

## The long-term behaviour of cement based backfill materials in salt formations

H.-J. Herbert & Th. Meyer

Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH,  
Theodor-Heuss-Str. 4, 38122 Braunschweig, Germany

The long-term behaviour of a cemented coal fly ash in high saline brines has been investigated by means of a time accelerating leaching experiment and by the geochemical modelling of the observed reactions. The investigated material (SFA) was a mixture of hard coal fly ash, Portland cement and saturated NaCl-solution. The leaching fluid was a high saline salt solution in equilibrium with the salt minerals halite, carnallite, sylvite, kainite and polyhalite (IP21 solution). This solution is likely to occur in salt and potash mines which are used in Germany as repositories for radioactive and hazardous chemical wastes. The employed leaching experiment was developed in the GRS specifically for the boundary conditions of underground repositories in salt formations. The experiment was conducted in several steps towards the thermodynamic equilibrium between the leaching fluid and the involved solid phases. In each step the resulting chemical composition of the leaching solution was determined as well as the dissolved and newly formed minerals. The experimentally observed reaction path was modelled using the computer code EQ3/6 and compared with results of a full-scale experiment in the Asse salt mine.

A good agreement between experimental data and the modelling results was obtained. The employed experimental and modelling tools have proved to be suitable for the evaluation of the long-term stability of cementitious materials in repositories in salt formations.

### 1. INTRODUCTION

The German concept for the final disposal of radioactive and hazardous wastes in salt formations includes the use of technical barriers like dams and backfill materials, which are partially based on cement. The safety assessment of the repository system implies detailed knowledge of the geochemical behaviour of cement and concrete in the salt environment. In case of a brine intrusion in the repository significant changes of the structure, the chemical and mineralogical composition as well as of the mechanical properties of the cemented materials can be expected. Dissolution and precipitation processes will result in changes of the brine composition and pH.

### 2. CASCADE EXPERIMENTS

In order to explain leaching and corrosion processes, a special laboratory scale experiment in

several steps (cascades) was developed. It is a rapid experimental method for the investigation of the reaction path of the fluid-solid interactions.

In a cascade experiment a weighed mass of this ground down powder is reacted with a certain mass of IP21 solution (first cascade). After 2-3 days of equilibration under continuous rotation of the reaction vessel at 25°C, the solution is extruded through a pressure filter onto unreacted SFA (second cascade). While these steps are repeated, the effective solid-solution ratio increases. The number of steps in the experiment ranges from 10 to 20. The number of steps is limited by the continuously decreasing volume of leachate. For each cascade the solution is analysed by ICP-MS and ICP-OES, in addition the solid material is analysed by ICP-MS, ICP-OES and XRD. Further experimental details are given in [1]. The results of this laboratory experiment are compared with the results of the geochemical modelling and with results of a full-scale in-situ experiment in the Asse salt mine.

### 3. GEOCHEMICAL MODELLING

The interpretation of the cement corrosion processes can be facilitated by means of thermodynamic modelling.

The experimentally observed reaction path was modelled using the computer code EQ3/6, release 7.2a, and the thermodynamic database for the seawater system of Harvie, Møller and Weare [2]. The solubility data used for concrete phases (Tab. 1) were those published by Reardon [3], Revertegat et al. [4] and Berner [5].

The initial composition of the IP21 solution and the composition of the SFA are given in tables 2 and 3.

Tab. 1: Solubility data of cement phases.

Cement phase	log $K_{sp}$
Brucite	17.11
CSH (0.8)	11.07
CSH (1.1)	16.71
Ettringite	55.35
Gibbsite	7.23
Gypsum	-4.58
Portlandite	22.80
Talc	22.41

Tab. 2: Main components of SFA.

Element	mg/kg
Al	81012
Ca	151214
Cl	40340
K	22553
Mg	9473
S	29099
Si	126750

Tab. 3: Composition of the IP21 solution.

element	mg/kg H <sub>2</sub> O
Na	0.463
K	0.556
Ca	0.001
Mg	4.250
SO <sub>4</sub>	0.314
Cl	8.892
density	1.293 [g/cm <sup>3</sup> ]

The IP21 solution was first computed via an EQNR3 run. The reaction path of the SFA interaction with the IP21 solution was modelled in an EQ6 run using the titration model. The steps of the EQ3/6 run (zi) correspond to the reaction i.e. the corrosion progress.

In order to simulate the corrosion of cementitious materials, the dissolution of portlandite, a main component in cement systems, was used to predict the solution composition. In a further modelling attempt the dissolution of a more complex special reactant was calculated. The chemical composition of the special reactant was defined by the SFA composition (Tab. 2).

### 4. RESULTS AND DISCUSSION

The comparison of the experimental results of the dissolution of the cemented fly ash with the modelled dissolution of portlandite in IP21 solution shows an excellent correspondence for the ions [Mg<sup>2+</sup>], [K<sup>+</sup>], [Na<sup>+</sup>], [Cl<sup>-</sup>] and [SO<sub>4</sub><sup>2-</sup>] in solution (Fig. 1). Major differences were found for [Ca<sup>2+</sup>] beginning with the second cascade. In the experiment the pH rose from 5.5 to 10.9. The calculated pH reached 10.4. This good agreement between experimental and modelling results, except for [Ca<sup>2+</sup>], shows that the reaction path of the SFA interaction with brine is mainly characterised by the dissolution of portlandite.

In a second attempt the dissolution of a special reactant with the chemical composition of the cemented fly ash was modelled. Fig. 2 shows the experimental and calculated development of [Na<sup>+</sup>], [K<sup>+</sup>], [Ca<sup>2+</sup>], [Mg<sup>2+</sup>] and [Cl<sup>-</sup>] in solution during the leaching process. The strong decrease of [Mg<sup>2+</sup>] in solution is very similar to that found with the modelling of portlandite dissolution

(compare with Fig. 1). This decrease is due to the precipitation of the mineral brucite ( $\text{Mg}(\text{OH})_2$ ). The formation of brucite is also responsible for the relative low pH in the first three cascades (Fig. 3).

Parallel to this process an increase of  $[\text{Ca}^{2+}]$  was found up to 2.06 mol/kg  $\text{H}_2\text{O}$  in the third cascade. After the third cascade a reduction of  $[\text{Ca}^{2+}]$  in solution could be observed accompanied with the precipitation of newly formed CSH and CSAH phases. The modelling with the special reactant reflects the decrease of  $[\text{Ca}^{2+}]$  in solution after the third cascade.

$[\text{K}^+]$  stayed nearly constant in the experiment and in the modelling. Due to the high concentration of NaCl in the SFA  $[\text{Na}^+]$  increased, whereas  $[\text{Cl}^-]$  decreased. These results were observed in the experiment as well as in the modelling.

During the first cascade  $[\text{SO}_4^{2-}]$  decreased to an amount of  $<10^{-4}$  mol/kg  $\text{H}_2\text{O}$  in the solution (Fig. 3). The same decrease was also observed in modelling of the portlandite dissolution. The sulfate ions were fixed in the newly formed phase gypsum, which could be identified in the XRD spectrum of the solid material after the first cascade. The difference between experimentally observed and calculated  $[\text{SO}_4^{2-}]$  after the sixth cascade (Fig. 3) is due to different boundary conditions in the experiment and in the modelling. In the cascade experiment the leached SFA was removed after each step. Thus the newly formed gypsum could not be redissolved in further steps. This was not considered in the calculations. The pH rose stepwise from 5.6 to 7.2 and 9.4.

Further phases involved in the reaction are brucite and CSH/CSAH. Whereas brucite is formed during the reaction the CSH/CSAH phases are present in the SFA as initial phases and later as new precipitated phases.

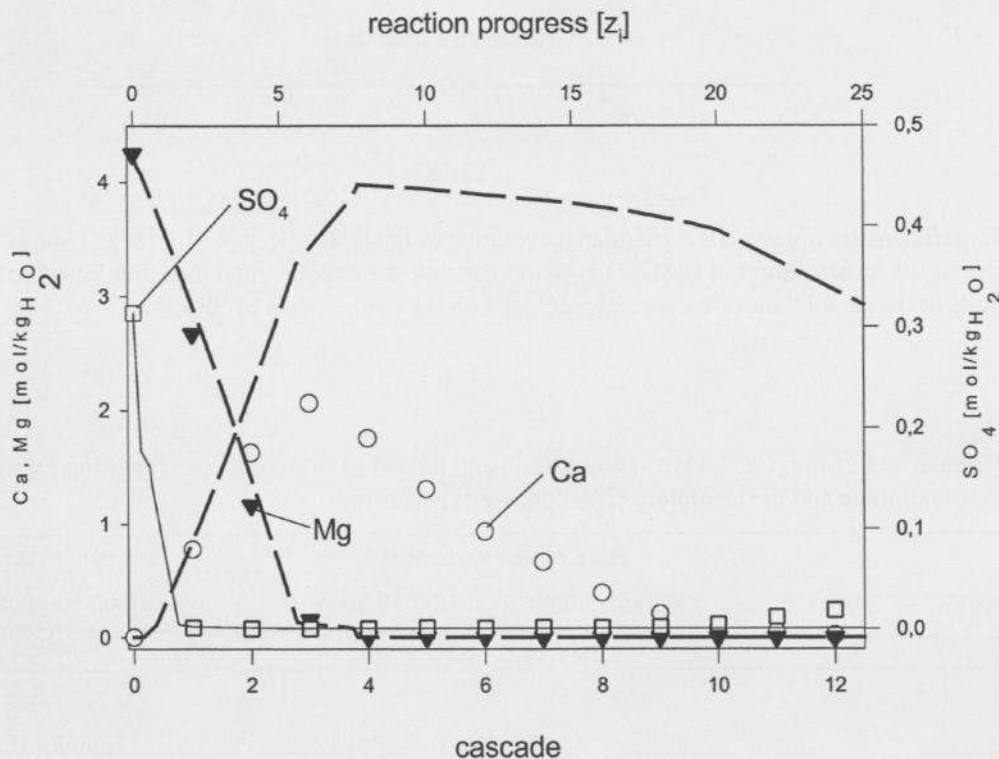


Fig. 1: Experimentally observed and calculated evolution of the  $[\text{Mg}^{2+}]$ ,  $[\text{Ca}^{2+}]$  and  $[\text{SO}_4^{2-}]$  in solution during SFA dissolution in IP21 brine. Symbols mark the experimental data and lines the calculated results of portlandite dissolution.

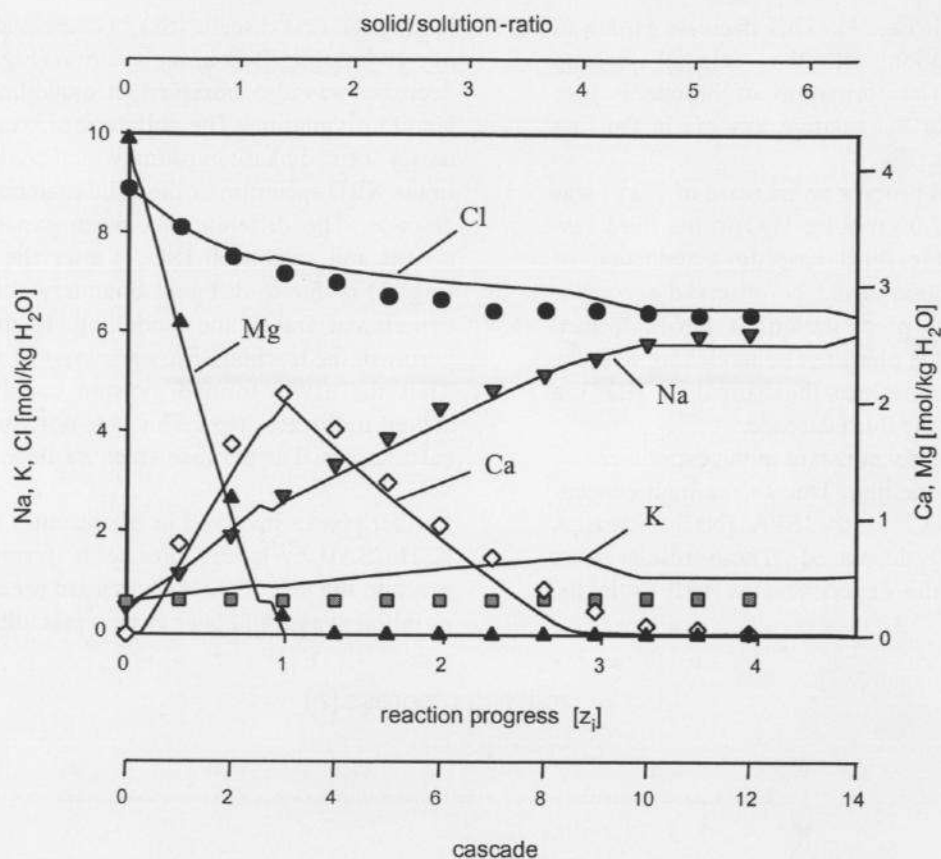


Fig. 2: Experimentally observed and calculated evolution of the  $[\text{Na}^+]$ ,  $[\text{K}^+]$ ,  $[\text{Ca}^{2+}]$ ,  $[\text{Mg}^{2+}]$  and  $[\text{Cl}^-]$  in solution during SFA dissolution in IP21 brine. Symbols mark the experimental data and lines the calculated results of the dissolution of the special reactant with the composition of SFA.

Tab. 4: Comparison of the  $[\text{Ca}^{2+}]$ ,  $[\text{Mg}^{2+}]$  and  $[\text{SO}_4^{2-}]$  and the pH in solution in the corrosion experiments in the Asse salt mine and the laboratory GRS cascade experiment.

parameter/element	Asse mine experiment	cascade experiment
	solution composition after 10 years	solution composition of cascade 2.25
pH	7,2	7,3
	[mol/kg $\text{H}_2\text{O}$ ]	[mol/kg $\text{H}_2\text{O}$ ]
$\text{Ca}^{2+}$	1,45 - 2,60	1,74
$\text{Mg}^{2+}$	0,90	0,92
$\text{SO}_4^{2-}$	$10^{-4}$	$< 10^{-4}$



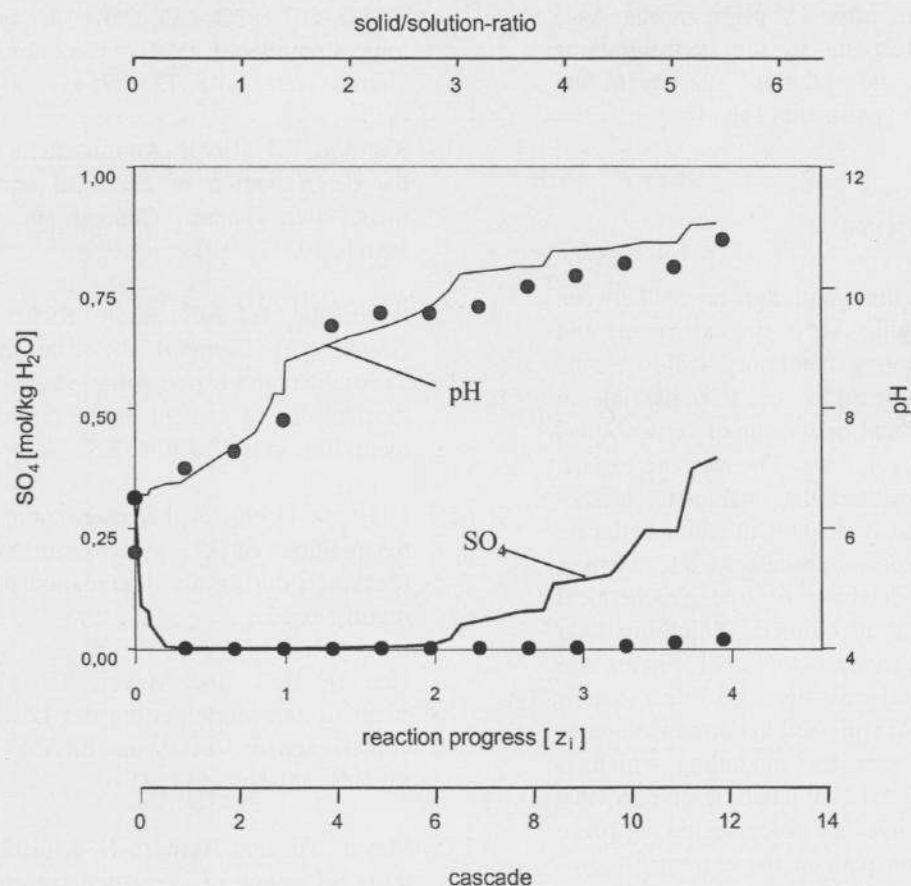


Fig. 3: Experimentally observed and calculated evolution of  $[\text{SO}_4^{2-}]$  and pH in solution during SFA dissolution in IP21 brine. Symbols mark the experimental data and lines the calculated results of the dissolution of the special reactant with the composition of the SFA.

Brucite is formed during the first four cascades in rather large quantities. The formation of this phase is controlled by the amount of  $[\text{Mg}^{2+}]$  in solution. Brucite precipitates as a gel like phase. This gel was observed macroscopically but it could not be detected by XRD as it is not in a crystalline state immediately after precipitation. It controls the pH during the first four cascades. After the consumption of all  $[\text{Mg}^{2+}]$  brucite precipitation ceases and the pH increases stepwise up to 10.9. The minerals detected in the cascade experiment correspond to those found in the geochemical modelling. In addition the modelling indicates that further minerals like talc and Mg-oxychloride may be involved in the reaction. Mg-oxychloride occurs as an interme-

diate phase which becomes stable at a certain step of the reaction path and disappears later on [6-8].

##### 5. COMPARISON OF THE LABORATORY EXPERIMENT WITH THE FULL-SCALE IN-SITU EXPERIMENT IN THE ASSE SALT MINE

In the Asse salt mine cemented waste forms in 200 litre drums were leached in IP21 solution over a period of about 10 years [9]. A comparison of the results of the laboratory scale cascade experiment with the full-scale in-situ experiment in the Asse salt mine shows a good agreement. The concentrations observed in the

leaching solution after 10 years in the Asse experiment correspond to the concentrations between the second and third cascade of the laboratory scale experiment (Tab. 4).

## 6. CONCLUSIONS

Considering the good agreement between the long lasting full-scale in-situ experiment and the time accelerating laboratory scale cascade experiment we conclude, that it is possible to predict the chemical behaviour of cementitious materials in salt solutions. The cascade experiment is a rapid method, that enables the prediction of the chemical changes in solution during the cement corrosion processes. The existing thermodynamic database for the geochemical modelling is still incomplete. Solubility data and dissolution models for CSH phases are incomplete or still missing. The Pitzer coefficients of Si and Al still need to be determined more accurately. However the modelling which is possible with the existing database gives a very valuable insight into the processes taking place along the reaction path in the extremely complex system. The employed experimental and modelling tools have proved to be suitable for a prediction of the long-term chemical behaviour of cementitious materials.

## REFERENCES

1. Herbert, H.-J. und Mönig, J.: Exemplarische Untersuchungen von Wechselwirkungsreaktionen UTD-relevanter chemisch-toxischer Abfälle mit hochsalinaren Lösungen, GRS-Bericht 126, (1996).
2. Harvie, C. E., Møller, N. and Weare, J. H. (1984): The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system to high ionic strengths at 25°C. - *Geochimica et Cosmochimica Acta*, v. 48, 723 - 751.
3. Reardon, E.J. (1990): An ion interaction model for the determination of chemical equilibria in cement/water systems, *Cement and Concrete Research*, 20, 175-192.
4. Revertegat, E.; Adenot, F.; Richet, C.; Wu, L.; Glasser, F.P.; Damidot, D.; Stronach, S.A. (1997): Theoretical and experimental study of degradation mechanisms of cement in the repository environment, Report EUR 17642 EN.
5. U. Berner (1990): A thermodynamic description of the evolution of pore water chemistry and uranium speciation during the degradation of cement, PSI report No. 62.
6. Herbert, H.-J. und Meyer, Th. (1998): Untersuchung und Modellierung des Lösungsverhaltens von tragendem Versatz im ERAM. - GRS report for BfS, AG-Nr. 1512, 71 p.
7. Meyer, Th. und Herbert, H.-J. (1999): The long-term behaviour of cemented materials in highly saline solutions, 2nd Geochemistry Workshop FZK Karlsruhe, Speyer, March 25.-26th 1999.
8. Meyer, Th. und Herbert, H.-J. (1999): Geochemische Modellierung der Betonkorrosion - International Symposium Environment 2000, Halle, Sept. 22.-25th. 1999.
9. Kienzler, B., Vejmělka, P., Herbert, H.-J. Meyer, H. and Altenhein-Haese, C. (2000): Long-term leaching experiments of full-scale cemented waste forms: Experimental and modelling results.- *Nuclear Technology*, vol. 129, 18p.