2010) use the term R_d, and K_d is used for the corrected value.

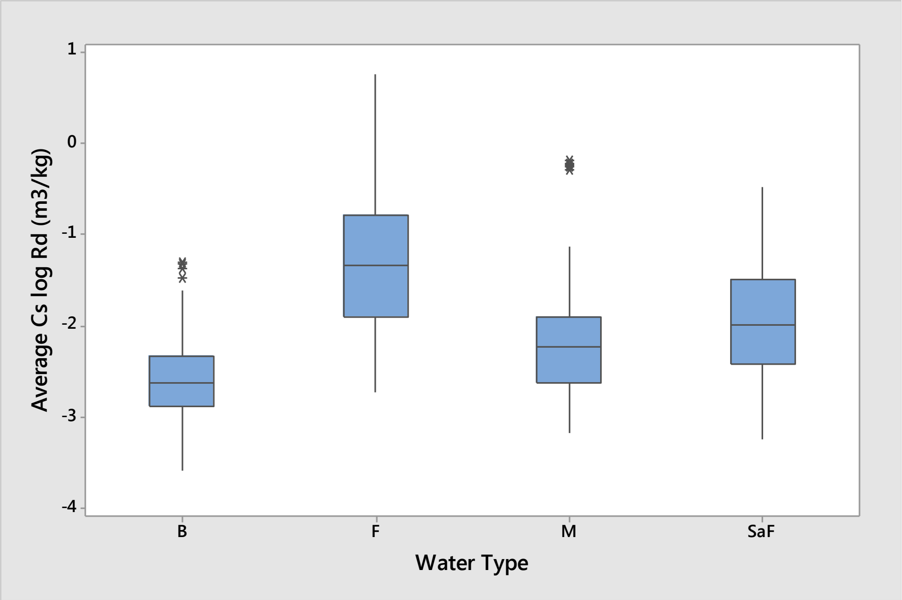

Figure 2.2.2-1. Results of Cs sorption on all rock types from the Forsmark site plotted as a function of water type (Selnert et al., 2008). When the variance of the different material is considered, the effect on sorption magnitude from the variation in ionic strength is reduced. Each box indicates the median (centre line) and 1st and 3rd quartiles (ends of the box) of the data. The whiskers are extended to data within ±1.5×IQR (interquartile range, 3Q−1Q) and data beyond ±1.5×IQR are represented as stars.

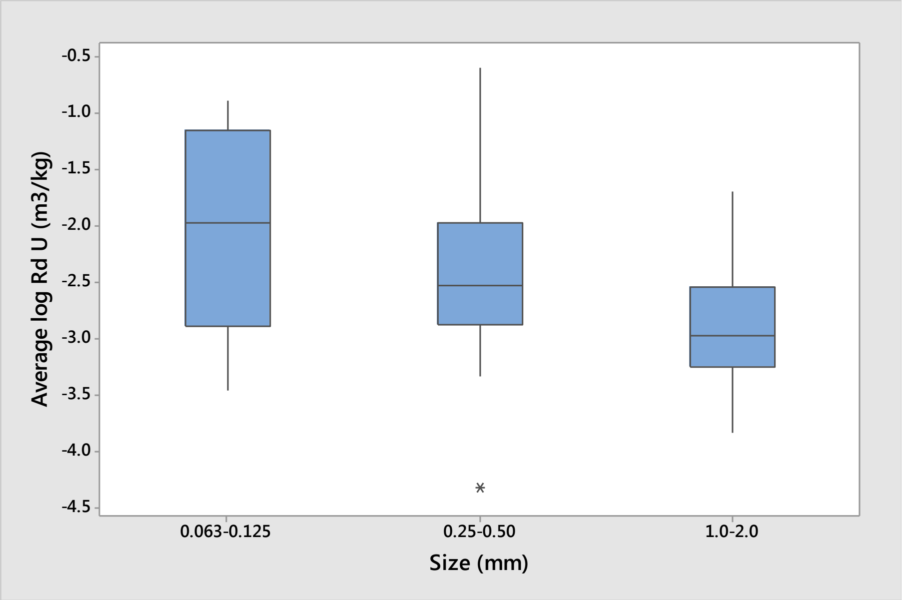

Figure 2.2.2-2. Results of U sorption on Forsmark site rocks as a function of grain size (Selnert et al., 2008). The mean U sorption values of the smaller grain sizes (0.063–0.125 and 0.25–0.50 mm) are significantly different than that of the larger size fraction. Each box indicates the median (centre line) and 1st and 3rd quartiles (ends of the box) of the data. The whiskers are extended to data within ±1.5×IQR (interquartile range, 3Q−1Q) and data beyond ±1.5×IQR are represented as stars.

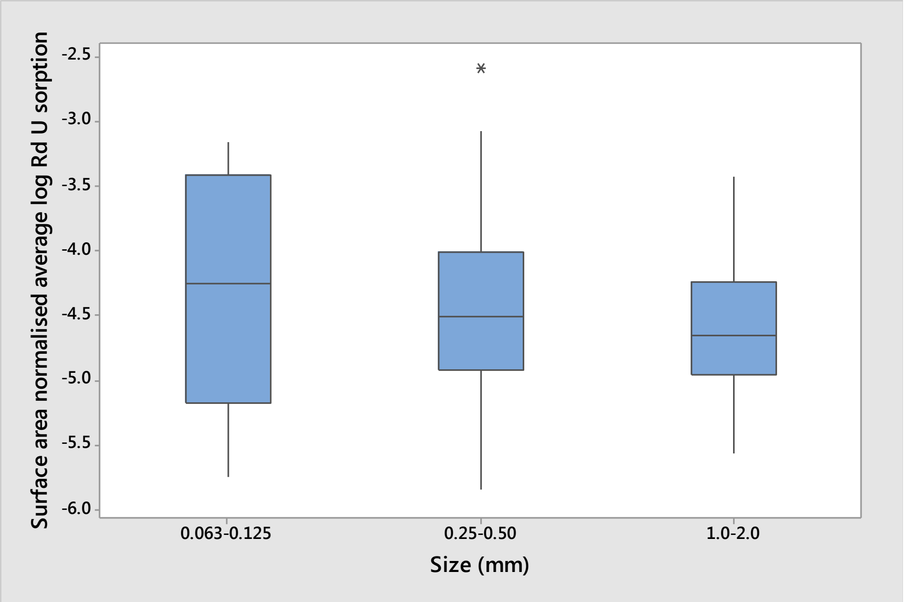

Figure 2.2.2-3. Results of U sorption on Forsmark site rocks as a function of grain size (Selnert et al., 2008). The sorption data were normalised with respect to specific surface area for each size fraction using the alternative surface area model described in Section 2.4.1. When normalised for surface area, the mean sorption values amongst the different size fractions are not distinguishable. Each box indicates the median (centre line) and 1st and 3rd quartiles (ends of the box) of the data. The whiskers are extended to data within ±1.5×IQR (interquartile range, 3Q−1Q) and data beyond ±1.5×IQR are represented as stars.

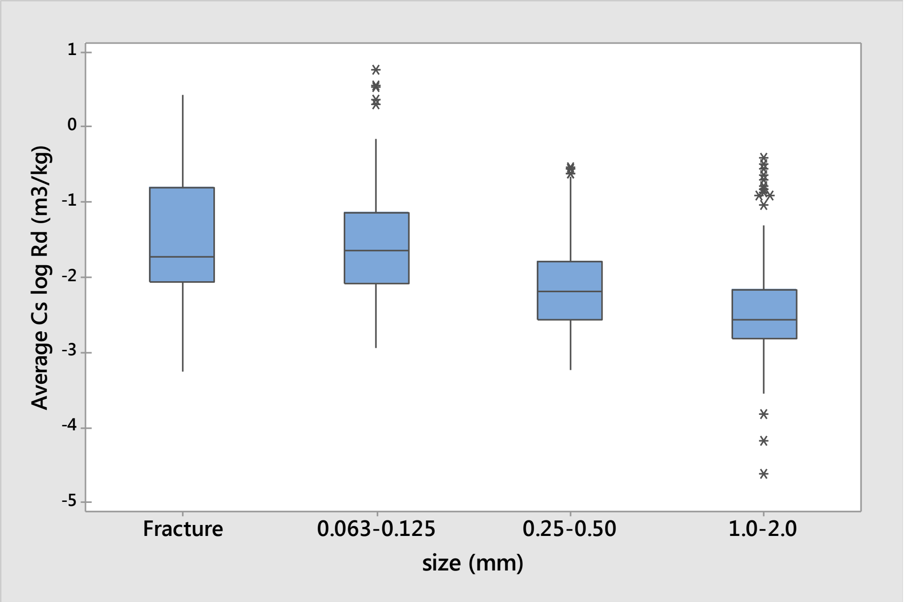

Figure 2.2.2-4. Results of Cs sorption experiments for all rocks types associated with the Forsmark site (Selnert et al., 2008). Mean sorption magnitudes on samples of fracture lining material and the 0.063–0.125mm grain size fraction are not distinguishable. Each box indicates the median (centre line) and 1st and 3rd quartiles (ends of the box) of the data. The whiskers are extended to data within ±1.5×IQR (interquartile range, 3Q−1Q) and data beyond ±1.5×IQR are represented as stars.

As noted in Crawford (2010), "Two key variables which govern a large portion of radionuclide speciation are the pH and carbonate concentration (or equivalent partial pressure of carbon dioxide, pCO_2). These are considered to be of primary relevance for many radionuclides, particularly those that sorb by way of a surface complexation mechanism." Another, and perhaps more important, major variable with respect to the Forsmark site is the redox condition (low Eh) of the groundwater (e.g., Sandström and Stephens, 2009).

As discussed in Widestrand et al. (2003) and Selnert et al. (2008; 2009a) establishing experimental conditions consistent with expected site conditions is essential. Selnert et al. (2008) made efforts to create an appropriate experimental environment by utilizing a controlled-atmosphere glove box and an N_2-atmosphere (in the absence of O_2). However, it appears that neither the actual O_2 concentration of the glove box atmosphere or the solutions nor the redox potential (ORP or Eh) of the solutions was monitored or measured during the experiments. An assumption of O_2 exclusion is usually not sufficient for experiments requiring low Eh conditions, and in the absence of any direct measurement, some proxy measurement, such as the concentration of a known redox pair or use of a tell-tale species [such as Tc used by Hiutti et al., (1996)] is warranted. Lack of adequate information about the redox state of the experiments obscured the fact that reducing conditions were not achieved and resulted in production of sorption data for oxidized forms of the important actinides Np and U instead of the reduced forms pertinent to the site (Selnert et al., 2008). The reviewer finds that this is a major deficiency in the program and has required the use of non-site-specific data to generate the K_d pdfs for important actinides (Crawford, 2010).

In addition, it appears that the N_2-gas used for the experiments did not contain any CO_2-gas. As noted by Crawford (2010) and in the early review by Randall (2012), there was significant pH drift in the solutions during the course of the experiments. Although not mentioned or presented by Selnert et al. (2008), some selected experimental and/or control solution were monitored for pH. Results of those measurements, shown in Figure 2.2.2-5 and summarized in Table 2.2.2-1, indicate a significant drift to more basic conditions. Although some alternative causes for the pH changes are discussed in Crawford (2010), the changes are almost certainly due to loss of CO_2 from the solutions as they equilibrated over time with the extremely low pCO_2 environment of the glove box atmosphere. Essentially, the sorption experiments were conducted in a CO_2-free system. This has significant impact on the potential sorption radioelements that form strong carbonate complexes (e.g., Np and U). The sorption of Np and U is also strongly influenced by solution pH (e.g., Bertetti et al., 1998; 2011; Pabalan et al., 1998). A shown in Figure 2.2.2-6, U sorption is dependent on both pH and pCO_2, and the evolution of the experimental solutions is toward conditions that generally favour greater U sorption. Furthermore, U sorption values as measured in the experiments, when corrected for surface area effects are within the bounds indicated by separately modelled data (Figure 2.2.2-6) (Selnert et al., 2008; Turner et al., 2006). The change in sorption with respect to pH and pCO_2 as measured is consistent with the model. This pH and pCO_2 drift could be part of the cause of the time-dependent sorption increase observed in the experiments. A complicating factor in this explanation is that the sorption of ion-exchangers such as Cs and Ra should not be impacted by variations in pH and pCO_2, yet they also display an increase in sorption over time (Figure 2.1.3-3). This might be explained by the slow sorption kinetics of Cs and Ra, which are explicitly accounted for in other programs (BSC, 2005). The primary concern with the resulting Np and U data is that sorption values collected under the experimental conditions (higher pH and low pCO_2) are likely to be larger than those collected at conditions more relevant to the Forsmark site.

Selnert et al. (2008) propose that the stronger sorption of Np and U on smaller size fractions (0.063–0.125 mm) relative to the largest fraction is not fully explained by specific surface area differences and is a result of localized reduction of species on the surfaces (presumably because more of the favorable mineral types facilitating reduction are exposed in the finer fraction). A check of mean logR_d values for Np confirms the sorption differences are statistically significant even after surface area corrections are made (Figure 2.2.2-7). However, there is no ability to account for the effects of pH and pCO_2 changes in the experiments. So it is difficult to explain the observed sorption behavior without additional information.

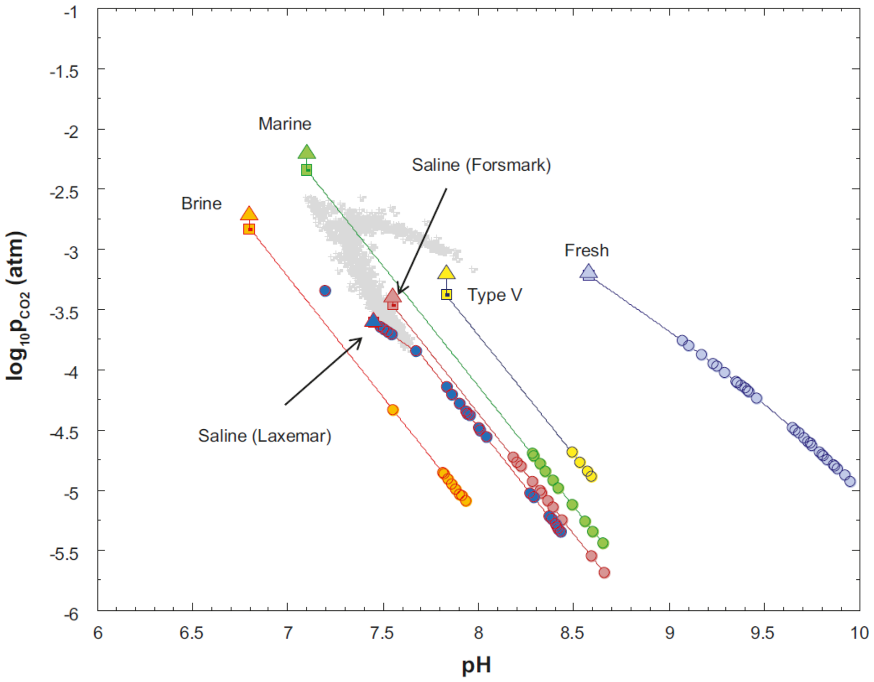

Figure 2.2.2-5. Figure 5-3 of Crawford (2010) showing the measured drift in pH and pCO_2 of the experimental solutions used in the sorption experiments of (Selnert et al., 2008; 2009a). The initial and final pH values are listed in Table 2.2.1-1. Note that all of the experimental solution types have final pCO_2 values that are well outside the expected range for Forsmark groundwater.

Table 2.2.1-1: Variation in pH for sorption experiments (Crawford, 2010)

Water Type	pH start	pH finish
Fresh	8.58	9.9
Marine	7.1	8.7
Saline Forsmark	7.55	8.7
Brine	6.8	8.0

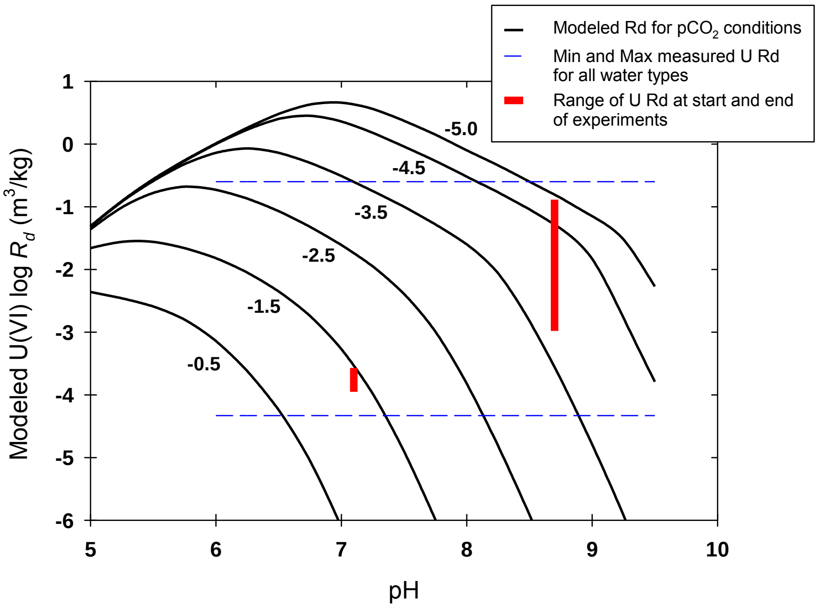

Figure 2.2.2-6. Plot of modelled U(IV) sorption on silicate and aluminosilicate rocks at various pCO_2 values ($\log_{10}$ atm). Model output is based on the surface complexation approach of Turner et al. (2006) and is corrected for surface area to be equivalent to Forsmark site host rock. As pCO_2 decreases U sorption is expected to increase. Also shown are the maximum and minimum U $\log_{10}R_d$ values for all experiments (blue lines) and the range of measured U $\log_{10}R_d$ at the start and at the end of the sorption experiments in Marine type water (red bars, these data are also corrected for surface area) (Selnert et al., 2008).

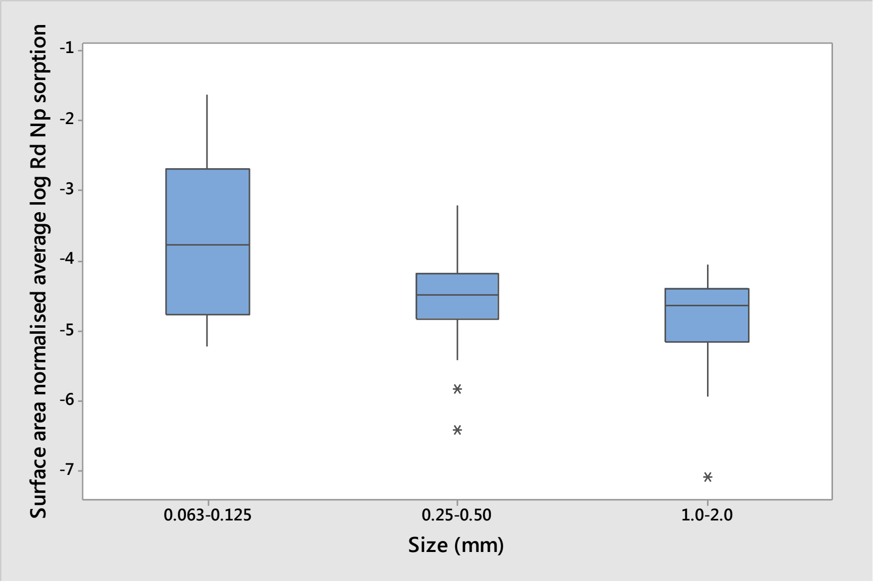

Figure 2.2.2-7. Results of Np sorption on Forsmark site rocks as a function of grain size (Selnert et al., 2008). The data have been normalised for specific surface area using the alternative model discussed in Section 2.4.1. Even after the correction, mean Np sorption on the finest size fraction (0.063–0.125 mm) remains significantly different than that of the larger size fractions. Each box indicates the median (centre line) and 1st and 3rd quartiles (ends of the box) of the data. The whiskers are extended to data within ±1.5×IQR (interquartile range, 3Q−1Q) and data beyond ±1.5×IQR are represented as stars.

Other issues arise when analysing the experimental protocols. Selnert et al. (2008) report that for strong sorbers, such as Am, there was significant sorption onto the walls of blank solution containers. Follow up analyses and experiments indicated that the actual amount of sorption onto container walls was quite limited in the presence of a competing substrate such as the rock samples (Selnert et al., 2008). Therefore, acidified blanks were used to minimize sorption onto blank container walls and these concentrations were used as initial values in calculating R_d values (Selnert et al., 2008). The reviewer concludes this is a reasonable approach, but these findings suggest other radioelements (Np and U in particular) may have also been affected by blank container sorption. Previous sorption studies have indicated that under solution conditions where sorption occurs, U (and Np) will sorb to many different types of materials, including container plastics and Teflon (e.g., Bertetti et al., 1998; 2011). In the presence of a competing substrate, the container wall sorption is diminished; but for low sorbing substrates like low surface area tectosilicates, a substantial amount of U may remain on the container (Figure 2.2.2-8). Systematic desorption experiments that explicitly determine experimental container wall residual sorption are required to fully account for this uncertainty. Conversely, if the blanks for moderate and low sorbers like Np and U are not acidified, there may be a substantial underestimate of experimental container sorption. The frequent calculation of negative sorption values for U and Np (Selnert et al., 2008, Appendix 5) indicates that sorption on the blank container walls may be underestimated.

Finally, a detailed review of Appendix 5 in Selnert et al. (2008) reveals several missing or non-measured R_d values for some nuclides. The cause of these missing values is explained in a footnote as being the result of low (non-measurable) sample radioactivity due to decay (Selnert et al., 2008). Selnert et al. (2008) do not provide important experimental information such as the target or measured starting concentrations of radioelements, the specific radionuclides used in the experiments, the analytical method used to quantify the radionuclide activities, or the actual amount of sample withdrawn for analyses. Widestrand et al. (2003) indicates ^{233}U and ^{237}Np would be used as tracers in the experiments. It is difficult to understand how these nuclides with very long half-lives could have decayed to non-detectable levels during the experiments. Thus, the explanation for the missing data provided in Appendix 5 is quite confusing to the reviewer. Selnert et al. (2008) indicate that the initial experimental conditions included 4 mL of solution to 1 g of solids. The actual volumes used are not provided. Information from other sources (Widestrand et al., 2003; Byegård et al., 1998) suggests that the actual volume and mass may have been 8 mL and 2 g, respectively. Selnert et al. (2008) report that less than 10% of the experiment solution volume was removed during sampling. Based on the information provided in Selnert et al. (2008), it is not possible to know if the experimental solution replicates were sampled multiple times over the course of the experiment (1, 7, 30, 90, and 180 days) or if a different set of replicates were used and sacrificed at each sampling interval. If the same solutions were sampled multiple times, that suggests the sampled volumes were on the order of 0.15 mL each. These are small volumes for experimental quantitation in which significant sorption has occurred because of the need to dilute and process the samples further. The relatively small experimental volumes may also indicate why other parameters such as pH and Eh were not directly measured for each experimental solution. Thus, the constraints imparted by the experimental design may have contributed to the large uncertainties in the results.

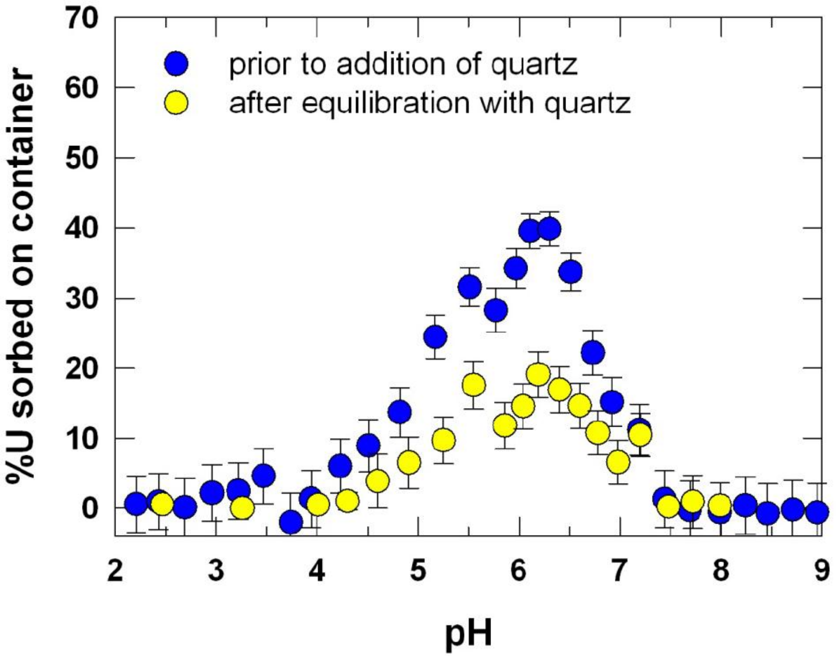

Figure 2.2.2-8. Results of U sorption onto experimental container surfaces before and after sorption on quartz solids (Bertetti et al., 2011). Although the sorption magnitude decreases with competition from the quartz, a significant fraction remains on the container. U sorption is highly dependent on pH.

2.3. Development of K_d Probability Distribution Functions

The second component of developing K_d values and K_d pdfs was to utilize data produced in the experimental program along with data derived from the open literature to assess uncertainty and generate representative sorption parameters for use in the SR-Site performance assessment. This second process is documented in detail in Crawford (2010).

The sorption data of Selnert et al. (2008) were initially processed to correct values to be equivalent for the site-specific rock type (SKB, 2010b). The corrections, known as transfer factors, account for differences in surface area and cation exchange capacity (CEC) between experimental samples and the host rock (SKB, 2010b; Crawford, 2010). Corrections are also made to account for the impacts of variations in groundwater compositions (SKB, 2010b; Crawford, 2010). The corrections are described in detail in Crawford (2010) and are discussed by Randall (2012) but are summarized again in this review for convenience and clarity.

The transfer factors of Crawford (2010) are (1) the surface area normalisation transfer factor (f_A), (2) the mechanical damage transfer factor (f_M), (3) the cation exchange capacity transfer factor (f_{CEC}), and (4) the groundwater chemistry transfer factor (f_{CHEM}). The transfer factors are applied to the experimental data as follows:

$$R_d^0 = R_d \times f_A \qquad \text{Eq. 1}$$

$$K_d^0 = R_d^0 \times f_M \times f_{CEC} \qquad \text{Eq. 2}$$

$$K_d = K_d^0 \otimes f_{CHEM} \qquad \text{Eq. 3}$$

where R_d is the sorption experiment result (m^3/kg), R_d^0 is the surface area adjusted value, K_d^0 is adjusted for mechanical damage and CEC, and K_d is the final corrected K_d value. If the f_{CHEM} correction is not applied (true for most surface complexation dependent radioelements), then K_d^0 is equal to K_d. Application of f_{CHEM} is by conjugation of two pdfs as discussed in Section 2.3.4. The transfer factors are discussed in more detail in the following sections.

2.3.1. Surface area normalisation (f_A)

The f_A factor accounts for the difference in sorptive surface areas between the different size fractions used in the laboratory investigations. It is defined as the ratio of the surface area of a reference size fraction of crushed rock (A_{ref}) relative to the actual size fraction used in the experiment (A_{sample}).

$$f_A = \frac{A_{sample}}{A_{ref}} \approx \frac{d_m}{d_{ref}} \qquad \text{Eq. 4}$$

where d_m and d_{ref} are the mean grain sizes for the size fractions used in the experiments. This allows data obtained for different size fractions to be converted into a mutually compatible form that can then be pooled before extrapolation to *in situ* conditions (Crawford, 2010). Because specific surface area measurements were not made for all size fractions of rock samples used in the sorption experiments, Crawford (2010) estimates mean particle size of the size fractions and assumes the surface area relationship can be conservatively represented by mean grain size ratios as shown in Equation 4 above. The mean grain size (d_m) is calculated using a model described by André et al. (2008) where a uniform distribution of particle sizes between the upper (d_2) and lower (d_1) sieve size is assumed (Crawford, 2010).

$$d_m = \frac{3}{4}\left(\frac{d_2^4 - d_1^4}{d_2^3 - d_1^3}\right) \qquad \text{Eq. 5}$$

The size fraction of 2.0–4.0 mm was selected as the reference size fraction (d_{ref}) (Crawford, 2010). The ratio of mean particle size of the fractions used in the experiments and the reference size fraction is used to calculate f_A. The resulting transfer factor values are listed in Table 2.3.1-1.

Table 2.3.1-1. Surface area normalisation transfer factors and associated surface areas (Crawford, 2010)

Sieve Size (mm)	Mean particle size (d_m) (mm)	f_A	$1/f_A$	Calculated surface area using f_A (m^2/g)	Calculated surface area using alternative model (m^2/g)†
0.063–0.125	0.101	0.0313	32	1.502	0.19
0.25–0.5	0.402	0.125	8	0.376	0.1
1.0–2.0	1.607	0.5	2	0.094	0.05
2.0–4.0	3.214	1	1	0.047	0.04

†Alternative model based on fit of measured surface areas. See text in Section 2.4.1 for discussion.

2.3.2. Mechanical damage (f_M)

The mechanical damage transfer factor (f_M) accounts for differences between the surface areas of the crushed rock or samples from literature data and Forsmark-representative undisturbed rock (Crawford, 2010). This factor employs the measured surface area (0.018 ± 0.005 m^2/g) of core samples (or monoliths) (400–500 g each) of the Forsmark host rock for the undisturbed rock values (André et al., 2009; Crawford, 2010). The mechanical damage transfer factor is calculated using

$$f_M = \frac{A_0}{A_{ref}} \qquad \text{Eq. 6}$$

where (A_{ref}) is the measured surface area of the reference size fraction (2.0–4.0 mm) of crushed rock used in experiments or the surface area of samples used in literature experiments and (A_0) is the measured surface area of the core sample (Crawford, 2010). The calculated (f_M) values of Crawford (2010) are provided in Table 2.3.2-1.

2.3.3. Cation exchange capacity (f_{CEC})

The cation exchange capacity (CEC) transfer factor (f_{CEC}) accounts for differences between the cation exchange capacity of the site-specific rock type and that of rock samples used in laboratory experiments (Crawford, 2010). Similar to the other transfer factors, the CEC correction is calculated as a ratio between the measured CEC of the site-specific host rock (CEC_0) and the CEC value of the rock samples used in experiments (CEC_{ref}) using the equation

$$f_{CEC} = \frac{CEC_0}{CEC_{ref}} \approx \frac{[Biotite\ \%]_0}{[Biotite\ \%]_{ref}} \approx \frac{Fe_0}{Fe_{ref}} \qquad \text{Eq. 7}$$

where $[Biotite\ \%]_0$ and $[Biotite\ \%]_{ref}$ are the percentages of biotite in the rock and the sample and Fe_0 and Fe_{ref} refer to the amount of iron in the host rock and sample rock (Crawford, 2010). As discussed previously, CEC values were measured for Forsmark rocks but the results are associated with significant uncertainties and have limited utility for direct comparison (Selnert et al., 2008; Crawford, 2010). To account for this and utilize a more robust data set to correct for CEC differences

Table 2.3.2-1. Mechanical damage transfer factors (f_M) from Crawford (2010, Table 5-3). Recalculated values are shown in the shaded columns. Possible errors are highlighted in bold text (see text in Section 2.4.1 for discussion).

Borehole (depth–m)	A_{ref} (m^2/g)	f_m	Check f_m	$\log_{10} f_m$	Check $\log_{10} f_m$
KFM01A (103)	0.024±0.022	0.74±1.39	0.75±1.42	0.14±0.56	***-0.13±0.82***†
KFM01A (487)	0.047±0.004	0.38±0.56	0.38***±0.22***†	-0.46±0.22	*-0.42±0.25*‡
KFM01A (908)	0.030±0.001	0.60±0.31	0.60±0.34	-0.27±0.21	*-0.22*±0.22†
KFM02A (552)	0.041±0.010	0.44±0.32	0.44±0.33	-0.35±0.30	-0.36±0.32
KFM03A (536)	0.013±0.003	1.38±0.91	1.38±*1.00*†	0.13±0.27	0.14±0.29
KFM06A (440)	0.035±0.005	0.52±0.30	0.51±0.32	-0.32±0.24	*-0.28*±0.25†
KFM07A (387)	0.032±0.008	0.56±0.41	0.56±0.42	-0.25±0.30	-0.25±0.32
KLX02 (217)	0.061±0.006	0.29±0.16	0.30±0.17	-0.57±0.23	*-0.54*±0.24†
KLX02 (753)	0.042±0.010	0.43±0.29	0.43±0.31	-0.38±0.28	-0.37±0.29
KLX02A (509)	0.029±0.006	0.62±0.40	0.62±0.43	-0.23±0.27	-0.21±0.28
KLX02A (682)	0.037±0.007	0.48±0.31	0.49±0.32	-0.34±0.26	-0.32±0.28
KLX02A (936)	0.096±0.004	0.19±0.10	0.19±0.11	-0.77±0.21	*-0.72*±0.23†
KLX03A (522)	0.035±0.0004	0.51±0.26	0.51±0.28	-0.34±0.21	*-0.29*±0.22†
KLX04A (489)	0.042±0.002	0.43±0.22	0.43±0.24	-0.41±0.21	*-0.37*±0.22†
KLX04A (718)	0.029±0.021	0.61±0.93	0.62±0.95	-0.02±0.50	***-0.21±0.66***†
KLX05 (482)	0.094±0.007	0.19±0.10	0.19±0.11	-0.76±0.22	*-0.72*±0.23†
KSH01A (981)	0.051±0.009	0.35±0.22	0.35±0.23	-0.48±0.25	-0.46±0.27

† Calculated discrepancies not explained by rounding differences are shown in *italics*.
Major discrepancies are shown in ***bold***.
‡ Error value calculated using corrected f_m error (± 0.22)

between Forsmark and Laxemar samples, Crawford (2010) relates biotite content, and derivatively, iron content to CEC. Using measured iron content data from Sidborn et al. (2010), a beta distribution of calculated f_{CEC} values is generated and then refit using a lognormal distribution to determine the f_{CEC} for the conversion from Laxemar data to the Forsmark host rock equivalent (Crawford, 2010). In practice, only the derived geometric mean value (0.63 ± 0.2) of the distribution is used as the f_{CEC} (Crawford, 2010). It is interesting to note that simply using average analytical results for Fe_2O_3 reported in Drake et al. (2006) and Sandström and Stephens (2009) for Forsmark and Laxemar reference rocks (types 101057 and 501044, respectively) results in calculated f_{CEC} values of 0.60–0.62, which are quite consistent with the 0.63 value of Crawford (2010).

For literature derived data, Crawford (2010) uses a generic value of 1.0 ± 0.5 cmol/kg for Forsmark metagranite (CEC_0) (rock type 10157) and the measured CEC of the literature source to calculate f_{CEC}. Where literature CEC values were not available, the biotite % was used, but only if the actual biotite contents of the samples and host rock differed by more than 50% (Crawford, 2010). The f_{CEC} is applied for ion-exchanging radionuclides, such as Ra and Cs, but is also applied for some radioelements that sorb via surface complexation. Crawford (2010) uses various lines of evidence that suggest preferential sorption U, Np, Tc, and sometimes Pu and Am, onto biotite and hornblende in granitic rocks. The application of this factor for those situations is “handled on a case by case basis in a partially subjective manner” (Crawford, 2010).

2.3.4. Groundwater chemistry (f_{CHEM})

The groundwater chemistry transfer factor (f_{CHEM}) accounts for differences between the groundwater chemistry under application conditions *in situ* and that used in laboratory investigations (Crawford, 2010). The chemistry of groundwater can and does vary spatially and temporally among values that are different than the bounding chemical conditions selected for use in the sorption experiments. Because sorption values are sensitive to changes in chemistry, it is important for K_d pdfs to account for those changes. For radioelements whose sorption is dominated by ion-exchange processes, such as Ra and Cs, ionic strength changes are most important; for those dominated by surface complexation processes, changes in pH and pCO_2 are most important (assuming that redox conditions are somewhat constant) (Crawford, 2010).

Conducting experiments to measure sorption of radioelements over the range of conceivable or predicted groundwater chemistry variations is not practical for many reasons. Thus, the available data often must be interpolated and extrapolated to chemical conditions outside of those used in the experiments. The variations and interactions of groundwater parameters are often non-linear, and as a result, some sort of geochemical modelling is typically required to calculate the values of important components like pH, pCO_2, and ionic strength. Crawford (2010) discusses at length the issues associated with use of surface complexation modelling to estimate sorption when important control data and thermodynamic values are lacking. Crawford (2010) concludes the uncertainties in the available data preclude the appropriate use of a chemical correction factor for surface complexing radioelements. However, Crawford (2010) found that data for radioelements sorbing via ion exchange were amenable to the application of an empirical correction factor.

Although the ion exchanging radioelements are impacted by changes in ionic strength, f_{CHEM} is not simply a relative ratio of reference versus predicted ionic strength values. Instead f_{CHEM} is based on the ratio of a calculated site-specific K_d value [$K_{d(app)}$] and a set of K_d values calculated for varying (both spatial and temporal) groundwater chemistries expected at the site [$K_{d(ref)}$] using the equation

$$f_{CHEM} = \frac{K_{d(app)}}{K_{d(ref)}} \qquad \text{Eq. 8}$$

The K_d values used to determine f_{CHEM} are derived from calculations of K_d using an ion exchange model originally developed by Byegård et al. (1995; 1998) (Crawford, 2010). Crawford (2010) updates the model to incorporate appropriate ion exchange selectivity coefficients and background concentrations of target radioelements. Forsmark marine-type groundwater is used for the site-specific chemistry to calculate the site-specific $K_{d(app)}$. The reference groundwater chemistry values are sampled from the SR-Site groundwater temperate domain geochemical modelling results of Salas et al. (2010), and the ion exchange model is used with those results to calculate the $K_{d(ref)}$. Using Equation 8 with each of the calculated $K_{d(ref)}$ values produces an f_{CHEM} distribution function. The f_{CHEM} pdf and the K_d^0 pdf obtained from the marine groundwater experimental sorption results are then sampled together and the values combined using Equation 3 to calculate the final corrected K_d distribution (Crawford, 2010).

2.3.5. Effects of redox

Because of the influence of redox conditions on sorption, the selection of appropriate K_d values and probability distributions depends on an understanding of the evolution of groundwater redox over time, and SKB considered the role of redox speciation as a separate factor when selecting K_d values for redox-sensitive elements (Crawford, 2010; SKB, 2010b).

SKB developed geochemical models to assess the potential long-term redox evolution of the Forsmark area for SR-Site (Salas et al., 2010; Crawford, 2010). The data generated from these models were used to calculate the aqueous speciation of redox sensitive radionuclides (Crawford, 2010). The speciation calculations were conducted for 20,000 randomly sampled groundwater compositions taken from the SR-Site temperate domain simulations (Salas et al., 2010). Additionally, sweep calculations were made for a range of hypothetical redox potentials in an effort to determine the aqueous chemical conditions (transition points) where reduced and oxidized radionuclide species were present in roughly equal concentrations (Crawford, 2010). These transition points were then used to evaluate the potential for a change in the redox state of the radionuclides during evolution of the system chemistry (Crawford, 2010; Salas et al., 2010). Crawford (2010) determined that, with the exception of U, the modelled changes in redox were insufficient to result in a change in oxidation state for the redox sensitive elements (Crawford, 2010). Citing the sensitivity and associated uncertainty of U speciation with respect to modelled redox conditions and carbonate concentration in the Forsmark groundwaters, K_d pdfs representing reduced as well as oxidized species of U were propagated for use in transport modelling for temperate and glacial periods (SKB, 2010b).

2.3.6. Selection of data

Crawford (2010) utilizes the results of sorption experiments conducted at Forsmark (Selnert et al, 2008) and Laxemar (Selnert et al., 2009a) whenever possible. The data are grouped by the water types used in the experiments, but are not filtered or excluded based on other factors. For instance, although the sorption data appear to exhibit a time-dependent trend of increasing sorption magnitudes with increasing contact times, Crawford (2010) notes that the cause of the time-dependent sorption behaviour is not clear. The behaviour is not fully compatible with simple models of diffusive uptake (Selnert et al., 2008; Crawford, 2010). Other factors, such as changes in the experimental solution compositions (observed), ion-exchange and surface complexation kinetic effects, and weathering of the rock samples in solution, are also possible contributors to the trend but cannot be accounted for given the data available from the experiments (Crawford, 2010). Since the time-dependent variance appears relatively small when compared to the overall variations in results, Crawford (2010) concludes that excluding or filtering data based on time is not warranted. Similarly, because the data are corrected for sorption differences due to variations in grain size, all data are used and equally weighted in that regard (Crawford, 2010). The number of available experiments is deemed adequate for reasonable statistical representation of uncertainty and variability, so except for the assumption that all experimentally derived data could be adequately interpreted using log-normal distributions, no additional transformations are made to adjust the mean values or uncertainty terms (Crawford, 2010).

For data derived from the open literature, specific methods are used to compensate for small sample sizes in order to establish more reasonable uncertainty bounds (Crawford, 2010, Appendix C). The methods are based on a statistical resampling of data created by estimating probability distributions from the original data (Crawford, 2010). Essentially, each sorption data value, in terms of %-sorbed ($S\%$) with an associated error term (± $S\%$), is recast as a beta distribution using the method of moments to estimate the beta distribution parameters (Crawford, 2010; NIST, 2014). The estimation is accomplished using the equations

$$\alpha = S\left(\frac{S(1-S)}{\sigma_S^2} - 1\right) \qquad \text{Eq. 9}$$

$$\beta = (1-S)\left(\frac{S(1-S)}{\sigma_S^2} - 1\right) \qquad \text{Eq. 10}$$

where α and β are the beta distribution parameters, S is the normalized sorption percentage (i.e., 99% = 0.99), and σ^2 is the normalized variance of S. The resulting beta distribution values are converted to R_d values using the equation

$$R_d = \frac{S\%}{(100-S\%)} \times \frac{V}{m} \qquad \text{Eq. 11}$$

where $S\%$ is the sorption entered as a percentage, m is the mass and V is the volume used in the sorption experiment. The calculated R_d values are fit using a log-normal distribution, corrected using f_M and f_{CEC}, and the resulting geometric mean and standard deviation are used (combined) to create a combined pdf for all the data points. The combined pdf (which now represents all the data from experiments on a given sample and water type) is merged with pdfs from other experiment sets to generate a final assembled pdf that represents the total amount of data and associated uncertainty. This is the pdf that is used for the K_d value recommendation. A detailed review of the calculations involved in the resampling procedure is provided in Appendix B of this report.

2.3.7. Individual element processing

Since this review focused on the development of K_d values and pdfs for five radioelements, the specific data and methods used for each are summarized in the following paragraphs.

Caesium (Cs) data were assembled from the sorption data collected in the Forsmark and Laxemar laboratory tests (Crawford, 2010). The data were processed to correct for surface area differences (f_A, f_M) and a CEC correction (f_{CEC}) was applied. The data were then corrected for chemistry differences (f_{CHEM}) using the Forsmark marine water as the application water type.

Radium data were assembled from the Forsmark and Laxemar experimental program results (Crawford, 2010). They were processed similar to the Cs data (i.e., all transfer factors applied) to produce the final recommended K_d values and pdf. Data from external sources (e.g.,Kulmala and Hakanen, 1995; Hiutti et al., 1996) were used as a comparison and verification of the results but were not included directly in the K_d value development.

Plutonium data were assembled from the data of Hiutti et al. (1996) and Kulmala et al. (1998) (Crawford, 2010). The data were processed to generate new re-sampled pdfs and an eventual combined pdf. The data were corrected for surface area (f_A, f_M) and CEC (f_{CEC}). Crawford (2010) conducted an analysis of expected Pu speciation for the projected geochemical conditions of the repository area over time to assess the proper redox state to use in the K_d value recommendations. The analytical and modelling results indicated that Pu would be in a reduced form as Pu (III or IV). In an effort to select a pessimistic K_d value, Pu (III) was assumed and the analyses of Am(III) sorption data were used to determine the K_d values and pdf. The Pu data were then used as an analogue for Np(IV), U(IV), Tc(IV, and Th(IV) (Crawford, 2010).

Neptunium data from the Forsmark and Laxemar sorption experiments were used to generate K_d values for Np(V). Since the geochemical analyses indicated that Np would most likely remain as Np(IV), and since Np(IV) data were not available from the site-specific program, data for Pu(IV) from Hiutti et al. (1996) and Kulmala et al. (1998) were used as analogues (Crawford, 2010). Although some data were available in Hiutti et al.(1996) for Np(IV), these were not used.

Uranium data from the Forsmark and Laxemar sorption experiments were used to generate K_d values for U(VI). The data were corrected for surface area (f_A, f_M) and CEC (f_{CEC}). Crawford's (2010) geochemical analyses indicated that the predicted variation in redox for the Forsmark repository area could produce conditions where U might exist in U(VI) form, although it most likely would remain in U(IV) form. Both U(IV) and U(VI) K_d pdfs were forwarded for use in the transport modelling program (Crawford, 2010) Since U(IV) data were not available from the site-specific program, data for Pu(IV) from Hiutti et al. (1996) and Kulmala et al. (1998) were used as analogues (Crawford, 2010). The U(VI) data were used to develop recommended U(VI) K_d values and associated pdf, which were used in sensitivity analyses for the SR-Ste performance assessment (SKB, 2010b).

2.4. Technical Review of K_d Probability Distribution Functions

The reviewer finds that the technical bases and methods used for the development of K_d values and K_d pdfs used in the SR-Site performance assessment are, for the most part, thoroughly and clearly presented in Crawford (2010). When combined with other technical documents supporting SKB's Forsmark application (e.g., SKB, 2010a; 2010b; 2010c), the technical and conceptual assumptions and considerations regarding the use of a K_d-based model for radionuclide retardation are adequately presented and discussed.

The available sorption data generated from the laboratory experimental program (Selnert et al., 2008; 2009a) are used whenever possible (Crawford, 2010). Although the final chemical conditions of the sorption experiments were not equivalent to any predicted or measured site conditions, some of the data, especially for radioelements that sorb primarily through ion exchange, were suitable for use. Crawford (2010) recognized the lack of site-specific sorption data for redox sensitive radioelements and appropriately selected data from open literature sources to provide the technical bases for K_d value selections for those elements. The most relevant data available are limited, however, and there are no described attempts to utilize other data sources to support K_d value selection (Crawford, 2010). Omitting other sources of data collected for widely varying substrates may be reasonable, since converting data for use often requires the incorporation of several assumptions and uncertainties that may result in values that are not valid for the application.

The reviewer finds that reliance on sorption data collected for one radioelement (Pu) to represent the sorption of several radioelements (Np, Tc, Th, and U) is a concern and highlights a potentially significant data gap remaining in SKB's repository program. There are clear and known differences in the speciation and complexation behaviour of the individual actinides and Tc. Moreover, much of the available data [including those of Hiutti et al. (1996) and Kulmala et al. (1998)] are poorly constrained with respect to pCO_2, a complexing agent that has known impacts on sorption. Continued reliance on data not specific to the Forsmark site and/or not supported by thermodynamic modelling is inconsistent with a goal of presenting the best supported safety case. Efforts should be made to undertake additional experiments or modelling efforts to support and verify the recommended K_d values and pdfs for these +4 valence elements. It is important to note, however, that valid literature-derived data collected from sites with adequately similar mineralogy and chemistry may also be found to be acceptable for establishing a safety case.

SKB has appropriately supported assumptions about past and present reducing conditions in fracture groundwaters with a detailed characterization of groundwater chemistry (e.g., Salas et al., 2010; Laaksoharju et al., 2008a; 2008b; Sidborn et al., 2010; SKB, 2010a). SKB conceptual models incorporated the Forsmark hydrochemical data and used them for detailed interpretations, appropriately providing support for the development of the reference end-member water compositions (Salas et al., 2010; Laaksoharju et al., 2008a; 2008b; SKB, 2008). The end-member water compositions are important because they form the basis for the detailed modelling SKB used to examine future hydrochemical evolution of the site (Salas et al., 2010). The geochemical modelling included appropriately screened site data and reasonable assumptions to address uncertainties about the mixing-related precipitation and dissolution of specific mineral phases, and about hydrogeological characteristics of the Forsmark flow system characteristics. These data and results are appropriately incorporated into the development of the K_d values and K_d pdfs (Crawford, 2010). Crawford (2010) also incorporates data regarding the concentration and distribution of Ra and radon (Rn) to provide a reasonable assessment of the validity of the final selected K_d pdfs for the current SR-Site conditions. The calculations also demonstrate the likely positive influence on radioelement retention resulting from sorption on fracture lining mineral phases (Crawford, 2010).

2.4.1. Surface area corrections (f_A and f_M)

Correcting sorption data for the effects of varying specific surface areas of experimental samples is required for most applications and/or extrapolations of laboratory data to field conditions. The use of the N_2-BET method to determine specific surface area and the use of specific surface area as an analogue for available sorption sites are reasonable and are accepted methodologies in nearly all repository programs (e.g., DOE, 2008; Andra, 2005; Bradbury and Baeyens, 2003). Crawford (2010), as did Selnert et al. (2008) and Byegård et al. (2008) previously, notes that the effects on sorption due to use of different grain size fractions may not only be a function of surface area differences but may be caused by differing mineral exposure and/or differences in diffusive behaviour. The uncertainties in the actual sorption results unfortunately did not support the application of a complex model to assess surface area effects, and a simple model was used instead (Crawford, 2010).

Rather than use measured surface area values directly to condition their estimates of grain size effects and apply a surface area correction, Crawford (2010) and Selnert et al. (2008) use a theoretical relationship that estimates surface area on the basis of the grain size of samples. Crawford (2010) uses a median grain size based on a particle distribution model (see Equation 5) to calculate the f_A. Crawford (2010) acknowledges this assumption tends to over-predict the correction needed for R_d^0. Unfortunately, this methodology appears to significantly overestimate the impacts of grain size on surface area, especially for smaller grain sizes. A comparison is made in Table 2.1.3-1 where the f_A correction ratio used for specific surface areas for the finest size fraction (0.063–0.125) is much higher (4 to 11 times) than the actual ratio of measured values for the Forsmark samples. Table 2.3.1-1 shows that use of the grain size-based f_A results in a significant overestimation of surface area for the smaller fractions.

A review of measured specific surface area data from other SKB sources suggests that the grain size estimation does not correspond well to the trend in measured data (Table 2.4.1-1). Table 2.4.1-1 displays specific surface data for Forsmark reference rock samples from several sources (Selnert et al., 2008; Andre et al., 2009; Byegård et al., 1998; Crawford, 2010). The data are shown in Figure 2.4.1-1 along with surface area estimates using the model of Crawford (2010). An alternative model fit using the 2.0–4.0 and 0.063–0.125 mm average data from Selnert et al. (2008) and the same function-type that adequately describes the trend in the Crawford (2010) model produces estimated surface area values that are much more consistent with those measured for site-specific materials (see Table 2.3.1-1). Note that the data from Byegård et al. (1998) and Andre et al. (2009) were not used in the alternate model, but they are well represented by the trend. Moreover, the Äspö diorite surface area measurements are similar to those of the Forsmark rocks. Data for the Äspö diorite is used by Crawford (2010) to estimate selectivity coefficients in the ion-exchange model. In short, the f_A correction used by Crawford (2010) clearly over estimates the relative surface area contribution by the crushed samples and thus produces a corrected R_d^0 that is likely too low.

Table 2.4.1-1. Comparison of measured surface areas for Forsmark and related rocks with those calculated using the f_A correction of Crawford (2010). The data are plotted in Figure 2.4.1-1. The Äspö rock is a diorite used in the ion-exchange model of Crawford (2010).

Source	Selnert et al., 2008	Selnert et al., 2008	Byegård et al., 1998	André et al., 2009			Selnert et al., 2008 average	Crawford, 2010
Borehole	KFM01A	KFM07A	Äspö	KFM02A	KFM02A	KFM07A		
Rock Type	101057	101057	N/A	101057	101057	101057	101057	101057
Equivalent dia. (mm)	Specific surface area (m^2/g)							
3.214	0.047	0.032	0.024				0.025	0.047
1.607			0.038	0.062	0.057	0.048		0.094
0.804				0.067	0.066			
0.402			0.077	0.092	0.075	0.063		0.376
0.201				0.132	0.12	0.109		
0.109			0.23					
0.103				0.205	0.191	0.165		
0.101	0.1635	0.2135					0.19	1.502
0.072			0.33					

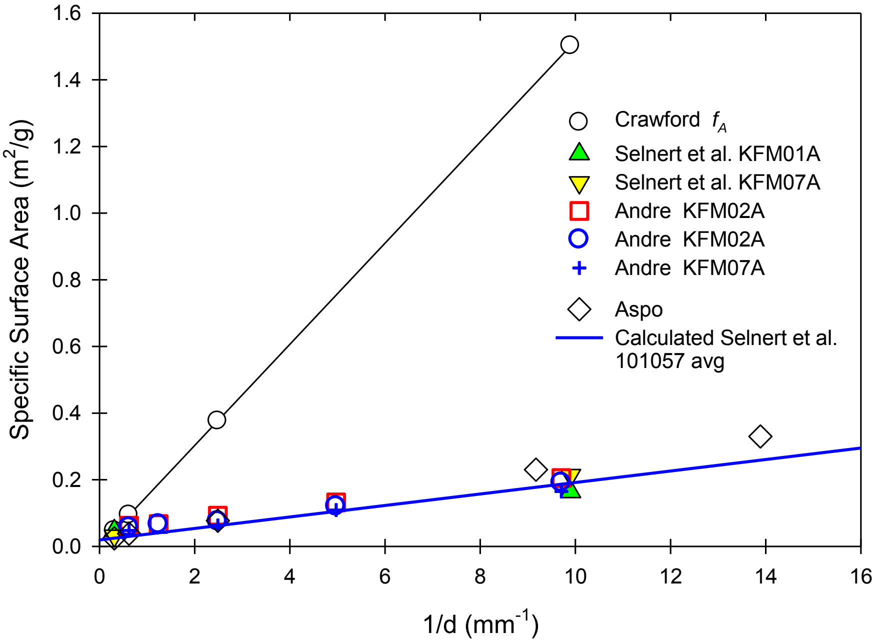

Figure 2.4.1-1. Comparison of measured surface areas for rocks from the Forsmark site and surface area estimates produced by the f_A correction used in Crawford (2010). An alternative model fit (blue line) representing the change in surface area with change in grain size is more consistent with measured data than the correction used by Crawford (2010).

For the mechanical damage correction factor (f_M), the reference standard (A_0) used is 0.018 ± 0.005 m^2/g, representing an average value for rock-type 101057 cores reported in Andre et al. (2009) (Crawford, 2010). This value overlaps with the 0.025 ± 0.015 m^2/g average measured surface area for all samples of the 2–4 mm size fraction of 101057-type rock reported in Selnert et al. (2008). The value also overlaps with the measured value (0.024 ± 0.012 m^2/g) for 101057-type core (Selnert et al., 2008). Laxemar rocks of the same size fraction had an average measured surface area of 0.025 ± 0.028 m^2/g, which is also quite similar to the average measured surface area of the 2–4 mm samples at Forsmark (Selnert et al., 2009a). While it seems reasonable to select a pessimistic surface area estimate for the *in situ* host rock given the difficulties and uncertainties in obtaining those values, it is unclear to the reviewer why an additional correction factor is needed. The f_M further reduces ("corrects") the measured R_d values when it appears that a one-time surface area normalization would suffice, and in any case, the range of f_M correction is only a factor from about 2 to 5. As applied, f_A and f_M corrections for rock samples of the 1–2 mm grain size fraction from borehole KFM01A at the 487-m depth (essentially, the host rock) reduce the measured R_d by a factor of 5 (2×2.63), whereas the actual surface areas differ by only a factor of 1.1. Similarly, for the 0.063–0.125 mm size fraction, the corrections reduce the R_d by a factor of 84 (32×2.63), while the actual surface area ratio is closer to 11. The f_M correction is needed for conversion of literature data, but its utility for the site-specific data is unclear.

An aspect of concern related to determination of the f_M is the presence of multiple apparent calculation errors. Closer inspection of the f_M summary Table 5-3 of Crawford (2010) (and reproduced here with check calculations as Table 2.3.2-1), reveals several apparent errors. With the exception of a few larger magnitude errors (shown in ***bold*** in Table 2.3.2-1) that might be attributed to typographic mistakes, there are multiple minor differences between the values produced by the check calculations and the values reported in Crawford (2010). These differences are minor, but they are associated with a standard calculation (conversion to $\log_{10}$) that is not uncertain. And since the f_M correction is small to begin with, they represent a larger component of error. It is confusing as to why the results are different than expected. The differences do not appear to be attributable to rounding. These types of errors also appear in the example table of transfer factor values associated with Ra sorption data conversion in Appendix C of Crawford (2010) (see Appendix A of this report for discussion). If these are indeed errors and have been carried through the K_d pdf development process, the magnitude and nature of the individual errors likely do not significantly change the recommended values or the results of the performance assessment. When taken together, however, errors such as these can erode confidence in the overall quality of results and lead to questions regarding the accuracy of more complex calculations (such as the f_{CHEM} transfer factor) for which there are substantially fewer transparent and traceable examples provided in SKB's technical reports.

2.4.2. f_{CEC} and f_{CHEM} corrections

Corrections for the differences in the CEC of the host rock and samples used in sorption experiments are made using the f_{CEC} transfer factor, and adjustments to account for potential changes in groundwater chemistry are made using the f_{CHEM} transfer factor. Like specific surface area, CEC is a physical property of the rock and is dependent on the rock mineral assemblage and how those minerals are exposed along rock surfaces. The f_{CHEM} factor, on the other hand, is a correction for the properties of the groundwater, and it is the only factor in which the effects on sorption of temporal and spatial variations in groundwater chemistry are applied.

The CEC's of the host rock and the rock samples used in the sorption experiments are potentially important because one of the main predicted contributors to dose at the Forsmark site, Ra, sorbs primarily through an ion exchange mechanism (SKB, 2010b; Crawford, 2010, Selnert et al., 2008). Crawford (2010) acknowledges the potential overlap in the measurement of surface area and CEC, and the two parameters are roughly correlated in the measurements (e.g., Selnert et al., 2008). There are adequate technical bases for development of the f_{CEC} parameter (Crawford (2010). Because the laboratory measurements of CEC exhibited larger than expected uncertainties, Crawford (2010) used the measured iron content of the Forsmark and Laxemar rocks to correct for CEC differences between them. The iron content values are presumably used because there are greater numbers of analyses available. Although it seems reasonable that CEC is related to biotite content (e.g., Drake et al., 2006), which is in turn related to iron content of the whole rock, there are no data or supporting information provided to support this claim. As is noted by Crawford (2010) in discussions regarding the f_{CHEM} parameter, exposed minerals and iron oxide surfaces can be occluded by precipitation films (armouring) of lesser sorbing minerals. This may be an important process in silica-rich environments such as the Forsmark site (Penn et al., 2001), but there is no discussion of why this process would not impact CEC. Crawford (2010) used the mean and standard deviation of the Forsmark and Laxemar iron content data to estimate and calculate a beta distribution, but the estimation method is not described. It is assumed Crawford (2010) used the method of moments described in his Appendix C. Additionally, there is no information provided to indicate the actual beta distribution parameters or value of iron content selected for the site-specific rock, so it is difficult to verify and trace the f_{CEC} distribution calculations. In the end, the CEC correction employed for the Laxemar rocks appears to be reasonable given that measured CEC values for the Laxemar rocks do indeed exceed those of the Forsmark rocks by an average factor of ~1.2–1.5 (Selnert et al., 2009), whereas the mean CEC correction used by Crawford (2010) has a factor of ~1.6. For sorption data from other sources, Crawford (2010) uses an estimated CEC value for the host rock and the measured CEC of the sample rock, if available.

Unfortunately, like the examples shown for f_M, calculation checks of f_{CEC} conversions reveal several discrepancies in the values listed in Crawford (2010). For example, the $\log_{10} f_{CEC}$ reported in Appendix C, Table C-1 for Kivetty porphyritic granodiorite is −1.04; however, using the CEC values provided in Table M-1 and Section 5.1 of Crawford (2010) the calculated $\log_{10} f_{CEC}$ is −0.89, as shown below:

$$f_{CEC} = \frac{CEC_0}{CEC_{ref}} = \frac{1\ \mathrm{cmol/kg}}{7.7\ \mathrm{cmol/kg}} = 0.13$$

$$\log_{10}(0.13) = -0.89 \neq -1.04$$

The cause of the discrepancy is unclear, but this example is indicative of similar discrepancies and/or errors observed for other calculations of $\log_{10} f_{CEC}$ and $\log_{10} f_M$. Additional examples of these types of errors are shown in Table A-2 and Tables B-5 and B-6 of this report. The particular K_d values for the Kivetty rocks were used only as a comparison to the K_d values developed for Ra for the Forsmark rocks (which were derived from the site-specific data), so any propagated errors are not incorporated directly into the SR-Site performance assessment. However, the

Kivetty data and associated transfer function errors are incorporated into the development of Pu K_d values. Review of the recommended K_d pdf for Pu indicates that the errors have an effect but that it is likely negligible in terms of performance (see Appendix B of this report).

Of the four transfer factors, calculation of the f_{CHEM} transfer factor is the most complex. Calculation of f_{CHEM} relies on an ion exchange model populated with estimates of selectivity coefficients for important components, such as Ra, and sampling of a generated, theoretical K_d pdf based on the ion exchange model (Crawford, 2010). Neither details of the model nor examples of input files for the PHREEQC calculations (Parkhurst and Appelo, 1999) are provided for review. Results of the f_{CHEM} calculations and sensitivity analyses for the model input parameters are plotted in graphical form, but there is no information to check or verify the $K_{d(app)}$ or $K_{d(ref)}$ values (see Equation 8) used to calculate f_{CHEM}, nor is there a plot of the f_{CHEM} distribution. As such, the f_{CHEM} values, and by extension associated final K_d values, cannot be independently calculated or checked with the information provided in any of the technical documents reviewed. Based on inspection of the graphs, however, Crawford’s (2010) calculated values for f_{CHEM} appear to be quite reasonable and are consistent with expectations of the influences of ionic strength on sorption. Part of this success is facilitated by use of a relatively simple ion exchange model that does incorporate estimates of background concentrations of the radioelements modeled and the extensive and well-supported geochemical characterization and modeling used for the groundwater chemistry variation of the Forsmark site (Laaksoharju et al., 2008a; 2008b; Gimeno et al., 2008; Salas et al., 2010). Plots of the results of final calculated K_d values versus predicted ionic strength values for future times [e.g., Figures E-5 through E-8, in Appendix E of Crawford (2010)] are particularly promising. Not only do the final corrected K_d values track with predicted changes in ionic strength in a manner consistent with the experiments, but the calculated K_d values confirm, at least for Cs and Ra, that the experimental results (those not used in the model calculation) are valid (Crawford, 2010, Appendices E and M). The reviewer realizes that the experimental data on these plots were intended to provide confidence in the ion-exchange and f_{CHEM} model as applied by Crawford (2010), but the conditions of the experiments were not similar to the Forsmark site in terms of pH and pCO_2. Thus the results also help to confirm the usefulness of the experimental data for ion exchangers.

2.4.3. Selection of data

SKB’s reliance on as much of the experimental data as is possible is a good approach. Crawford (2010) has elected to include most of the data without filtering for differences in size fractions or length of experiments. The use of data for all size fractions is acceptable, particularly in light of the carefully considered corrections for potential surface area and CEC differences (Crawford, 2010). Use of the data without filtering with respect to time is acceptable but ignores obvious kinetics effects with respect to sorption at early times. These effect are apparent and expected. Numerous other studies of radioelement sorption present information to suggest that at least 7 and as many as 30 days are needed to achieve equilibrium with respect to sorption (e.g., Bertetti et al., 1998; Pabalan et al., 1998). The continued change in measured sorption at longer times is more difficult to explain but the relative changes in sorption are small at the longer times (>30 days) (Selnert et al., 2008). The net effect of using the early sampling data is to bias the results downward to lower average K_d values.

Use of the data from the Finnish program (e.g., Hiutti et al., 1996; Kulmala and Hakanen, 1995; Kumala et al., 1998) is reasonable given the similarities in the rock types and generally similar water chemistries. It is important to note, however, that the Finnish experimental data also have uncertainties with respect to pH and pCO_2 control. Uncertainties are estimated for single measurement points and are propagated rigorously through the data correction process for data derived from literature sources (Crawford, 2010). The application of this process is commendable in that uncertainties are often not carried forward, but it is difficult to know if the carefully calculated uncertainties, which add to the total variance in the data, are potentially misleading. The statistical manipulations are reasonable, but it is difficult to argue that the resulting uncertainty distribution is anything more than an estimate. Crawford (2010) acknowledges this limitation, but this added uncertainty for the developed distributions will continue to be an issue unless site-relevant sorption data for the actinides and Tc can be produced.

The calculations of propagated uncertainties are not presented in detail, and for the reviewer, the text is sometimes confusing. For example, Crawford often, but not always, uses 2σ error values for propagation, and 1σ values are always listed in tables and text. Moreover, the specific calculations of uncertainty are dependent on several factors and assumptions, yet there are no examples. The lack of example calculations makes it more difficult to assess the discrepancies between independently calculated uncertainties (e.g., Table 2.3.2-1 among many others) and those reported in Crawford (2010). These issues are discussed in more detail in Appendix A of this report. The uncertainties are not carried forward for site-specific data in the same manner because it was judged that this would be a small effect relative to the existing uncertainty/variation in the experiments (Crawford, 2010).

One concern noted in previous reviews (e.g., Randall, 2012) was that the recommended K_d pdfs may be too broad, and inspection of the data reveals the spread of the experiments are within the tails of the recommended K_d pdfs (e.g., Figure M-9 of Crawford, 2010). However, the truncation of the K_d pdfs at 2.5% and 97.5% values, in addition to the pessimistic approach in correcting experimental sorption values, suggests that the potential for risk dilution is minimal. Additionally, the neglect of including fracture minerals in the K_d assessment may be balanced by the small extension of the pdfs at high K_ds relative to the experimental results.

The reviewer finds that the detailed presentation in Crawford is generally very good, but there are many discussions that make it difficult to see the real process and end results. For example, much work is spent to fit and process pdfs for each of the water types used in the experiments, but in the end only the data from the Forsmark marine composition is used to develop the final pdfs for Cs and Ra. This is not apparent initially. In fact, the reviewer found that the discussion of the most complex process (f_{CHEM} application) is the most difficult to extract from the text. Nonetheless, the development and use of f_{CHEM} is a valuable addition to Crawford's (2010) K_d value assessment. Not only does the factor aid in the understanding of the effects of water chemistry changes on the distribution of K_d values, but it provides a direct means to evaluate the experimental data for internal consistency. Additional work, such as that presented in Crawford (2013), should be considered to evaluate spatial effects on sorption of important nuclides.

Crawford (2010) discusses the potential for the actinides and Tc to be preferentially sorbed onto dark minerals, especially biotite. An attempt to incorporate this into the correction factors is made using the CEC, but the CEC measures were not particularly well-constrained (Selnert et al., 2008). It is recommended that a more extended analysis of the experimental samples be conducted to determine the differences, if any, in the extent of biotite on the surfaces of the samples. This seems like a more direct way of accounting for this effect. Moreover, in the case of actinides, the correction is mostly important for rocks that are not site-specific. This again highlights a need for some site-specific data. Also, the actual method used to combine the pdfs from individual data points is not described in detail. It appears that new pdfs are used to generate random data that is subsequently combined and fit, but it could also assumed that the central values (in $\log_{10}$ form) are averaged and the uncertainties propagated accordingly.

2.4.4. Recommended K_d values

Results for Cs sorption from the experimental program were useful for development of K_d values (Selnert et al., 2008; Crawford, 2010), and the recommended K_d values and pdfs are consistent with the data and analyses presented in Crawford (2010). Because it was one of the radioelements included in both the Level A and Level B experiments, there is a greater amount of data for Cs as compared to the other radioelements reviewed in detail in this report. The high solubility of Cs can result in dissolved concentrations where its sorption behaviour is non-linear. Crawford (2010) discusses this aspect and provides a reasonable basis for linear behaviour through the K_d range selected.

Like the data for Cs, the experimental data for Ra are useful for development of K_d values and the recommended K_d pdf (Selnert et al., 2008; Crawford, 2010). Although there are fewer data than for Cs, there is enough for the observed trends and values to be statistically significant. As with all the radioelements, the final K_d values are likely biased low, but comparison to experimental data after all corrections are applied indicates the Ra K_d pdfs are reasonable (Crawford, 2010). The analysis in Appendix B of Crawford (2010) is quite helpful in providing confidence in the final selected K_d pdf for Ra. Finally, as discussed in Section 2.4.2, some reported values in Crawford (2010) for transfer factor calculations associated with Ra sorption coefficients exhibit discrepancies when compared to independent check calculations (see Appendix A of this report).

The K_d pdf for Pu is a complex data manipulation process that is not well detailed for the amount of work involved. Like the creation of the beta distribution for the f_{CEC} parameter, there are no listed α or β scaling values for the beta distributions to provide for independent verification. Another issue is that it is difficult to understand just how the individual pdfs were combined. Detailed calculations attempting to reproduce the Pu K_d value development process are presented in Appendix B of this report. Unfortunately, after much examination and development of Pu data, these are not used directly for Pu K_d values. Instead, the Pu information is used as an analogue for the pdfs of Np, U, Th, and Tc (Crawford, 2010). Crawford's (2010) calculations to estimate redox conditions are appropriate

(McMurry and Bertetti, 2014). For Pu, speciation calculations suggest Pu(III) as the major valence state for SR-Site conditions (Crawford, 2010). This is based on the same thermodynamic data that Crawford (2010) argues is unsuitable for SCM assessment of Pu sorption. Use of Am(III) as an analogue seems inconsistent with the data at hand, given that the Hiutti et al. (1996) and Kulmala et al. (1998) data are collected under Eh conditions relevant to the SR-Site. The Finnish data are real, why eliminate them in favour of a theoretical construct for the sake of pessimistic choices?

The processing and development of the oxidized Np and U K_d values are reasonable and consistent with the experimental data (Crawford, 2010). Except for the sensitivity analysis of U(VI) conducted as part of the transport modelling (SKB, 2010b), the U and Np data are not used. Use of Pu(IV) sorption information as an analogue for U(IV) or Np(IV) may or may not be reasonable as there are no data or models presented to support the equivalence of sorption behaviour for these actinides. Certainly, U(VI) and Np(V) exhibit very different behaviours depending on solution chemical conditions (e,g., Bertetti et al., 2011). It is strongly recommended that some sort of verification experiments under relevant conditions be conducted.

3. Conclusions

The objectives of this review were to provide a comprehensive assessment of (i) the scientific bases for SKB's selection of K_d values for the geosphere surrounding a deep geologic repository at the Forsmark site and (ii) the data and methodologies employed to establish the probability distribution functions (pdfs) used in transport modelling. The review examined SKB's approach to the assessment and modelling of radionuclide sorption, including the methods and results of sorption experiments and the relevance of data derived from those experiments. The detailed review also examined the methods used to translate experimental data from SKB's program, as well as data derived from literature sources, into the set of K_d values. The transfer factors used to correct sorption data for surface area, mechanical damage, cation exchange capacity, and groundwater chemistry variations were reviewed in detail. The review considered data from a limited number of radioelements (Cs, Ra, Np, Pu, and U) that span a range of characteristics including sources of data, primary mechanisms of sorption, and importance to performance.

The review incorporated information from the technical documents used to develop the K_d values (Selnert et al., 2008; 2009a; Crawford, 2010) and multiple supporting or summary documents, from both SKB and the open literature, associated with radionuclide transport at the Forsmark site.

The reviewer found that SKB has conducted a carefully planned and extensive experimental program to support K_d value development (e.g., Selnert et al., 2008; 2009a) and has integrated data from that program into a rigorous and well documented technical report describing the development of the recommended K_d values and K_d pdfs for the SR-Site performance assessment (Crawford, 2010). Despite some technical gaps from the experimental studies, overall, the program has produced a set of technically defensible distribution coefficients that are likely to be conservative. Crawford (2010) substituted data from the literature to account for the site-specific experimental data gaps. The program as reviewed appears to have several areas in which improvements can be made. Additionally, the data gaps should be addressed as the licensing process moves forward. A summary of issues includes:

1. It is acknowledged that experiments to investigate sorption at geochemical conditions different from laboratory atmospheric conditions are extremely challenging. The SKB work was rigorously conducted and took years to complete. However, the net results of the extensive and carefully considered experimental program are that ***very little to no data were collected under conditions relevant to the repository site conditions***. Some examples of the experimental program deficiencies include:

    a. There were no measurements of solution compositions designed to assess the actual redox state of the experiments. As a result, the failure to achieve reducing conditions was not apparent to the investigators and the experiments were effectively conducted under oxidizing conditions (as indicated by the low sorption behavior of Np and U).

    b. The experimental design did not include control of pCO_2. As a result, there was significant pH drift during the course of the experiments and the final experimental conditions were effectively CO_2-free. This essentially produced sorption data for the actinides that were not useful to the program and that would not likely be technically defensible if used.

    c. The method of correction for experimental container wall adsorption likely resulted in incorrect estimates of wall sorption for most nuclides that sorb via a surface complexation mechanism.

    d. Fortunately, the drift of experimental chemistries away from site-relevant conditions had a minor impact on the utility of sorption data for radium, a primary radionuclide of interest for the SR-Site assessment.

2. The reviewer finds that the methodology used by Crawford (2010) to develop the pdfs for radionuclide K_d values is reasonable and likely produces a set of pessimistic values. Arguments can be made for and against the specific approaches and values used for the transfer factors, but changes to these would be unlikely to alter the proposed K_d values or pdf ranges in a manner that is significant to safety or the performance assessment results. Use of literature data relevant to the Forsmark site accounted for the lack of site-specific sorption data for redox sensitive radioelements, but the literature data also have uncertainties with respect to pCO_2.

3. The review finds that the methodology of Crawford (2010) is explained clearly but does not provide sufficient information to provide transparency in the application of certain transfer factors. It is not possible to reproduce values at each step because the correction values are not explicitly presented for each nuclide. This issue is exacerbated by the presence of many apparent calculation errors in Crawford et al. (2010). Although the

magnitude of the discrepancies is often small, the calculations are associated with well-defined functions and should not vary (for instance, the values of $\log_{10}$ conversions should be exact at the precision used in the SKB report). The number of errors erodes confidence in the process and the reported results.

4. The corrections incorporated as transfer factors often appear to be overly conservative, especially with respect to surface area corrections.

5. Crawford (2010) incorporated adequate consideration of the experimental uncertainties/gaps resulting from deficiencies in the experimental design, but the net effect is that most of the K_d values for redox sensitive radionuclides are derived from a rather small set of data from the literature.

6. SKB's general approach to development of K_d value pdfs and use of the K_d approach in performance assessment is reasonable and consistent with current approaches of other national waste repository programs. A primary weakness of the methodology as utilized is a lack of predictive capability regarding the timing(s) and actual magnitude(s) of potential releases from the repository to the environment. Further analyses consistent with what is done in Crawford (2013) are warranted.

7. SKB's considerable discussion of reasons to eschew surface complexation modelling (SCM) in support of K_d value development seems inconsistent with the vast amount of available geochemical data and characterization of the SR-Site. Ion-exchange and speciation models and calculations are used extensively in SKB's development of the technical bases for some K_d value selections. Use of SCMs could provide a significant tool for the validation of sensitivity analyses of temporal and spatial uncertainties (that is, the ranges of pdfs) incorporated into the proposed K_d values.

8. Regarding relevant comments made in previous reviews such as Technical Note 2012:63 (Randall, 2012), Technical Note 2012:55 (Little, et al., 2012), and the review by Stenhouse et al. (2008):

    a. The pdf ranges appear neither too wide nor too narrow for radionuclides whose sorption is governed primarily by ion-exchange. The range and distribution types as selected appear to adequately cover the range and variability of values as observed in experiments and as impacted by chemical changes. For most of the actinides, there is little or no assessment of the impact of the expected variations in pH or CO_2 at the SR-Site, so the proposed ranges remain uncertain.

    b. SKB documents contain more than adequate discussion and reasoning devoted to the assumptions, limitations, caveats, and considerations for implementing the linear K_d approach.

    c. Use of analogues to develop the K_d values and pdfs for redox sensitive actinides is a major weakness in SKB's development of K_d values. The lack of relevant experimental data is the primary limitation in this regard, but it is also impacted by a lack of utilization SCMs to develop insights.

Recommendations:

1. SSM should ask SKB to conduct limited surface complexation modelling to evaluate the sensitivity of the sorption of actinides to changes in pH and pCO_2. This would help to validate the proposed pdfs. The methods used by SKB to develop pdfs from the literature incorporated some uncertainties, but none that explicitly consider the very important impact of pH and pCO_2 variation on actinide sorption (especially for Np, Pu, and U). The net result of the modeling will not supply values for sorption because there are no site relevant data to check the models, but would provide insight into (i) the correlated or non-correlated sorption behavior of the nuclides, (ii) the impacts of assumptions associated with use of analogues, and (iii) the range of possible changes in sorption magnitudes resulting from spatial variations in groundwater chemistry.

2. SSM should strongly recommend that SKB conduct a limited set of sorption experiments under site-relevant conditions (or SSM should independently conduct these experiments). The experiments could be limited to one particular water type (for example, the marine type used as the baseline for K_d value selections) but should include variations in and control of pH and pCO_2. These experiments would be a critically needed confirmation of the adequacy of SKB's selected K_d values, which are currently based solely on literature data. Radioelements should include Tc, Np, and U (with Th and Pu as options, though neither is likely to be required).

4. REFERENCES

Alliot, I., C. Alliot, P.Vitorge, and M. Fattahi. 2009. "Speciation of Technetium(IV) in Bicarbonate Media". *Environ Sci Technol*, Vol. 43, pp. 9174-9182.

Andra. 2005. "Dossier 2005 Argile. Tome: Safety Evaluation of a Geological Repository." ANDRA Report Series. Châtenay-Malabry, France: Agence Nationale pour la gestion des Déchets Radioactifs.

André, M., M.E. Malmström, and I. Neretnieks. 2008. "Determination of sorption properties of intact rock samples: New methods based on electromigration." *Journal of Contaminant Hydrology*, Vol. 103, pp 71–81.

André, M., M.E. Malmström, and I. Neretnieks. 2009. "Specific surface area determinations on intact drillcores and evaluation of extrapolation methods for rock matrix surfaces." *Journal of Contaminant Hydrology*, vol. 110, pp. 1–8.

Bertetti, F.P., R.T. Pabalan, and M.G. Almendarez. 1998. "Studies of Neptunium^{V} Sorption on Quartz, Clinoptilolite, Montmorillonite, and α-alumina." *Adsorption of Metals by Geomedia*. E.A. Jenne, ed. New York City, New York: Academic Press, Inc. pp. 131–148.

Bertetti, F.P., R. Pabalan, D. Pickett, and R.T. Palaban. 2011. "Radionuclide Sorption Technical Assistance Activities at the Center for Nuclear Waste Regulatory

Analyses.” San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. Available at: http://adamswebsearch2.nrc.gov/webSearch2/main.jsp?AccessionNumber=ML112490545

Bechtel SAIC Company (BSC). 2005. “Saturated Zone Flow and Transport Model Abstraction.” MDL–NBS–HS–000021. Rev. 03. AD 01, AD 02, ERD 01. Las Vegas, Nevada: Bechtel SAIC Company, LLC. Available at: http://pbadupws.nrc.gov/docs/ML0908/ML090890567.html

Bradbury, M.H. and B. Baeyens. 2003. “Far-Field Sorption Data Bases for Performance Assessment of a High-Level Radioactive Waste Repository in an Undisturbed Opalinus Clay Host Rock.” Technical Report 02-19. National Cooperative for the Disposal of Radioactive Waste (NAGRA).

Brunauer, S., P. Emmet, and E. Teller. 1938. “Adsorption of gases in multimolecular layers.” *Journal of the American Chemical Society*, Vol. 60. pp 309–319.

Byegård, J., H. Johansson, M. Skålberg, and E-L. Tullborg. 1998. “The interaction of sorbing and non-sorbing tracers with different Äspö rock types. Sorption and diffusion experiments in the laboratory scale.” SKB TR-98-18, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Byegård, J., E. Selnert, E-L. Tullborg. 2008. “Bedrock transport properties. Data evaluation and retardation model. Site descriptive modelling, SDM-Site Forsmark.” SKB R-08-98, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Chapman, N.A. and I.G. McKinley. 1987. *The Geological Disposal of Nuclear Waste*. New York City, New York: John Wiley and Sons.

Coleman, H.W. and W.G. Steele. 1989. *Experimentation and Uncertainty Analysis for Engineers*. New York City, New York: John Wiley and Sons.

Crawford, J. 2010. “Bedrock K_d data and uncertainty assessment for application in SR-Site geosphere transport calculations.” SKB R-10-48. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Crawford , J. 2008. “Bedrock transport properties Forsmark. “Site descriptive modelling SDM-Site Forsmark.” SKB R-08-48, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Crawford, J., I. Neretnieks, and M. Malmström, M. 2006. “Data and uncertainty assessment for radionuclide Kd partitioning coefficients in granitic rock for use in SRT-Can calculations.” SKB R-06-75, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Drake, H., B. Sandström, and E-L. Tullborg. 2006. “Mineralogy and geochemistry of rocks and fracture fillings from Forsmark and Oskarshamn: Compilation of data for SR-Can.” SKB R-06-109, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Follin, S. 2008. “Bedrock hydrogeology Forsmark. Site descriptive modelling, SDM-Site Forsmark.” SKB R-08-95, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Gimeno, M.J., L.F. Auqué, J.B. Gómez, and P. Acero. 2008. “Water-rock interaction modelling and uncertainties of mixing modelling.” SKB R-08-86, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Huitti, T., M. Hakanen, and A. Lindberg, 1998. “Sorption of cesium on Olkiluoto mica gneiss, granodiorite and granite.” Posiva 98-11. Helsinki, Finland: Posiva Oy.

Huitti T, M. Hakanen, and A. Lindberg. 1996. “Sorption of cesium, radium, protactinium, uranium, neptunium, and plutonium on Rapakivi granite.” Posiva 96-23. Helsinki, Finland: Posiva Oy.

International Organization for Standardization (ISO). 1995. Soil quality — Determination of the potential cation exchange capacity and exchangeable cations using barium chloride solution buffered at pH = 8.1 (ISO 13536).

Ku, H.H. 1966. “Notes on the Use of Propagation of Error Formulas.” *Journal of Research of the National Bureau of Standards - C. Engineering and Instrumentation*, Vol. 70C, No.4, pp. 263–273. Available at: http://nistdigitalarchives.contentdm.oclc.org/cdm/compoundobject/collection/p13011coll6/id/78003/rec/5

Kulmala, S. and M. Hakanen. 1995. “Sorption of alkaline-earth elements Sr, Ba and Ra from groundwater on rocks from TVO investigation areas.” Report YJT-95-03. Nuclear Waste Commission of Finnish Power Companies.

Kulmala, S., M. Hakanen, and A. Lindberg. 1998. “Sorption of plutonium on rocks in groundwaters from Posiva investigation sites.” Posiva 98-12. Helsinki, Finland: Posiva Oy.

Laaksoharju, M., M. Gascoyne, and I. Gurban. 2008a. “Understanding groundwater chemistry using mixing models.” *Applied Geochemistry* (23), p. 1921-1940.

Laaksoharju, M., J. Smellie, E.-L. Tullborg, M. Gimeno, L. Hallbeck, J. Molinero, and N. Waber. 2008b. “Bedrock hydrogeochemistry Forsmark.” SKB R-08-47. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Little, R., P. Maul, P. Robinson, and C. Watson. 2012. “Review of SKB’s Radionuclide Transport Methodology.” Technical Note 2012:55, Stockholm, Sweden: Swedish Radiation Safety Authority (SSM).

National Institute of Standards and Technology (NIST). 2014. *NIST/SEMATECH e-Handbook of Statistical Methods*, http://www.itl.nist.gov/div898/handbook/, accessed March 10, 2014.

McMurry, J. and F.P. Bertetti. 2012. “Review of groundwater chemistry in SKB’s safety assessment SR–Site.” Technical Note 2012:33. Stockholm, Sweden: Swedish Radiation Safety Authority (SSM).

McMurry, J. and F.P. Bertetti. 2014. "Review of groundwater chemistry in SKB's safety assessment SR–Site." Technical Note 2012:33. Stockholm, Sweden: Swedish Radiation Safety Authority (SSM).

Pabalan, R.T., D.R. Turner, F.P. Bertetti, and J.D. Prikryl. 1998. "Uranium^{VI} Sorption onto Selected Mineral Surfaces." *Adsorption of Metals by Geomedia*. E.A. Jenne, ed. New York City, New York: Academic Press, Inc. pp. 99−130.

Painter, S., V. Cvetkovic, and D.R. Turner. 2001. Effect of Heterogeneity on Radionuclide Retardation in the Alluvial Aquifer Near Yucca Mountain, Nevada. *Groundwater*, vol. 39(3), pp. 326–338.

Parkhurst, D.L. and C.A.J. Appelo. 1999. "User's guide to PHREEQC (version 2): a computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculation." Water Resources Investigation Report 99-4259. Denver, Colorado: U.S. Geological Survey.

Penn, R.L., C. Zhu, H. Xu, and D.R. Veblen. 2001. Iron oxide coatings on sand grains from the Atlantic coastal plain: High-resolution transmission electron microscopy characterization. *Geology*, v. 29, no. 9. pp. 843–846.

Randall, M. 2012. "Review of Radionuclide Sorption on Bentonite and Forsmark Bedrock Material." Technical Note 2012:63, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Salas, J., M.J. Gimeno, L. Auqué, J. Molinero, J. Gómez, and I. Juárez. 2010. "SR-Site – hydrogeochemical evolution of the Forsmark site." SKB TR-10-58, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Sandström, B. and M.B. Stephens. 2009. "Mineralogy, geochemistry, porosity and redox properties of rocks from Forsmark. Compilation of data fom the regional model volume for SR-Site." SKB R-09-51, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Sandström, B., E.-L. Tullborg, J. Smellie, A.B. MacKenzie, and J. Suksi. 2008. "Fracture mineralogy of the Forsmark site." SKB R-08-102. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Selnert, E., J. Byegård and H. Widestrand. 2008. "Forsmark site investigation Laboratory measurements within the site investigation programme for the transport properties of the rock — Final report." SKB P-07-139, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Selnert, E., J. Byegård and H. Widestrand. 2009a. "Oskarshamn site investigation. Laboratory measurements within the site investigation programme for the transport properties of the rock — Final report." SKB P-07-179, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Selnert, E., J. Byegård, H. Widestrand, S. Carlsten, C. Döse, and E-L. Tullborg. 2009b. "Bedrock transport properties data evaluation and retardation model. Site descriptive modelling SDM-Site Laxemar." SKB R-08-100, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Sidborn, M., B. Sandström, E-L. Tullborg, J. Salas, F. Maia, A. Delos, J. Molinero, L. Hallbeck, and K. Pedersen. 2010. “SR-Site: Oxygen ingress in the rock at Forsmark during a glacial cycle.” SKB TR-10-57, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

SKB. 2011. “Long-term safety for the final repository for spent nuclear fuel at Forsmark: Main report of the SR-Site project.” SKB TR-11-01. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company (SKB).

SKB. 2010a. “Geosphere process report for the safety assessment SR-Site.” SKB TR-10-48. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company (SKB).

SKB. 2010b. “Radionuclide transport report for the safety assessment SR-Site.” SKB TR-10-50. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company (SKB).

SKB. 2010c. “Data report for the safety assessment SR-Site.” SKB TR-10-52. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company (SKB).

SKB. 2008. “Site description of Forsmark at completion of the site investigation phase.” SKB TR-08-05. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company (SKB).

Stenhouse, M., C. Jégou, P. Bown, G. Meinrath, H. Nitsche, and C. Ekberg. 2008. “Review of SR-Can: Evaluation of SKB’s handling of spent fuel performance, radionuclide chemistry and geosphere transport parameters.” SKI Report 2008:17. Stockholm, Sweden: Swedish Nuclear Power Inspectorate (SKI).

Turner, D.R., F.P. Bertetti, and R.T. Pabalan. 2002. “The Role of Radionuclide Sorption in High-Level Waste Performance Assessment: Approaches for the Abstraction of Detailed Models.” *Geochemistry of Soil Radionuclides*. P.-C. Zhang and P.V. Brady, eds. Special Publication 59. Madison, Wisconsin: Soil Science Society of America. pp. 211–252.

Turner, D.R., R.T. Pabalan, and F.P. Bertetti. 2006. “Applying Surface Complexation Modeling to Radionuclide Sorption.” *Surface Complexation Modeling*. F. Lützenkirchen, ed. Amsterdam: Elsevier, Ltd. pp. 553–604.

U.S. Department of Energy (DOE). 2008. DOE/RW–0573, “Safety Analysis Report Yucca Mountain Repository License Application.” Rev. 00. Las Vegas, Nevada: DOE, Office of Civilian Radioactive Waste Management. Available at: http://www.nrc.gov/waste/hlw-disposal/yucca-lic-app.html

White A. F., T.F. Bullen, M.S. Schulz, A.E. Blum, T.G. Huntington, and N.E. Peters. 2001. “Differential rates of feldspar weathering in granitic regoliths. *Geochim. Cosmochim. Acta*, Vol. 65 (6), pp. 847–869.

Widestrand, H., J. Byegård, Y. Ohlsson, and E-L. Tullborg. 2003. “Strategy for the use of laboratory methods in the site investigations programme for the transport properties of the rock." SKB R-03-20, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

Widestrand, H., J. Byegård, E. Selnert, M. Skålberg, S. Höglund, and E. Gustafsson. 2010. "Long Term Sorption Diffusion Experiment (LTDE-SD). Supporting laboratory program – Sorption diffusion experiments and rock material characterisation. With supplement of adsorption studies on intact rock samples from the Forsmark and Laxemar site investigations." R-10-66, Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.

5. Appendix A: Assessment and propagation of uncertainties

Crawford (2010) formally propagates uncertainties in measurement data through calculations for several transfer factors. The specific methods used in the uncertainty propagation are not presented in Crawford (2010) nor are examples of the calculations provided. However, Crawford (2010) does provide several tables that provide intermediate results of transfer factor calculations. The description of the uncertainty analyses is associated with various statements such as:

> "...area measurements of the crushed rock samples used in the site investigations were also based on small numbers of replicates, 2σ errors were propagated in the Gaussian error analysis as is standard laboratory practice for such small sample sizes." (Crawford, 2010, p. 66)
>
> "The error estimates for f_M are derived for 2σ errors using Gaussian error propagation." (Crawford, 2010, p. 67)
>
> "Since the transfer factors themselves are uncertain, the estimated errors of the transfer factors are propagated formally in the calculations using Gauss error propagation rules and assuming no correlation between f_M and f_{CEC}." (Crawford, 2010, p. 141)
>
> "Extrapolated K_d values and their uncertainties are obtained by Gauss error propagation in log space." (Crawford, 2010, p. 141)
>
> "In this report it is assumed that the uncertainty distribution for both the numerator and denominator of Equation 5-7 is log-normally distributed. This gives slightly more pessimistic mechanical transfer factors than if normal uncertainties were to be assumed." (Crawford, 2010, p. 66)
>
> "This was achieved using a re-sampling technique based on aggregation of the underlying uncertainty distributions for individual data points (assuming a Gaussian mixture model for uncertainty aggregation)." (Crawford, 2010, p. 78)

These statements of Crawford (2010) provide a substantial amount of additional information that it used in the uncertainty calculations. For instance, when errors are propagated, 2σ errors should be used. This typically requires doubling of the reported 1σ values provided in Crawford (2010). Assumption of log-normally distributed data implies that the mean values used for the transfer value calculations are geometric mean values and not arithmetic mean values. Another important aspect of uncertainty calculations is that the data reduction equation be solved for the experimental result before the uncertainty analysis is started (Coleman and Steele, 1989).

A general formula for the propagation of uncertainty for $Y = f(X, Z, \ldots)$, where Y is a function of one or more variables (X, Z, …), can be written as

$$\sigma_y = \sqrt{\left(\frac{\partial Y}{\partial X}\right)^2 \sigma_X^2 + \left(\frac{\partial Y}{\partial Z}\right)^2 \sigma_z^2 + \cdots + \left(\frac{\partial r}{\partial X}\right)\left(\frac{\partial y}{\partial Z}\right)\sigma_{zx}^2 + \cdots}$$

where σ_x, σ_y, and σ_z are the standard deviations of X, Y, and Z measurements, σ_{zx} is the estimated covariance between the X and Z measurements, and $\frac{\partial Y}{\partial X}$ is the partial derivative of the function Y with respect to X (NIST, 2014; Ku, 1966; Coleman and Steel, 1989).

When the variables are considered independent and uncorrelated we can write:

$$\sigma_y = \sqrt{\sum_{j=1}^{m} \left(\frac{\partial y}{\partial x_j} \sigma_{x_j} \right)^2}$$

which is commonly known as the Gaussian propagation of error form of the equation (NIST, 2014; Ku, 1966; Coleman and Steel, 1989).

Several examples from Crawford (2010) are provided to examine the uncertainty calculations. Table A-1 below is a subset (the first few rows) of Table 2.3.2-1 shown in the text of this report. The table reproduces data from Crawford (2010) and provides columns for the results of check calculations.

Table A-1. Extracted portion of Table 2.3.2-1.

Borehole (depth–m)	**A_{ref} (m^2/g)**	**f_m**	**Check f_m**	**log$_{10}f_m$**	**Check log$_{10}f_m$**
KFM01A (103)	0.024±0.022	0.74±1.39	0.75±1.42	0.14±0.56	***-0.13±0.82***†
KFM01A (487)	0.047±0.004	0.38±0.56	0.38***±0.22***†	-0.46±0.22	***-0.42±0.25***‡
KFM01A (908)	0.030±0.001	0.60±0.31	0.60±0.34	-0.27±0.21	***-0.22***±0.22†

Let us consider the calculation of uncertainty (or error as listed in the table) for the KFM01A, 487-m sample. Recall that the A_0 value for Forsmark host rock is 0.018±0.005 m^2/g and that

$$f_M = \frac{A_0}{A_{ref}}$$

The uncertainty in f_M is

$$\sigma_{f_M} = \sqrt{\left(\frac{\partial f_M}{\partial A_0} \sigma_{A_0} \right)^2 + \left(\frac{\partial f_M}{\partial A_{ref}} \sigma_{A_{ref}} \right)^2}$$

which equates to

$$\sigma_{f_M} = \sqrt{\left(\frac{1}{A_{ref0}} \right)^2 (0.005 \times 2)^2 + \left(-\frac{A_0}{A_{ref}^2} \right)^2 (0.004 \times 2)^2}$$

Dividing by f_M gives

$$\sigma_{f_M} = f_M \sqrt{\left(\frac{1}{A_0} \right)^2 (0.01)^2 + \left(-\frac{1}{A_{ref}} \right)^2 (0.008)^2}$$

$$\sigma_{f_M} = (0.38)\sqrt{\left(\frac{1}{0.018}\right)^2 (0.01)^2 + \left(-\frac{1}{0.047}\right)^2 (0.008)^2}$$

$$\sigma_{f_M} = (0.38)\sqrt{0.30864 + 0.02897} = (0.38)(0.58104)$$

$$\boldsymbol{\sigma_{f_M} = 0.22}$$

Thus, the calculated uncertainty in f_M is ±0.22. There is a discrepancy between the value calculated for sample 487-m as listed in the table and this value. A similar calculation for KFM01, 103-m sample produces an uncertainty of ±0.142, which is consistent within possible rounding errors with the original value in the table. It is important to note that the uncertainty value as calculated now represents the cumulative 2σ error, so in subsequent calculations it does not need to be doubled as was done when using the measurement uncertainties. The uncertainty in the $\log_{10} f_M$ can be calculated using

$$\sigma_{log10f_M} = \sqrt{\left(\frac{\partial f_M}{\partial f_M}\sigma_{f_M}\right)^2}$$

$$\sigma_{log10f_M} = \sqrt{\left(\frac{\sigma f_M}{f_M \ln(10)}\right)^2}$$

$$\sigma_{log10f_M} = \sqrt{\left(\frac{0.22}{(0.38)\ln(10)}\right)^2} = \mathbf{0.25}$$

Thus, the uncertainty in $\log_{10} f_M$ is ±0.25 when the uncertainty f_M in is ±0.22. This also implies that the uncertainty in f_M of ±0.56 listed for this sample may be a typographical error, because propagating that value through the uncertainty calculation produces a result of ±0.64, instead of the ±0.22 value reported in the table (Crawford, 2010).

Several of these calculations can be reviewed using some examples taken from Appendix K, Table K-2 of Crawford (2010) as shown in Table A-2. As can be seen in the table, there are numerous discrepancies (both in $\log_{10}$ and uncertainty) between the listed and the calculated values. The potential impact of these discrepancies is evaluated in Appendix B.

Table A-2. Comparison of selected reported values from Table K-2 (Crawford, 2010) and independent check calculations.

Rock Type	Reported surface area (m^2/g)	Reported CEC (cmol/kg)	Reported $\log_{10} f_M$	Calculated $\log_{10} f_M$	Reported $\log_{10} f_{CEC}$	Calculated $\log_{10} f_{CEC}$
Host₀	0.018±0.005	1±0.5				
OL1	0.95±0.01	1.5±0.4	−1.78±0.23	**−1.73±0.25**	−0.27±0.42	**−0.18±0.49**
Ro1A	0.28±0.01	1.8±0.4	−1.25±0.23	**−1.20±0.25**	−0.37±0.41	**−0.26±0.48**
Ki4A	0.21±0.01	1.2±0.4	−1.13±0.23	**−1.08±0.25**	−0.15±0.45	**−0.18±0.52**

6. Appendix B: Evaluation of the processing of literature-derived data

To complete the detailed review of the K_d value development process, the specific procedure for manipulation of literature data is verified with check calculations in this appendix. This verification focuses on two issues (i) an effort to reproduce the magnitude and general form of the K_d pdfs for individual experiments, and (ii) an effort to reproduce the final combined pdf as reported in Crawford (2010).

The verification and calculation check includes data for Ra and Pu, both of which are important to performance at the Forsmark site. Ra is a primary dose contributor based on transport modelling results, and Pu K_d values are used as analogues to determine the distributions for Np (and other actinides), which is also an important contributor to dose (SKB, 2010b). We begin with Ra, since Ra data are also used as the example in Appendix C of Crawford (2010).

Because of the relatively small sample size of relevant sorption data sets available from the open literature, Crawford (2010) developed procedures to help establish uncertainty bounds for the data. The procedures were based on statistical processing and resampling of the original data (Crawford, 2010). A detailed description of the resampling process is provided in Appendix C of Crawford (2010) and details of the processing for individual radioelements are provided in separate appendices (Appendix M for Ra and Appendix K for Pu; Crawford, 2010). As described, the data were processed as follows:

1. Each sorption data value, in terms of %-sorbed (*S%*) with an associated error term (± *S%*), is recast as a beta distribution using the method of moments to estimate the beta distribution parameters (Crawford, 2010; NIST, 2014). The estimation is accomplished using the equations

   $$\alpha = S\left(\frac{S(1-S)}{\sigma_S^2} - 1\right) \qquad \text{Eq. B-1}$$

   and

   $$\beta = (1-S)\left(\frac{S(1-S)}{\sigma_S^2} - 1\right) \qquad \text{Eq. B-2}$$

   where α and β are the beta distribution parameters, S is the normalized sorption percentage (i.e., 99% = 0.99), and σ^2 is the normalized variance of S.

2. The resulting beta distribution values are converted to R_d values using the equation

   $$R_d = \frac{S\%}{(100-S\%)} \times \frac{V}{m} \qquad \text{Eq. B-3}$$

   Where *S%* is the sorption entered as a percentage, *m* is the mass and *V* is the volume used in the sorption experiment. The *V/m* ratio is converted to appropriate units of m^3/kg. The literature data are in units of mL/g, so each value must be divided by a factor of 1000. Note that each value in the distribution is converted to an equivalent R_d. Completion of Steps 1 and 2 produces an equivalent R_d data set (or R_d^0 since no f_A transfer factor is needed for the literature data).

3. “After re-calculation of the individual R_d values and their uncertainty ranges, the raw data are then individually extrapolated to *in situ* conditions using the mechanical and CEC transfer factors.” And “…the estimated errors of the transfer factors are propagated formally in the calculations using Gauss error propagation rules and assuming no correlation…[t]he transfer factor corrections and the error calculations are carried out on the log-transformed R_d values” (Crawford 2010, Appendix C).

   This is interpreted to mean that the calculated R_d values are fit using a log-normal distribution (more specifically, a normal distribution fit to $\log_{10}$ transformed data) and corrected using f_M and f_{CEC}. The correction is applied by finding the mean and standard deviation of the log-normal fit and adding the $\log_{10}$ values of the transfer factors. Uncertainty is calculated similarly using the log transformed values. If the transfer factors are not applied by simple addition to the $\log_{10}\mu$ and $\log_{10}\sigma$ values of the distribution, the only way to add uncertainty is to process each value of the R_d distribution with a sampled value representing the range of each the transfer factor. Since this sampling/conversion method is not mentioned, the addition of $\log_{10}$ transfer function values is assumed. Completion of step 3 produces distributions in terms of K_d^0 for each experimental data point.

4. In the next step the pdf from the individual data points (now represented as log-normal distribution mean and standard deviation values) are combined into a composite distribution for a particular experiment.

   Crawford (2010) states combining the pdfs is “…achieved by random sampling of the individual K_d uncertainty distributions where the overall distribution is then obtained as the ensemble of resampled values” (Appendix C) and “…re-sampled assuming a convex combination of the underlying lognormal distributions, now including the additional uncertainty of the f_M and f_{CEC} transfer factors” (Appendix K).

   Thus, it appears that new model data is generated and resampled from the corrected individual data point distributions and then combined into one large data set (with equal weighting to all values). A log-normal distribution is fit to the combined data set to produce the combined experiment pdf. Completion of step 4 produces a distribution of K_d^0 values for each experiment.

5. The combined experiment pdf (which now represents all the data from an experiment on a given sample and water type) is merged with pdfs from other experiments to generate a final assembled pdf that represents the total amount of data and associated uncertainty. This is the pdf that is used for the K_d value recommendation. The final recommended K_d pdf is created by “pooling” the data sets or “aggregating the data sets together” (Crawford, 2010, Appendix C; Appendix K). For the site-specific data for radioelements to which f_{CHEM} is applied, this process is different. In those cases only the pdf for the experimental results from marine type water are used. The marine water K_d^0 pdf is then combined with the f_{CHEM} distribution to create the final K_d pdf.

   The aggregation of data sets implies that samples are again generated for the combined experiment distributions and then resampled to form another combined data set to which a log-normal distribution is fit to produce the μ and σ for the final recommended pdf. Completion of step 5 produces a cumulative K_d pdf. The f_{CHEM} transfer factor was not applied to the literature data.

6.1. Step 1–Recasting of sorption data points into beta distributions.

Using the summary data provided in Crawford (2010, Appendix C, Table C-1) and Equations B-1 and B-2, the beta distribution location parameters (α and β) were calculated. The results are provided in Table B-1. It is important to note that 1σ and not 2σ uncertainties must be used to generate the beta distributions. Use of 2σ values produces a pdf that has a much larger final σ than calculated by Crawford (2010) (Figure B-1).

Table B-1. Summary of independently calculated beta distribution location parameters using data from Crawford (2010, Appendix C, Table C-1).

Experiment Point	Sorption (%)	Sorption error (%)	Normalized sorption	Normalized error	α	β
1	98.3	1	0.983	0.01	163.286	2.77586
2	99.2	0.1	0.992	0.001	7871.52	62.9722
3	96.3	0.4	0.963	0.004	2143.58	79.3124
4	94.8	0.7	0.948	0.007	952.779	49.5445
5	89.0	0.5	0.890	0.005	3484.35	383.279
6	93.5	0.2	0.935	0.002	14205.2	923.339

6.2. Step 2–Conversion to R_d values

The beta distribution parameters were used to generate random samples (n=200) for each experimental data point. The sampled data were converted to R_d (m^3/kg) form using Equation B-3 and the *V/m* ratios listed in Crawford (2010, Appendix C, Table C-1). The ratios were converted from mL/g to m^3/kg. The results of the independently calculated R_d means and errors ($\log_{10}$ transformed) are listed in Table B-2 with the results of Crawford (2010). Since the generated data set is likely smaller than Crawford's (2010)[3], some variation is expected. Nonetheless, the values are quite close. This is illustrated graphically in Figures B-2 and B-3.

Rather than generate new sets of data from each probability distribution, a simpler methodology can be used and was tested. In this method, the uncertainty in each probability distribution is estimated using a combination of distribution mixture functions and the uncertainty propagation approach discussed in Appendix A. For this step, the $\log_{10}R_d$ is calculated directly from the individual sorption data point using Equation B-3, and the error is estimated directly by solving the uncertainty propagation equation for the datum.

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[3] Crawford (2010) states that "a large number of random deviates" were generated from the beta distributions but does not provide an actual value for the number of deviates. It is assumed that many more re-modeled data were generated than the 200 per distribution used for this review.

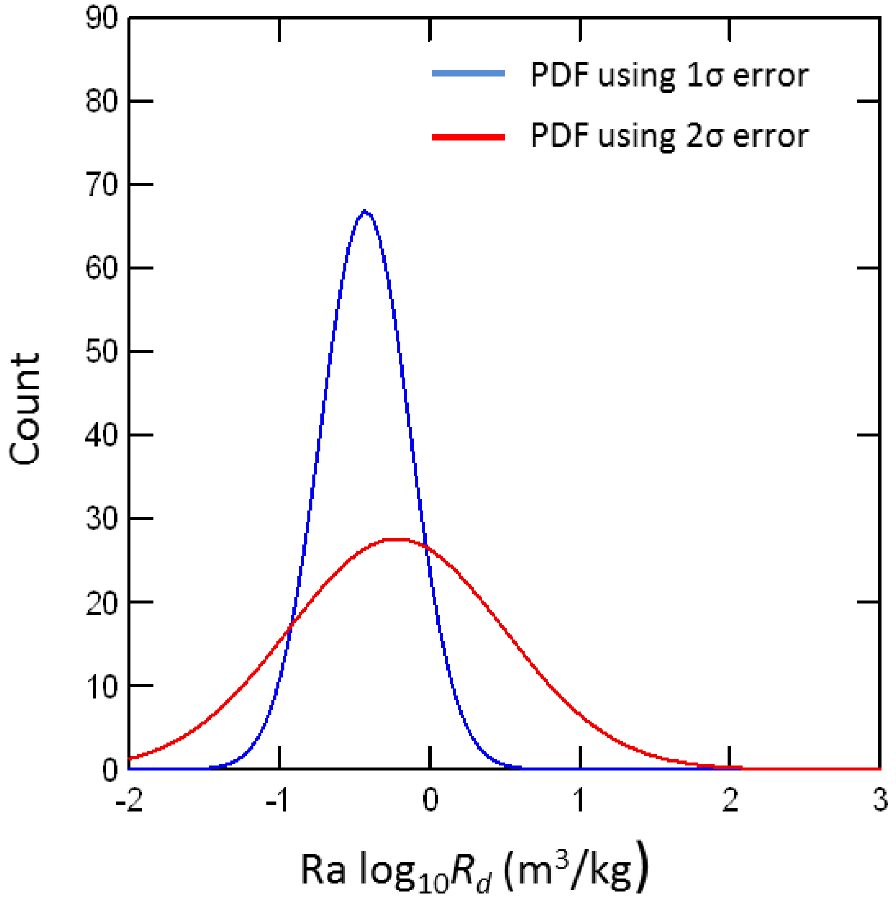

Figure B-1. Comparison of independently calculated $\log_{10}R_d$ pdfs for one Ra sorption experimental data point when using 1σ error or 2σ error to inform the generated beta distribution. The 1σ error pdf ($\log_{10}R_d$ μ = -0.429±0.3) is more consistent with results of Crawford (2010) for the same datum ($\log_{10}R_d$ μ = -0.459±0.3).

Table B-2. Summary of calculated $\log_{10}R_d$ μ and σ values from sampled beta distributions along with a comparison of the results to those of Crawford (2010).

Experiment Point	Calc. $\mathrm{Log}_{10}R_d$ (m^3/kg)	Calc. $\mathrm{Log}_{10}R_d$ error	Crawford calc. $\mathrm{Log}_{10}R_d$	Crawford calc. error	Alternate $\mathrm{Log}_{10}R_d$ (m^3/kg)	Alternate $\mathrm{Log}_{10}R_d$ error
1	-0.429	0.298	-0.459	0.285	-0.539	0.260
2	0.100	0.056	0.097	0.055	0.093	0.055
3	0.130	0.047	0.117	0.049	0.114	0.049
4	0.280	0.064	0.265	0.062	0.261	0.062
5	0.261	0.021	0.209	0.022	0.209	0.022
6	-0.812	0.015	-0.842	0.014	-0.842	0.014

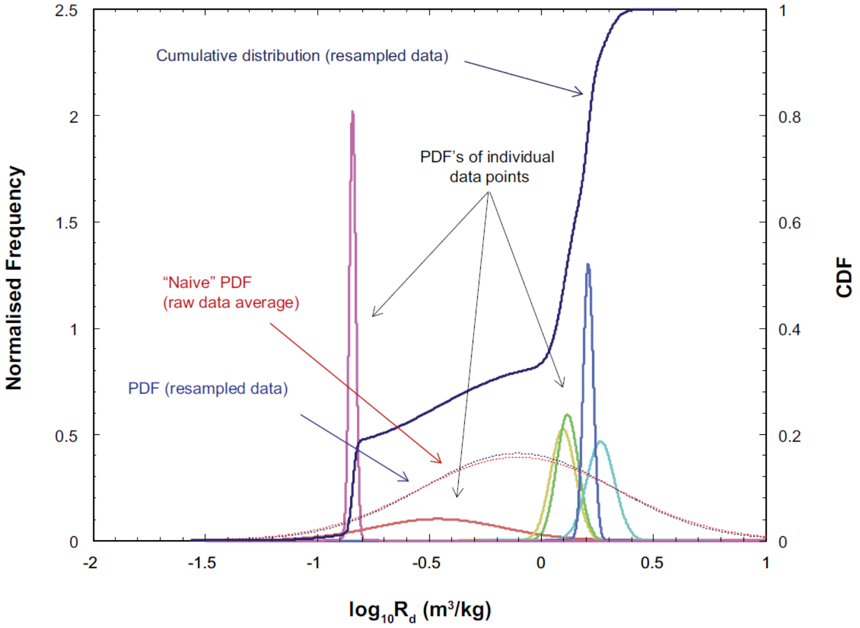

Figure B-2. Figure C-3 of Crawford (2010) showing the Ra R_d pdfs resulting from (i) resampling the beta distributions (individual data point pdfs), (ii) calculating log-normal parameters, and (iii) resampling the cumulative data from the log-normal distributions (resampled data pdf). Compare this output to the independently calculated pdfs in Figure B-3.

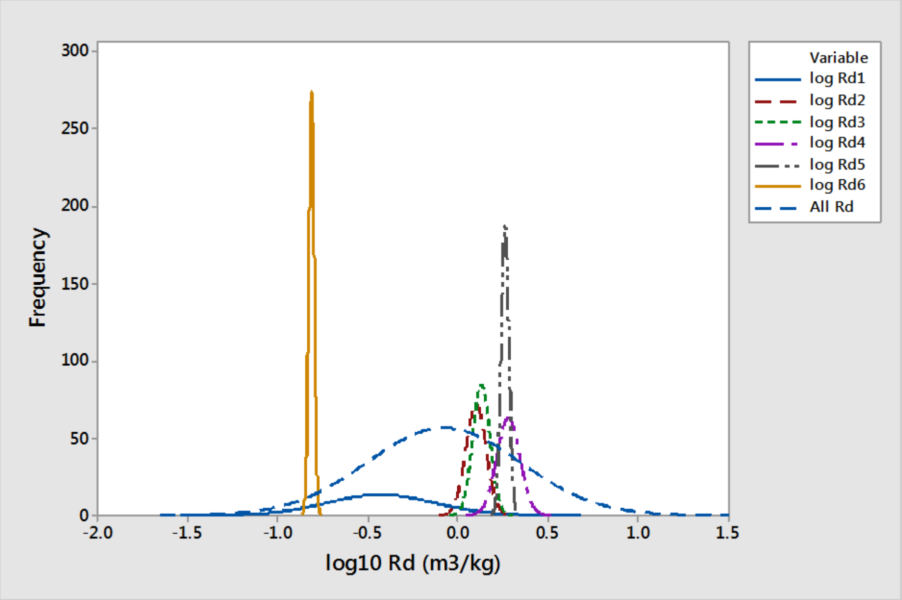

Figure B-3. Plot of independently calculated R_d pdfs representing Ra sorption on Kivetty rocks as listed in Table C-1 of Crawford (2010). Position and width of the pdfs are quite similar to those produced by Crawford (2010) for the same data (compare to Figure B-2).

For example, using Experimental Point 1 in Table B-1

$$log_{10}R_d = log_{10}\left[\left(\frac{98.3}{(100-98.3)}\right)\times\frac{5\ \text{mL}}{1\ \text{g}\times 1000\ \left({}^{\text{mL/g}}\big/_{\text{m}^3/\text{kg}}\right)}\right] = -0.539$$

Likewise, the error (uncertainty) is calculated using

$$\sigma_{log_{10}R_d} = \sqrt{\left(\frac{\partial log_{10}R_d}{\partial S}\right)^2 + (\sigma_S)^2}$$

$$\sigma_{log_{10}R_d} = \sqrt{\left(\frac{-43.4294}{(98.3-100)98.3}\right)^2 + (1)^2} = 0.260$$

Using this alternate calculation method, the predicted $\log_{10}$ μ and σ are reasonably close to the values produced by re-sampling the created probability distribution (Table B-2). In fact, the high uncertainty associated with Experimental Point 1 appears to be an exception as the remaining predicted values are quite close to the values predicted by Crawford (2010) and the independently re-sampled data.

6.3. Step 3 – Application of transfer factors

Once the sample $\log_{10}R_d$ μ and σ are generated for each data point, the data are corrected for specific surface area and CEC differences by applying the f_M and f_{CEC} transfer factors. The $\log_{10}f_M$ and $\log_{10}f_{CEC}$ for the example data set are provided by Crawford (2010, Appendix C, Table C-1). Multiplication of these factors (or addition of $\log_{10}$ transformed values) produces $\log_{10}K_d^0$ μ and σ for each Experimental Point. As is discussed in Sections 2.4.2 and Appendix A, there are numerous discrepancies in the reported values for $\log_{10}f_M$ and $\log_{10}f_{CEC}$ reported in Crawford (2010) as compared to those calculated independently. For this verification, the values found in Crawford (2010) are used. The uncertainties are propagated through the summations. Results of step 3 are shown in Table B-3. As can be seen in the table, the independently calculated $\log_{10}K_d^0$ values agree well with the values from Crawford (2010).

Table B-3. Comparison of independently calculated K_d^0 values with those of Crawford (2010).

Calculated $\log_{10}R_d$ (m^3/kg)	**$\log_{10}f_M$**	**$\log_{10}f_{CEC}$**	**Crawford $\log_{10}K_d^0$ (m^3/kg)**	**Calculated $\log_{10}K_d^0$ (m^3/kg)**
-0.429 ± 0.298	-2.1 ± 0.23	-1.04 ± 0.37	-3.59 ± 0.52	-3.569 ± 0.528
0.100 ± 0.056	-2.1 ± 0.23	-1.04 ± 0.37	-3.04 ± 0.43	-3.040 ± 0.439
0.130 ± 0.047	-2.1 ± 0.23	-1.04 ± 0.37	-3.02 ± 0.43	-3.010 ± 0.438
0.280 ± 0.064	-2.1 ± 0.23	-1.04 ± 0.37	-2.87 ± 0.43	-2.860 ± 0.440
0.261 ± 0.021	-2.1 ± 0.23	-1.04 ± 0.37	-2.93 ± 0.43	-2.879 ± 0.436
-0.812 ± 0.015	-1.06 ± 0.23	-1.04 ± 0.37	-2.93 ± 0.43	-2.912 ± 0.436

6.4. Step 4 – Creation of composite K_d^0 for one experiment (6 data points)

The $\log_{10}K_d^0$ μ and σ values produced in step 3 were used to randomly generate six log-normal distributions (actually, six normal distributions with log-transformed data). Each distribution was generated with 200 data points. All the data (1200 data points) were combined to form a composite distribution. Statistics for the combined data were computed to calculate a composite $\log_{10}K_d^0$ μ and σ for all the data in the example experiment. Crawford (2010) does not provide a data table with the final calculated K_d^0 values for the Ra example, nor are these values reported in the detailed Ra K_d development Appendix M. Instead, a graph illustrating the K_d^0 cumulative distribution is provided with a $\log_{10}$ scale (not $\log_{10}$ transformed) (Crawford, 2010). Therefore, the reported individual Experimental Point distribution location factors given in Crawford (2010, Appendix C, Table C-1) were used to randomly generate data for six log-normal distributions (n=200). These data were combined (n=1200) and $\log_{10}K_d^0$ μ and σ were calculated for the composite data set. The results are shown in Table B-4 and are illustrated in Figure B-4.

Table B-4. Comparison of independently calculated final K_d^0-values for Ra with those calculated from Crawford (2010) data.

Source	Calculated $\log_{10} K_d^0$ μ and σ (m^3/kg)	Mean K_d^0 (m^3/kg)
Fit of independent values	-3.03 ± 0.49	9.3×10^{-4}
Fit of Crawford values	-3.08 ± 0.51	8.3×10^{-4} (~7×10^{-4})†
Convex combination of Crawford values	-3.06 ± 0.51	8.7×10^{-4}
Convex combination of independent values	-3.04 ± 0.52	9.1×10^{-4}

† As estimated from Figure M-5 of Crawford (2010)

The alternative method of calculating the final K_d^0 pdf is also continued in this step. Instead of generating new random samples, the $\log_{10}$ μ and σ are used directly to calculate the combined pdf parameters. For example, a convex combination Z, of probability distributions X_i can be derived as a weighted sum (where the weights w_i, satisfy the constraints $w_i \geq 0$ and $w_1 + w_2 + \ldots + w_n = 1$) of its component probability distributions, with probability density function:

$$f_Z(x) = \sum_{i=1}^{n} w_i f_{X_i}(x) \qquad \text{Eq. B-4}$$

For a convex combination of univariate normal distributions with weights w_i, means μ_i, and variances σ_i^2, the total mean (μ) and variance (σ^2) will be

$$\mu = \sum_{i=1}^{n} w_i \mu_i \qquad \text{Eq. B-5}$$

and

$$\sigma^2 = \sum_{i=1}^{n} w_i((\mu_i - \mu)^2 + \sigma_i^2). \qquad \text{Eq. B-6}$$

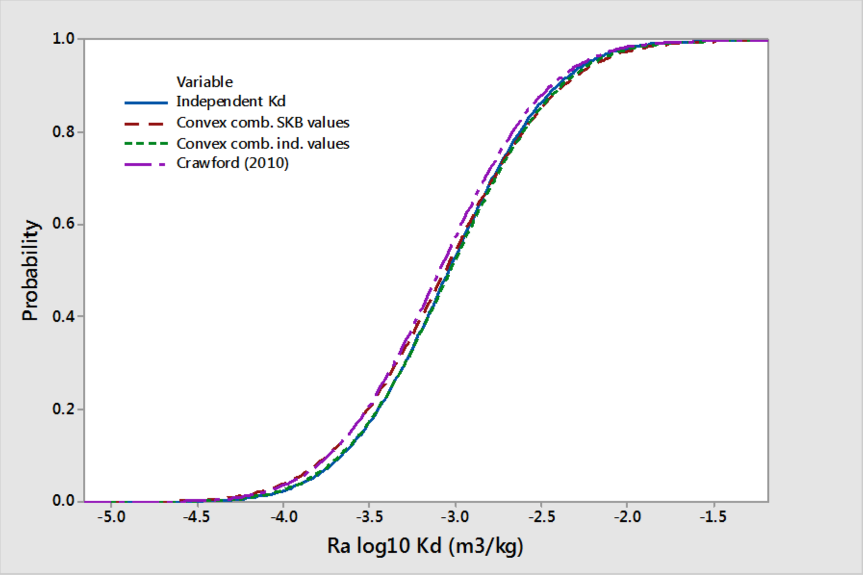

Figure B-4. Plot of Ra K_d^0 pdfs. The pdfs represent the combined K_d^0 pdf for the experimental data in Appendix C, Table C-1 of Crawford (2010). The pdfs were calculated using different methods. The independent K_d pdf was calculated using the original data, transfer factors presented in Crawford (2010), and the resampling method. The convex combination SKB pdf was calculated using the alternative methods described in Section B-6.4 and using transfer factors values provided in Crawford (2010), while the convex combination independent pdf utilized independently calculated transfer factors values. The independently calculated pdfs and the Ra pdf derived by Crawford (2010) are virtually indistinguishable.

Thus, the calculated K_d^0-pdf parameters listed in Table B-3 were processed using Equations B-5 and B-6 to derive estimated final composite $\log_{10}$ μ and σ values. The method was applied to both the independent data and the data provided by Crawford (2010, Appendix C, Table C-1). The results of these calculations are shown in Table B-4. The alternate method produces very similar results to the distribution resampling method of Crawford (2010). A graphical illustration is provided in Figure B-4.

6.5. Step 5 – Creation of final K_d by combining all experimental data (i.e., composite K_d^0 pdfs)

The calculation of the final K_d value is difficult to verify for those radioelements (such as Ra) that are further processed using the f_{CHEM} transfer factor. In any case, the combined K_d^0 pdf data for Ra are not presented in any form in Crawford (2010). The K_d value development for Pu, however, is completed by combining the K_d pdf data, and the final K_d cumulative distribution is presented in graphical form in Crawford (2010, Appendix K, Figure K-6). Calculations and distribution re-sampling of selected experiments were checked for Pu K_d-value development using Crawford's (2010) methodology. The results (not shown) are comparable to those reported in Crawford (2010). To facilitate a comprehensive examination, the original Pu sorption data under anoxic conditions from Hiutti et al. (1996) and Kulmala et al. (1998) were processed using the alternate methods discussed in sections B-6.2 and B-6.4 to produce final K_d values for Pu. Namely, the R_d pdfs were generated directly from the single experimental data points and the pdfs were then processed using the convex combination method (no resampling of data). In addition, the data were processed separately using f_M and f_{CEC} values that were provided in Crawford (2010) and values that were calculated independently to examine the effect of the noted discrepancies. The results are listed in Tables B-5, B-6, and B-7, and are illustrated in Figures B-5 and B-6.

Table B-5. Independently calculated K_d values for Pu under anoxic conditions using f_M and f_{CEC} values from Crawford (2010).

Sorption Expt.	Calculated $\log_{10}R_d$ (m^3/kg)	$\log_{10} f_M$	$\log_{10} f_{CEC}$	Calculated $\log_{10}R_d^0$ (m^3/kg)
Ol1	0.600 ± 0.45	-1.78 ± 0.23	-0.27 ± 0.42	-1.45 ± 0.44
Ol2A	0.331 ± 0.27	-1.15 ± 0.23	-0.44 ± 0.40	-1.26 ± 0.28
Ol2B	0.277 ± 0.33	-1.36 ± 0.23	-0.37 ± 0.41	-1.45 ± 0.33
Ro1A	-0.209 ± 0.20	-1.25 ± 0.23	-0.37 ± 0.41	-1.83 ± 0.26
Ro1B	-0.315 ± 0.19	-1.17± 0.23	-0.38 ± 0.39	-1.87 ± 0.24
Ro1C	0.039 ± 0.39	-1.06 ± 0.23	-0.20 ± 0.44	-1.22 ± 0.40
Ki4A	0.038 ± 0.31	-1.13 ± 0.23	-0.15 ± 0.45	-1.24 ± 0.35
Ki4B	-0.009 ± 0.27	-1.15 ± 0.23	-0.42 ± 0.37	-1.58 ± 0.26
YT5-1	-0.073 ± 0.68	-1.29 ± 0.23	-0.10 ± 0.43	-1.46 ± 0.69

Table B-6. Independently calculated K_d values for Pu under anoxic conditions using f_M and f_{CEC} values calculated independently.

Sorption Expt.	Calculated $\log_{10}R_d$ (m^3/kg)	$\log_{10} f_M$	$\log_{10} f_{CEC}$	Calculated $\log_{10}R_d^0$ (m^3/kg)
Ol1	0.600 ± 0.45	-1.73 ± 0.25	-0.18 ± 0.49	-1.31 ± 0.51
Ol2A	0.331 ± 0.27	-1.10 ± 0.25	-0.32 ± 0.46	-1.09 ± 0.35
Ol2B	0.277 ± 0.33	-1.31 ± 0.25	-0.26 ± 0.48	-1.29 ± 0.40
Ro1A	-0.209 ± 0.20	-1.20 ± 0.25	-0.26 ± 0.48	-1.67 ± 0.33
Ro1B	-0.315 ± 0.19	-1.12 ± 0.25	-0.26 ± 0.46	-1.69 ± 0.31
Ro1C	0.039 ± 0.39	-1.01 ± 0.25	-0.11 ± 0.51	-1.09 ± 0.48
Ki4A	0.038 ± 0.31	-1.08 ± 0.25	-0.08 ± 0.52	-1.12 ± 0.43
Ki4B	-0.009 ± 0.27	-1.10 ± 0.25	-0.28 ± 0.44	-1.38 ± 0.33
YT5-1	-0.073 ± 0.68	-1.25 ± 0.25	0.00 ± 0.50	-1.32 ± 0.76

Table B-7. Final calculated K_d values for Pu under anoxic conditions.

Source	Calculated $\log_{10}K_d$ (m^3/kg)	Mean K_d (m^3/kg)
Independently calculated using Crawford (2010) f_M and f_{CEC}	−1.49 ± 0.45	3.2×10^{-2}
Independently calculated using independent f_M and f_{CEC}	−1.33 ± 0.53	4.7×10^{-2}
Reported value in Crawford (2010)	−1.28 ± 0.65	5.2×10^{-2}

Independent calculation of the K_d values and K_d pdfs derived from literature data appears to verify the reasonableness of the approach and calculations used in Crawford (2010) (Figure B-7). The independent calculation final K_d pdf for Pu is quite similar to Crawford's (2010) final recommended Pu K_d pdf. Assessment of the influence of the apparent discrepancies in the reported f_M and f_{CEC} values results in calculated mean K_d values that differ by less than a factor of 4 (see Table B-7). Though these are different values, the difference is minimal with respect to the impact on performance assessment results. Thus the potential errors observed in Crawford (2010) likely have more of an impact on confidence in quality assurance and more complex calculations for which no verification can be made.

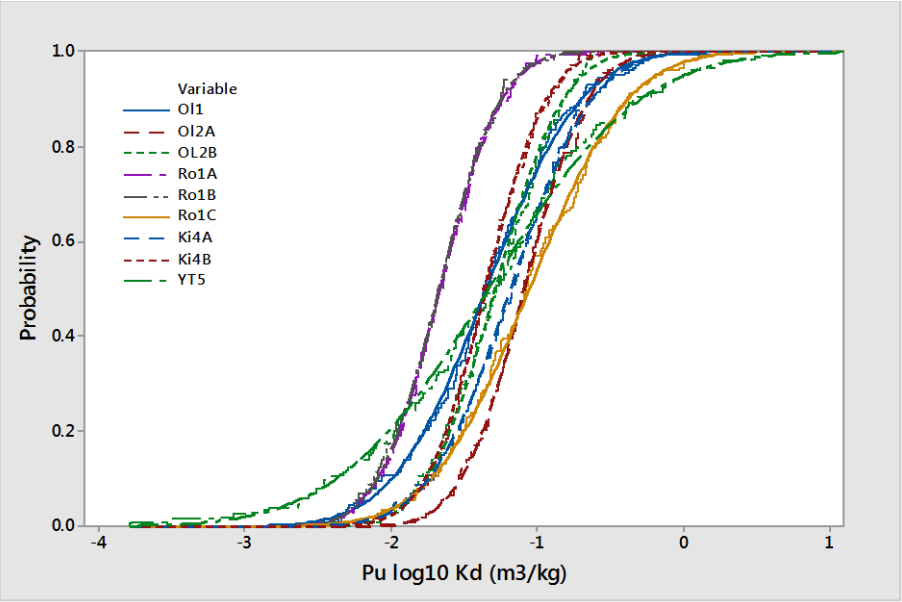

Figure B-5. Independently calculated combined empirical K_d^0 pdfs for the experiments used to develop Pu K_d values under anoxic conditions. The range and spread of the pdfs are similar to those calculated by Crawford (see Figure B-6).

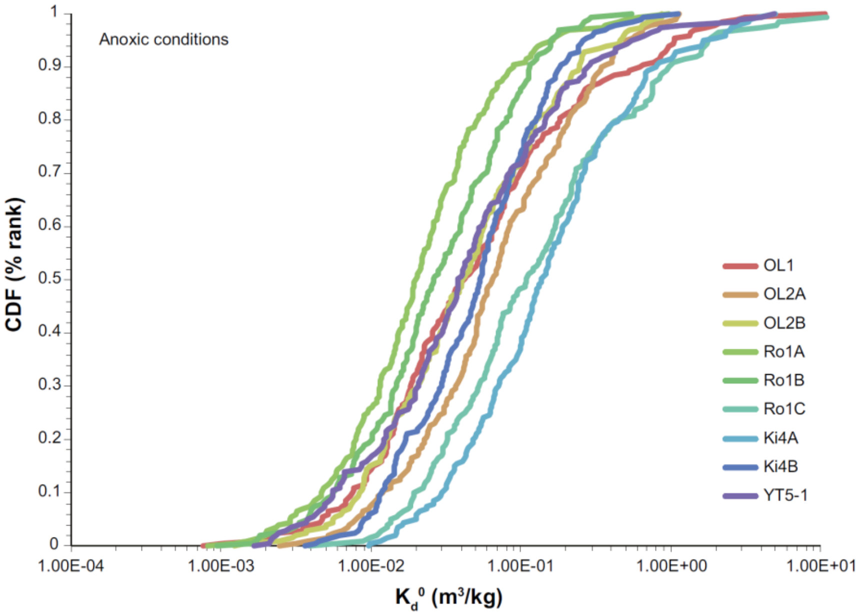

Figure B-6. Figure K-4 of Crawford (2010) showing the calculated combined K_d^0 pdfs for the experiments used to develop Pu K_d values under anoxic conditions. The range and spread of the pdfs are similar to those calculated independently (see Figure B-5).

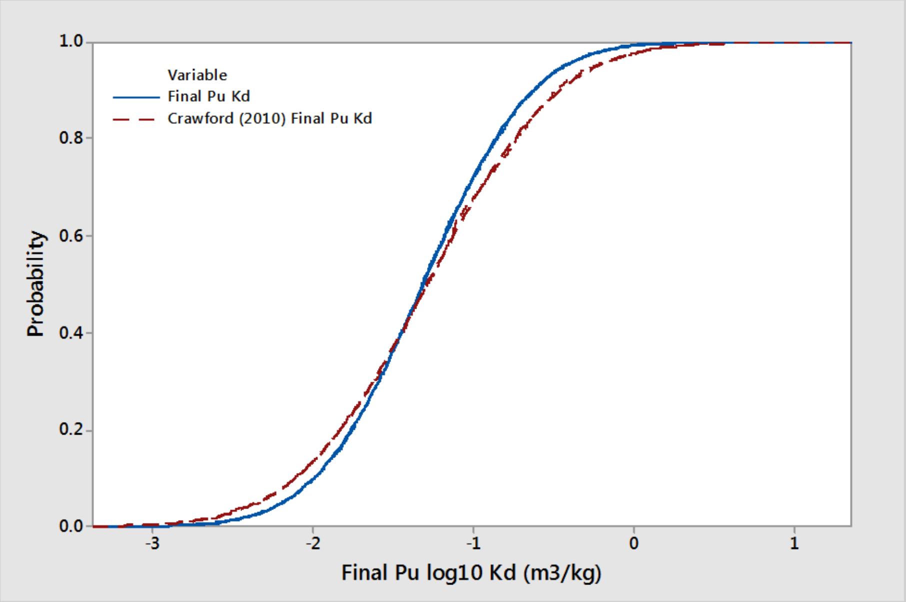

Figure B-7. Plot of independently calculated final Pu K_d pdf as compared to the final Pu K_d pdf derived by Crawford (2010). The $\log_{10}K_d$ μ and σ values are quite similar (see Table B-7). A slightly lower variance was calculated in the review using the convex combination method as opposed to the resampling method used by Crawford (2010).

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The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 315 employees with competencies in the fields of engineering, natural and behavioural sciences, law, economics and communications. We have received quality, environmental and working environment certification.

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