

**Physico-Chemical Phenomena Governing
the Behaviour of Radioactive Substances.
State-of-the-Art Description**

Restoration Strategies for Radioactively Contaminated
Sites and their Close Surroundings
RESTRAT - WP2

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Summary

Work package WP2.1 of the EC project RESTRAT characterizes the main parameters, namely physico-chemical ones, determining the source term evolution in radioactively contaminated sites with regard to their importance and availability for risk assessment models, ensuring a more profound chemical base for restoration scenarios.

This report summarizes the physico-chemical phenomena and their main parameters. It points out the ways to get the available data from sources like databases, scientific publications, or own experimental determinations and measurements. Such a database establishment for each site to be remediated has to be accompanied by an integration of chemical speciation into existing risk assessment codes. Therefore the state-of-the-art of chemical speciation and migration modelling is described, leading to the conclusion that it is necessary to unfold the wide-spread K_d -concept. K_d values have generally both large uncertainties and important effects on the risk assessment predictions, particularly as models are often sensitive towards changes in K_d . Hence an unfolding makes it possible to perform more detailed sensitivity analysis, to find the most critical parameters, to reduce parameter space, and finally to prepare the way for more reliable models.

Consequently, the models for surface complexation most often used in geochemical modelling are presented here. For both non-electrostatic and electrostatic adsorption models the defining equations, theoretical background and the main parameters are given. Because surface complexation models, together with chemical speciation, are to be combined with currently used risk assessment software, the implementation of such surface complexation models in the geochemical code MINTEQA2 [Allison *et al.*, 1991] is explained.

In its last part, this work describes data structures and data flows for the proposed strategy of a K_d unfolding, namely the combination of MINTEQA2 with the PRISM / BIOPATH [Gardner *et al.*, 1983; Bergström *et al.*, 1982] package.

It is hoped that the work performed under the RESTRAT project, and especially the part presented in this report, will help to define and use a common language among all the different group of scientists, involved and required in such a true multi-disciplinary and complex challenge as the risk assessment for radioactively contaminated sites.

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1. Introduction

The main objective of the overall RESTRAT project is to develop a generic methodology for the ranking of restoration techniques as a function of site and contamination characteristics. The work has been broken down into several work packages. This technical deliverable, as required by the contract, summarizes the work performed in work package WP 2: Physico-chemical phenomena during Phase 1: State-of-the-art description.

The focus is on the characterization of the main parameters, namely physico-chemical ones, determining the source term evolution with regard to their importance and availability for risk assessment models. The aim is to deliver a more profound chemical base for risk assessment scenarios, which is accompanied by a general improvement of the communication and mutual understanding between risk assessment researchers and physico-chemists. In order to take properly into account the physico-chemical phenomena governing the contamination source term development in time and space, it is necessary to extend the knowledge about these phenomena and the underlying basic processes and interactions. This allows a better integration of chemical speciation into existing risk assessment codes.

Up to now, the physico-chemical phenomena were considered (if at all) by applying distribution coefficients (K_d) in order to model the distribution of a contaminant between solid and aqueous phases. Such distribution coefficients generally have large uncertainties. In many cases sensitivity analysis for risk assessments revealed, that the uncertainty of the K_d was propagated throughout the whole model, contributing to a large extent to the overall uncertainty of a prediction. In other words, risk assessment models are particularly sensitive towards changes in K_d . To overcome this problem, strategies are required to “unfold” the K_d approach into more basic processes. This should make it possible to perform more detailed sensitivity analysis, to find the most critical parameters, to reduce parameter space and, finally, to pave the way to more reliable models.

2. Important physico-chemical processes

A contaminant can occur in many different forms in an environmental compartment, each of them having different mobility, transfer coefficients to and between living matter, and even toxicity. This variety of existing forms for a given element is termed chemical speciation, defined as the distribution of one or more elements between all its possible species¹ (distinct chemical entities) in a given system². It should be noted that the term “speciation” is also used in another context to describe all the experimental methods applied to investigate the above discussed species distribution.

Species distributions determine whether a contaminant is mainly a component - and thus easily transported and taken up - or is immobilized through precipitation or adsorption onto a surface. Therefore, changes in speciation can either accelerate or slow down radionuclide migration. Many of the processes affecting the source term are influenced by the speciation. Their importance may vary, so the following list should not be considered a ranking:

- radioactive decay;
- complexation reactions (with organic and inorganic ligands), through:
 - hydrolysis;
 - dissociation;
 - association / polymerization;
- oxidation state changes / redox reactions;
- precipitation and dissolution of solid phases;
- co-precipitation (inclusion & surface precipitation) of trace components;
- physical and chemical sorption onto mineral surfaces or colloids;
- formation of solid solutions (mixed mineral phases);
- ion exchange;
- extraction (in case of several fluid phases);
- formation of colloids;
- formation of aerosols;
- processes involving biological material, such as biosorption, biologically catalysed redox reactions, enzymatic reactions, metabolisms.

Many of these processes are controlled by parameters from outside, which can be considered as fixed by certain environmental (natural and man-made) conditions. But for some of these parameters feedback can be observed; the internal physico-chemical processes of an environmental compartment will influence parameters such as pH or redox potential, either amplifying or extenuating already established trends from outside the compartment. Without a thorough description of all parameters and processes, leading to a comprehensive, “full-system” modelling, no sound prognostics are possible.

¹ simple ions or neutral molecules, ion pairs, associates, complexes, hydrolysis products, pure minerals, solid solutions, gases, surface complexes

² aqueous solution in contact with all solid phases and the gas phase, maybe also other fluid phases (organics), colloids and aerosols

3. Physico-chemical parameters necessary to describe natural systems

The various processes listed above can be described quantitatively by their respective functional terms, each requiring a unique set of parameters. Fortunately, many parameters are used simultaneously for many or all of the above reactions, like temperature or concentrations. In general, the parameters can be divided into system-specific parameters (subdivided into the stationary state and the dynamic evolution) and into reaction-specific parameters. Many of these parameters also depend on the chemical or physical models applied to the system. The most obvious case is the number and kind of species thought to be present in the system of interest, i.e. the selected speciation model [Appelo and Postma, 1993; Manahan, 1994; Ure and Davidson, 1995]. When the ionic strength I of the system exceeds the validity range of the Debye-Hückel Limiting Law, one has the choice between various activity coefficient models, such as the Davies Equation [Davies, 1962], the Specific Ion Interaction Theory / SIT or Brønsted-Guggenheim-Scatchard Model [Grenthe *et al.*, 1997], the Pitzer Model [Pitzer, 1973; Pitzer, 1991], the Mean Spherical Approximation (MSA) [Blum, 1988], and the models from Scatchard or Lim [Scatchard, 1968; Lim, 1987]. The next step of complexity is added with the introduction of a Surface Complexation Model (SCM) [Stumm, 1992]. Constant-Capacitance, Diffuse-Layer, Stern, Triple-Layer, Four-Layer-Model: all require their special set of parameters. In the case of mixed fluid phases one has to choose between mixing models such as Flory/Huggins, NRTL, UNIFAC, Wilson, van Laar, UNIQUAC, and ASOG. Kinetic rate laws or the models for the formation and interaction of colloids or aerosols also have their own set of parameters [Connors, 1990; Schmalzried, 1995]. The thermodynamics of water and aqueous solutions are dealt with in detail by various papers [Horne, 1971; Stumm and Morgan, 1996; Deutsch, 1997].

3.1. Site-specific parameters

The parameters described below are all specific to a given site and must be determined by field studies or from samples in the laboratory (see also Chapter 4). They either define the stationary state of a system or its dynamic evolution.

3.1.1. Description of the stationary state (composition) of a system

- Temperature.
- Pressure (total system and partial pressure of all gaseous components).
- Elementary composition, concentrations for all components (total or, better, for each species separately):
 - This includes pH , ionic strength , humidity.
- Composition of solid phases:
 - Identification of rocks and their mineral matrix.
- Redox state:
 - Eh, oxygen partial pressure, potentials of important redox pairs.
- Surface properties:
 - Specific surface area, active sites, site densities, crystal size, structural disorders, charge distribution, surface films (biological matter!).
- Total water content.

3.1.2. Description of the system's evolution in time and space

The parameters describing the temporal and spatial evolution of a system come from several disciplines, including chemistry, biology, hydrodynamics, meteorology, and geophysics. Therefore, this list is rather heterogeneous.

- Flow rates.
- Geometries of flow paths.
- Porosity of geomatrix.
- Gradients (spatial or temporal) of temperature, pressure, concentrations, density.
- Diffusion coefficients.
- Biological activities (e.g., bioturbation).

3.2. Reaction-specific (system independent) parameters

Such parameters describe the underlying basic reactions in a given system, they are universal and, therefore, the same for all sites. They can, hopefully, be extracted from databases or the literature. In some cases it may also become necessary to determine them in specifically designed laboratory experiments. Many of these parameter sets are not unique in the sense that they are not dependent on a chosen model.

- Thermodynamic parameters:
 - equilibrium constants;
 - solubilities;
 - enthalpies, entropies, and Gibbs free energies;
 - heat capacities;
 - partial molar properties;
 - activity coefficients.
- Kinetic parameters:
 - rate constants with the corresponding rate laws.
- Radioactive decay rates.
- Degradation rates for biological material.
- Parameters for biosorption.

4. Database establishment

The previous section may suggest, wrongly, that the number of parameters necessary to describe natural systems is immense. Fortunately, the vast majority of natural sites have a chemistry determined by just a few of the afore-mentioned processes. Hence, the number of parameters is maintainable if one can identify the dominating physico-chemical phenomena. However, some problems with the modelling of natural systems still persist. These will be tackled in the next sections, mainly focussing on the proper determination of site-specific data.

4.1. Problems with the determination of site-specific parameters

All site-specific parameters have to be determined from field and laboratory data. The most critical step is the very first one, the sampling itself. Collecting a probe from a natural system or installing a sensor or other devices in it to perform measurements on site means a more or less serious disturbance to the system. The next step, taking the sample to an analytical laboratory for further analysis presents an even greater danger of changing the sample irreversibly. The greatest care, therefore, has to be applied to the sampling procedure, with preference given to *in-situ* determinations of sensitive parameters such as pH, gas content (oxygen, carbon dioxide) or redox potential. A good introduction to the matter is given in Chapter 9 - "Geochemistry and the design of sampling programs" in [Deutsch, 1997]. Other interesting monographs are also recommendable [Broekart *et al.*, 1990; Fränze, 1993; Manahan, 1994].

Field and laboratory data can be checked for internal consistency to a certain degree by means of chemical speciation modelling. The modelling will help to establish a ranking for all necessary information. Then it can also be decided whether additional experiments need to be carried out. The following items can be used as a guidance:

- initial charge balance;
- comparison of computed and experimental pH;
- comparison of various redox systems and field measurements;
- solids that seem to be oversaturated;
- computed partial pressure of CO₂.

In some cases the model for the chemical system can be made more realistic by specifying some components to be in equilibrium with either a mineral that is in excess or a large gas reservoir (namely CO₂). Simultaneous chemical equilibrium is the exception to the rule in natural systems, even on large time scale. This is especially true in the case of redox pairs and in heterogeneous phase reactions, such as precipitation and dissolution. The kinetics of many such processes are not yet well enough understood and some are not reversible. Modelling must take this into account, e.g. by applying kinetic rate laws (when available) or at least by excluding some kinetically-hindered minerals from consideration.

4.2. Sampling recommendations

At the beginning of the project data were already accessible for the RESTRAT test sites (Ranstad, Mol, Drigg and Ravenglass). Based on these data, on further extra sampling campaigns, on the authors' experience from field data collection and laboratory analysis, and on some general considerations, recommendations have been formulated concerning the sampling procedures. They include a recommended minimum set of basic properties necessary for realistic physico-chemical modelling, which is listed in Table 1. Some general recommendations are:

- Due to the heterogeneity of most natural systems it is difficult to collect representative samples, or make *in-situ* measurements at representative locations. Therefore, rather large sample sets are required to obtain error estimates. Another side effect of this heterogeneity is that matrix effects may falsify analytical results for contaminants, which usually are only present in trace amounts compared to the major chemical components, both in minerals and in aqueous solutions.
- Natural systems are especially sensitive to small changes in external parameters like temperature, pressure, oxygen content or redox potential. Such changes occur already when taking a sample, later during transport and storage, and finally also in the course of many analytical methods themselves. Definitely the best way to investigate a system is to do it *in-situ*, without disturbing it.
- If this is not feasible, it is always good practise to limit any delays between sampling and investigation to the absolute minimum, and to store samples under conditions equal to the field: air-tight, at original temperature, without gas bubbles over liquid samples, hidden from light if necessary.
- Last, but not least, quality assurance requires precise records for all analytical steps with times, locations, applied procedures and methods, observations, data processing and results.

4.2.1. Quantitative analysis for anions and cations in aqueous solutions

Table 1: Anions and cations to be analysed in aqueous solutions

CO ₃ ²⁻	# %	Ca ²⁺	# %	As ³⁺	# *
Cl ⁻	%	Mg ²⁺	# %	Pb ²⁺	# *
SO ₄ ²⁻	# %	Fe ²⁺ & Fe ³⁺	# %	Cd ²⁺	# *
PO ₄ ³⁻	#	Al ³⁺	# %	Zn ²⁺	# *
NO ₃ ⁻ / NO ₂ ⁻ / NH ₄ ⁺	%	Na ⁺	%	all radionuclides of interest	*
SiO ₃ ²⁻	#	K ⁺	%		

Annotations indicate the main reasons requiring specific measurements:

- # - Component shows strong complexing capabilities
- % - Component is needed to calculate the ionic strength
- * - Component is a contaminant itself

The main difficulties concern the CO₃²⁻ content which is in equilibrium with dissolved CO₂(g) and also strongly dependent on pH and temperature. Thus *in-situ* determinations would be the best. The SiO₃²⁻ content is often overestimated because not only the true dissolved content is measured but also the finely dispersed, or colloidal silicate. The same holds for iron and alumina. It is therefore advised to filter before analysis (at best in 2 or 3 steps down to 10 nm pore filters) using tangential filtering techniques or centrifugation.

4.2.2. pH

In-situ measurements are to be strongly encouraged. A good calibration is essential, which means using standard buffers, calibrate immediately before measurement, store electrodes as recommended by the supplier, take temperature effects into account, check long-time stability / drift of the used electrodes.

4.2.3. Gas phase composition

This is only necessary, if there are indications that it differs from the global atmosphere composition. The following components should be checked: CO₂, O₂, H₂S, NH₃, CH₄.

4.2.4. Temperature

Annual fluctuations should be taken into account, maybe resulting in different modelling scenarios for different seasons. The temperature amplitude will become smaller, and thus less important, the deeper the investigated water layer or mineral horizon is situated. Increasing temperature will generally cause a faster kinetic, which makes metastable intermediate phases less important. This makes modelling easier in a sense that the assumption of thermodynamic equilibrium is more justified than at room temperature. On the other side it must be noted that the thermodynamic data situation for temperatures lower than 20 °C or higher than 25 °C is far less satisfactory than for ambient temperature.

4.2.5. Redox state

It must be kept in mind, that there is nothing like a "global" Eh in a given natural system. However, this is what usually is performed: a measurement of the Eh with special commercial electrodes. It is certainly better to also determine the dissolved oxygen content. This is very sensitive to changes in the sampling conditions, thus in-situ measurements are to be preferred. However, the best way to measure Eh is to undertake independent determinations of the concentration of the constituents of various redox couples. The more redox couples are determined the more reliable will be the redox state characteristic. Examples for redox couples which can be measured separately are: Fe²⁺ / Fe³⁺ ; As³⁺ / AsO₃⁻ ; SO₄²⁻ / SO₃²⁻ ; SO₄²⁻ / S²⁻ ; NO₃⁻ / NO₂⁻ ; NO₃⁻ / NH₄⁺ ; Br⁻ / Br₂ ; Mn²⁺ / MnO₄⁻.

4.2.6. Organics

Values for the total organic carbon (TOC) are of limited use for speciation modelling. A real step forward is an analysis of functional groups (especially carboxylic and phenolic groups). This requires more analytical effort and can probably only be done from external analytical services. It should nevertheless be undertaken, at least, with a few representative samples to indicate which organics are present at all. In the best case they do not play an important role, so modelling becomes much easier. But simply to assume: "no problems with organics" is the wrong strategy.

4.2.7. Qualitative analysis of solid phases / minerals

The most important question is: "Which phases are the dominant ones ?" A second step is to check, whether the surfaces of the minerals are different from the core (e.g. due to weathering or bio-films). For surface complexing modelling it is necessary to determine the specific surface area (in m² g⁻¹) and the type and concentration of reactive sites. If possible, a specialist in petrology, mineralogy or geochemistry should be involved in such determinations. Several books can also be of great help, either concerning more general questions [Jeffery and Hutchinson, 1986; Crompton, 1996] or the determination of surface properties [Perry, 1990].

4.2.8. Size distribution of dispersed or colloidal material

Filtering or centrifugation techniques can give at least some information about size. More advanced methods include Photon Correlation Spectroscopy (PCS) [Pecora, 1985; Schurtenberger and Newman, 1993; Phillies, 1990] , Flow Field Flow Fractionation techniques (FFFF) [Beckett and Hart, 1993; Schimpf and Wahlund, 1997; Klein and Nießner, 1998] or, especially with regard to humic substances, Size Exclusion Chromatography / Gel Permeation Chromatography [Swift, 1985; De Nobili *et al.*, 1989].

4.3. Database situation for reaction specific parameters

Reaction specific parameters can usually be taken from the literature, ranging from large databases down to single values from a publication. Nevertheless, available data are often not sufficient in scope or quality (experimental conditions, reproducibility, internal consistency), and there are a variety of other problems. Many equilibrium constants are conditional ones, they are not transformed to the standard state (and to do it *a-posteriori* is often impossible). It is quite common that even the encompassed species-set differs among databases. Some of the species reported in literature are rather speculative, they are results of “best fits”, often based on additional assumptions of the authors. There is rarely direct spectroscopic or other evidence for a species. Database entries are not reviewed or the review criteria are not clear. In the worst case even the original reference is missing. It is common that the uncertainties are unstated, or they are strongly correlated. In some cases the format of the database may be important, since this can determine, whether it is possible to substitute database entries by one’s own values, or to extend the database with new values. Another question is, which activity coefficient model is supported by the database, and whether the thermodynamic parameters are temperature (and to a lesser degree pressure) dependent. Concerning both commercial and freely available databases, quality and quantity decrease in the order:

Thermodynamics > Kinetics > Sorption > Colloids.

Recently, a comprehensive report about currently available thermodynamic and kinetic databases was published by the NEA [Mason *et al.*, 1996]. A thorough analysis of existing thermodynamic and sorption databases can also be found in Chapter 2 of the RESTRAT TD5 [Brendler, 1999].

A common way to improve the situation are laboratory experiments performed by ourselves or by contractors. Limitations are, that they are expensive (for time rather than for costs) and restricted due to radiation safety regulations. Moreover, there are problems with the scaling-up of experimental conditions in size and time. In general it is difficult to mimic natural environments. The set-up of the experiments must ensure, that the experimental data are sensitive enough towards the desired parameter, otherwise the consequence is an “overfitting” of the model, giving strongly correlated parameters. As an example, at the moment several experiments are under way in the author’s institution, the Institute of Radiochemistry at the Forschungszentrum Rossendorf e.V. (FZR), to obtain thermodynamic properties for selected systems:

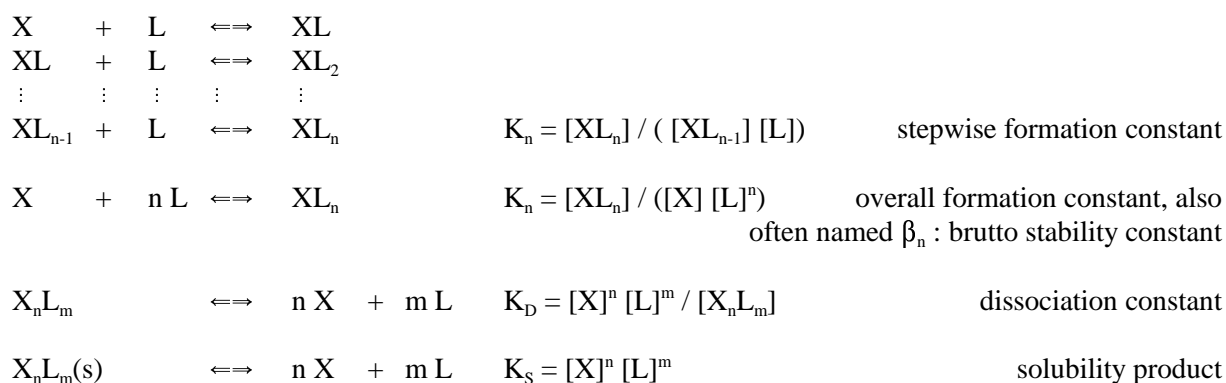
- Direct speciation determinations, e.g. conventional UV/Vis spectroscopy, Time-resolved laser-induced fluorescence spectroscopy (TRLFS) [Geipel *et al.*, 1997a; Moll *et al.*, 1998], Laser-induced photoacoustic spectroscopy (LIPAS), X-ray absorption near edge structure (XANES) [Denecke *et al.*, 1997], Extended X-ray absorption fine structure (EXAFS) [Reich *et al.*, 1996; Allen *et al.*, 1997], X-ray photoelectron spectroscopy (XPS) [Teterin *et al.*, 1996; Geipel *et al.*, 1997b], or Nuclear magnetic resonance spectroscopy (NMR) [Moll *et al.*, 1995]. These methods deliver information about the complex constitution, the coordination structure and bond lengths, or the oxidation state.
- Determination of complexation constants (potentiometry, UV/Vis, TRLFS, LIPAS) [Brendler *et al.*, 1996].
- Determination of sorption properties in batch and column experiments [Arnold *et al.*, 1998].
- Determination of solubilities [Moll *et al.*, 1996].

5. State-of-the-art chemical modelling

In the past two decades software packages have become an increasingly common tool for the modelling of complex environmental scenarios down to simple speciation problems. How do such conventional speciation codes work ?

5.1. Terms and definitions

In the following formulae **X** stands for a metal ion and **L** for a complexing ligand.



Often chemical equilibrium constants are used as negative logarithms: $pK = -\log K$. When formulating the framework of a chemical reaction for a specific system, it is very important to give the appropriate chemical reaction equation to which each parameter is associated.

5.2. Defining a chemical system

As has been already pointed out in Chapter 3, there are different ways to define a chemical system, resulting in different parameter sets. In any case, a chemical system must be defined completely and unambiguously. Here, the concept of components and compounds is helpful.

Each chemical element in a given system is represented by exactly one chemical entity, which is termed the component (also called the basic species or master species). No component can be obtained through chemical reactions of other components. In contrast, all the other constituents of the system (compounds, hydrolysis products, complexes, minerals, ion pairs, surface complexes etc.) are reaction products from the set of components. Literature values for equilibrium constants for the formation of such compounds often have to be transformed from the literature-specified reaction to the reaction based on the chosen set of master species. This sometimes results in negative stoichiometric coefficients. It should be noted, that for each chemical system there are various sets of components possible. This is illustrated by the example in Table 2 which gives a set of components for the system "*aqueous solution of uranyl phosphate in contact with the atmosphere*", and also shows alternative components. In most modelling software packages, a master species is allowed to only contain the element it represents and, additionally, oxygen or hydrogen. Although this assigns a considerable degree of freedom to the choice of a proper set of master species, in reality one should keep to master species which are expected to be actually present in the natural system under consideration. This will drastically improve the convergence of the numerical system to be solved for the chemical speciation. As an example, a good representant for uranium in oxidized systems at normal pH would be the uranyl cation UO_2^{2+} , whereas in reducing environments $U(OH)_4(aq)$

would be the better choice. Furthermore, for many inorganic strong acids, the first protonation steps, such as H_2PO_4^- or HSO_4^- , are appropriate master species. This is also outlined in Table 2.

Table 2: Chemical system set-up: master species for an aqueous solution of uranyl phosphate in contact with the atmosphere under normal pH.

Element	Master species	Other theoretically possible master species
Uranium	UO_2^{2+}	U^{4+} , $\text{U}(\text{OH})_4(\text{aq})$
Phosphorus	H_2PO_4^-	$\text{H}_3\text{PO}_4(\text{aq})$, HPO_4^{2-} , PO_4^{3-}
Carbon	HCO_3^-	$\text{CO}_2(\text{g})$, $\text{CO}_2(\text{aq})$, CO_3^{2-}
Oxygen ¹⁾	H_2O	$\text{O}_2(\text{g})$
Hydrogen ¹⁾	H^+	OH^- , $\text{H}_2(\text{g})$

¹⁾ Often master species for these components are already predefined by the software.

5.3. Mathematical formulation

The chemical speciation is computed at discrete points in time and space by means of either a minimization of the overall Gibbs Free Energy of the system or by solving a set of nonlinear equations constructed from a mass balance matrix. Here we deal only with the second case, which is the more wide spread approach. After the chemical system of interest has been properly defined, the mass balances must be formulated for each chemical element. Equation (1) describes, for a given chemical component i , its partition of the total concentration T_i (e.g. its analytically determined total concentration). Here, F_i is the free concentration of the respective master species i (i.e. that proportion of a component which really exists in form of its master species and has not reacted to form some other compound). The second term on the right side of equation (1) sums all reaction products that may have formed in the solution, with R denoting the number of independent chemical reactions (i.e. number of compounds). In most cases, the stoichiometric coefficient x_{ij} of master species i in compound j will be zero.

$$T_i = F_i + \sum_{j=1}^R [x_{ij} C_j] \quad (1)$$

The concentration C_j of any compound j can be expressed by the mass action law according to equation (2), with β_j as the equilibrium constant for the reaction forming compound j (e.g. brutto stability constant of a complex), b as an index over all components, and N as the number of components in the chemical system. Thus, x_{bj} is the stoichiometric coefficient of master species b in the reaction product (compound, complex etc.) j .

$$C_j = \beta_j \prod_{b=1}^N (F_b)^{x_{bj}} \quad (2)$$

Combining equations (1) and (2) then gives equation (3):

$$T_i = F_i + \sum_{j=1}^R \left[x_{ij} \beta_j \prod_{b=1}^N (F_b)^{x_{bj}} \right] \quad (3)$$

Because the concentrations must be substituted by the respective activities in all calculations, there is a dependence on the ionic strength too (and of course on temperature and pressure). The relation between activity and concentration is given as in equation (4), here for the molal activity a with γ being the (dimensionless) molal activity coefficient and m being the molality = amount of species in mole per kg H_2O . This can of course also be formulated for other concentration units like molarity, mole ratio or partial pressure.

$$a = \gamma * m \quad (4)$$

Finally, this leads to a system of nonlinear equations of degree N , where all the F_i values are unknown. To solve this system, N restrictions are necessary. These are the total concentrations of all elements. Instead of total concentrations a restriction may also be formulated by a given free concentration, directly determined or defined by an equilibrium with a mineral or an external gas phase. However, the following exceptions must be considered in most speciation programs:

- An additional restriction in ionic systems is the charge balance. Thus, one activity (mostly H^+ / pH, but any other charged species will also do) can not be varied.
- The internal norm is that the concentration of the solute H_2O is fixed, so yet another component must not be specified. Therefore, oxygen is usually not explicitly represented by a master species.

The resulting system of non-linear equations is solved iteratively by varying the free concentrations F_i . This involves for example the following steps:

- Solution of all reactions in the homogeneous (aqueous) solution and on surfaces.
- Iteration for activity coefficient corrections.
- Check of saturation indices: does any precipitation / dissolution occur ?
- Test new multi-phase assemblages, if necessary.
- Compute changes in mass for every phase.

The most popular numerical approach consists of a two-step process. First, starting values for the variable parameters are estimated and a robust minimization method is applied. In a second step a hybrid Newton-Raphson procedure with incorporated relaxation is used. During each iteration step the activity coefficients are held constant, they are computed again after all concentrations have been determined. The result is the species distribution for all chemical elements (maybe even split according to their various redox states), the activity and activity coefficients of all species, the redox potentials, and the saturation indices for all minerals.

5.4. Migration modelling

All the above equations describe a situation of thermodynamic equilibrium, but in natural systems this state is often approached only after very long times. Reactions involving solid phases like dissolution and precipitation, or redox reactions that involve re-arrangement of structural elements of molecules or ions tend to be very slow, leaving the system in a steady state, but not in thermodynamic equilibrium. To

describe such states, one needs to consider kinetic rate laws. The key principle is the definition of a reaction progress variable:

$$d\xi_r = \frac{dn_{ir}}{x_{ir}} \quad (5)$$

ξ_r = reaction progress of reaction r
 n_{ir} = moles of species i in reaction r
 x_{ir} = stoichiometric coefficient of species i in reaction r

Then we can define a reaction progress rate:

$$v = \frac{d\xi}{dt} \quad ; \quad v_r^{rel} = \frac{v_r}{v} \quad (6)$$

v = absolute reaction progress rate of reaction r
 v_r^{rel} = relative reaction progress rate of reaction r

Consideration of kinetics does not necessarily mean a real transport in space, since all reactants can be locally fixed. Evolution, both in time and space, needs a transport equation and this is done by solution of (partial) differential equations. The chemical speciation equations can either be directly substituted into the transport equations, or speciation and transport equations are solved in turn iteratively. To compute migration an additional set of parameters is necessary that describes the geometry of flow paths and various transport properties (e.g. diffusion coefficients, flow rates, porosities, tortuosities).

5.5. Available speciation and migration software

This, and the following section, give an overview of speciation and migration modelling software available. Programs tested at the Institute of Radiochemistry (to the end of 1998) are marked with an asterisk (*). In Table 3 some of the most popular modelling software for speciation and migration problems are compared with respect to some of the above mentioned decision criteria.

The chemical modelling software can be divided into three main groups: computation of speciations with given thermodynamic parameters, combination of speciation modules with a transport code, and programs to iterate thermodynamic and/or kinetic parameters from experimental data.

5.5.1. Programs to compute speciations with given thermodynamic parameters

MTDATA [Davies *et al.*, 1989] *
 VICTORIA [Heames *et al.*, 1992] *
 EQ3/6 [Wolery, 1992] *

MINEQL - family: MINEQL [Westall *et al.*, 1976]
HYDRAQL [Papelis *et al.*, 1988] *
MINTEQA2 [Allison *et al.*, 1991] *
MINEQL+ [Schecher and McAvoy, 1994] *
CHIMERE [Coudrain-Ribstein and Jamet, 1988]
PHREEQE - family: PHREEQE [Parkhurst *et al.*, 1980]
HARPHRQ [Brown *et al.*, 1988]
PHREEQC [Parkhurst, 1995]
PHREEQPITZ [Plummer *et al.*, 1988]
WATEQ - family: WATEQ [Truesdell and Jones, 1973]
WATEQ4F [Ball *et al.*, 1981]
WATEQP [Appelo and Postma, 1994]
RAMESES [Leung *et al.*, 1988] *
C-HALTAFALL [Östhols, 1994] *
GEOCHEM [Sposito and Mattigod, 1980]
SOLGASWATER [Eriksson, 1979]
CHEMSAGE [Eriksson and Hack, 1990]
SOLMINEQ.88 [Perkins *et al.*, 1990]

5.5.2. Programs combining speciation modules with a transport code

PHREEQM [Appelo and Postma, 1994]
CHEMTARD [Bennett *et al.*, 1992] *, with extensions towards colloids [Ivanovich *et al.*, 1993]
OS3D/GIMRT [Steeffel and Yabusaki, 1995] *
HYDROGEOCHEM [Yeh and Tripathi, 1990]
TReAC [Nitzsche, 1997]
CHEQMATE [Haworth *et al.*, 1988]
CHEMTRNS [Noorishad *et al.*, 1987]
THCC [Carnahan, 1987]
UNSATCHEM-2D [Simunek and Suarez, 1993] *
TRANSEQL [Kienzler, 1995]
DYNAMIX [Liu and Narasimhan, 1989a & 1989b]
COTAM [Hamer and Sieger, 1994]
MINTRAN [Walter *et al.*, 1994]
MT3DMS [Zheng and Wang, 1998]
COLTRAP [Van der Lee *et al.*, 1997]

These programs are often called reactive transport codes or coupled transport codes. There are two main methodologies applied here: either the equations describing the geochemical reactions are directly incorporated into the transport equations enabling analytical solutions (only feasible for small and simple geochemical systems), or the chemical speciation is calculated separately and iteratively for each transport step.

There are several excellent reviews of speciation and migration modelling [Jenne, 1979; Melchior and Bassett, 1990; Read, 1994; Lichtner *et al.*, 1996]. Interesting application cases can be found in [Schnoor, 1996; Deutsch, 1997]. However, it is worth noting that only two of the models mentioned above (COLTRAP and the CHEMTARD modification) include a specific treatment for colloids; they are simply ignored in all other cases.

Table 3: Comparison of features of some programs modelling speciation and reactive transport

	MTDAT A	EQ3/6	HYDRA QL	MINEQL +	MINTEQ A2	C- HALTA- FALL	PHREE QE	CHEM- TARD
Manual	X	X	X	X	X	X	-	X
Source Code	-	X ¹	X	-	X	X	X	X
Solid Phases	X	X	X	X	X	X	X	X
Activity coefficients	X	X	X	X	X	X	X	X
Adsorption	-	-	X	X	X	X	-	X
Redox	X	X	X	X	X	X	X	X
Kinetic	-	X	-	-	-	-	-	X
Transport	X	-	-	-	-	-	-	X
Database	X	X	X ²	X ²	X ²	-	X ²	-
Graphic Output	X	-	-	X	-	-	-	-
Operating System	DOS	UNIX, DOS	DOS	Windows	UNIX, DOS	UNIX, DOS	UNIX, DOS	UNIX
Programming Language	FOR- TRAN	FOR- TRAN	FOR- TRAN	FOR- TRAN	FOR- TRAN	C	FOR- TRAN and C	FOR- TRAN

x: Indication that the feature is available for the program.

¹: Extra fee for source code.

²: Database selection is not critically evaluated and poorly documented.

5.5.3. Programs to iterate thermodynamic and/or kinetic parameters

These programs start from experimental data sets, most often obtained by spectrophotometric, potentiometric or extraction techniques. They necessarily contain subroutines for the determination of species distributions, thus there is a strong relation between all three types of speciation modelling software. Valuable overviews about correct usage and limitations of software for speciation data treatment are given in several monographs [Meloun *et al.*, 1988; Leggett, 1985; Gans, 1992].

SQUAD [Leggett, 1985] *

MINIQUAD85 [Vacca and Sabatini, 1985] *

C-LETAGROP [Östhols, 1994] *

FITEQL [Westall, 1982] *

PKAS [Martell and Motekaitis, 1992]

LAKE [Ingri *et al.*, 1996]

5.6. Criteria to select appropriate modelling software

From the above it is clear that there are many programs in use. Each has a number of options to cover different areas of physico-chemical phenomena. Some of them require high learning efforts. Therefore it is hard for the potential user to judge, which is the proper approach for a particular application ? To ease such decisions, the scope of this section is to determine the major selection criteria, and to apply them to some representative software packages. Their strengths and weaknesses will be worked out and recommendations as to their application given.

Features to be considered when evaluating speciation modelling software are:

- Can the program handle redox reactions, kinetic rate laws, adsorption, multiple phase equilibria?
- Is the applied activity coefficient models adequate for the system under investigation?
- Which mathematical methods, especially minimization approaches, are applied?
- What is the performance of computational speed and numerical robustness?
- Can the user access an internal database? If so: is it possible to introduce changes, exclusions, additions via input file options?
- Does the software provide graphical output or other postprocessing tools?
- Which operating system and programming language is necessary?
- Are manual and/or source code available, how can support be obtained?

Additionally, features which may be important include: upper concentration limit, charge balance check, initial values, ability to cope with changes in volume, temperature or pressure etc. Other questions arise especially for parameter iteration programs:

- What is the maximal dimension of the problem (number of species & reactions)?
- What kind of experimental data can be processed: spectrometry, potentiometry, solubility experiments, extraction, coulometry, NMR, ...?
- Which parameters are adjustable: electrode potential, liquid junction potential, electrode drift, initial concentrations?
- Which statistics are applied to allow judgement of the final parameter set? How are uncertainties computed?
- How is the convergence criteria defined? Is there a procedure to avoid local minima?

6. Description of PRISM / BIOPATH

The mathematical method included in the BIOPATH code is based on compartment theory with first-order kinetics. Therefore, the cycling and content of radioactive matter in different ecosystems is described by a system of first order differential equations with constant or time varying transfer coefficients and a number of physically defined areas or volumes (compartments). The premises are that the outflow for reservoir "j" is solely dependent upon the quantity Y_j of the radionuclide in that reservoir. The reservoir is instantaneously well mixed, all atoms, molecules or other elementary units have the same probability of leaving the reservoir. The amount of activity in a given reservoir is dependent on the outflow to, and inflow from, other reservoirs. The source term for the reservoir, such as release to the reservoir or generation within by radioactive decay.

The PRISM system consists of three main parts. First, in PRISM1, random values of model parameters are generated by using a systematic sampling method, the Latin Hypercube Sampling. In addition correlations between model parameters can be taken into account no matter what distributions they are drawn from. Second, in PRISM2, model predictions are made for each set of input parameter values. Finally, PRISM3 statistically evaluates and summarizes the joint set of model parameter values and respective results. This includes the identification of the parameters most relevant for the overall uncertainty of each response.

This short description of BIOPATH and PRISM was taken from Moreno *et al.* (1995). Both software packages are written in FORTRAN77. Further information about BIOPATH is given in Bergström *et al.* (1982). A very detailed description of the methodology behind PRISM and its code implementation, including the structure of input and output files can be found in Gardner *et al.* (1983). Recently, various applications of the PRISM / BIOPATH software are shown [Nordlinder *et al.*, 1993; Nordlinder *et al.*, 1995; Bergström and Nordlinder, 1991]. For more details, please also refer to the Technical Deliverables TD6 [Stiglund and Nordlinder, 1999] and TD7 [Brendler *et al.*, 1999] of this project.

7. Unfolding the K_d value

7.1. Why are the K_d values not satisfactory ?

The K_d framework is built on the concept of distribution (or retardation) coefficients. This is defined as the ratio of the sorbed (fixed, immobilized) and unsorbed (free, truly dissolved) fraction of a component (chemical element) under equilibrium conditions. That means, however, subsuming many physico-chemical processes into one parameter, which is a severe weakness of the K_d principle [Hayes *et al.*, 1991; Puigdomenech and Bergström, 1994]. Distribution coefficients are very difficult to measure with a good precision and accuracy. Literally by definition, because of their incorporation of very different basic physico-chemical phenomena, they are dependent on so many parameters that even slight changes in one system parameter (say the Eh or the content of a major cation, or the occurrence of a new mineral phase, etc) can drastically change the distribution coefficient. To measure the effect of all combinations of these parameters is impossible. That means, all K_d values used nowadays in risk assessment or other prognostic studies are just snapshots for specific locations of the site valid only for the time of the measurement. This in turn assigns them very large uncertainties.

A much better strategy is the decomposition of the K_d value into the main basic processes defining it. Such an approach will unfold the single value K_d into a vector of parameters, such as Eh, pH, concentrations of the various components, surface areas, and temperature. Apparently this is a step backwards. But it has the great advantage that all these parameters can be measured with more reliability and precision. Knowing the functional relationships between these processes and how they contribute to the K_d allows a computation of K_d rather than a measurement. Moreover, simulations with variable parameter values may easily yield a K_d surface as a function of the "primary" parameter vector, even for hypothetical conditions. Also, some long-term effects that can render conventional distribution coefficients meaningless (co-precipitation, diffusion of the trace element into crystal lattices) can be accounted for in a better way. Another application is expressing K_d as a function of time, related to better-defined time dependencies of other basic parameters. Furthermore, it becomes possible to identify those parameters affecting the K_d strongest. Consequently, extra measurements can be designed efficaciously to reduce the K_d uncertainty.

7.2. Guidelines for unfolding the K_d

The unfolding of the K_d has to ensure that a broad spectrum of physico-chemical processes governing the source term evolution is covered. But to make the model development efficacious and fast, both the original risk assessment code and the chemical speciation code should be left mainly unchanged. The focus should be on the creation of simple interfaces between these codes. Ideally, it would be that, after each speciation modelling step, there are still only one or two parameters delivered, but now as a function of time (and space), to take into account the changes in speciation. In general there are three different approaches possible for an unfolding of the K_d value. K_d values can be made available to the risk assessment code (here the PRISM / BIOPATH program suite):

- a) as pre-processed matrices (values and associated error distributions). That means the uncoupling of speciation from the risk assessment calculation. It is certainly the fastest way when it comes to computing time, but to cover the whole parameter space defining K_d inter- and extrapolations are necessary which will increase uncertainty significantly.
- b) via on-line calls of external speciation programs. This will slow down the computing, but gives a much higher accuracy of the results. On the other hand, the programs are still kept quite flexible.

- c) from directly incorporated subroutine calls performing the speciation calculations. This ensures a faster computation than in case b), but requires the largest programming efforts and makes the whole software rather inflexible.

Approach b) has been chosen in this work because of the high flexibility which allows for later corrections in the code that may be necessary in the course of program testing and verification. Since PRISM / BIOPATH can only handle the transport of the contaminant itself, but not of all the other major components in the system, internal physico-chemical conditions of a compartment will only change when respective parameters are defined as time-dependent. So far this is not used. Hence, as a first approximation it is sufficient to compute the speciation only once for each compartment, resulting in corresponding new K_d values.

There are various ways to improve computational speed further in the future. Arranged with increasing programming efforts, this comprises:

- reduction of the output from the chemical speciation modelling to ease output processing by PRISM2;
- reduction of the input files for the chemical speciation modelling to include only necessary components;
- propagating of previous equilibrium concentration as initial values when performing time-dependent calculations;
- shift the PRISM2 call to the chemical speciation software from an external "system()" call to an entirely internal subroutine. This means full integration of chemical speciation into PRISM and BIOPATH.

7.3. Selection of speciation programs

As described in Section 5.5, there is a variety of speciation programs to choose from when it comes to an integration with the PRISM / BIOPATH software. The processes mainly influencing the species distribution can roughly be grouped into three categories:

- reactions in homogeneous solution (redox reactions, hydrolysis, complexation, etc);
- the formation of pure and mixed solid phases;
- and reactions on mineral surfaces.

The modelling of chemical speciation has to take them all into account, which does not pose a problem with regard to the first two categories. Nearly all programs available now can handle them, including redox reactions, which is essential for the reasons outlined in Chapter 3. When it comes to the third category, many programs have to give up or can just offer the simplistic K_d approach, that was already critically discussed in the previous two sections of this chapter. One of the few programs that is capable of modelling reactions between dissolved ions and mineral surfaces is MINTEQA2 from the U.S. Environmental Protection Agency [Allison *et al.*, 1991]. It has three different surface complexation models incorporated to choose from. Another program, EQ3/6 from the Lawrence Livermore National Laboratory [Wolery, 1992], can not compute surface reaction equilibria but has the big advantage to take kinetic rate laws into account. So in a certain sense these two programs complement each other. There are more reasons, why these two programs were selected for the speciation modelling part in the integrated risk assessment package to be developed. Both are available in source code, which is essential for any adaptations which are necessary to create interfaces between chemical modelling and risk assessment modules. Moreover, they have been in use for many years, have been checked by a number of validation programs and are recommended by international organizations.

At the moment no program is available that could act as a kind of superset of EQ3/6 and MINTEQA2, and include both kinetics and surface complexation. There are two reasons, why from these two candidates the

MINTEQA2 code (a more detailed description of the software is given in RESTRAT TD7 [Brendler *et al.*, 1999]) was initially chosen for incorporation into the risk assessment code. First, surface complexation is the most dominant process directly effecting distribution coefficients. Second, the database situation for kinetic parameters is worse than the one for surface complexation. So the focussing on surface reactions will faster led to results. The great importance of surface reactions for both the mobilization and retardation of radionuclides in the environment requires a deeper insight in the respective theories and models, which is done in the following chapter. Details about the actual implementation of an interface between the speciation and the risk assessment codes will be given later in Chapter 9.

However, the actual combination strategy to incorporate speciation codes into the PRISM / BIOPATH software is so flexible that it needs comparatively little effort to substitute the present speciation modules by another, better program.

8. Models to describe sorption phenomena

In the literature there are many attempts to describe the interactions between ions in solution and a mineral surface in contact with them. The resulting interactions can be grouped into various phenomena, such as physisorption, chemisorption, co-precipitation, inclusion, diffusion, surface-precipitation, or even formation of solid solutions. Surface complexation in a strict sense only describes the chemisorption and has, therefore, to be combined with models for the other effects to ensure a proper thermodynamically based speciation model for the elements of interest. Nevertheless, on shorter timescales it is often the dominating process, having a fast kinetics. Processes like diffusion of sorbed ions into the host mineral and the subsequent formation of mixed crystals or solid solutions may then follow, but these require much more time. This chapter briefly explains the models most often applied in sorption chemistry. Much more detailed information can be obtained from various textbooks [Dzombak and Morel, 1990] and publications [Davies *et al.*, 1978; Davies and Leckie, 1978; Davies and Leckie, 1980; Sposito, 1983; Sposito, 1989; Davies and Kent, 1990; Goldberg, 1991].

For all the formulae the following conventions apply: Brackets, [], specify concentrations in mol / L, braces, {}, specify free activities in mol / L. The index **T** indicates total concentration or activity, **M** stands for a metal species (pure cation, hydrolytic or complex species) that can sorb onto a surface, =SOH denotes the protonated, unreacted sorption site. The activity coefficient (dimension depends on reaction equation) of a species *i* is given by γ_i .

Whereas the simplest (and older) sorption models do not distinguish between the various processes outlined above that contribute to the overall sorption, newer model approaches at least describe separately the effects of the electrostatic attraction between a surface and an ion having charges of opposite sign, and the effects coming from a chemical reaction of an ion with a reactive surface site. Therefore, the sorption models will be grouped into two classes, the non-electrostatic and the electrostatic models. The latter are the surface complexation models (SCM) in a strict sense.

8.1. Non-electrostatic adsorption models

This section discusses four different approaches all of which neglect the contribution of the electrostatic effects of charged surfaces to the overall stability of surface complexes. This allows them to be rather simple in terms of defining equations and amount of model parameters. Of course this often does not reflect reality with the necessary accuracy, so the usefulness of the following four models is restricted to only a few cases. More often electrostatic adsorption models will be of greater benefit.

8.1.1. Distribution coefficient (K_d) model

This model is the one most often applied in geochemistry at present. It is used in two different versions, based on either of the following definitions:

a) Conventional K_d model:

$$K_d = \frac{[=SOH-M]_{sp}}{[M]_T} \quad (7)$$

Here K_d represents the ratio of the specific concentration of the metal sorbed onto the surface (given in mol / g solid) to the concentration of the dissolved metal (sum over all aqueous species containing the metal, given in mol / L solution).

B) Activity K_d model:

$$K_d^{act} = \frac{\{=SOH-M\}}{\{M\}} \quad (8)$$

Contrary to the above definition, here the activity of the sorbed species and the free metal cation in solution is considered.

8.1.2. Langmuir adsorption model

The Langmuir adsorption differs from the K_d approach only in that it requires specification of the total number of surface sites available. It assumes a reaction between a distinct surface site and the free metal cation, giving an equilibrium constant according to the equation:

$$K_L^{act} = \frac{\{=SOH-M\}}{\{M\} \{=SOH\}} \quad (9)$$

This formulation is equal to the expression most often given as:

$$[=SOH-M] = K_L^{act} \frac{[=SOH]_T \gamma_M[M]}{1 + K_L^{act} \gamma_M[M]} \quad (10)$$

Whether a description with the Langmuir isotherm is correct can easily be verified by plotting $[M] / [SOH-M]$, using a linearized version of the defining equation:

$$\frac{[M]}{[=SOH-M]} = \frac{1}{K_L[=SOH]_T} + \frac{[M]}{[=SOH]_T} \quad (11)$$

The introduction of total surface site densities certainly improves the sorption isotherm concept, because this takes into consideration saturation effects due to the limited number of reactive surface sites that are really accessible in a reaction. This surface site density, however, is a parameter not so easily to determine. It can be obtained from measurements of maximum sorption values (maximum proton uptake), by tritium exchange methods, or through theoretical considerations, for details see Dzombak and Morel (1990). Values determined for the same surface may differ by a factor of two to three. The surface site density is often given the symbol Γ with the units mol/m² or sites/nm², but also mol/L solution, mol/mol metal or mol/g solids are reported; so care must be taken when using such values.

8.1.3. Freundlich adsorption model

The Freundlich model again is very similar to the K_d approach, assuming infinite numbers of surface sites. The difference is that the reacting species **M** is assigned a mass action stoichiometric coefficient of 1/n:

$$K_F^{act} = \frac{\{=SOH-M\}}{\{M\}^{1/n} \{=SOH\}} \quad (12)$$

The applicability of the model can also be checked through a linearized version of the above equation:

$$\log [=SOH-M] = \log K_F + \frac{1}{n} \log[M] \quad (13)$$

8.1.4. Ion exchange model

This model describes the process of exchanging an ion from the solution with an ion on the surface of a mineral. Such an ion can also be the proton H^+ . The reaction parameter K_{ex} actually measures the competition between two ions M_A (initially occupying the site) and M_B (replacing ion) for a surface site, therefore K_{ex} is also called selectivity coefficient:

$$K_{ex} = \frac{\{M_A\} \{=SOH-M_B\}}{\{M_B\} \{=SOH-M_A\}} \quad (14)$$

8.2. Electrostatic adsorption models

The models dealt with in this section all treat surface reactions as complexation reactions analogous to such reactions in homogeneous aqueous solutions. Therefore these models are called Surface Complexation Models (SCM). This requires the definition of surface sites with a finite concentration. Usually such surface sites are represented as $=SOH$ groups with S denoting a metal from the solid structure, located at the solid-liquid interface. Many mineral surfaces, but especially colloids carry a significant surface charge, creating an electrostatic potential extending into the aqueous solution. Depending of the charge of the ions they are either attracted or repelled, thus greatly influencing the sorption behaviour of charged species (and due to dipolar effects even neutral species). To account in a proper way for this charge effect, additional terms have been introduced into adsorption models, modifying the activity of sorbate ions. These terms describe the electrical work necessary to penetrate the zone of electrostatic potentials, resulting in a difference between the activity of ions M_s with the charge $z+$ near the surface and the same ions M in the bulk solution:

$$\{M_s^{z+}\} = \{M^{z+}\} [e^{-\Psi F/RT}]^{z+} \quad (15)$$

where the second term of the right side, the Boltzmann factor, is defined by the Faraday constant F , the ideal gas constant R , the absolute temperature T , and the electric potential Ψ near the surface. The activity of surface species is set to one by definition. Another essential assumption is the diprotic acid model used to describe the protonation and deprotonation of surface sites.



During some surface complexation experiments it turned out, that the observations could only be explained satisfactory when assuming two site categories on one surface, having different binding properties: "strong" and "weak" binding sites with differing surface site densities. The strong binding surface sites are considered to be acidic, with a large degree of polarization. Weak binding sites are basic sites, with a much lesser degree of polarization, very similar to anion exchange sites. This concept is applied mostly to cation sorption, for anions no significant difference in sorbing on strong and weak sites could be detected. So identical complex stability constants are used (which reduces the number of parameters somewhat) for both site types. Fortunately, when dealing for sorption of contaminants in natural systems, the concentration of contaminants is near to trace levels. However, in cases, where the concentration of the sorbing ions is considerably larger, surface precipitation may become important. It is worthwhile to note, that such

precipitations onto a surface will already occur at concentrations below the values that must be exceeded in the bulk solution, because the solid activity on surfaces is less than unity.

8.2.1. Constant capacitance model

The constant capacitance model assumes only one layer or plane between surface and bulk solution. All specifically adsorbed ions contribute to the surface charge in this layer. The total charge T_{σ_o} is computed using a constant capacitance term C according to:

$$T_{\sigma_o} = C \Psi_o \quad (17)$$

Actually, the constant capacitance model is just a special case of the diffuse layer model for solutions of high ionic strength ($I > 0.01$ mol/L) and surfaces of low potential, see especially Hayes *et al.* (1991). It is strongly dependent from the ionic strength, and requires one more parameter than the Diffuse Double Layer model.

8.2.2. Diffuse double layer model

Here, the total charge T_{σ_o} is defined by the following equation, with all parameters being defined already before:

$$T_{\sigma_o} = 0.1174 \sqrt{I} \sinh \left(Z \Psi_o \frac{F}{2RT} \right) \quad (18)$$

An important advantage of this rather simple approach is, that there are no electrostatic parameters required at all. This reduces data needs and consequently data uncertainty, for a detailed discussion see Dzombak and Morel (1990). Ionic strength dependence is taken into account as long as I is below 0.1 mol/L. However, there are other cases, where this approach can not be applied because of a more complex surface chemistry.

8.2.3. Triple layer model

In the triple layer model, two different planes are assumed for the surface: The innermost or o-plane does only incorporate protonation or deprotonation of surface sites. All other specifically adsorbed ions are assigned to the outer or β -plane. Therefore, each plane has its own charge and potential. The third layer (to justify the name of the model) is as in the above models the diffuse layer. The total charge for these three planes are computed from the respective capacitances C and potentials Ψ :

$$\begin{aligned} T_{\sigma_o} &= C_{o-\beta} (\Psi_o - \Psi_{\beta}) \\ T_{\sigma_{\beta}} &= C_{o-\beta} (\Psi_{\beta} - \Psi_o) + C_{\beta-d} (\Psi_{\beta} - \Psi_d) \\ T_{\sigma_d} &= C_{\beta-d} (\Psi_d - \Psi_{\beta}) \end{aligned} \quad (19)$$

The charge σ_d of the diffuse layer is for monovalent symmetric electrolytes given by the Gouy-Chapman equation with the dielectric constant ϵ und the permittivity in vacuum ϵ_0 :

$$\sigma_o = - \sqrt{\epsilon \epsilon_0 RT I} \sinh \left(\Psi_d \frac{F}{2RT} \right) \quad (20)$$

Here we have thus two additional electrostatic parameters, $C_{\alpha-\beta}$ and $C_{\beta-d}$, often just referred as C_1 and C_2 . To reduce the number of variable model parameters, C_2 is generally fixed to 0.2, whereas C_1 is a fitting parameter inside a range between 0.1 and 2.0, which is supported by theoretical considerations.

8.3. Implementation of sorption models in the MINTEQA2 software

All seven sorption models described above can be dealt with in the MINTEQA2 code. However, in contrast to the reaction in homogeneous aqueous solutions (such as complexation), there is no default database for surface complexation delivered together with the program. The only exception is a database containing several surface reactions of trace metals onto an iron oxide surface, using the diffuse layer model. The user has to supply all the necessary data to set up an appropriate database himself, details will be given later. When it comes to the modelling of a speciation, the user first has to decide which SCM to apply, i.e. it must be capable of describing reality, and the necessary parameter sets must be available. Once this decision is made, up to five different surfaces can be defined simultaneously, e.g. to model a rock consisting of several minerals. And each of these surfaces can have up to two types of site.

In the overall modelling framework each of these up to five surfaces is treated like a set of pseudo-component. Such a set comprises of the following members (the internal species name is given in parentheses with # denoting the number of the surface/mineral, in the present realization of the integrated software this value will always be one):

- surface site 1 (ADS#TYP1)
- surface site 2 (ADS#TYP2)
- electrostatic component for the α -plane (ADS#PSI0)
- electrostatic component for the β -plane (ADS#PSIB)
- electrostatic component for the d -plane (ADS#PSID)

These components have also predefined internal species codes (from 811 through 859) that can not be altered by the user. When using non-electrostatic adsorption models or the diffuse double layer model then, of course, the latter three components become meaningless. For the constant capacitance model only the first electrostatic component is used. Pseudo-species that are meaningless for the selected sorption model must not appear in the species list. The general approach is to write all surface complexation reactions in terms of the solved ions and the above pseudo components. Contrary to the aqueous species no activity coefficients are calculated for both the sorbed species and the unreacted surface sites.

Now the algorithms used to apply the electrostatic adsorption models shall be explained in more detail. In all of these models a charge σ is associated with the surface (or with both the α - and β -plane for the triple layer model) which has to be equal (with opposite sign due to the charge balance) to a charge σ_d associated with a diffuse layer of counter ions. The electrostatic components that are essentially Boltzmann factors are defined as components just to fit them into the general computation scheme. They are incorporated as stoichiometric components in the surface complexation reactions but are no real chemical entities. Also no total concentration can be assigned to them, rather the total charge is computed using the equations presented in the previous section. Instead of mass balance equations, charge balance equations are used to iterate the equilibrium concentrations for sorbed species. They have the form:

$$\sum_i x_{\sigma i} Z_i - T_{\sigma} = 0 \quad (21)$$

where Z_i is the charge of sorbed ion i , x_{oi} is its stoichiometric coefficient, and T_σ is the total charge for the surface according to the applied model (see equations **17** to **19**).

As pointed out at the beginning of this section, the user has to set up his own database containing all the thermodynamic information necessary to apply SCM. This means formulating all relevant chemical reactions with the proper stoichiometric coefficients, the latter being directly inserted into the database. When writing the surface complexation reaction, one should keep in mind that MINTEQA2 expects formation constants for the complexes, and that all reactions have to be re-written if necessary in terms of the unreacted site =SOH. Moreover, the Boltzmann factors also have to appear explicitly in the reaction. This means, MINTEQA2 uses intrinsic reaction constants K^{int} compared to the apparent constants K^{app} directly determined from experiment. Their relationship is derived from equation **15** and given below, where Δz stands for the change in charge of the surface species in the course of the considered reaction.

$$K^{int} = K^{app} \left[e^{-\Psi F \Delta z / RT} \right] \quad (22)$$

Two examples will help to understand the formalism. It is important to keep this relationship in mind when extracting surface complexation data from publications or databases as sometimes it is not stated, whether intrinsic or apparent values are reported.

The first example is about the sorption of a monovalent metal ion onto a deprotonated surface site described with the triple layer model. The corresponding reaction, starting from =SOH, is as follows:



The index s for proton and metal ion indicates, that both are not in the bulk solution but already in the charged surface region, i.e. energy had to be spent to move them in an electrical potential. This is accounted for by applying equation **15** to correct the respective activities. It gives for the proton:

$$\{H_s^+\} = \{H^+\} \left[e^{-\Psi_o F / RT} \right] \quad (24)$$

The equation for the metal ion is similar, but whereas the proton is bound in the o-plane, the metal ion is bound in the β -plane, thus the Boltzmann factors have different potentials Ψ . By substituting these expressions into equation **22**, one derives:

$$K = \frac{\{=SO-M\} \{H^+\} \left[e^{-\Psi_o F / RT} \right]}{\{=SOH\} \{M^+\} \left[e^{-\Psi_\beta F / RT} \right]} \quad (25)$$

This corresponds to the following reaction written in terms of the MINTEQA2 components:



The second example is the sorption of a divalent metal ion on a surface using the diffuse layer model. The conventional reaction formalism would be:



After transforming again the activity of proton and metal ion (this time the model requires them both to be in the o-plane !), the mass action expression is:

$$K = \frac{\{=SO-M^+\} \{H^+\} \left[e^{-\Psi_o F/RT} \right]}{\{=SOH\} \{M^{2+}\} \left[e^{-\Psi_o F/RT} \right]^2} \quad (28)$$

$$= \frac{\{=SO-M^+\} \{H^+\}}{\{=SOH\} \{M^{2+}\} \left[e^{-\Psi_o F/RT} \right]}$$

The stoichiometry in MINTEQA2 therefore is expressed as:



Besides the thermodynamic database, the user has to specify all surface sites with their parameters in the input file. Then, the total analytical input concentration T_{SOH} for a surface site in mol / L must be given. It is calculated from:

$$T_{SOH} = \frac{N_s S_A C_s}{N_A} \quad (30)$$

where N_s is the surface site density in sites / m², S_A is the specific surface area of the mineral in m² / g, C_s is the concentration of the solid in the suspension in g / L, and N_A is Avogadro's number.

After the surface complexation models available in MINTEQA2, together with their actual implementation, were discussed, the next chapter will focus on the interaction between MINTEQA2 and the risk assessment package PRISM / BIOPATH.

9. Combination of MINTEQA2 with PRISM and BIOPATH

9.1. Chemical data input: internal structure and handling

There are several premises concerning the internal data structure and data processing of the chemical part of the parameter vector for the **PRISM / BIOPATH / MINTEQA2** project:

- To keep the chemical model as simple as possible, and thereby speeding up the processing, the set of chemical components can differ from compartment to compartment.
- Only a subset of the features offered by **MINTEQA2** is used, again to keep the overall program as simple and fast as possible.
- The concentration of each component is given either as numerical value (several concentration units are possible), as being in equilibrium with a gas phase (then the appropriate partial pressure is required), or as being in equilibrium with an (infinite) mineral. In the last case, this will add no variable parameter to the **PRISM** input vector.
- Adsorption phenomena can be included utilizing different models. At present just one surface (i.e. mineral type) with up to two different surface site types may be specified. This will add up to five variable parameters **S1 .. S5** to the **PRISM** input vector, depending on the chosen SCM model.
- One can chose different reaction constants β to be modified depending on the actual components for each compartment. But the same constant should be modified in an identical manner for each compartment where it is relevant. The reaction constants may include complexation, precipitation/dissolution and sorption.
- There is also an option to suppress certain reactions totally, this will of course not contribute to the parameter vector for **PRISM**.
- All parameters are stored sequentially in a vector of structures in the fixed order shown below for a system consisting of **z** different compartments. The indices **n** for the concentrations **C** and **m** for the stability constants β do not necessarily have the same value in each compartment. It should be noted that the term box is used as a synonym for compartment from here on.

T	S1 ... S5		Eh		pH		C₁ ... C_n		β₁ ... β_m	(box #1)
			:							
			:							
	S1 ... S5		Eh		pH		C₁ ... C_n		β₁ ... β_m	(box #z)

9.2. Application scheme

The following scheme lists all actions necessary to set up and run the integrated **PRISM / BIOPATH / MINTEQA2** model properly. The approach for the incorporation of the **EQ3/6** code will be quite similar, then of course no surface parameters are required because **EQ3/6** is not able to handle SCM.

Step: Action:

- 1 Define the compartment structure:
 - 1.1 Write a FORTRAN file with a function **users()**. It includes the **BIOPATH** routines that computes the contaminant transfer between the compartments and makes the dose calculations. Here also the call to the speciation code interface must be inserted, followed by appropriate assignments of the thus computed K_d values.
 - 1.2 Compile the source code and link it with other routines and libraries to get an executable **PRISM2**.
 - 1.3 Create a file **model.box** in PRISM1.INP style, containing all non-chemical parameters for all compartments.
 - 1.4 Create input files PRISM2.INP (containing identifiers for the response functions, and also some nuclide-specific data) and PRISM3.INP (defining the ranking method).
- 2 Identify each compartment that requires a K_d and collect all the necessary data:
 - 2.1 Determine analytical concentrations for the major anions and cations, and the contaminants, including also probable equilibria with solid phases or the atmosphere. Data consistency should be checked separately with a chemical speciation modelling program.
 - 2.2 Select thermodynamic data for the reactions, which in fact means a critical assessment, correction and extension of the default **MINTEQA2** database THERMO.DBS.
 - 2.3 Collect surface complexation data (for the contaminant and competing ions) to build an SCM input file for **MINTEQA2**:
 - Identify the relevant mineral phases and their concentration.
 - Select a suitable SCM (Surface Complexation Model) from the available list.
 - Collect intrinsic surface properties.
 - Collect stability constants of surface complexes.
- 3 Create a file **model.chem**. Every parameter can be assigned uncertainties with corresponding distribution functions, see Section 9.3.1 for details.
 - Specify the temperature.
 - Specify the file with the SCM database, depending on the mineral dominating sorption processes.
 - Specify intrinsic surface data, both site-specific and mineral-specific ones, see Section 9.3.2 for details.
 - Specify redox potential (as Eh or pe) and pH.
 - Specify the number of master species (chemical components), their formulas, concentrations and (optionally) guesses for free concentrations.
 - Specify any reaction that should have a reaction constant different from the entry in the thermodynamic database. Again, uncertainties can be specified.
 - Specify any species that should be excluded from consideration.
 - Specify the species used to keep the charge balance (not used by **MINTEQA2** at present).
- 4 Scan **model.chem** with a separate preprocessor executable **CHEM2MIN** that build from it (in parallel to guarantee consistency between all files):
 - a **MINTEQA2** input template **minteq.template**, see Section 9.3.2 for details;
 - a **PRISM1** input file PRISM1.INP, which optionally can be edited by the user to introduce correlations between parameters;
 - a further input file **dim.chem** containing the **MINTEQA2** species code for the contaminant, the number of compartments and for each compartment the number of components, the number of modified log β 's, the number of SCM parameters, the type of the redox value, and the number of infinite minerals.

- 5 Run of **PRISM1**: generation of all parameter set variations, stored in binary format in the file PRISM1.RSL. The output file PRISM1.OUT allows a check for correct running.
- 6 Run of **PRISM2**: loop over all parameter sets, for each vector the FORTRAN subroutine **users()** is called that performs the following operations:
 - 6.1 Analyse the parameter vector, extract the relevant values and build a **MINTEQA2** input file for each compartment (also including the constant parameters). Concatenate them to one large input file MININ.DAT.
 - 6.2 Run **MINTEQA2** to get for all compartments the speciation of the aqueous phase and the amount of precipitated minerals. In case that **MINTEQA2** fails for one or more parameter sets, please check the monitoring file PRISM2.LOG. If serious problems remain, further clues can be obtained when compiling the interface modules with the compiler option “-DDEBUG”.
 - 6.3 Calculate K_d values for all compartments, using the results from the **MINTEQA2** output file MINOUT.OUT, and store them in the appropriate **BIOPATH** variables.
 - 6.4 Run **BIOPATH** for each time step. K_d is considered to be constant, because the only transport accounted for in **BIOPATH** is the contaminant. In case of time-dependent parameters, K_d will be calculated for each time step separately.
 - 6.5 Collect the final response sets together with the respective input parameter sets and write a binary output file PRISM2.RSL. The file PRISM2.OUT contains some additional information.
- 7 Run of **PRISM3**: Sensitivity analysis with respect to all parameters (delivering also covariance matrices) based on the file PRISM2.RSL. The results are summarized in PRISM3.OUT and PRISM3.TBL.
- 8 Analyse the ranking and correlation information, create graphs and reports.

9.3. Description of data structures

The input for the chemical and non-chemical part of the risk assessment model is separated and defined in extra files. They are both processed by the **CHEM2MIN** or **CHEM2EQ** executables to produce input templates for **MINTEQA2** or **EQ3/6**, respectively, and for the **PRISM** code. Thus it is assured that the model description is consistent for both parts of the modelling. The file containing the chemical information is called `model.chem` and has to be written by the user.

9.3.1. Chemical model description file (`model.chem`)

It has a well-defined, line-oriented structure. The first lines contain some general information for documentation purposes. Then detailed chemical data for each compartment of the model set-up are specified. The following model parameters and their respective error function will be transferred to the **PRISM** code: temperature, sorption parameters, redox state, pH, and all concentration values (aqueous and gas phase).

Each such model parameter has its own entry line. It always consists of the acronym for the parameter (the chemical formula in case of species), an integer to indicate the concentration unit (in case of redox state and master components) or the species type (in case of suppressed or modified species), a character to specify the type of the error distribution, the numerical value for the parameter, and finally the parameter(s) describing the error distribution function. At present, there are eight uncertainty distribution functions implemented in **PRISM**. They are listed below together with their identification codes and required parameters. Only the one- or two-letter code and all the non-zero parameters must be given in `model.chem`. Optionally as last entry on a line, guesses for the true free equilibrium concentration of a

master species can be given. This will be used to initialize the iteration of chemical speciation, thereby enhancing its convergence.

```
'C ' -- CONSTANT      (const. value, zero, zero, zero)
'H ' -- HISTOGRAM     (zero, zero, zero, zero)
'U ' -- UNIFORM       (zero, zero, minimum, maximum)
'LU' -- LOG-UNIFORM   (zero, zero, minimum, maximum)
'T ' -- TRIANGULAR    (midpoint, zero, minimum, maximum)
'LT' -- LOG-TRIANGULAR (midpoint, zero, minimum, maximum)
'N ' -- NORMAL        (mean, std.dev., minimum, maximum)
'LN' -- LOG-NORMAL    (mean, std.dev., minimum, maximum)
```

The type 'H' gives a random order of numbers from 1 to the number of iterations (set of parameters). It is important to note, that the above codes reflect FORTRAN string conventions. In this project here, only the respective characters without apostrophes are required.

To incorporate adsorption phenomena into the calculation (not possible with **EQ3/6**), an adsorption isotherm type or a surface complexation model (**SCM**) must be specified. The following options are available:

```
0 -- No sorption model at all
1 -- Simple  $K_d$  approach
2 -- Langmuir adsorption isotherm
3 -- Freundlich adsorption isotherm
4 -- Ion exchange
5 -- Constant capacitance SCM model
6 -- Triple layer SCM model
7 -- Diffuse double layer SCM model
```

If there is sorption to be considered, a file with the appropriate thermodynamic database for the sorption reaction must be given, its name defaults to **SCM.DBS**. Several parameters are necessary to describe the sorption processes, for their identification fixed, pre-defined keywords must be used as (pseudo-) species names, as specified in the following paragraph. The first sorption parameter, the concentration of the sorbent phase (in gram suspended solids per litre solution, including only the fraction of the reactive component) is a site-specific one that must be determined experimentally (keyword: **ADS1CONC**). The specific surface area (in m^2 per gram solid) of the sorbing mineral must be provided as next item (keyword: **ADS1AREA**). Then the number of distinct surface sites must be given, followed by the respective site concentration(s) in mol / L (keywords: **ADS1TYP1** and **ADS1TYP2**), with the first one usually assigned to the strong, and the second one to the weak binding site type. These values must be computed from site-specific (the solid concentration) and from mineral-specific (specific surface area and binding site density) parameters. Finally, only in the case of the Constant Capacitance SCM or Triple Layer SCM, a value for the inner layer capacitance (in F / m^2) is required (keyword: **ADS1CAPI** - with the last character being the letter I, not the digit 1). The outer layer capacitance additionally required in the Triple Layer SCM is set in the source code of **CHEM2MIN** to a default constant value of 0.2 for all minerals, as recommended in Dzombak and Morel (1990). For all surface parameters, the concentration unit flag is meaningless and can be set to zero. Here, it should explicitly be mentioned that K_d values computed for mixed solids with only a fraction sorbing must be multiplied with that fraction before any comparison with conventional (default or experimental) K_d values.

For the redox state definition, the concentration unit type specifies whether **Eh** (-1) or **pe** (-2) is used. Any other values of this type will be interpreted to be zero, i.e. there is no redox aspect in the problem.

CHEM2MIN or **CHEM2EQ** will pass the redox type for each box to the file `dim.chem`. The redox value is always included in the parameter list for **PRISM1**, even if not defined. Before passing the redox state value to `MININ.DAT`, **Eh** values (in V) will be converted to **pe** according to:

$$pe = \frac{F \cdot Eh}{2.303 \cdot R \cdot T} \quad (31)$$

with **F** being the Faraday constant (in C mol⁻¹), **Eh** the redox potential (in V), **R** the universal gas constant (in J mol⁻¹ K⁻¹), and **T** the temperature (in K).

In case of any species (major ions = master species, components, contaminants, minerals, species to be suppressed or to be assigned modified stability constants) its formula is dependent both on the speciation software and the thermodynamic database that are used. For **MINTEQA2**, e.g., it has to be in accordance with the one in `THERMO.DBS` (for aqueous species, solids and gases) and `COMP.DBS` (for components). If such formulas in the *.DBS files contain any spaces, they must be substituted then by underscores in the input file `model.chem`. A formula is followed on the same line by a concentration type flag, specifying the unit of the concentration parameter value. Valid concentration types for species are:

- 0 mol / kg H₂O (molality);
- 2 mol / L H₂O(molarity);
- 3 mg / kg H₂O;
- 19 a mineral is in equilibrium with the aqueous species and thus determines its activity. The name of this mineral then follows immediately, a concentration value and its distribution function is not required in such cases. Therefore the respective parameters are omitted. If a mineral is defined as “infinite” and thus determining a component, all other minerals containing the same component and exhibiting a higher solubility must explicitly suppressed, due to a bug in the **MINTEQA2** software.
- 21 an infinite gas reservoir determines the activity of the aqueous species (e.g. for CO₂(g) determining carbonate activity), the logarithm of the partial pressure of the gas in equilibrium with the species must then be given as concentration value.

The concentration type flag of the first component per compartment defines all other concentration type flags in that compartment. Therefore values other than 0, 2 or 3 are not valid for the first component in a compartment.

Lines starting with a hash sign, #, are comments. They can be inserted everywhere to guide the user and are consequently skipped by the program. If there are several contaminants relevant for a site, for each of them a separate input file must be created. But this simply means making copies from a “master” file and changing the entry after “# Contaminant”.

In case of species declared to be explicitly excluded from consideration, or to be assigned a modified stability constant, the meaning of the concentration type flag changes to a species type flag. Valid species types are:

- 0 - aqueous species
- 1 - mineral
- 2 - gas

An example for `model.chem` can be found in Appendix A.

9.3.2. Conventional PRISM / BIOPATH input file (**model.box**)

The file **model.box**, delivering all non-chemical input to PRISM / BIOPATH, follows the special input file format required for **PRISM1**, with a structure of four blocks. The first block is just a single line, giving (in free format) a short description of the problem, the first 40 characters will be printed to the output file. The second block, again just one line, consists of three integers: The number of parameter variations, the number of parameters, and a seed for the random number generator (i.e. an arbitrary selection). The third block consists of one line for each parameter, starting with the name of the parameter (a string with a maximum of 12 characters, delimited by apostrophes), then the acronym for the chosen error distribution function for this parameter (two characters enclosed in apostrophes, for valid options see the previous section), and finally four floating point numbers describing the error distribution. The fourth block gives all the parameter correlation, with one line for each correlation. It starts with the two names of the two correlated parameters (as specified in the third block and in the same format), then the floating point number for the correlation coefficient follows.

There are no empty lines between the blocks or after the last block. Strings may contain spaces. Floating point numbers with exponents must have an upper-case **E** and up to three digits for the exponent. An example of a **model.box** input file is given in Appendix B. All input is in free format, i.e. the amount of space between the various input items is not relevant. After being processed by **CHEM2MIN**, all parameter names, together with the values (and distribution type, parameters, initial guesses) are used to extend this original **PRISM1** input file, generating a new “combined” input file named **PRISM1.INP**.

9.3.3. Template file for the chemical speciation (**minteq.template**)

To reduce the overhead of computing the chemical speciation for each of the parameter sets, a template file is used. Actually this file is a stack of templates for all boxes of the model. So the reading of the extensive database becomes necessary only once per time step.

The template comes with the exact structure required by the respective chemical speciation modelling software, here **MINTEQA2**. However, for each parameter sampled by **PRISM**, an unique tag of the form **#@#PARAiii##** is inserted into this template instead of an actual value, with **iii** standing for the respective three-digits number of the parameter (= position in the vector obtained from **PRISM** as shown in Section 9.1). The physical order in the template can differ from the logical order, and there can be several tags on one input line. Some constant parameters of the chemical model are not forwarded to **PRISM** but rather already incorporated directly into the template to make the model and thus the computing lean and fast. An example of a **MINTEQA2** input template file is given in Appendix C.

For each parameter set generated by **PRISM1**, the template is later scanned by the interface module of the integrated software. Tag numbers are recognized and the tags themselves substituted by the actual correct parameter values, independent from the position in the input file.

9.3.4. Input file for PRISM2 (**PRISM2.INP**)

This input file delivers information for **PRISM2** in a line-oriented manner. The first line simply contains the number of response functions created by **PRISM2**, this value of course must be in correspondence with **users()**. The second line is just a (problem-descriptive) text with its first 40 characters to reappear in various output files. The following lines then contain for each response a label / string, delimited by apostrophes. Here, several strings can be grouped on the same line. Usually the end of the file is reached

after these strings. But because this input file stays open when the subroutine *users()* is entered, additional parameters can then be read in from PRISM2.INP. This can be used, e.g., to pass on some constant values such as the half-life of isotopes.

9.3.5. Input file for PRISM3 (PRISM3.INP)

PRISM3 needs also some specific information that is delivered through PRISM3.INP. It is, however the smallest input file, just containing two lines in its minimal version. The first line is a descriptive text used in the output files (40 characters long). The second line contains values for various control variables: the type of regression to be performed (IRNK), the significance level for entrance of a variable into the regression model (ALFAI), the significance level for rejection of a variable previously entered into the model (ALFAO), the minimum improvement in R2 that a variable can make for regression analysis to continue (RCRIT) and the minimum correlation between two parameters and/or responses for inclusion in printout (EPR). Finally, a third line may contain the number of previous dose pathways (NRD) considered in the last response if the last response name is "TOTAL DOSE". It is possible to invoke the default initialization by just ending the second input line with a slash. The following values are valid entries for the variable IRNK:

- 1 For both unranked and ranked regression,
- 0 For unranked regression,
- 1 For ranked regression,
- 2 For no regression,

The default settings for all control variables are as follows:

- IRNK = 1,
- ALFAI = 0.1,
- ALFAO = 0.5 (Demand: ALFAO > ALFAI),
- RCRIT = 1,
- EPR = 0.25,
- NRD = 7.

9.4. Data flow between PRISM, BIOPATH and MINTEQA2

The flow chart in Fig. 1 depicts the data transfer and processing between the preprocessor, the various **PRISM** modules, **BIOPATH**, **MINTEQA2**, and the new interface routines connecting them all. Boxes with rounded corners are data files. Rectangular "buttons" stand for programs or subroutine modules: black for **PRISM**, light grey for **BIOPATH**, dark grey for **MINTEQA2** and the new interface **CHEM2MIN**. Arrows show the data processing, which follows the paths outlined in Section 9.2. The box SCM.DBS stands for any appropriate database of surface complexation constants.

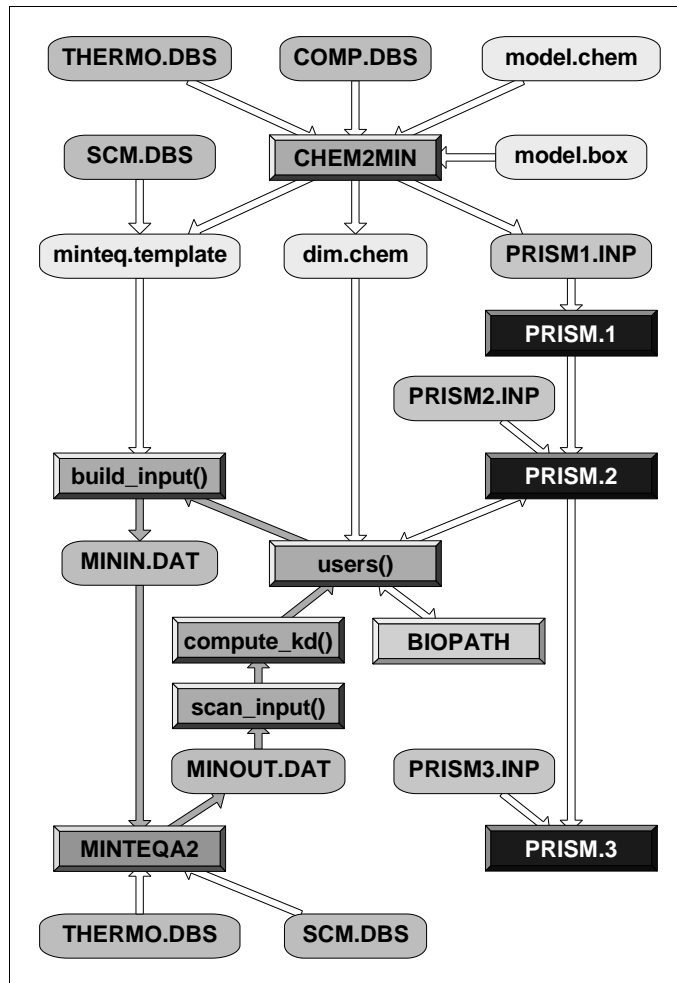


Figure 1: Data flow between preprocessor, PRISM, BIOPATH, MINTEQA2, and the interface modules

10. Conclusions

Reliable risk prognostics for radioactively contaminated sites requires detailed information on the source term. It was demonstrated, that in order to properly describe the evolution of the source term in space and time an essential part of the information is related to physico-chemical phenomena. An overview over the most important of these phenomena were elaborated, together with their parameter that are necessary for modelling. These parameters can be grouped into three classes:

- system-specific parameters for the stationary state;
- system-specific parameters for the dynamic evolution;
- reaction-specific parameters.

The two classes of system-specific parameters must be determined on the given site. A multidisciplinary approach, including radiologists, geologists, hydrologists, chemists, engineers and mathematicians, is not only required for all later modelling purposes but also to ensure high-quality input data. Especially for the stationary state data, recommendations for sampling techniques and analytical methods were given. The reaction-specific parameters most often will be extracted from literature, several valuable sources were pointed out, also guidance on the critical evaluation and on the proper usage of such databases is given. This is accompanied by a list of useful methods to be applied in cases were, e.g. thermodynamic, data must be determined through own experiments. Most of the discussed physico-chemical phenomena directly contribute to the chemical speciation of the contaminant of interest. Namely, these are reactions in homogeneous solution (redox reactions, hydrolysis, complexation, etc), the formation of pure and mixed solid phases, and reactions on mineral surfaces. The modelling of chemical speciation has to take them all into account.

This reports describes in detail the state-of-the-art of chemical speciation and migration modelling, giving many examples of the transition of modelling approaches into software. So far, the complexity of physico-chemical phenomena has not been properly accounted for in risk assessment software. The mainly applied K_d concept has several drawbacks but can be substituted by better approaches (unfolding the K_d into its main determining processes). This was demonstrated through the development of a new methodology, based on a comprehensive chemical speciation modelling with inclusion of surface complexation reactions (MINTEQA2 [Allison *et al.*, 1991]) and on the full integration of this part into an existing risk assessment software package (PRISM / BIOPATH [Gardner *et al.*, 1983; Bergström *et al.*, 1982]). Appropriate software has been developed and tested (RESTRAT TD7 [Brendler *et al.*, 1999]). Applications of the newly developed methodology towards five different test cases are demonstrated in the RESTRAT TD5 [Brendler, 1999]. The new approach, and especially the unfolding of the K_d , makes it possible to perform more detailed sensitivity analysis, to find the most critical parameters, to reduce the parameter space, and finally to prepare the way for more reliable models. Thus the objectives of work package WP2.1 are met.

As an outlook the further development of the new approach should be mentioned. This could address, e.g., the introduction of time-dependence for various chemical parameters coupled to the incorporation of kinetics to properly describe real geochemical processes with involvement of meta-stable phases. Another direction of further research could be the move to other types of transport models such as the ones described in Section 5.5.2.

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Appendices

Appendix A: Example for an input file model.chem

```
# Text for overall problem description (just one line)
Generic Rock Pile Site (RESTRAT PROJECT) - Full Model
# Database to be used (3 characters)
fzr
# Name and date of model creator
V.Brendler
21.09.1998
# Number of boxes
1
# (average) Temperature in Celsius
TCELSIUS 0 c 15
# Contaminant
UO2+2
# For each box: Comment line
Aquifer Layer (Box 1)
# Type of adsorption model
7
# Sorption database
HFO_DDL.DBS
# Sorption parameters; Type; Distribution; Values
ADS1CONC 0 t 1.967e3 1.0e3 2.0e3
ADS1AREA 0 c 600
2
ADS1TYP1 0 c 0.106 -0.2
ADS1TYP2 0 c 4.43 -0.2
# Redox state and pH
Eh -1 n 0.346 0.02
pH 0 n 7.46 0.15
# Number of components
10
# Component formula; Concentration type; Distribution; Values
UO2+2 0 n 1.004e-6 2.36e-7 1.0e-15
NO3-1 0 c 1.188e-4
SO4-2 0 n 2.248e-2 1.92e-3
CO3-2 21 n -2.49 0.25
Cl-1 0 n 5.639e-4 6.47e-5
H4SiO4 19 QUARTZ
K+1 0 n 1.175e-3 8.91e-5
Na+1 0 n 8.647e-4 4.44e-5
Ca+2 19 CALCITE
Mg+2 0 n 1.038e-2 3.33e-5
# Number of reactions with varied equilibrium constant
0
# Number of minerals or complexes to be suppressed
2
# Species formula; Species type
PYROPHYLLITE 1
DIASPORE 1
# Species for charge balancing
SO4-2
#
```

RESTRAT - Physico-Chemical Phenomena: State-of-the-Art Description

Appendix B: Example for a model.box input file

```

Ravenglass Estuary - Americium
1000 54 2555512
'MCumbCost' 'T' 27 0 26 28
'MSedChan' 'T' 3.5E8 0 3E8 4E8
'MBankLow' 'T' 0.13 0 0.12 0.14
'MBankUpp' 'T' 0.4 0 0.35 0.45
'MBankEro' 'T' 3.5E8 0 3E8 4E8
'SedAccLow' 'T' 6 0 5.5 6.5
'SedAccUp' 'T' 9.5 0 9 10
'ResTiLow' 'T' 20 0 10 30
'SedRat' 'T' 12 0 10 14
'SuspRa' 'N' 5E-3 4E-3 1E-4 1
'ResuspEr' 'U' 0 0 0 6
'BulkDens' 'LT' 1100 0 1000 1600
'ChanYta' 'T' 1 0 0.9 1.1
'ErYta' 'T' 1 0 0.9 1.1
'FracToEr' 'U' 0.3 0 0.1 0.9
'Outflow' 'T' 355 0 340 370
'SedRatIr' 'T' 10 0 5 15
'SuspIr' 'T' 5E-3 0 4E-3 6E-3
'MeanDepth' 'T' 26 0 24 27
'UpBaArea' 'T' 1.98 0 1.95 2.0
'TotArea' 'T' 4.2 0 4.1 4.3
'PasYield' 'T' 1.5 0 1 2
'FrMilkCow' 'U' 0.5 0 0 1
'MeatProd' 'T' 150 0 100 200
'MilkProd' 'T' 5000 0 4000 6000
'FrSheep' 'U' 0.5 0 0 1
'ShMeetPr' 'T' 10 0 5 15
'FishProd' 'T' 10 0 5 15
'SheFiProd' 'T' 10 0 5 15
'Occupancy' 'N' 1000 -0.2 1E-10 1E10
'Pop' 'N' 1000 -0.2 1E-10 1E10
'CoPaCon' 'T' 16 0 10 25
'ShPaCon' 'T' 1.1 0 0.5 2
'DF' 'C' 1 0 0 0
'Soluble_Ir' 'LT' 0.054 0 0.01 0.097
'Part_Ir' 'LT' 22.2 0 0.1 53.2
'In_Ir_3' 'T' 7.5E15 0 6E15 9E15
'In_Chan_4' 'T' 3.3E12 0 1E12 6E12
'In_Ba_L_5' 'T' 4.3E12 0 2E12 7E12
'In_Ba_U_6' 'T' 1.2E13 0 5E12 2E13
'In_Ero_7' 'T' 2.8E12 0 1E12 5E12
'Source_Ir' 'C' 0 0 1E13 2E13
'DF_milk' 'LT' 1.5E-6 0 4E-7 2E-5
'DF_meat' 'LT' 4E-5 0 4E-6 1E-4
'DF_sheep' 'LT' 3E-3 0 3E-4 3E-2
'CF_plant' 'LT' 1E-3 0 2E-4 0.2
'BF_fish' 'LT' 50 0 0.5 200
'BF_Shellf' 'LT' 500 0 100 1000
'Kd_sed' 'LT' 552 0 30 790
'T_halv' 'C' 7380 0 0 0
'Dosfakt' 'C' 2.1E-7 0 0 0
'ExtDosF' 'C' 1.1E-15 0 0 0
'Soluble_Ir' 'Part_Ir' 0.85
    
```

RESTRAT - Physico-Chemical Phenomena: State-of-the-Art Description

Appendix C: Example for a MINTEQA2 input template

```
Generic Rock Pile Site (RESTRAT PROJECT) - Full Model
Created at: 21.09.1998
Created by: V.Brendler
Box 1: Aquifer Layer (Box 1)
###PARA001## MOLAL 0.000
0 0 1 1 2 0 0 0 1 3 0 0 0
4 1 7
###PARA002## ##PARA003## ##PARA006## ##PARA007## 81
1 0.0 0.0 /E-1
330 0.0 0.0 /H+1
893 ##PARA010## -15.00 n /UO2+2
492 ##PARA011## 0.00 /NO3-1
732 ##PARA012## 0.00 /SO4-2
140 0.0 0.0 /CO3-2
180 ##PARA014## 0.00 /Cl-1
770 0.0 0.0 /H4SiO4
410 ##PARA015## 0.00 /K+1
500 ##PARA016## 0.00 /Na+1
150 0.0 0.0 /Ca+2
460 ##PARA017## 0.00 /Mg+2
811 ##PARA004## 0.00 /ADS1TYP1
812 ##PARA005## 0.00 /ADS1TYP2
813 0.0 0.00 /ADS1PSIo

3 5
330 ##PARA009## 0.00 /H+1
3301403 ##PARA013## 0.00 /CO2 (g)
1 ##PARA008## 0.00 /E-1
2077002 4.0060 0.00 /QUARTZ
5015001 8.4750 0.00 /CALCITE
6 3
8603002 0.0 0.00 /PYROPHYLLITE
2003002 0.0 0.00 /DIASPORE
813 0.0 0.00 /ADS1PSIo
```

This example was generated based on the chemical input file shown in Appendix A, but it does not show the sorption database that will also be appended automatically on the MINTEQA2 input file template.