Multi-mineral reactions controlling secondary phase evolution in a hyper-alkaline plume

XiaoHui Chen[1*], Steven Thornton[2]

[*1]School of Civil Engineering, University of Leeds.

[*]Telephone: +44 (0)113 3430350

[*]Email: x.chen@leeds.ac.uk

[2] Groundwater Protection and Restoration Group, Dept of Civil and Structural Engineering,

The University of Sheffield, S1 3JD, UK

* Address for correspondence

Abstract

This paper presents a modelling study of the influence of a hyper alkaline leachate on a host rock in a geological disposal facility (GDF) for low-intermediate level nuclear waste disposal, when compared with a 15-year experiment designed to simulate the geochemical and mineralogical evolution of the system. The hyper alkaline leachate may be produced by the interaction of groundwater with the cementitious backfill surrounding the waste form. The rock sample is from the Borrowdale Volcanic Group, which comprises orthoclase, quartz, dolomite, muscovite, hematite, and calcite as the major mineral phases, with various kinetic dissolution / precipitation rates. Multi-mineral reactions with the multiple chemicals in the leachate is responsible for the variation of chemical concentration and temporal evolution of different primary and secondary phases observed in the experimental study. The temporal variation in concentration of Ca^{2+}, SiO_3^{2-}, Mg^{2+}, CO_3^{2-}, and pH has been modelled, which agrees well with the experimental results. The mineral evolution process has confirmed that dolomite and CSH gel will dissolve and generate new secondary phases, such as calcite and saponite-K over the 15 year experiment.

1 Introduction

Intermediate/Low-Level (I'LL) Waste disposal in the UK is based on a concept of waste encapsulation within multiple barriers in a deep geological repository (Nirex, 2003). The key engineering components comprise (1) a suitable host rock environment, around 100s of metres or several kilometres below the biosphere, as a residence for the nuclear waste; (2) the immobilization of waste (usually in a cementitious waste form) and emplaced in stainless steel containers; (3) a cementitious backfill material around the waste and for the whole facility to maintain high pH conditions, to promote hydrolysis and minimize radionuclide mobility. A hyper-alkaline plume will be formed by the permeation of groundwater through the cementitious barrier and waste form into the near-field environment around the repository. As different mineral phases in the cementitious barrier contribute to reactions with groundwater, the alkaline leachate composition will evolve over time.

Research on natural analogs of alkaline plumes has been conducted at two sites: Khushayms Matruk and Maqarin in Jordan. The research at Kushayms Matruk shows the influence of an alkaline plume on an argillaceous formation, studied as a natural analogue of an engineered clayey barrier (Techer et al. 2006). At Maqarin, the research has focused on the characterisation and evolution of the high pH waste leachate pore fluids over time (Alexander at al. 1992; Khoury et al. 1992; Clark et al. 1994). In these studies, the hyper-alkaline groundwater compositions have been grouped into 3 stages which are analogous to the three stages in the theoretical cementitious repository evolution of nuclear waste i.e. "Western Springs" – early, active, high-pH NaOH/KOH leachate; "Eastern Springs" – intermediate, active, lower-pH $Ca(OH)_2$ or buffered leachate; and "Daba Region" – late, inactive fossil, lower pH silica-dominated leachate.

However, most of the research has been conducted in a relatively short time (e.g. months to a few years) due to experimental limitations. Multiple chemical reactions and mineralogical evolution in the long-term are significant for nuclear waste disposal, given that the half-life of most radionuclides in I/LL waste could be 10s -1000s of years. Recently chemical mass transfer between groundwater and a host

rock for an idealised GDF (Geological Disposal Facility) site for nuclear waste disposal, has been evaluated in a 15 year experiment (i.e. 184 month experiment, equal to 15 years and 3 months, referred as 15 years for simplification in this paper) (Rochelle et al., 2001; Moyce et al., 2014a). This experiment presents a benchmark for understanding the long-term reaction of a hyper alkaline pore fluid on nominal host rocks for a GDF .

Geochemical models often assume local thermodynamic equilibrium to evaluate mineral alteration (Westall et al., 1986, Bethke, 1994, Bethke, 1996, van der Lee, 1997a). While this assumption may be appropriate for the bulk chemistry of most natural waters dominated by fast reactions, this is not the case for slow reactions, which may typify conditions in the host rock of a GDF, where non-equilibrium and kinetically controlled precipitation and dissolution must be considered (Soetaert et al., 1996). Such kinetics may be expressed in terms of first- or second-order kinetic formulations, which leads to a full kinetic approach. The problem with the kinetic approach is that not all information needed to fully describe kinetic parameters, such as surface area, initial moles and final moles of reactants or reaction rates, can be obtained. Moreover, the database of rates for mineral dissolution/precipitation reactions is still under development. For example, in the widely used PHREEQC geochemical model (Parkhurst and Appelo, 2010), the kinetics database includes rates for only 6 minerals, such as calcite, k-feldspar etc, which is not adequate for modelling the complex georeaction system considered in this study. In addition, the influence of physical coupling with chemical concentrations in the experiment (e.g. evaporation), presents a barrier for chemistry modelling.

This paper uses a coupled evaporation and chemical reaction process method with the assumption of linear kinetics for both physical and chemical processes, and compares the predicted chemical evolution of the system against experimental results. Such a modelling study will offer a deeper understanding of the reaction processes, and provide a foundation for very long-term prediction (e.g. 10-100s of years) for nuclear safety assessment.

2 Experiment introduction

Experiments were conducted in 150 ml (for both rock sample and solution) and 100 ml (for solution blanks) stainless steel pressure vessels lined with Teflon® by the British Geological Survey (BGS) since 1995 (Rochelle et al., 2001). The experiments were established to investigate the chemical mass transfer between samples of the Borrowdale Volcanic Group (BVG) and Young Near-Feld Porewater (YNFP. It has similar chemical compositions to the "Western Springs) or Evolved Near-Field Groundwater (ENFG). The BVG rock used in these experiments was taken from Sellafield borehole BH14A at 859.02 m depth (BRT). Sampling of these experiments was conducted at 4, 9 and 15 months of reaction (Rochelle et al., 2001), but several experiments were allowed to continue. One set of these remaining samples was sacrificed for analysis, to provide a 15-year time point for data. Further experiments are being allowed to continue (Moyce et al., 2014a).

The 15 years experiment was divided into 2 separate time periods, with a different experimental objective: the first period is from 0-15 months, with a focus on mineral evolution in the short term, whereas the second period was from 15 months to 15 years, with a focus was on long-term mineral evolution. The modelling strategy has also been divided into two sections, respectively. In this paper, modelling will be focused on Young Near-Field Porewater reaction with BVG rock from 15 months to 15 years only, to develop a deeper understanding of the mineral evolution and chemical transfer at an early active stage of nuclear waste disposal (YNFP is given in Table 1).

The mineralogical composition of BVG wall rock is given in Table 2 (Rochelle et al., 2001). Note that the fracture fill and clay phases have not been considered here even the if starting material has indicated their presence. This is because this fraction exists in a very small amount in the rock sample, with a similar overall mineral composition to the BVG rock, which is the primary focus of the study. Six minerals are presented in the BVG rock and all of them can dissolve and react with YNFP.

3 Modelling approach

3.1 Conceptual model

PHREEQC (Parkhurst et al., 1980), a geochemical model used to study aqueous geochemical reactions in water systems, was used to conduct the modelling. Functionally, it provides saturated speciation calculations, batch-reaction, transport with reversible reactions (such as aqueous, mineral, surface-complexion, and ion-exchange equilibrium etc.). The default thermodynamic database named "llnl", has been modified to "llnl-BGS" for this modelling. The thermodynamic information for key phases ii provided in Appendix 1. Python (Kuhlman, 2012), which is a interpreted high-level programming language, has been used for the post processing progress of PHREEQC.

The conceptual model of BVG reacted with YNFP is described in Table 3. From a theoretical and experimental analysis it is assumed that BVG alteration progresses according to the following processes (Moyce et al., 2014a):

- Dissolution of primary minerals to release Ca, Mg, K, Al and Si into solution.

- Precipitation of CSH phases/incorporation of Ca from solution into leached silicates to form CSH phases. Note that various secondary phases may form during the reaction process in the 15 year period, but attention was focused on CSH phases as they most strongly influence the microstructure of the porous materials and consequently affect radionuclide transport (Moyce et al., 2014).

- Decrease in pH leading to transformation of CSH to MSH and formation of secondary calcite.

The modelling focuses on the reaction from the 15th month to the 15th year. Only two data points were available during this 15 year time: data for the 15th month from the start, and for the 15th year, as the end. Also attention has been focused on the reaction path rather than reaction kinetics, therefore it is assumed that a linear dissolution and precipitation process is appropriate for the minerals. The dissolution of CSH is incongruent over its range of composition, but in part of this range, a linear relationship may be valid (Chen et al., 2004; Glasser et al., 1987). Eighteen reaction steps have been chosen to represent the time period of the reaction. The quantitative XRD analysis for the experiment shows that ~ 0.019 moles of dolomite dissolved in the YNFP system between t=0 and 15 years of

reaction. Thus from t=15 months to t=15 years, the amount of dolomite dissolved can be calculated as follows, based on linear kinetics.

Dolomite in YNFP: 0.019-0.019*15/184= 0.017451 moles (184 months total for the experiment)

As CSH gel has been observed at t=15 months but disappeared at t=15 years time in the experiment, it is necessary to assume that there is a small amount of CSH gel dissolving simultaneously with the dolomite. Without XRD data for the 15 month reaction, it is assumed that 0.00021 moles CSH gel dissolved in the YNFP. The assumed amount of CSH gel is obtained by trial and error to obtain agreement between experimental data and the modelling results after 15 years for both pH and Ca concentration, as the CSH gel dissolution may directly influence both pH and Ca concentration at this time if the amount of dolomite has been fixed as mentioned above.

3.2 Secondary phases

Various secondary phases may precipitate and dissolve during the reaction process over 15 years. The PHREEQC database includes thermodynamic data for Brucite, Talc, Geothite and Calcite, although there is insufficient data for CSH phases. This section focuses on investigating the secondary development of potential CSH phases.

CSH phases can be defined as $xCaO.ySiO_2.zH_2O$, which is a result of the reaction between the silicate phases of Portland cement and water. For example, one of the chemical reactions which generate CSH phases can be defined as :

$$2\ Ca_3SiO_5 + 7\ H_2O \rightarrow 3\ CaO \cdot 2\ SiO_2 \cdot 4\ H_2O + 3\ Ca(OH)_2 + 173.6\ kJ$$

There exist more than 30 calcium silicate hydrate (also shown as C-S-H or CSH) phases (Taylor, 1997). It may be difficult to identify the exact CSH phases which precipitate from the experiment due to a remarkable level of structural complexity that calcium silicate hydrates possess (Chen et al., 2004). The summary of the CSH structure is shown in Table 4, in which CSH phases have been classified as crystalline phases and fewer crystalline phases. The experiment has identified that the CSH phase

should be CSHgel (Moyce et al., 2014a). As the ratio of Ca: Si is not constant during the reaction observed in the experiment, to simply the discussion, the CSH gel in the modelling is assumed to be CSH tob2 (the thermodynamic data is in Appendix. Note that CSHjen and Tobermorite have been tried in the modelling without significant difference observed).

4 Results and discussion

There are two separate modelling processes (Figure 1 to Figure 6) for the respective experiments: (1) a chemical concentration change in the solution (only) blank; (2) a chemical concertation change and phase evolution of the solution and reacting rock sample. "YNFP (Exp)" and "YNFP (Num)" designate process (1), whereas "YNFP Reacted (Exp)" and "YNFP Reacted (Num)" designate process (2). Evaporation will have the major influence on chemical concentration changes in process (1), whereas, process (2) is coupled with chemical reaction and minerals evolution.

The initial YNFP solution in the 15 month modelling is from the experiment results. Dolomite and CSHtob2 then dissolve into the YNFP solution. The saturation indexes of dolomite and CSHtob2 are both blow zero, which confirms that they can dissolve into the YNFP solution, whereas, the saturation indexes of calcite, talc and saponite-K are above zero, and these phases can precipitate as secondary phases. Saponite-k may be the "platy' Mg(Al)(K)-silicate secondary phase" found from the experiment. (Moyce et al., 2014a).

The concentration of Ca^{2+} in processes 1 and 2 (Figure 1) decreases due to precipitation of secondary calcite (Figure 6). This can be confirmed from an experimental and modelling study for self-sealing of cementitious low- and intermediate-level waste repository be calcite precipitation (Pfingsten, 2002). Note that the attention for mineral evolution in Figure (6) will be only focused on YNFP reacted (process 2), as for the process (1) there are nearly no external chemical intrusions.

Si, which was not in the initial concentration in YNFP, remains at zero for YNFP (only) (Figure 2), however, the high Si concentration from "YNFP Reacted", which was released by dissolution of quartz

and k-feldspar in the first 15 months (Rochelle et al., 2001), drops to 0 due to precipitation of Saponite-k ((Moyce et al., 2014b), Figure 6).

CO_3^{2-} (Figure 4) and Mg^{2+} (Figure 3) increase with time for "YNFP" due to the evaporation only, but for reacted YNFP, the increase is caused by the combined effects of evaporation and dissolution of dolomite caused by the pH decrease in Figure 5. Experimental studies of the interaction of Tournemire argillite with hyper alkaline fluids has indicated the dissolution of dolomite along with pH change (Devol-Brown et al., 2007).

The pH for "YNFP" remains constant as there are no strong chemical reactions (Figure 5). The pH for "YNFP reacted" decreases due to the precipitation of secondary phases such as calcite and saponite-k, which has been confirmed in the experimental study (Moyce, 2014). Figure 6 shows the dissolution of dolomite and CSH gel transferred to precipitation of calcite and sponite-k (Moyce, 2014)..

5 Conclusion

This study presents the first geochemical modelling interpretation of this unique 15 year experiment, by combined analysis of physical corporation, chemical reaction and linear kinetics. The results provide important new insight into the geochemical and mineralogical evolution that occurs by reaction of hyper-alkaline pore fluids with silicate rocks over extended contact times, as may occur during migration of alkaline pH leachates from an I/LLW nuclear waste repository. These observations are : (1) Dolomite may be the most significant mineralogical control during reaction of the hyper alkaline pore fluid with BVG rock in the long term; (2) CSH phases (with K) may be a key control for the formation of secondary phases; (3) Ca^{2+} from dolomite dissolution may be precipitated in the reaction. (4) Saponite-K may be the key secondary phase during the process. This study modelled the key reaction processes and their mineralogical controls during 15 years of the experiment, Secondary mineral phases are likely to evolve in spatial and temporal significance as the hyper-alkaline leachate chemistry changes during migration through the CDZ, This will potentially influence the porosity evolution of the host rock, as this changes in response to respective dissolution of primary phases and precipitation of secondary phases. The results of this study will provide a fundamental basis for numerical analysis and

prediction of scenarios for the nuclear waste disposal safety case. The issue of non-linear kinetics should be addressed in future research to further refine the observations herein.

Acknowledgement

Reference

BETHKE, C. 1994. The Geochemist's Workbench™. A User's Guide to Rxn, Act2, Tact, React and Gtplot. University of Illinois, Urbana-Champaign.

BETHKE, C. M. 1996. *Geochemical reaction modeling. Concepts and applications,* New York, Oxford Univ.

BONACCORSI, E., MERLINO, S. & TAYLOR, H. F. W. 2004. The crystal structure of jennite, Ca9Si6O18(OH)6 路 8H2O. *Cement and Concrete Research,* 34**,** 1481-1488.

CHEN, J. J., THOMAS, J. J., TAYLOR, H. F. W. & JENNINGS, H. M. 2004. Solubility and structure of calcium silicate hydrate. *Cement and Concrete Research,* 34**,** 1499-1519.

DENT GLASSER, L. S., LACHOWSKI, E. E., QURESHI, M. Y., CALHOUN, H. P., EMBREE, D. J., JAMIESON, W. D. & MASSON, C. R. 1981. Identification of some of the polysilicate components of trimethylsilylated cement paste. *Cement and Concrete Research,* 11**,** 775-780.

DEVOL-BROWN, I., TINSEAU, E., BARTIER, D., MIFSUD, A. & STAMMOSE, D. 2007. Interaction of Tournemire argillite (Aveyron, France) with hyperalkaline fluids: Batch experiments performed with powdered and/or compact materials. *Physics and Chemistry of the Earth, Parts A/B/C,* 32**,** 320-333.

GARD, J. A. & TAYLOR, H. F. W. 1976. Calcium silicate hydrate (II) ("C-S-H(II)"). *Cement and Concrete Research,* 6**,** 667-677.

GRUTZECK, M. W. & ROY, D. M. 1969. Electron microprobe studies of the hydration of 3CaOSiO2. *Nature***,** 492-494.

HIRLJAC, J., WU, Z. Q. & YOUNG, J. F. 1983. Silicate polymerization during the hydration of alite. *Cement and Concrete Research,* 13**,** 877-886.

KUHLMAN, D. 2012. *A Python Book: Beginning Python, Advanced Python, and Python Exercises*, MIT License.

MERLINO, S., BONACCORSI, E. & KAMPF, A. R. 2000. Tobermorite 14A° : crystal structure and OD character. *In:* RAMMLMAIR, D., MEDERER, J., OBERTHUR, T., HEIMANN, R. B. & PENTINGHAUS, H. (eds.) *Applied Mineralogy.* Balkema, Rotterdam.

MOHAN, K. & TAYLOR, H. F. W. 1982. A trimethylsilylation study of tricalcium silicate pastes. *Cement and Concrete Research,* 12**,** 25-31.

MOYCE, E., B.A. , MORRIS, K., MILODOWSKI, A., E. , ROCHELLE, C., CHEN, X., THORNTON, S. & SHAW, S. 2014a. Rock alteration in alkaline cement waters over 15 years and its relevance to the geological disposal of nuclear waste. *Applied Geochemistry,* 50**,** 91-105.

MOYCE, E. B. A. 2014. *Rock alteration at high pH relevant to the geological disposal of radioactive waste.* University of Leeds.

MOYCE, E. B. A., ROCHELLE, C., MORRIS, K., MILODOWSKI, A. E., CHEN, X., THORNTON, S., SMALL, J. S. & SHAW, S. 2014b. Rock alteration in alkaline cement waters over 15 years and its relevance to the geological disposal of nuclear waste. *Applied Geochemistry,* 50**,** 91-105.

NIREX 2003. Generic post-closure performance assessment.: Nirex Report N/080,UK Nirex Ltd.

PARKHURST, D. L. & APPELO, C. A. J. 2010. User's Guide to PHREEQC (Version 2)-A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and lnverse Geochemical Calculations. *http://web.inter.nl.net/users/pyriet/bijlage%206.pdf*.

PARKHURST, D. L., THORSTENSON, D. C. & PLUMMER, L. N. 1980. PHREEQE—Acomputer program for geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report

PFINGSTEN, W. 2002. Experimental and modeling indications for self-sealing of a cementitious low- and intermediate-level waste repository by calcite precipitation. *Nuclear Technology,* 140**,** 63-82.

ROCHELLE, C., PEARCE, J., BATEMAN, K., COOMBS, P. & WETTON, P. 2001. The Evaluation of Chemical Mass Transfer in the Disturbed Zone of a Deep Geological Disposal Facility For Radioactive Waste: X. Interaction Between Synthetic Cement Porefluids and BVG: Observations from Experiments of 4, 9 and 15 Months Duration. *BGS technical report* WE/97/16

SOETAERT, K., HERMAN, P. M. J. & MIDDELBURG, J. J. 1996. A model of early diagenetic processes from the shelf to abyssal depths. *Geochimica Et Cosmochimica Acta,* 60**,** 1019-1040.

TAYLOR, H. F. W. 1997. *Cement Chemistry,2nd ed.,* London, Thomas Telford.

VAN DER LEE, J. 1997a. HYTEC, un modèle couplé hydro-géochimique de migration de polluants et de colloïdes. *Technical Report LHM/RD/97/02.* CIG, École des Mines de Paris, Fontainebleau.

WESTALL, J., ZACHARY, J. & MOREL, F. 1986. MINEQL-A computer program for the calculation of the chemical equilibrium composition of aqueous systems. *Technical Report 86-01.* Department of Chemistry, Oregon State University.

Chen, J.J., Thomas, J.J., Taylor, H.F.W., Jennings, H.M., 2004. Solubility and structure of calcium silicate hydrate. Cement and Concrete Research 34, 1499-1519.

Glasser, F.P., Lachowski, E.E., Macphee, D.E., 1987. Compositional Model for Calcium Silicate Hydrate (C‐S‐H) Gels, Their Solubilities, and Free Energies of Formation. Journal of the American Ceramic Society 70, 481-485.

Moyce, E., B.A. , Morris, K., Milodowski, A., E. , Rochelle, C., Chen, X., Thornton, S., Shaw, S., 2014. Rock alteration in alkaline cement waters over 15 years and its relevance to the geological disposal of nuclear waste. Applied Geochemistry 50, 91-105.