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# REVIEW OF THERMODYNAMIC AND ADSORPTION DATABASES

**Cementitious Barriers Partnership** 

November 2009 CBP-TR-2009-002-C8, Rev. 0

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### FOREWORD

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Waste Processing. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications.

A multi-disciplinary partnership of federal, academic, private sector, and international expertise has been formed to accomplish the project objective. In addition to the US DOE, the CBP partners are the United States Nuclear Regulatory Commission (NRC), the National Institute of Standards and Technology (NIST), the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) / Consortium for Risk Evaluation with Stakeholder Participation (CRESP), Energy Research Center of the Netherlands (ECN), and SIMCO Technologies, Inc.

The periods of cementitious performance being evaluated are >100 years for operating facilities and > 1000 years for waste management. The set of simulation tools and data developed under this project will be used to evaluate and predict the behavior of cementitious barriers used in nearsurface engineered waste disposal systems, e.g., waste forms, containment structures, entombments, and environmental remediation, including decontamination and decommissioning (D&D) activities. The simulation tools also will support analysis of structural concrete components of nuclear facilities (spent-fuel pools, dry spent-fuel storage units, and recycling facilities such as fuel fabrication, separations processes). Simulation parameters will be obtained from prior literature and will be experimentally measured under this project, as necessary, to demonstrate application of the simulation tools for three prototype applications (waste form in concrete vault, high-level waste tank grouting, and spent-fuel pool). Test methods and data needs to support use of the simulation tools for future applications will be defined.

The CBP project is a five-year effort focused on reducing the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will enable improved risk-informed, performance-based decision-making and support several of the strategic initiatives in the DOE Office of Environmental Management Engineering & Technology Roadmap. Those strategic initiatives include 1) enhanced tank closure processes; 2) enhanced stabilization technologies; 3) advanced predictive capabilities; 4) enhanced remediation methods; 5) adapted technologies for site-specific and complex-wide D&D applications; 6) improved SNF storage, stabilization and disposal preparation; 7) enhanced storage, monitoring and stabilization systems; and 8) enhanced long-term performance evaluation and monitoring.

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## LIST OF ABBREVIATIONS AND ACRONYMS

BRGM	Bureau de Recherches Géologiques et Minières
CBP	Cementitious Barriers Partnership
CD-MUSIC	Charge distribution multi-site competitive adsorption model
CEN	European Committee for Standardization
EN	European norm
GTLM	Generalized two layer model
HFO	Hydrous ferric oxide
JAEA	Japanese Atomic Energy Agency
$K_{d}$	Partition coefficient between solid and liquid phase
LFER	Linear Free Energy relationships
LLNL	Lawrence Livermore National Laboratory
NICA	Non-ideal competitive adsorption model (NICA-Donan)
NIST	National Institute of Standards and Technology
PSI	Paul Scherrer Institute
PZC	Point of zero charge
TS	Technical specification
WHAM	Windermere humic aqueous model

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## ABSTRACT

The objective of this chapter provide a summary of thermodynamic databases that have been used and are available to predict 1) equilibrium phase assemblages in cementitious materials and 2) the impact of sorption processes on the concentrations of ionic species in an aqueous phase in contact with cementitious materials and soils. In addition, a brief summary of approaches to thermodynamic modeling is provided.

## **1.0 INTRODUCTION**

The specific chemical form of individual substances defines to a large extent how constituents present in materials are distributed amongst solid phases and susceptible to reactive transport processes. For cementitious materials and barriers, multi-phase thermodynamic equilibrium and reactive transport are the basis for understanding the distribution and release of solid phase constituents, either primary matrix components or trace constituents of concern, and the ingress of chemical species that may cause transformations of the properties of the material (e.g., chemical degradation). Chemical "speciation" refers to the different chemical forms in which an element may be present, such as, free ions, dissolved complexes, mineral phases, other solid phases, ions adsorbed onto hydrated mineral surfaces or dispersed as colloids. In addition to chemical speciation, the mobility of contaminants in the environment is also a function of transport processes (convection, diffusion) and time-dependent processes, such as, chemical reactions (represented as reaction kinetics) and slow

changes in the geochemical properties of materials (e.g., weathering/ aging reactions). Table 1 provides a summary of the typical interactions considered for systems comprised of cementitious materials and trace ionic species, such as, radionuclides and metals.

Thermodynamic data form the basis for chemical speciation modeling of equilibrium and reactive transport of constituents within cementitious materials. These data consist of reliable equilibrium constants for the (1) dissolution and precipitation of solid phases of interest between aqueous and solid phases and (2) formation of dissolved species in aqueous solution. Several databases are available which contain information for the matrix phases present in cementitious materials and for phases and elements found in a variety of waste streams including radionuclides.

In practice however, there are many instances, where thermodynamic data are limited, have not been measured, or where it is not possible to provide accurate quantification of the equilibrium

## Table 1. Fundamental Phases and Speciation to be Considered as Part of Multi-Phase ChemicalEquilibrium

#### Solid Phases (dissolution and precipitation phenomena)

Crystalline (mineral) phases Amorphous (non crystalline) phases Solid solutions (crystalline and amorphous)

#### Reactive Solid Surfaces (adsorption, desorption and ion-exchange phenomena)

Iron oxides (i.e., iron (hydr)oxides) Aluminum oxides (i.e., aluminum (hydr)oxides) Manganese oxides (i.e., manganese (hydr)oxides) Clay minerals Organic matter (e.g., precipitated humic and fulvic acids)

#### **Aqueous Phase**

Free dissolved species Chelated and complexed species Species associated with dissolved organic carbon Colloids

#### **Gas Phase**

Inert gases present as major constituents (i.e., nitrogen) Reactive gases present as major (i.e., oxygen, water) or trace (i.e., carbon dioxide) constituents

chemistry and individual solid-liquid partitioning processes. In such cases, partition coefficients  $(K_{\lambda})$  are often used as an approximation to describe and predict the concentrations of ionic species in the aqueous phase relative to the concentrations in the associated solid phases. They are applicable under specific conditions where sorption and desorption processes are the dominant partitioning mechanism (i.e., dilute solutions), rather than when aqueous saturation of a species with respect to a specific mineral phase or congruent dissolution are the controlling partitioning mechanisms. Partition coefficients are linear extrapolations of an empirical value applicable to a specific set of chemical conditions (solid phases, aqueous concentration, ionic strength, pH, temperature, etc.). Partition coefficients are not mechanistic except in the Henry's Law regime (i.e., very dilute solution) and therefore their application to aqueous concentrations and conditions beyond their initial definition should be performed with care. Often

in practice,  $K_d$  values are extrapolated to extend the range of estimating partitioning beyond where measurements are available.

#### 1.1 Mechanistic and Deterministic Models

Models used to describe speciation may be either empirical, mechanistic, or a combination thereof. Empirical models typically are case and material specific and are based on specific experiments or observations, which limit their extension to predictions beyond the conditions of their initial definition. Since fundamental processes on a molecular scale are valid across a wide variety of materials, application scenarios, and environmental conditions, models that explicitly reflect individual component chemical processes (hereafter referred to as mechanistic models) have a much wider applicability than empirical models. Examples of empirical models include linear partition coefficients and Freundlich adsorption models. During the past decades, mechanistic models have been developed that describe the chemical interactions that various cementitious phases and inorganic contaminants undergo as the result of aging and exposure to environmental conditions (including contact with soils, sediments, and the aquatic environment). In addition, mechanistic models have been developed to describe sorption processes on reactive surfaces (clay minerals, natural organic matter and iron (hydr)oxides)<sup>1</sup> found in natural and anthropogenic environments. Several models include "generic" thermodynamic and sorption binding parameter data sets which have been derived for a wide range of inorganic species which are frequently of interest, such as, various metals, oxyanions and radionuclides. These models can be applied to a variety of systems and conditions.

Due to the process-based character of the underlying process models and parameter data amongst material systems and scenarios, a mechanistic geochemical modeling approach is well suited for predicting longterm release properties from contaminated materials in the environment.

#### 1.1.1 Internal Consistency of the Mechanistic Modeling Approach

The long-term predictive value of a mechanistic model strongly depends on the way the model is parameterized, i.e., the way in which the specific thermodynamic and sorption parameters and estimates of material-specific properties/input parameters are selected for use in the model. The mechanistic modeling approach described in this chapter relies on consistency between the:

- Hypothesized component processes (i.e., system conceptual model),
- Chosen (sorption) sub-models to simulate these processes,

- · Necessary model input parameters, and
- Experimental methods or pre-existing data to define these parameters.

For the selection of sub-models (e.g., sorption), models are preferred for which "generic" parameter sets for a wide range of substances (major, minor and trace constituents) have been derived. Although such generic parameter sets may not provide the best description of measurements for a particular system, these parameter sets are internally consistent and are therefore more generally valid. In addition, when the purpose is to model long-term and complex (natural and waste) systems, there is a need for parameter sets that cover a broad range of major, minor and trace elements in order to account for multi-component interactions. Examples of multi-component interactions are competition between different elements for the (limited) sorption "sites" on reactive surfaces, as well as the formation of precipitates and soluble complexes.

In order to achieve a generally valid modeling approach, the models and associated parameter sets selected must have consistent reference states and underlying assumptions. Only peer-reviewed thermodynamic and binding parameter data should be used. In this respect, it is important to note that mechanistic sorption models and associated generic parameter sets may not be available for all of the potentially important sorption processes. In those cases, an attempt can be made to derive the necessary sorption characteristics from those of similar reactive surfaces for which this type of information is available. When sorption models are used in this way the amount of the reactive surface area of this material also must be determined. Important reactive surfaces that are treated in this way include amorphous and crystalline iron and aluminum (hydr) oxides, clays, and reactive fractions of dissolved and particulate organic matter (humic and fulvic acids).

<sup>&</sup>lt;sup>1</sup>The terminology (hydr)oxides refers to the range of hydrated states of metal oxide surfaces (e.g., iron, aluminum, manganese).

A number of widely used (geo)chemical reaction or thermodynamic and binding parameter databases and sorption models are discussed in the sections that follow. In each case, the models and databases are internally consistent in the way that they are initially formulated (e.g., reference state, temperature, units). However, transfer of database information (parameters or sub-models) from one modeling framework to another must be accomplished with care to insure that internal consistency is maintained.

#### 1.2 Database vs. Conceptual Model

A clear distinction is needed between a thermodynamic database and a thermodynamic conceptual model. The thermodynamic database contains stability constants derived from experimental work and parameters which are used as input for models describing sorption processes (e.g., iron-oxide and organic matter), dissolution and precipitation, and aqueous speciation (e.g., complexation and chelation reactions).

A conceptual thermodynamic model includes a number of important aspects:

- Definition of the scenario to be evaluated including identification of the control volume, key processes taking place, bulk and trace element chemistry, solid phases present (including amorphous phases and solid solutions such as C-S-H and trace species incorporated in ettringite), and boundary conditions;
- Methods for calculating activity coefficients (e.g., Debye-Hückel, Pitzer);
- Reaction temperature dependence (e.g., Van't Hoff, empirical reaction constant temperature coefficients, temperature-dependent heat capacity); Models and parameters for binding to solid phases

(e.g., empirical equations, surface complexation, ion-exchange); and

• Models and parameters for aqueous phase speciation (e.g., aqueous complexation, association with dissolved organic carbon).

Each feature of the model will have its own set of coefficients that must be included in the thermodynamic database. However, for each of the enumerated aspects, there are multiple valid approaches for construction a system model. Because there are no truly ab initio calculations (calculations on a molecular statistical thermodynamics basis without underlying measured coefficients), the only way to test a conceptual model is to compare model predictions to measured data.

In theory, for a given conceptual model, one could optimize the thermodynamic parameters to best agree with a single observation. In practice, however, one tries to achieve a conceptual model that can handle a range of scenarios and conditions with minimal or no change in thermodynamic properties. To achieve this, the researcher seeks a constrained optimization where, for a given conceptual model, the model calculation "best" agrees with the full range of scenarios.

## 2.0 THERMODYNAMIC DATA SOURCES AND TYPES

#### 2.1 Equilibrium Between Solid Phases and Dissolved Species

The minimum thermodynamic data required to calculate equilibrium between dissolved species and precipitated solid phases consists of a complete set of solid phase formation reactions<sup>2</sup> plus solubility

<sup>&</sup>lt;sup>2</sup>Formation reactions are the stoichiometric chemical equations for the precipitation and dissolution equilibrium between the solid and aqueous phases. Solubility constants are the equilibrium constants for the formation reactions assuming that the solid phase has unit activity.

constants. The minimum thermodynamic data required to calculate equilibrium concentrations of soluble species consists of aqueous formation reaction equations, including the complete reaction stoichiometry of the aqueous species plus an accompanying equilibrium constant. To describe the temperature dependence of a reaction, entropy and enthalpy changes are needed to calculate the theoretical temperature dependency of the reaction constants

Formation constants of aqueous species and solid phases are based on (assumed) chemical equilibrium. In practice, chemical equilibrium between solid and liquid phases is rarely met, while equilibrium amongst dissolved aqueous species is achieved rapidly. In short-term laboratory leaching experiments, concentrations have been shown to approach equilibrium even in case of strongly heterogeneous waste materials (Dijkstra et al., 2006a). In case of slow dissolution-precipitation reactions, a kinetic description (formation/solubility as a function of time) is required to reflect the extent of approach to equilibrium, either on an empirical basis or a thermodynamic basis where the difference in Gibbs Free energy between the current system state and the equilibrium state provides the driving force for reaction. Kinetic parameters, however, are rarely available for most chemical reactions.

Compilations of thermodynamic data commonly used in equilibrium computer speciation software are available for public use. These databases consist of reactions, constants and parameters for the formation of solid phases and dissolved species. Publically available databases applicable to the CBP project are described below.

#### 2.1.1 MINTEQA2 Database

The MINTEQA2 V4 chemical reaction database version 4 (U.S.EPA, 1999) is freely available on the Internet *(http://www.rockware.com/product/data.* 

*php?id=132;* see also, *http://www.epa.gov/ceampubl/ mmedia/minteq/)* in different formats compatible with common geochemical speciation programs (MINTEO, Geochemist's WorkBench, PHREEOC). It contains a large set of aqueous complexation and precipitation reactions and probably is the most extensively used source of thermodynamic data for chemical speciation purposes in the world. Thermodynamic data in version 4.0 and later versions have been expanded and been strongly improved over earlier versions. The main difference with other commonly used thermodynamic databases is that version 4.0 and later versions rely largely on the Critically Selected Stability Constants of Metal Complexes Database published by the National Institute of Standards and Technology (NIST). This NIST database includes an objective evaluation of the quality of the thermodynamic data. This database contains solubility constants for a number of solid phases that are constituents of cementitious materials. Furthermore, it contains thermodynamic data for a limited set of radioactive elements, and a set of surface complexation reactions for the Generalized Two Layer Model (GTLM) of Dzombak and Morel (1990).

#### 2.1.2 Lawrence Livermore National Laboratory Database

The Lawrence Livermore National Laboratory (LLNL) thermodynamic database is the default thermodynamic database used in the popular geochemical speciation program Geochemist's Workbench (Bethke, 1998). Like MINTEQA2, this database (referred to as thermo.com.V8.R6.230, available at *http://www.rockware.com/product/data. php?id=132*) contains many aqueous complexation and precipitation reactions with references to the original literature sources. The LLNL database is also available in different formats, such as a format compatible with PHREEQC. In comparison with the MINTEQA2 database the LLNL thermo.com. V8R6230 database contains a much larger data set for

radioactive elements. However, this database does not contain thermodynamic data for adsorption reactions.

# 2.1.3 Yucca Mountain Geochemistry Database

A database (data0.ymp.R2) that includes thermodynamic data, sorption parameters and radionuclide  $K_d$  values for cement and geologic materials was developed for the Yucca Mountain Geologic Repository Project and was extensively reviewed.

#### 2.1.4 Nagra/PSI Thermodynamic Database

The Swiss Nagra/PSI Chemical Thermodynamic Data Base 01/01 by Hummel, Berner et al (2002) contains thermodynamic data for a range of radioactive elements. The Nagra/PSI database defines a basic set of components and phases (available at *http://les.web. psi.ch/TDBbook/index.htm*). This database does not contain sorption data.

#### 2.1.5 CEMDATA07

The Lothenbach et al. (2007 and 2008) cements database, CEMDATA07, was developed within the context of and supplements the Nagra / PSI database. This database is the most complete set of thermodynamic cement chemistry reactions (available at *http://www.empa.ch/plugin/template/ empa/\*/74250/---/l=1*). CEMDATA07 has detailed information on cement hydration phases and includes descriptions of the behavior of major elements in cement chemistry (e.g., calcium, alumina, silica). CEMDATA07 was developed by combining the equilibrium model GEMS (*http://gems.web.psi. ch/*) and the Nagra/PSI database. This database has no sorption data and does not contain radionuclide information.

## 2.1.6 Japanese Atomic Energy Agency Database

The Japanese Atomic Energy Agency (JAEA) developed a thermodynamic database that includes a wide range of radioactive species. This database can be downloaded in different formats, such as the one for PHREEQC (available at *http://migrationdb.jaea. go.jp/english.html*). The database is quite extensive but English documentation is limited. With respect to speciation of radionuclides, this database may be a valuable addition to MINTEQA2 v4. Data on adsorption reactions for radionuclides and other species are included in this database.

#### 2.1.7 Thermoddem Database

In France, the Bureau de Recherches Géologiques et Minieres (BRGM) has taken the initiative to collect thermodynamic data and provide detailed descriptions of the possible relevance of minerals for use in given situations (Piantone et al. 2006). So, in contrast with the other databases described here, the Thermoddem database (available at http://thermoddem.brgm.fr/ presentation.asp) not only contains a large set of chemical reactions, but helps users select a subset of relevant reactions for specific materials (e.g., cement, soil, fly ash) and conditions. Consequently this database is potentially useful for non-specialist users. For example, selecting a solid phase only found under very special exposure conditions for solving an ambient temperature problem is identified as being unlikely.

# 2.1.8 Additional Database for Selected Solid Solutions

In cement paste and mortar, the anion precipitation has been described as a solid solution in ettringite (Klemm 1998). The parameters for  $CrO_4^{2-}$ ,  $AsO_3^{3-}$ ,  $MoO_4^{-}$ ,  $VO_4^{3-}$ ,  $PO_4^{3-}$ ,  $SeO_3^{2-}$ ,  $SO_4^{2-}$ ,  $BO_3^{3-}$ ,  $Ba^{2+}$  and

Formula	log(K <sub>so</sub> )
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>4</sub> .12H <sub>2</sub> O	45
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (CrO4) <sub>3</sub> .(OH) <sub>4</sub> .12 H <sub>2</sub> O	47.40
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (AsO <sub>4</sub> ) <sub>3</sub> .(OH).9 H <sub>2</sub> O	40.79
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (H <sub>3</sub> BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>10</sub> .18 H <sub>2</sub> O	66.38
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (SeO <sub>4</sub> ) <sub>3</sub> .(OH) <sub>4</sub> .12 H <sub>2</sub> O	44.40
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (VO <sub>4</sub> ) <sub>3</sub> (OH).9 H <sub>2</sub> O	45.40
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (Sb(OH) <sub>6</sub> ) <sub>3</sub> .(OH) <sub>7</sub> .24 H <sub>2</sub> O	58.18
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> (OH) <sub>4</sub> .12 H <sub>2</sub> O	46.40
Ca <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH). 9 H <sub>2</sub> O	-11.89
Ba <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>4</sub> .12 H <sub>2</sub> O	60
Sr <sub>6</sub> (Al(OH) <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>4</sub> .12 H <sub>2</sub> O	60

#### Table 2. Stability Constants for Cement Solid Solutions Containing Specific Anionic Species\*

\*Species on which the solubility products are based:  $Ca^{2+}$ ,  $Al(OH)^{4-}$ ,  $SO_4^{2-}$ ,  $OH^-$ ,  $CrO_4^{2-}$ ,  $MoO_4^{-}$ ,  $PO_4^{3-}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Sb(OH)_6^{-}$ ,  $SeO_4^{2-}$ ,  $AsO_4^{3-}$ 

Sr<sup>2+</sup> have been derived from modeling the dissolved concentration as obtained from two cement mortars (prepared according to EN 197-1) and tested in a pH dependence leaching test (CEN/TS 14429). One of the two cements is a regular Portland cement and the other a cement with increased trace element levels prepared in a small kiln. Stability constants are provided in Table 2.

Other cement mortars with varying concentrations of oxyanions and cement stabilized wastes modeled with these parameter settings generally indicate good agreement between measured and predicted concentrations. Obviously, independent experimental verification of the constants is desirable, but at present the descriptions provide an adequate quantification, which provides adequate prediction even at low liquid to solid conditions such as occurs for pore water, which is very helpful in subsequent transport modeling runs.

Solid solutions can be modeled as ideal solid solutions described by (Parkhurst and Appelo, 1999).

This means that the activity of each member phase is equal to its mole fraction. By choosing the solubility products of the end members equal to the equivalent pure phases, the solid solution will always be less soluble than the pure phases of any of the member solids. As a result, the pure phases will not form in the calculations. The solid solution will dissolve completely if the product of saturation indices of all member phases is less than 1.

#### 2.2 Sorption of Soluble Species on Solid Surfaces

In addition to the formation of solution complexes and precipitates, sorption processes influence the distribution of ions and chemicals dissolved in an aqueous phase that is in contact with solids. Sorption processes can occur between dissolved ions or molecules and suspended colloids, including large organic molecules of natural origin (e.g., humic substances), organic material, or inorganic solids. Sorption processes apply to a wide variety of solid surfaces including the external and internal surface area of the phases making up cementitious materials and soils.

The most dominant colloidal and solid reactive surfaces for metals in soils are believed to be dissolved and natural humic substances (i.e., humic and fulvic acids), surfaces of clay minerals and (hydr)oxides of iron, aluminum and manganese. Sorption onto these surfaces, can occur through electrostatic interaction or by chemical reactions with reactive groups, such as, carboxylic or phenolic groups on organic molecules. Sorption of most inorganic contaminants is generally non-linear, i.e., the sorbed amount depends in a non-linear way on the concentration in solution, and is influenced by many multi-component interactions, e.g., competition between different species in solution for the same adsorption sites. For these reasons empirically-based models that are based on a single species in dilute or ideal aqueous solution are unsuitable to describe reactive transport processes on longer time and distance scales.

During the past decades, models have been developed that describe multi-component sorption interactions on the reactive surfaces identified above. Adsorption models most relevant to the performance of cementitious materials and stabilization of chemical and radioactive species are described below.

# 2.2.1 Sorption Parameters for Hydrated Metal Oxides

Adsorption behavior of (hydr)oxide surfaces can described by a variety of semi-mechanistic models that are consistent with thermodynamic databases, such as, MINTEQA2, that describe solution complexation behavior. The first one discussed here is the generalized two layer model GTLM by Dzombak and Morel (1990), which is the most widely used model. The second one is the CD-MUSIC (charge

distribution multi-site competitive adsorption model) developed by Hiemstra et al., (1996; 1989a, 1989b). The CD-MUSIC approach is more recent and more in line with latest mechanistic insights and is better able describe competitive interactions. However, the GTLM model comes with an extended set of databases with "generic" adsorption reactions and constants, while the set of available reactions for the CD-MUSIC is more limited. Both models use a similar format for the description of the adsorption reactions, consisting of an equilibrium reaction plus reaction constant for each adsorbing species. However, reactions and constants determined for one model cannot be used with another model. Although default parameters for both models have been shown to lead to acceptable predictions of contaminant release in soils and cementitious materials over a wide range of conditions (Weng et al., 2001; Dijkstra et al., 2004, and Kaplan, 2008), system specific parameters, such as, specific surface area and point of zero charge (PZC), must be determined.

Most reactions and parameters for dissolved species are available for sorption on iron (hydr)oxides such as hydrous ferric oxides (HFO) and goethite ( $\alpha$ -FeOOH), for which these models were originally developed. Recently, GTLM and CD-MUSIC have also been applied to multi-component sorption to aluminum (hydr)oxides (e.g., Meima and Comans, 1998) and manganese oxides (Tonkin et al., 2004).

Surface precipitation is a term for the process where, at very high surface coverages of a species onto a sorbent surface, a surface phase may be formed whose composition varies continuously between that of the original sorbent metal (hydr)oxide and a solid crystalline or amorphous precipitate of the sorbing cation (Dzombak and Morel, 1990). Surface precipitation is an integral part of the GTLM of Dzombak and Morel (1990) and can be described fairly well as the formation of an ideal solid solution. Conditions under which surface precipitation may be expected can be met in waste materials with high concentrations of metal contaminants (Dijkstra et al., 2006)

# 2.2.2 Sorption Parameters for Dissolved and Particulate Organic Matter

Interactions between solutes and organic matter are important, especially in determining behavior of cationic trace elements. In contrast with oxides that have well defined surfaces with well defined binding sites, organic matter surfaces are composed of a heterogeneous mixture of binding sites. There are currently two ways in which interaction with these surfaces are modeled. The first is to mimic a heterogeneous collection of sites by defining a large set of discrete surface sites with slightly varying chemical properties (binding constants). An example of this approach is the well known WHAM model of Tipping (1994). The second approach is a numerical approach which assumes a continuous distribution of reactive surface sites with different binding properties, as in the NICA-Donnan model (Kinniburgh et al., 1999). As with the metal (hydr) oxides, adsorption reactions and parameters for the WHAM and NICA-Donnan models are not interchangeable, but for both models adsorption reactions and constants are available for a wide range of solutes.

The advantage of the discrete approach (WHAM model) is that this fits relatively easily within existing numerical equilibrium frameworks, although it is computationally intensive because of the large number of chemical entities (sites and species). The advantage of the continuous approach (NICA– Donnan model) is its elegance, small set of required parameters, numerical efficiency, and applicability in a wider concentration range in comparison with the discrete model. The NICA model has demonstrated better predictive capabilities that are well tested on multi-component natural and waste systems (Dijkstra et al., 2004; 2008). The disadvantage of this approach is that it is difficult to implement numerically in combination with existing frameworks.

#### 2.2.3 Clay Interaction Parameters

Ion exchange reactions for clays are available in databases, such as, MINTEQ, PHREEQC, and Geochemist's Workbench. They are mathematically represented in the form of the so-called Gaines-Thomas convention (Gaines and Thomas, 1953)<sup>3</sup>. The resulting equations require ion-specific and surface-specific parameters. Sorption onto clay minerals is predominantly electrostatic and associated with the permanently charged surfaces of many common clay minerals. In general, the relative importance of this process in concrete and cement stabilized wastes is generally low in contrast to greater significance in soils (Dijkstra et al., 2004). However, specific and strong interactions between radionuclides and clays are known for cadmium and radiocesium (De Koning and Comans, 2004 and references therein). Ion exchange can also be modeled with a fairly simple Donnan-approach, which is based on electrostatic interactions between the sorbing ion and the charge of the surface, and requires no ionspecific exchange parameters.

### 2.2.4 K<sub>d</sub> Values for Radionuclides

In the performance assessments carried out at nuclear sites,  $K_d$ 's are frequently used to describe both the source term release as well as the transport in the near and the far field. Examples of  $K_d$  data used for suites of radionuclides in waste form and concrete

<sup>&</sup>lt;sup>3</sup> Equilibrium among aqueous and exchange species requires that all mass-action equations for the exchange species are satisfied. For example, the association reaction for the exchange species  $CaX_2$  is  $Ca^{2^+} + 2X^- = CaX_2$ , where  $X^-$  is the exchange master species for the default database. The use of equivalent fractions for activities and this form for the chemical reaction is known as the Gaines-Thomas convention (Gaines and Thomas, 1953) and is the convention used in the PHREEQC and some other databases.

performance assessments are given in Kaplan et al. (2008), Krupta et al. (2004) and by Krupka and Serne (1998). The JAEA thermodynamic database (see Section 2.1.6) includes  $K_d$  values for a wide range of radionuclides and other constituents on cementitious and other materials.

#### 2.3 Use of Combined Thermodynamic and Sorption Data

For modeling interactions of contaminants in the environment and in cementitious materials, often a combination is made between reactions from a common thermodynamic database such as MINTEQA2, and several of the listed sorption models. This approach is often referred to as a "multisurface" modeling approach, which describes the dominant interactions that contaminants undergo in the natural and anthropogenic environment. There are several good overview/review papers in which the approach is discussed more thoroughly (Merdy et al. 2006, van Riemsdijk et al. 2006).

This approach has been used for modeling interactions in natural waters (Lofts et al., 1998; Unsworth, 2004), extensively in soils (Lofts et al., 2001; Weng et al., 2001, Cances et al., 2003, Dijkstra et al., 2004; Fest et al., 2005;), river floodplains (Schroder et al., 2005), and granular and monolithic waste materials (van der Sloot et al., 2006; Carter et al., 2008; Dijkstra et al., 2008; Tiruta-Barna et al., 2005).

## **3.0 SUMMARY**

Table 3 provides a summary comparison of the main contents of the thermodynamic databases described above.

#### Table 3. Overview of Main Contents of Different Thermodynamic Databases

	Aqueous Speciation	Mineral Precipitation	Adsorption			Radio
Database			Oxides	Organic Matter	Clay	nuclides
MINTEQA2 V4	Yes	Yes (>400)	Yes, HFO	No	No	Some
LLNL (thermo.cem.V8.R6.230)	Yes	Yes		No	No	Yes
Nagra/PSI Chemical Thermodynamic Data Base 01/01	Yes	Yes	No	No	No	Yes
BRGM (Thermoddem)	Yes	Yes	Yes	No	No	Yes
Cement 07	Yes (Cement specific)	Yes (Cement specific)	No	No	No	No
JAEA	Yes	Yes	No	No	No	Yes

Thermodynamic data (for aqueous solution speciation and precipitates) is estimated to be rather well covered by the databases listed in Section 2.1. However, temperature dependence parameters in the currently available thermodynamic databases are incomplete and most data are reported at a standard state of  $25^{\circ}$ C.

For sorption processes, the available "generic" parameter data sets contain parameters for a few actinide, transuranic and rare earth elements (Am, Cm, Dy, Eu, Th, U, Be, Pu, Np, Pd), but an evaluation has to be made as to which relevant parameters are missing. Sorption parameters that are not readily available can often be derived using published LFER's (Linear Free Energy Relationships) or by assuming "surrogate" behavior of a compound for which information is more complete. Information on the temperature dependence of sorption processes is virtually absent.

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