

Modeling of Near Field Actinide Concentrations in Radioactive Waste Repositories in Salt Formations: Effect of Buffer Materials

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ABSTRACT

Engineered barrier systems are designed to reduce the near field actinide concentrations in case of water penetration into a repository. In this paper, the influence of buffer materials, such as MgO/CaO and clays, on the solubilities of Am, Np, Pu, and U is studied. The analysis is performed for low level cemented waste forms in a rock salt formation in contact with MgCl₂ saturated salt brine (Q-brine).

The evolution of the geochemical milieu by cement corrosion is calculated using reaction path modeling supported by the code EQ3/6. The influence of different buffer materials is analyzed with respect to their impact on the solution chemistry and corresponding actinide concentrations.

INTRODUCTION

Safe disposal of radioactive waste relies on multi-barrier systems [1]. Part of these systems are engineered barriers which provide for a plugging of the openings as well as for the chemical buffering of solutions and sorption capacity. Geochemical evaluation of buffer and backfill materials under repository relevant conditions focuses on two main topics i) the long-term geochemical stability and the chemical properties in case of solution access and ii) the geochemical buffering of the solution with respect to Eh, pH, and pCO₂ [2,3].

The geochemical stability of buffer and backfill materials in contact with salt solutions and the evolution of the solution composition depends on the waste forms (cement and organic components), the remaining void volume, and different boundary conditions, such as pH and temperature etc.

In this paper the actinide solubility is investigated. In the case of radioactive waste disposal in German salt formations, brines having a high ionic strength have to be considered in this analysis. Different buffer materials, i.e., MgO, CaO and clays, were selected and their behavior in contact with cemented waste forms and with a MgCl₂ saturated salt brine (Q-brine (Table 1)) was investigated.

Table 1. Composition of Q-brine [mol·(1000 mol H₂O)⁻¹] [4]

NaCl	KCl	MgCl ₂	MgSO ₄	pH	T	ρ
$\left[\frac{\text{mol}}{10^3 \text{ mol } H_2O} \right]$		$[^{\circ}C]$	$\left[\frac{g}{cm^3} \right]$			
6.8	17.4	77.3	3.2	5.5	55	1.30

Methods

The geochemical milieu, actinide concentrations, and possible precipitation of solid phases are computed by geochemical model calculations using the EQ3/6 Rel.7.2a package [5]. A thermodynamic equilibrium between the solution and solid phases is assumed. The initial solution composition is computed, including all species involved in further reactions.

The cemented waste forms consist of different solid mineral phases. After cement corrosion in Q-brine most important are portlandite (Ca(OH)₂) and calcium-silicate-hydrate phases (CSH). Further phases identified experimentally are Friedel's salt, quartz, and ettringite [4]. It was shown [4], that application of the special reactant approach is valid and computed and experimental results agree well. The special reactant approach is preferred for modeling in this work, because different types of cements are deposited in real disposal having different compositions. The element composition of the cemented waste form used is given in Table 2.

Table 2. Element composition of cement and smectite used in EQ6 calculations

element	O	H	Ca	Si	Al	Mg	Fe	Mn
cement composition mol·(kg cement) ⁻¹	46.9	30.3	8.2	2.4	0.7	0.3	0.2	0.01

In contrast the influence of clay, CaO and MgO is modeled using the pure phases compositions of Smectite-low-Fe-Mg, Portlandite and Brucite (data base data0.com.R22a EQ3/6 [5]).

To simulate corrosion of cemented waste forms or the influence of buffer materials by reaction path modeling, small amounts of a "special reactant" having the element composition of the waste form or buffer material are "added" numerically to the solutions. The new equilibrium is determined by EQ6 computations including precipitation of super-saturated mineral phases. In the next step (additional special reactant added) all phases precipitated in the first reaction step are retained and allowed to dissolve again, if they are under-saturated in the new reaction step.

The steps of the EQ6 reaction path modeling run are considered to represent the progress of waste form corrosion or buffer material dissolution (including precipitation of secondary phases). The model bases on thermodynamic equilibrium exclusively. Time dependencies of the corrosion/precipitation processes involved can be considered by application of empirical rate constants. However, this rates are not available.

The data base used for all calculations is based on the data of Harvie, Møller, Weare (1980) [6]. All calculations were done using the Pitzer formalism [7,8]. For calculation of cement systems silicate and aluminate species as well as additional phases had to be incorporated to the data base. The new data base was checked for consistency ([9,10]). Thermodynamic data of

actinides used base on the NEA-TDB [11,12], literature compilations and new measurements [13-15]. Reliability and consistency of the database was checked by comparison with experimental data [13-15].

Scenarios

The evolution of the solution composition and the actinide solubilities are calculated for three different scenarios corresponding to different backfill concepts. For all three scenarios it is assumed that Q-brine penetrates the disposal rooms. Here, the brine comes into contact with the waste forms and the buffer and backfill materials. Inert backfill materials, i.e. crushed rock salt, have no influence on the solution composition. Such materials provide for mechanical stabilization of the disposal rooms.

In the following sections, the three different disposal scenarios used in the model calculations shall be described.

Scenario I: Q-brine in contact with cemented waste forms and inert backfill

Scenario II: Q-brine in contact with cemented waste forms, inert backfill, and additional MgO buffer material

Scenario III: Q-brine in contact with cemented waste forms, inert backfill and MgO buffer material, and additional smectite backfill

The first scenario represents the disposal of cemented low level waste forms. In this disposal concept, the typically remaining void volumes and amounts of cemented waste forms are taken into consideration.

In the second scenario, MgO buffer material is used additionally. In the presence of organic waste material, considerable amounts of CO₂ may be produced by microbial decomposition. Enhanced CO₂ concentrations cause enhanced concentrations of DIC (dissolved inorganic carbon). DIC is in equilibrium with the carbonate concentration which influences the actinide solubility. In particular at pH values above 9, actinide solubilities would be controlled mainly by actinide carbonate complexation. Therefore, the use of MgO as buffer material is supposed to buffer pH and limit the carbonate concentration by magnesite precipitation to values below 10⁻⁵ mol per kg H₂O.

In the third scenario, additional smectite buffer material is added to serve as actinide sorption material. It is not expected, that smectite will remain stable in salt brines [16]. Hence, the reaction of smectite in Q-brine has to be modeled.

Development of the Geochemical Milieu

In the following section, the development of the geochemical milieu in case of cement corrosion shall be calculated. The influence of different buffer materials is analyzed with respect to their impact on the solution chemistry. If the corrosion and reaction rates of waste forms and buffer materials would be known, the temporal evolution of the geochemical milieu could be modeled in a reaction path calculation. Unfortunately, these rates are not available or uncertain to rely on such an approach. Therefore, the evolution of the geochemical milieu is calculated using an equilibrium approach, i.e. first the geochemical milieu resulting from waste form corrosion is calculated. Then, a certain progress of reaction path is selected, preferably one which is identified to provide low actinide solubilities, and the influence of buffer materials on this milieu is calculated.

Cemented Waste Forms

Cement corrosion in salt brines depends on the composition of the brine [4]. In case of MgCl_2 rich brine pH is buffered to values around 8.5. This buffer is obtained by precipitation of brucite. Under certain conditions the complete Mg content of the brine can be precipitated and the pH may increase to values above 10 (Figure 1). In this pH range negatively charged actinide complexes (hydroxo and/or carbonato complexes) are formed, increasing the dissolved actinide concentration. A pH range between 7 and 9 provides for low actinide solubilities. The calculations show that this pH range may be established for cement to brine ratios ranging from 0.05 to 0.65 [kg cement / kg H_2O] for Q-brine under various CO_2 partial pressures (0.35–1013 hPa).

For further calculations of the geochemical milieu at a cement corrosion progress of $0.4 \text{ kg cement} \cdot (\text{kg H}_2\text{O})^{-1}$ is considered. Additional calculations showed, that any other value in the range 0.05 to 0.65 kg cement corroded per kg H_2O in Q-brine could be selected for further calculations due to the stable and almost constant geochemical milieu.

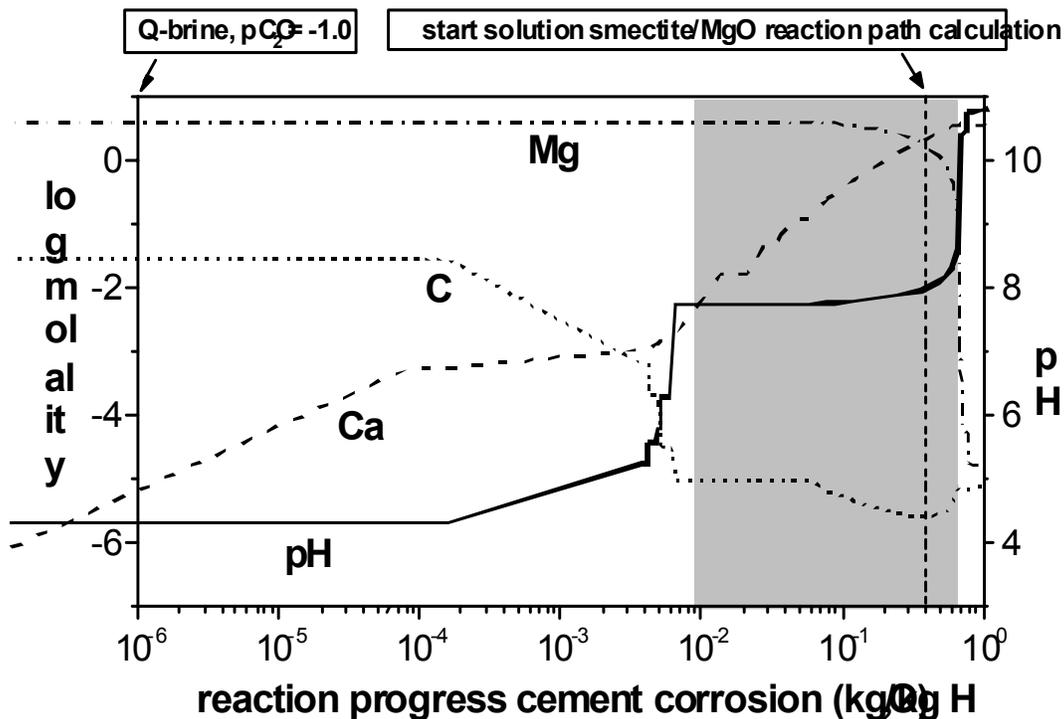


Figure 1. Evolution of the solution composition in the case of scenario I. Grey: Range of preferred cement to water ratio, for which a pH between 7 and 9 is maintained. (low actinide solubilities).

MgO/CaO Buffer Materials

Modeling of the geochemical milieu showed that the reaction of MgO with Q-brine ensures optimum buffer properties (Figure 2). Using a MgO/CaO mixture, the buffer capacity decreases with increasing Ca content of the mixture with respect to DIC. As far as Q-brine is concerned, the addition of solid MgO has no significant impact on the brine composition except for the reduction of the CO_3^{2-} concentration.

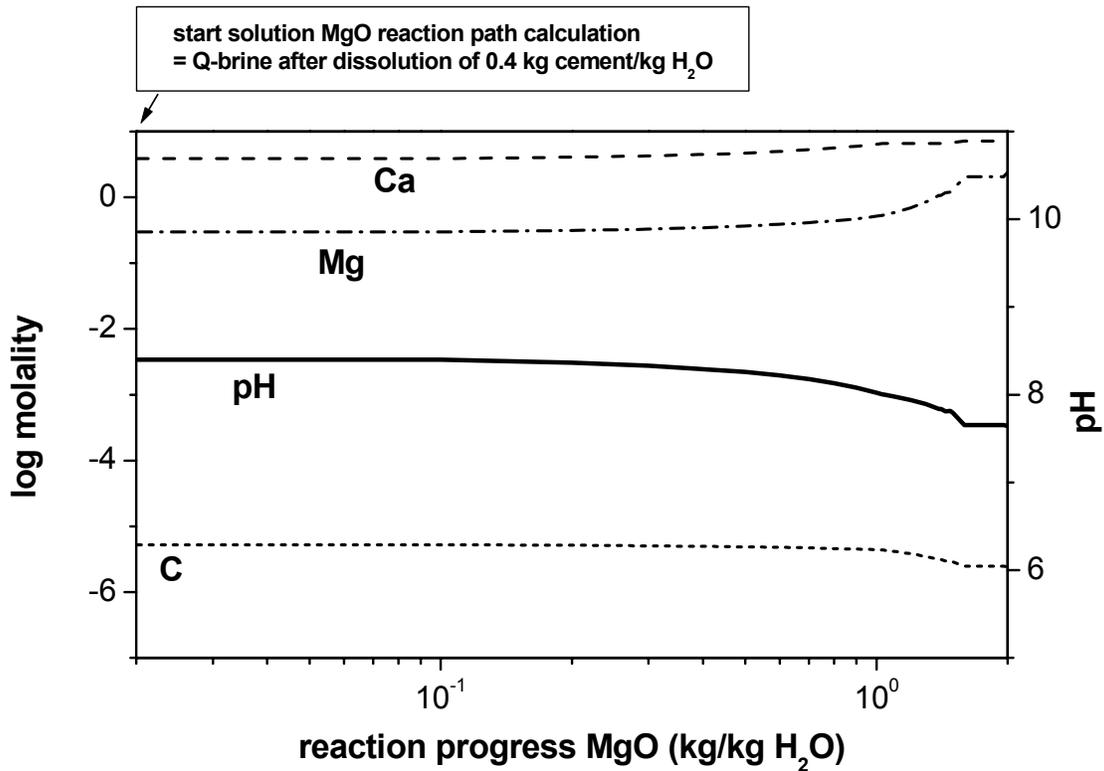


Figure 2. Evolution of the solution composition in case of scenario II.

“Smectite-low-Fe-Mg”

Of the variety of clays with different properties, Smectite-low-Fe-Mg was selected due to its reducing capacity. Computations show, that smectite would not change the brine composition significantly. However, the calculations demonstrated that the pH may decrease to values of about 6 (Figure 3). This drop in pH is correlated with the formation of secondary phases. At this pH, enhanced actinide concentrations are computed due to the increased actinide solid-phase solubility. Whether an enhanced solubility or sorption onto smectite dominates the actinide concentration in solution is determined by the amount of smectite applied, its sorption properties, and its reaction rate.

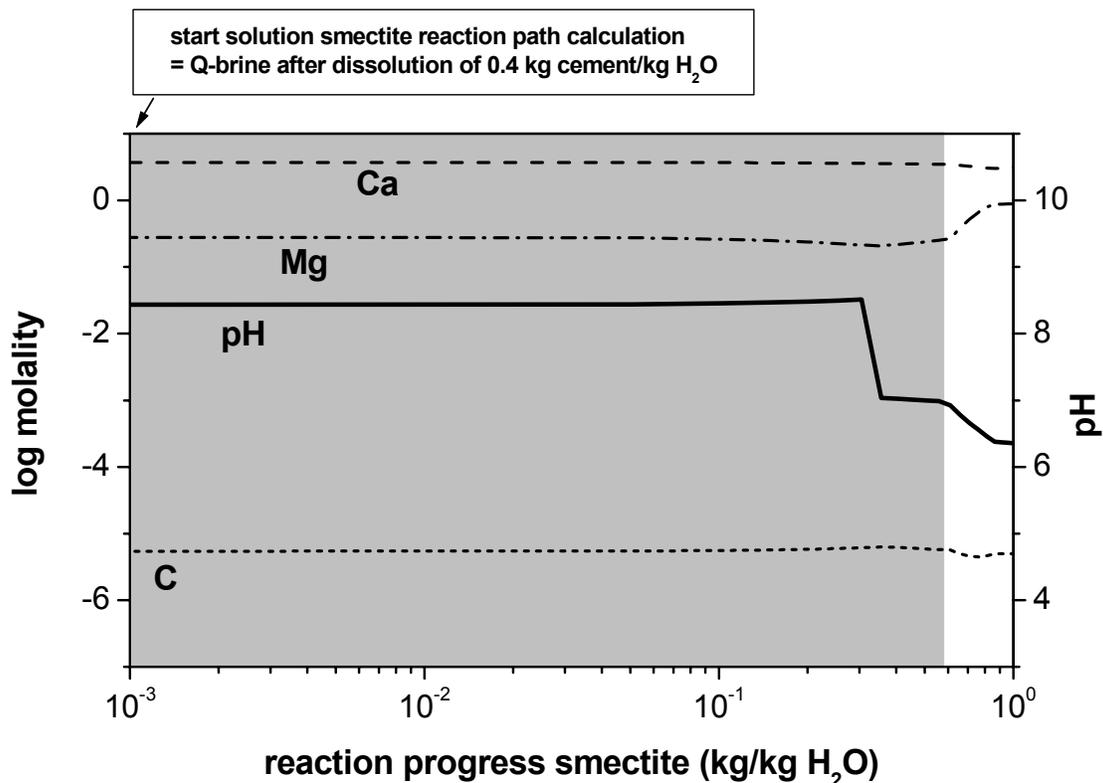


Figure 3. Evolution of the solution composition in case of scenario III. Grey: Range of preferred smectite to water ratio for which a pH between 7 and 9 is maintained (low actinide solubilities).

Actinide Solubility

Actinide solubilities are calculated for solution compositions defined by the reaction path calculations of the geochemical milieu. Here we calculate actinide solubilities for a system with 0.4 kg cement corroded per kg H₂O, 0.25 kg MgO reacted per kg H₂O, and additionally 3.0 kg smectite reacted per kg H₂O. The values of cement and MgO reaction progress correspond to the given ranges of preferable conditions identified in the reaction path modeling of the geochemical milieu. The value for smectite is chosen outside the preferred range to demonstrate the influence of lower pH on the calculated actinide solubilities.

After closing a low level radioactive waste repository, the evolution of moderate reducing conditions (-100 – 0 mV) is expected due to the large Fe inventories (canisters) in the disposal rooms. H₂ production by corrosion of Fe-containing materials may decrease the redox potential. Radiolytic processes do not have to be considered for low level radioactive waste. Only the predominant actinide oxidation states, i.e., Am(III), Pu(IV), Np(V) and U(VI), shall be applied below to calculate the solubilities under moderate reducing conditions in the pH range from 7 to 9. In case of neptunium, also the tetravalent oxidation state may be relevant under these conditions. As an example, the Np(V) solubility is calculated here. As far as performance assessment calculations are concerned, Np(V) solubility may be a conservative limit of the Np concentration in the solution, as a much smaller solubility is expected for Np(IV).

In Table 1 the actinide concentrations resulting for the different scenarios are listed together with the solubility limiting phases used in the calculations. The solubility limiting phases have

been selected on the basis of a number of geochemical modeling exercises and a comparison of the results with experimental findings.

Table 3. Calculated actinide solubilities for different disposal concepts

Solubility limiting phase		Solubility [mol (kg H ₂ O) ⁻¹]		
		Scenario I Q-brine, cemented waste forms, inert backfill	Scenario II Q-brine, cemented waste forms, inert and MgO backfill	Scenario III Q-brine, cemented waste forms, inert, MgO, and smectite backfill
Am(III)	Am(OH) ₃ (cr)	2.2 · 10 ⁻⁶	3.3 · 10 ⁻⁶	1.4 · 10 ⁻⁴
Pu(IV)	PuO ₂ · xH ₂ O(am)	6.7 · 10 ⁻¹²	6.5 · 10 ⁻¹²	2.9 · 10 ⁻¹¹
Np(V)	NpO ₂ (OH) (altered)	3.4 · 10 ⁻⁴	2.9 · 10 ⁻⁴	6.5 · 10 ⁻³
U(VI)	Na ₂ U ₂ O ₇	1.2 · 10 ⁻⁷	1.4 · 10 ⁻⁷	1.7 · 10 ⁻⁷

Table 1 shows that the use of MgO as buffer material will not change significantly the actinide solubility (scenario II compared to scenario I). The effect of MgO would be dramatic, if a certain amount of CO₂/CO₃²⁻ would be present in the solution. MgO will limit the CO₃²⁻ concentration and, thus, also the actinide carbonate complexation.

The use of smectite (scenario III) will enhance the actinide solubility due to the lower pH (6.6 compared to 8). On the other hand, the sorption capacity of smectite is not considered in this calculation. Therefore, the pros and cons of the use of smectite as buffer material have to be evaluated critically.

CONCLUSIONS

Geochemical modeling is a powerful tool to assess the near field geochemistry of a radioactive waste repository. Buffer materials providing low actinide solubilities can be identified by reaction path modeling. Unfortunately, certain buffer materials with experimentally proved beneficial effects on actinide solubility cannot be included in such an analysis at the moment, as data are lacking, e.g. apatite in MgCl₂ systems.

Based on the present state of knowledge, it may be concluded that the cement to water ratio is the most effective parameter to control the pH and, thus, the actinide solubility for cemented waste forms in Q-brine systems. The amount of MgO in a repository room has to be selected such that the CO₃²⁻ concentration is low and the carbonate complexation of dissolved actinides in the solution is negligible. Smectite may reduce the actinide concentration in the solution by sorption processes. Enhanced actinide solubilities due to a decrease of pH by smectite dissolution have to be considered.

The amount of buffer materials to be used in a repository depends on the boundary conditions defined by the storage concept. If the actinide inventories are far below the thermodynamic solubilities, the actinide solution concentrations are limited by the inventories. If the actinide concentrations are solubility-controlled, the remaining void volume and the waste form inventory determine the kind and amount of buffer and backfill materials that provide for low actinide solubilities. For each disposal room a specific analysis of backfill measures has to be performed.

The present evaluation of the benefits of buffer materials in a salt environment is based on geochemical modeling. To confirm the model results, experimental checking of at least some of the model results is required.

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