Geochemical Modelling of Repository Systems: Limitations of the Thermodynamic Approach

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Thermodynamic modelling / Cement degradation / Solubility limits

Summary

In the light of their relevance for performance assessment, results from cement degradation modelling and solubility limit evaluations in cementitious systems are illustrated, but the main emphasis is put on the role and limitations of the thermodynamic approach. It is concluded that research on flow system properties is needed to further improve our understanding of cement performance. It is proposed to complement thermodynamic modelling with system-dependent features and processes like inventories, sorption and co-precipitation, isotopic dilution etc.

Introduction

To demonstrate the safety of waste repository systems requires an accurate quantitative description of ongoing processes. Considering the complexity of such systems, these requirements are hard to meet. Fortunately, it is in many cases, sufficient to show that parameters do not exceed given limits or that individual processes have only limited consequences (conservative approach). Anyway, a detailed system knowledge and a profound understanding of the relevant processes are important prerequisites, and reliable tools for performing actual calculations and predictions are needed.

Today, the most widely used tools for making quantitative predictions are geochemical models based on equilibrium thermodynamics. Due to the broad availability of computing resources, user-friendly code systems and large varieties of thermodynamic databases available world-wide, this research field has become very popular.

Using the Swiss, cement-based repository for long-lived, intermediate level radioactive waste (LMA-repository, in Swiss terminology) as an example, this report aims at demonstrating how we use thermodynamic modelling in this research field. In the first part of this paper, we give an overview of PSI work related to understanding and modelling of cement systems. The second part shows the evaluation of expected maximum concentrations for some safety relevant radionuclides in a distinct cementitious environment. We do, however, not give a detailed compilation of all quantitative calculations contributing to the safety of the repository, nor do we give a deep insight into the different thermodynamic considerations used through-out the various studies. For this, we refer to the extensive reporting on this subject. Our intention is to point out the relevance of the results for repository safety and to identify gaps and weak points of the selected approaches. We also propose measures to be taken to correct identified shortcomings.

Cement degradation

To understand the chemical long-term evolution of cementitious matrix-, backfill- and construction materials, cement degradation models have been and are currently being developed at PSI. A first step included the development of a thermodynamic description of CSH-gels (<u>C</u>alcium <u>S</u>ilicate <u>H</u>ydrate-gels) with main emphasis on their incongruent dissolution behavior [1]. By combining this dissolution model with a simple single box model, we obtained a first order type description of the long-term chemical behavior of cementitious materials in contact with host rock fluids. In a second step, we improved the model by including the aluminates hydrogarnet ($3CaO \cdot Al_2O_3 \cdot 12H_2O$) and ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$). Thermodynamic constants for these phases were carefully evaluated from recent literature data. Additionally, a multi box model allowed for a better representation of the heterogeneous distribution of repository compartments [2]. Predictions were made for various cementitious repository systems degrading in different groundwaters under several flow scenarios.

From a safety assessment point of view, many important results were obtained from this type of models:

– A quantitative thermodynamic description of hydrated cement is a feasible task.

– The desired high pH conditions will maintain for a very long time. Up to [$10^5 \dots 10^6$] years of chemical lifetime under reasonable water flow rates are predicted.

– Considering chemical longevity, the composition of the groundwater turned out to be much more important than the cement composition. Due to calcite precipitation, carbonate was identified as a key solute in groundwaters.

– Porosity and associated flow properties are key issues for the chemical longevity. Complete pore system sealing by calcite precipitation is predicted in carbonate groundwaters. Therefore, changes in porosity due to dissolution/precipitation processes were
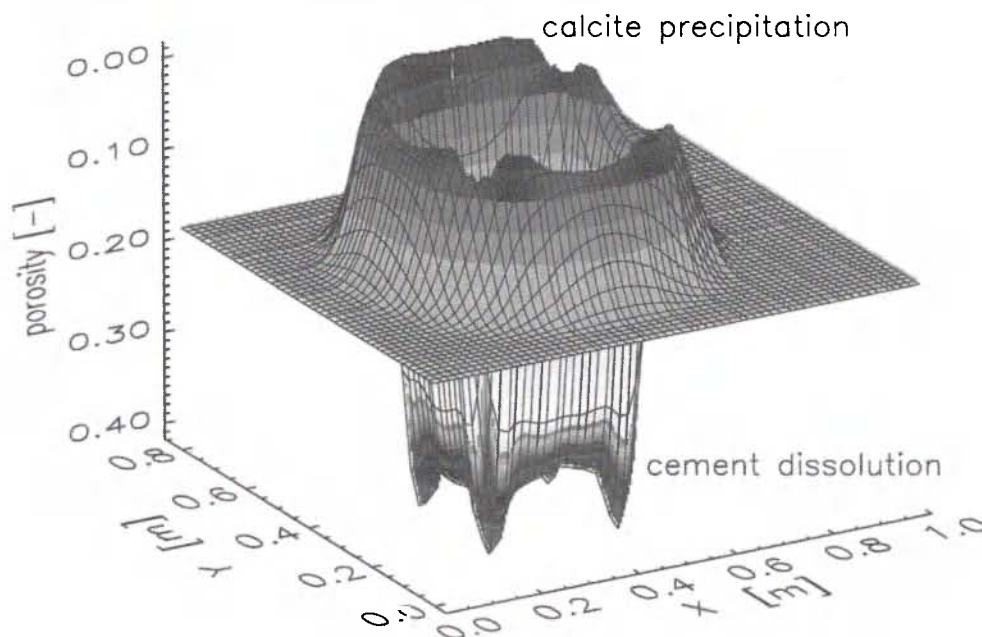
Fig. 1. MCOTAC [4] model results showing the porosity development after 1000 years in and around a cementitious repository of strongly simplified composition $(Ca(OH)_2$ only; $\varepsilon = 17\%$) degrading in carbonate groundwater (pH 8.2; total $CO_3^{2-} = 1.5 \cdot 10^{-2}$ M). The present system is diffusion dominated $(D_{eff} = 5 \cdot 10^{-10}$ m²/s), but the impact of slow advection $(10^{-12}$ m/s) is indicated in the downstream part.

identified as one of the key areas for further model development.

− Degradation products of organic wastes may neutralize significant portions of the cement, which in turn has a strong impact on the overall chemical environment.

Apart from these very promising results and from identifying new and potentially important features (i.e. the role of organic degradation products), the box models also include several shortcomings:

− Alkali hydroxides fix the chemical regime at an early stage of the repository lifetime, but no thermodynamic description of their release from the cement is included.

− Compared to recent experimental cement degradation data [3], the thermodynamic model for the aluminates (including sulfates) does not yet give correct predictions. Such phases are important in retaining (sorption/uptake) many of the radiotoxic nuclides and will control the chemical regime when CSH-gels become exhausted.

− Box models, assuming a homogeneous mixture of all repository constituents, is a too simplistic description. Heterogeneities among the different cementitious structures will establish preferential flow paths and must not be neglected.

− The present multi box approach suffers from mass balance problems associated with the feed-back of porosity changes to water throughput.

A second type of models started from a completely different point. A transport model based on random walk of multispecies particles was iteratively coupled with an ordinary geochemical speciation module [4]. The chemistry module of this system of coupled

models (MCOTAC: modular coupling of transport and chemistry) includes sorption, and, as one of the most interesting features, allows for feeding back porosity changes to the hydraulic system properties using a Kozeny-Carman type equation [5].

A most relevant result of preliminary predictions with MCOTAC is presented in Fig. 1. The volcano type porosity distribution demonstrates, how alkaline Ca solutions react with the groundwater carbonate to precipitate a "wall" of calcite around the repository. The model confirms the system sealing already predicted, but now the sealing front may be located in space and time. MCOTAC also answers the alkali release problem:

Presuming that the whole alkali inventory is reversible sorbed on hydrated cement and by applying reasonable K_d's, the experimental alkali release is very well reproduced (Fig. 2). Obvious benefits, but also disadvantages, escape from this model type:

− All of the nice features offered by MCOTAC need many additional parameters to be determined (i.e. individual diffusion coefficients).

− The quantitative examination usually requires substantial computer power, which may restrict system size and/or the level of sophistication.

− Very slow chemical processes interfere with the transport part of the model. Unfortunately, data on chemical kinetics for these processes are sparse.

More detailed conclusions on these model results were already discussed in [4, 5], it is not the aim to repeat them here. We would rather like to use some distinct key results to address the second part of the present report title. Geochemical models based on thermodynamic principles are the most often used
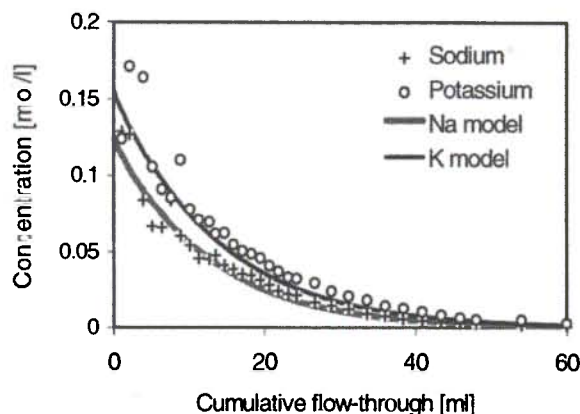
Fig. 2. Alkali release from cement [3], modelled with MCOTAC [5]. Cylindrical cement discs (13.2·1.0 cm³; ε = 65%) were degraded with pure water under advective flow conditions (3 · 10^{-8} m/s). Model curves were calculated by assuming reversible sorption (K_d = 0.3 ... 0.4 ml/g) of the alkalis on hydrated cement.

tools in waste management. Our models are not an exception to this. But where are the limits of this approach?

Modelling cement degradation revealed that several solid phases are not yet understood (i.e. the aluminates), and their thermodynamics clearly need improvement. Despite the fact that the early release of alkalis may be reproduced with a simple sorption approach (notably by using well established thermodynamic equilibrium formalisms), it is not yet understood from a thermodynamic point of view. However, these shortcomings are not the limitations addressed in the title. We are convinced that these "little" problems are solvable with reasonable additional effort. Major limitations of the thermodynamic approach will be induced by processes like those visualized in Fig. 1. Precipitation of secondary phases may completely change the system geometry, and, hence, the transport characteristics of the cement structures.

Let us consider the extreme case of an advection dominated flow system which completely seals by secondary calcite. The flow field will change, most likely in a way that the streamlines may encompass this low porosity structure. Further release may then become diffusion dominated which would increase the lifetime by orders of magnitude. The example tries to demonstrate that uncertainties introduced by the water throughput and its dependence on geometrical factors are much larger than uncertainties caused by thermodynamics will ever be. With respect to cement degradation, there is no chance to get a significantly improved system understanding by just improving the thermodynamics of cement minerals. Although the thermodynamic model explains which solids dissolve or precipitate (an unalterable and essential condition), it will not tell us at which place this will happen, and what the impacts on flow properties will be. It is therefore concluded that further improvement of understanding the degradation of cementitious structures

needs research on the geometrical aspects of the flow system and on their changes.

However, understanding and modelling the cement system of a repository is just half of the story. Much more important for safety considerations is the release of radionuclides. This leads to the second part of the present contribution.

Expected maximum radionuclide concentrations in a cementitious environment

This subject is the real play-ground of thermodynamic modelling. Many of the limitations and problems associated with the thermodynamic approach may be demonstrated in this field. None of them are fundamentally new, and sometimes we are astonished why they are often ignored.

A main feature of the chemistry of cement systems are the high pH pore solutions. The examples presented in this work are based on a cement system in an early stage of degradation, when the pore solution is still dominated by high alkali hydroxide concentrations (NaOH, KOH: 0.35 mol/l; pH = 13.4), saturated with respect to portlandite. Our question is simple: What maximum concentrations do we expect for safety relevant radionuclides? As usual in this type of studies, we tried to model the solubility of nuclides in the pre-defined solution with the help of a geochemical code. Unfortunately, we failed in many cases, i.e., the geochemical model did not give a sensible answer. It would, however, go far beyond the limits of this report to give all details of this study. We refer to the corresponding report [6]. We also do not make comments on how we performed the modelling, we suppose that the majority of the readers is very familiar with this subject. However, by selecting some characteristic examples, we explain why the thermodynamic prediction failed and which measures we took to nevertheless fix the maximum concentration.

Uranium

A first type of limitations was encountered when we tried to select potential limiting solids. Which one? Inverse modelling using data from [7] indicated α-$Na_2U_2O_7$ to be the limiting solid at 5 · 10^{-7} mol/l of U, whereby the hydroxo complexes of U(VI) dominate the speciation. These findings are in contradiction to recent experiments in the CaO-SiO_2-UO_3-H_2O system [8], which positively identified several potential U-bearing solids, some of them even in phase pure form. Unfortunately, the data are not conclusively enough to unambiguously derive identity and thermodynamic properties of the limiting solid. However, these most important experiments clearly demonstrate that U(VI)-solubility in cement-like systems does not exceed 10^{-8} mol/l (Fig. 3).
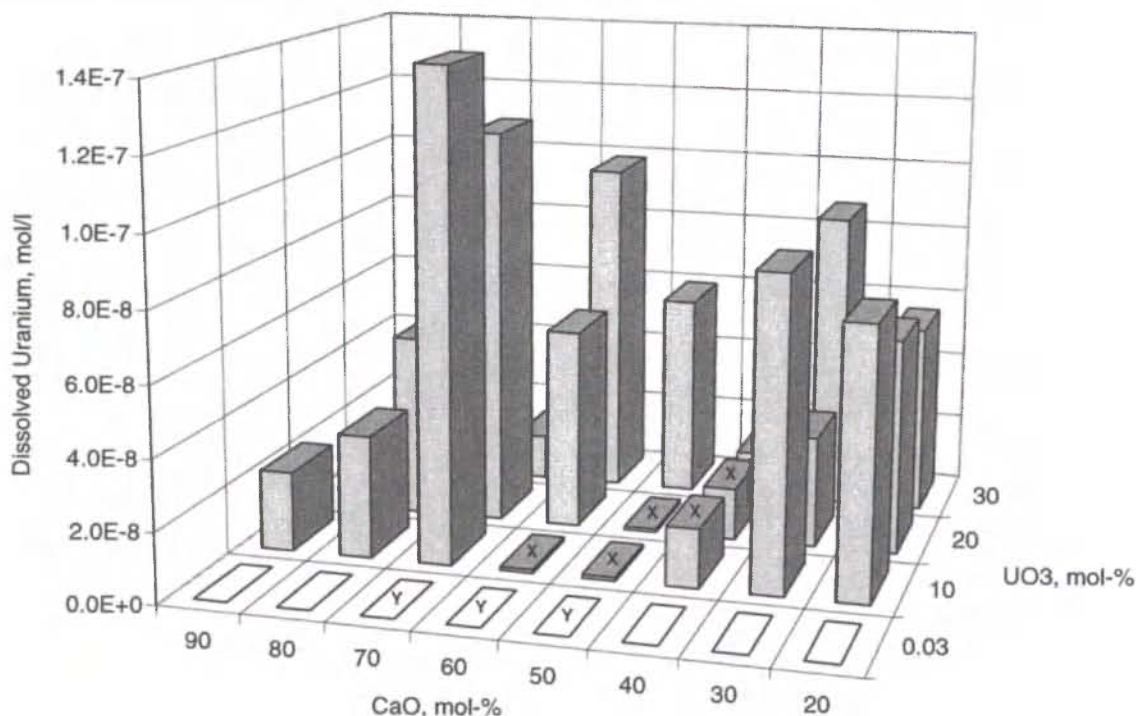
Fig. 3. Uranium concentrations in the CaO-SiO_2-UO_3-H_2O system, measured at 85°C after several months [8]. The initial portion of SiO_2 in the mixtures (not shown) completes $(CaO + UO_3)$ to 100 mol-%. Crosses (X) mark conditions where CSH-gels were observed in the course of the experiment, and Y's mark conditions where CSH-gels would exist in hydrated cements of potentially low UO_3-loadings as foreseen in the Swiss repository design.
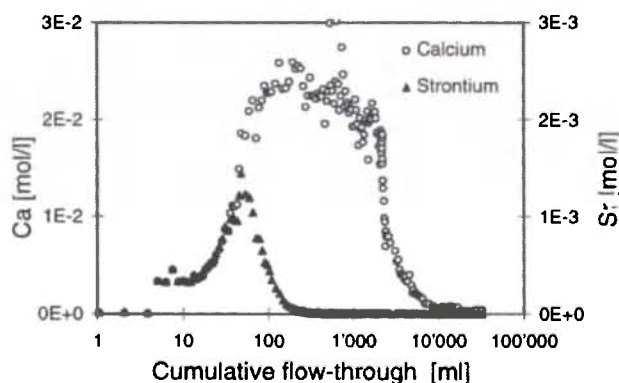

Fig. 4. Strontium and calcium concentrations in the leachate of degrading cement [3] (see also caption of Fig. 2). Ca^{2+} concentration is clearly determined by the thermodynamics of portlandite $(Ca(OH)_2)$ [1, 2], but Sr^{2+} is not limited by $Sr(OH)_2$. There is evidence that the similarity of curves may be traced back to co-precipitating phenomena. Note that an identical curve is also obtained for Ba^{2+} at a level of 10^{-5} mol/l (not shown).

Strontium

Since Ca obeys the thermodynamic laws in a classical way, the well-defined solubility behavior of portlandite $(Ca(OH)_2)$ is one of the pillars of thermodynamic cement modelling. Sr, usually regarded as chemically similar to Ca, behaves differently. Experiments in the porewater of degrading cement [3] show a solubility curve (dependent on the degradation progress) similar to that of Ca, but at a lower level (Fig. 4). A sparingly soluble Sr-hydroxide is not formed, the usual thermodynamic approach of using a pure Sr-bearing solid is

therefore not applicable. However, experimental observations are compatible with co-precipitation phenomena. Their (thermodynamic) description is still open, but a promising approach was recently given by Curti [9].

Protactinium

The total inventory in the repository is very small. Based on the current repository design, only 20 mmoles of ^{231}Pa (from ^{235}U) are distributed over 6000 tons of hydrated cement. Thermodynamic data on Pa are very scarce, but this is not the point here. The open question is its distribution among the matrix. If these 4.6 g of PaO_2 were localized in a small volume (i.e. spent fuel), thermodynamics would have to be considered. For the more homogeneous-type distribution in the present design, a matrix concentration below 1 ppb is calculated. At such low "sub-trace" levels thermodynamic predictions based on single (pure) phases usually fail, since the element is most likely associated with a variety of potential host phases. For the performance assessment the solution to this problem is rather simple. Completely dissolved in the 600 tons of porewater, the very low inventory gives a maximum concentration of only $3 \cdot 10^{-8}$ mol/l of Pa.

Cesium

No sparingly soluble Cs-bearing solids are known, the (thermodynamically) not well characterized pollucite

being an exception. Therefore, the usual approach gives no answer. A more empirical, "semi-thermo-dynamic" way to guess an upper concentration limit for Cs is based on its sorption on hydrated cement $(K_d \sim 2 \cdot 10^{-3}$ m³/kg). A reasonable low inventory (130 moles) combined with a huge amount of hydrated cement (6000 tons) gives a low $(10^{-5}$ mol/l) solution concentration if sorption is operative. The site occupancy on the cement remains negligible low (73 ppm), even if all Cs sorbs on the cement.

Zirconium

With 1200 tons, Zr is the most abundant waste element in the repository. Thermodynamic data of reasonable quality are available and lead to $4 \cdot 10^{-5}$ mol/l of dissolved Zr with ZrO_2 being the limiting solid. Everything seems fine, but a potential limitation of the thermodynamic approach lies with the fact that Zr is disposed in its metallic form, whereas the thermodynamic prediction considers the oxidized form. How is Zr oxidized under repository conditions? Are sufficient oxidizers delivered by radiolysis of the porewater or by the groundwater? This is not a question of thermodynamics, but depends on the disposed radioactivity and/or on the transport properties of the cementitious matrix. An additional feature is worth mentioning here: The radiotoxic ^{93}Zr contributes only about 200 ppm to the total Zr. An isotopic dilution factor of at least 5000 is therefore applicable. This means that the toxic ^{93}Zr concentration will be 3 to 4 orders of magnitude below total dissolved Zr.

Conclusions

What are the lessons learned from the briefly presented studies and what do we conclude with emphasis on the reports subtitle? We focus on the given examples and find three main reasons for "limitations of the thermodynamic approach":

1. Although thermodynamic considerations usually contribute significantly to the overall system performance, other features or processes (e.g. the system transport properties) may be much more important.

2. The thermodynamic approach has a restricted applicability. Several system dependent gradations were recognized:

i) Thermodynamic properties are well known, but not applicable under given conditions (example: Sr at very high pH).

ii) Concentrations are too small to form independent solids. This is a rather common shortcoming in geochemical modelling of trace concentrations.

iii) In the given environment, no sparingly soluble solids exist for particular elements (example: Cs or other alkalis).

3. For a given element the relevant solubility limiting solids are not, or at least not conclusively, predictable. This also includes an unknown control based on kinetic constraints.

However, from the few presented examples, one should by no means get the impression that thermodynamic modelling is a useless tool. The opposite is true. The thermodynamic approach is still the most important and meaningful instrument in predicting the chemical behavior of many elements. For instance, we did not have substantial problems in predicting maximum concentrations for Pu, Am, Np, Mo or Sn. There is no question that thermodynamics are the basic form into which experimental work has to be condensed. Reliable thermodynamic properties are a most important basis for investigating reaction mechanisms and for understanding the behavior in different chemical environments. There is no doubt that research in this field must go on.

On the other side, it is important to recognize that thermodynamic modelling is not the only method for obtaining reliable, quantitative predictions in the performance assessment of radioactive waste repositories. As briefly outlined in the examples, other methods may also give good results, with even less effort needed for evaluation. These include experimental results from relevant systems, total inventories, sorption- and/or co-precipitation processes (which in fact imply sound thermodynamic system knowledge), dilution with stable isotopes and in some cases also the similar chemical behavior of comparable elements.

Many limitations may be attributed to the fact that quantitative geochemical modelling has to be performed in a very complex, scenario dependent and usually not well understood chemical environment. Repository specific boundary conditions, water conducting features, not well defined groundwater compositions, variable inventories, temperature gradients, waste forms and waste distributions etc. need to be defined prior to any quantitative modelling work. The way to these boundary conditions is a most important first step, essentially not yet related to the foreseen quantitative calculations or predictions. However, in most cases this step is as thorny as is the real computer calculation, which often (and wrongly) is identified as "geochemical modelling".

Acknowledgments

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