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Long-Term Cement Studies (LCS) at the Grimsel Test Site – Modelling of the in-situ Experiment 2

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J.M. Soler\textsuperscript{1,2}, C. Watson\textsuperscript{3}, F. Bultmark\textsuperscript{4}, M.C. Chaparro\textsuperscript{1,2}, M. Manette\textsuperscript{2,5}, M.W. Saaltink\textsuperscript{2,5}, D. Savage\textsuperscript{6} & J. Wilson\textsuperscript{3}

\textsuperscript{1}Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Catalonia, Spain
\textsuperscript{2}Associated Unit: Hydrogeology Group (UPC-CSIC)
\textsuperscript{3}Quintessa Ltd., Henley-on-Thames, UK
\textsuperscript{4}Svensk Kärnbränslehantering AB (SKB), Solna, Sweden
\textsuperscript{5}Universitat Politècnica de Catalunya (UPC)
Barcelona, Catalonia, Spain
\textsuperscript{6}Savage Earth Associates Ltd., Bournemouth, UK
Foreword

The Grimsel Test Site

Nagra and its partners have been conducting underground research at the Grimsel Test Site (GTS) since 1984. The projects have contributed substantially to the development and confirmation of safe geological disposal concepts and to the characterisation of potential host rock formations. The GTS is reached by an access tunnel belonging to the Kraftwerke Oberhasli AG (KWO), the local hydropower company. The KWO has operated hydropower plants in the Grimsel area since 1925.

The main tunnels of the GTS were excavated in 1983 and 1984 using both a tunnel boring machine and drill and blast techniques. Expansion of the site in 1995 and 1998 provided space for two large-scale demonstration experiments. The branching tunnel system of more than 1 km in length is located at an elevation of 1730 m a.s.l., about 350 to 520 m beneath the flanks of the Juchlistock, in the 300-million-year-old granitoid of the Aar Massif. The local geology is ideal for the investigation of a wide range of experimental concepts and scientific issues in both tectonically overprinted and fractured areas, as well as in zones of relatively homogeneous intact rock. More than 5000 m of cored boreholes have been drilled.

More than two dozen organisations and research institutes from twelve countries, together with the European Union, have participated in the six phases of the research programme. Each phase has focused on the key issues at the time, attempting to anticipate the next steps in national programmes for the long-term management of radioactive waste. The current Phase VI began in 2003 and is dedicated to integrative projects with: a) field experiments under repository-relevant boundary conditions, i.e. large-scale, long-term experiments with realistic hydrogeological settings; and b) focal points addressing the implementation of a geological repository in terms of engineering feasibility, potential construction impacts on the surrounding rock, operational aspects, closure, and monitoring. A radiation-controlled zone of IAEA Level B/C allows field experiments to be carried out with radioactive tracers.

The GTS has established itself as an internationally renowned research laboratory in the field of safe disposal of radioactive waste in deep geological repositories. It fulfils a multitude of roles, such as providing a strong driving-force for scientific and technological progress, an effective platform for international cooperation, a hands-on training centre for knowledge transfer to the younger generation, and a forum for dialogue between numerous parties including decision-makers, academics, politicians, authorities and the public.
Location of Nagra's Grimsel Test Site (GTS) at the Grimsel Pass in the Central Alps (Bernese Alps) of Switzerland
Grimsel area (view to the west)

1 Grimsel Test Site         2 Lake Raeterichsboden        3 Lake Grimsel         4 Juchlistock

Grimsel Test Site
Abstract

Portland cement and concrete are major components of the engineered barrier system and of structural supports in different concepts for the geological disposal of low- and intermediate-level radioactive waste, high-level waste and spent fuel. The interaction between groundwater and cement causes the generation of hyperalkaline solutions (pH 12 – 13.5), which may react with the rocks hosting the repositories and may cause changes in their physical and chemical properties. Within the framework of the GTS-LCS project (Grimsel Test Site – Long-Term Cement Studies), a collaboration between JAEA (Japan), NAGRA (Switzerland), NUMO (Japan), POSIVA (Finland), RWM (UK) and SKB (Sweden), an in-situ experiment lasting about 6 years was started in 2009 at the Grimsel Test Site. The objective was the study of water-cement-rock interactions and their effect on water flow and solute transport properties under realistic flow conditions. Pre-hardened Ordinary Portland Cement cylindrical pieces were placed in a borehole intersecting fracture F16. Another two boreholes (observation and extraction boreholes) were placed at about 0.56 and 1.12 metres away from the emplacement borehole. Grimsel groundwater was circulated and injected in the emplacement borehole. Water was extracted at the observation and extraction boreholes and the chemical composition of the different solutions was monitored. Elevated pH and solute concentrations reflecting interaction with the cement were observed in the observation and extraction boreholes after injection was started in the emplacement borehole. Prior to and during the experiment, tracer tests were performed to characterise the flow and transport properties of the rock around the 3 experimental boreholes. Analyses of the cement and rock next to the emplacement borehole were performed at the end of the experiment.

Flow, tracer transport and reactive transport modelling of the in-situ experiment has been performed by different teams (SKB, IDAEA-CSIC/UPC (POSIVA), QUINTESSA (RWM)). The results from the different modelling exercises (tracer transport and reactive transport) have shown that it is possible to model and interpret the results of the in-situ experiment assuming either a homogeneous fracture or a fracture where flow is along preferential flow paths or channels. A real discrimination between the different flow models is not possible. Emphasis was put on the geochemical aspects of cement-groundwater-rock interaction and the main characteristics of the observed alteration of both cement and rock could be reproduced with the use of current thermodynamic and kinetic data (e.g. portlandite dissolution in the cement, calcite precipitation at the cement-gap and gap-rock interfaces, primary mineral dissolution in the rock, C-S-H/C-A-S-H precipitation in the rock), with improved results being obtained when using the most recent data for phases such as C-A-S-H. Finer details, such as the observed range in compositions of C-S-H/ C-A-S-H in the rock or the presence of minor amounts of CaCO$_3$ precursor phases (aragonite, vaterite) could not be resolved in the modelling approaches used here. Overall, the understanding of the geochemical processes involved seems sound.

It is to be noted that the setup of the experiment was such that most information was obtained from the monitoring of solution composition at the 3 boreholes during the experiment, together with characterisation of the cement source and rock at the emplacement borehole at the end of the experiment. Therefore, while the main mineralogical and geochemical aspects of the alteration could be qualitatively reproduced, the calculated spatial extent and distribution pattern of alteration in the fracture were controlled by the implemented model concept (homogeneous fracture vs. discrete channels). Discrimination and further formulation of the concepts would depend on the characterisation of the flow field and of the mineralogical alteration in the fracture plane beyond the boreholes.
Zusammenfassung


Résumé

Le ciment Portland et le béton sont des composants essentiels des systèmes de barrière ouvrées et des structures de soutènement prévus par différents concepts de stockage géologique destinés aux déchets radioactifs, qu'il s'agisse des déchets de faible et de moyenne activité, de haute activité ou des assemblages combustibles usés. L'interaction entre l'eau souterraine et le ciment entraîne la formation de solutions hyperalcalines (pH de 12 à 13,5), lesquelles peuvent réagir avec les roches d'accueil des dépôts et ainsi causer des modifications de leurs propriétés physiques et chimiques. Une collaboration entre JAEA (Japon), la NAGRA (Suisse), NUMO (Japon), POSIVA (Finlande), RWM (Royaume-Uni) et SKB (Suède) a débuté en 2009 sur le projet GTS-LCS (« Grimsel Test Site – Long-Term Cement Studies » – Études à long terme sur le ciment), un essai in situ d’une durée de six ans environ, mis en œuvre au Laboratoire souterrain du Grimsel. L’objectif était d’étudier les interactions entre eau, ciment et roche afin de connaître leurs effets, dans des conditions réalistes, sur la circulation de l’eau et les caractéristiques du transport de solutés.

Des cylindres de ciment Portland ordinaire prédurcès ont été placés dans un trou de forage traversant la faille F16. Deux autres trous de forage (l’un destiné à l’observation, l’autre à l’extraction) ont été placés à 0,56 et 1,12 mètre respectivement du premier. De l’eau souterraine du Grimsel a été injectée et a circulé dans le trou principal. On a ensuite extrait de l’eau dans les deux autres trous et observé la composition chimique des différentes solutions. Après le début de l’injection d’eau dans le trou de forage principal, on a observé une augmentation du pH ainsi que des concentrations de solutés reflétant l’interaction avec le ciment dans les trous d’observation et d’extraction. Avant et pendant cet essai, des expériences de traçage ont été réalisées afin de déterminer les flux caractéristiques dans la roche entourant les trois trous de forage. Le ciment et la roche proche du forage principal ont été analysés à l’issue de l’essai.

La modélisation des circulations d’eau, du transport de traceurs et du transport réactif dans le cadre de cet essai in situ a été mise en œuvre par différentes équipes (SKB, IDAEA-CSIC/UPC (POSIVA), QUINTESSA (RWM)). Les résultats des différents essais de modélisation (transport de traceurs et transport réactif) ont montré qu’il était possible de modéliser et d’interpréter les données tirées de l’essai in situ, en postulant soit une faille homogène, soit une faille où le flux suit des cheminements préférentiels. Une véritable discrimination entre les différents modèles de flux n’est pas possible. L’accent a été placé sur les aspects géochimiques des interactions ciment/eau souterraine/roche ; il a été possible de reproduire les principales caractéristiques des altérations observées dans le ciment et la roche à l’aide de données thermodynamiques et cinétiques courantes (p. ex. dissolution de la portlandite dans le ciment ; précipitation de la calcite aux interfaces entre ciment et vide ainsi que entre vide et roche ; dissolution minérale primaire dans la roche ; précipitation C-S-H/C-A-S-H dans la roche), de meilleurs résultats ayant été obtenus lorsque les données les plus récentes avaient été utilisées pour des phases telles que C-A-S-H. Certaines particularités – à l’instar des importantes variations constatées dans la composition de C-S-H/C-A-S-H dans la roche ou la présence de quantités mineures de précursieurs de CaCO₃ (aragonite, vätérite) – n’ont pas pu être reproduites à l’aide des modélisations utilisées. Globalement, il est permis de dire que nous avons une bonne compréhension des processus géochimiques impliqués.
Par ailleurs, il faut relever que pour cet essai, l’essentiel des informations provenait de l’observation de la composition des solutions extraites dans les trois trous de forage pendant l’expérience ainsi que de la caractérisation du ciment et de la roche dans le trou principal à l’issue de l’essai. En conséquence, si l’on a pu caractériser, d’une manière générale, les altérations au plan minéralogique et géochimique, il demeure que le calcul de l’étendue et de la répartition des altérations dans la fracture est dépendant du modèle conceptuel utilisé (fracture homogène vs cheminement discrets). Pour évaluer, puis préciser les modèles conceptuels, il faudrait pouvoir caractériser le champ de propagation des altérations minéralogiques dans le plan de la faille au-delà des trous de forage.
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1 Introduction

Portland cement and concrete are major components of the engineered barrier system and of structural supports in different concepts for the geological disposal of low- and intermediate-level radioactive waste, high-level waste and spent fuel. The interaction between groundwater and cement causes the generation of hyperalkaline solutions (pH 12 – 13.5), which may react with the rocks hosting the repositories and may cause changes in their physical and chemical properties. Experimental and modelling studies of such interactions at different scales have been numerous in the last years (e.g. Adler, 2001; Bartier et al., 2013; Dähn et al., 2014; De Windt et al., 2008; Gaboreau et al., 2011, 2012; Gaucher et al., 2004; Hoch et al., 2004; Honty et al., 2010; Jenni et al., 2014; Kosakowski & Berner, 2013; Mäder et al., 2006, 2017; Martin et al., 2016; Marty et al., 2009, 2014; Moyce et al., 2014; Read et al., 2001; Savage et al., 2011; Shao et al., 2013; Soler, 2003, 2013, 2016; Soler & Mäder, 2005, 2007, 2010; Soler et al., 2011; Techer et al., 2012; Trottignon et al., 2007; Watson et al., 2012, 2016b). A common finding of these studies has been an increase in porosity in the cement due mainly to portlandite dissolution together with a decrease in porosity near the cement-rock interface due to the precipitation of secondary phases. This decrease in porosity would, in principle, be beneficial for the performance of a repository (decrease in flow and transport properties), with a possible exception when gas is produced by the waste.

The interaction between high-pH solutions and fractured granite was already studied during the GTS­HPF project (Grimsel Test Site – Hyperalkaline Plume in Fractured Rock; Soler et al., 2006). The conclusions from the project pointed to a need to perform in-situ experiments under more realistic conditions, specifically through the use of solid cement sources and realistic water flow conditions. In the HPF in-situ experiment, synthetic high-pH solution (pH 13.36, OH-K-Na-Ca dominated) had been actively injected into a fracture.

Within the framework of the GTS-LCS project (Grimsel Test Site – Long-Term Cement Studies), a collaboration between JAEA (Japan), NAGRA (Switzerland), NUMO (Japan), POSIVA (Finland), RWM (UK) and SKB (Sweden), an in-situ experiment lasting about 6 years was started in 2009 at the Grimsel Test Site. The geological description of the rock mass around the GTS together with geoscientific knowledge from the experiments performed is provided in Schneeberger et al. (2019). The publication also compiles milestone publications to facilitate in-depth studies.

The objective of the LCS project was the study of water-cement-rock interactions and their effect on water flow and solute transport properties under realistic flow conditions. Pre-hardened Ordinary Portland Cement (OPC) cylindrical pieces were placed in a borehole (LSC 08.003) intersecting fracture F16. Another two boreholes (observation and extraction boreholes) were placed at about 0.56 (LCS 07.002) and 1.12 (LCS LSC 08.001) metres away from the emplacement borehole (Fig. 1.1). A fourth borehole (LCS 07.001) was only poorly hydraulically connected to the other boreholes and was used to test injection techniques.

Grimsel groundwater was circulated and injected in the emplacement borehole (LCS 08.003). Water was extracted at the observation (LCS 07.002) and extraction (LCS LCS 08.001) boreholes and the chemical composition of the different solutions was monitored (cf. Fig 1-1). Elevated pH and solute concentrations reflecting interaction with the cement were observed in the observation and extraction boreholes after injection was started in the emplacement borehole. Prior to and during the experiment, tracer tests were performed to characterise the flow and transport properties of the rock around the 3 experimental boreholes. Analyses of the cement and rock next to the emplacement borehole were performed at the end of the experiment.

Flow and transport modelling (tracer tests) and reactive transport modelling (water-cement-rock interaction) performed during the project are reported here. These calculations were carried out by IDAEA-CSIC/UPC (on behalf of POSIVA), QUINTESSA (on behalf of RWM) and SKB.
Fig. 1-1: Experimental setup with the three boreholes (emplacement, observation, extraction) intersecting the F16 fracture (from Lanyon & Mäder, 2020)

In this report, a summary of the LCS in-situ experiment is provided first (chapter 2), followed by the flow, tracer transport and reactive transport modelling exercises performed by the different teams (chapters 3 to 8). Finally, chapter 9 summarises the modelling work and provides global conclusions followed by a discussion of the outcome (chapter 10).
2 LCS project

Prior to introducing the LCS in-situ experiment as a part of the LCS project, it is worthwhile briefly discussing the precursor to LCS, the Hyperalkaline Plume in Fractured Rock (HPF) project. The HPF project was funded by ANDRA (France), JNC (now JAEA, Japan), Nagra (Switzerland), SKB (Sweden), Posiva (Finland) and the DoE (USA), and ran from 1997 until 2004. In addition to laboratory and modelling studies (Soler et al., 2006), a large scale in-situ dipole test was conducted at the Grimsel Test Site (Mäder et al., 2006). During this experiment, which ran for 3 years, a hyperalkaline solution was injected via a borehole into a natural heterogeneous shear zone within the Grimsel granite. The injection was performed at a constant rate over the course of 3 years, and adjacent boreholes were used to monitor the migration of the hyperalkaline solution in the shear zone.

A series of uranine dye and Br-82 dipole tracer tests were run over the course of the HPF experiment. Tracer peaks became higher and moved towards earlier breakthrough during the experiment (Fig. 2-1). These results pointed to a channelling effect, which severely limited the mixing of the injected high-pH solution with background Grimsel groundwater at late stages of the experiment. The fracture zone itself was found to be heterogeneous and random, meaning that conclusions drawn from one tracer test could not be applied deterministically to other similar tests in the same fracture or indeed at another time in the same borehole. The lack of information about the flow path geometry, coupled with other missing information such as the ion exchange/surface complexation processes acting in the fault gouge material and the minerals precipitating and dissolving, resulted in a wide range of possible breakthrough times and solute concentration distributions from the models.

Fig. 2-1: Non-reactive tracer tests results (breakthrough curves) from the HPF experiment at the GTS before and after starting (run #4 and following) the high-pH solution injection (from Soler et al., 2006)
The HPF experiment confirmed that hyperalkaline fluids are very reactive in ambient conditions and cause significant mineral alteration, which in turn induces observable changes to the flow field. The observed trend indicated self-sealing of flow paths, leading to reduced transmissivity. The HPF experiment was one of the most chemically complex and difficult to be carried out at the Grimsel Test Site. During the course of the experiment, equipment, materials and measurement techniques were updated and refined, providing invaluable experience for future experiments of this kind. However, at the conclusion of the project, some areas were identified in which the experiment could be improved upon (Soler et al., 2006). Potential changes included:

- The use of more realistic flow conditions.
  - The constant injection rate used resulted in continuously increasing injection pressures and flow rate overall, which is not comparable to any type of natural system, in that they were too fast and they did not slow as the system sealed.

- Use of evolving cement sources.
  - The hyperalkaline solution injected represented a ‘young’ fluid, corresponding to a worst-case scenario and not necessarily representative of the actual or realistic source in an underground disposal facility.

- Improved characterisation and understanding of the mineralogy.
  - This includes the effects of sorption (via ion exchange or surface complexation) and the formation of secondary phases.

At the conclusion of the HPF project, a new in-situ experiment was planned to address some of the perceived shortcomings of the HPF experiment. The HPF experiment was already described as one of the most chemically complex and difficult to be conducted at the Grimsel Test Site; the LCS experiment seems to be even more challenging. Difficulties are always encountered in running large-scale in-situ experiments and interpreting the results, given the less well-constrained and often not fully understood environment compared to the laboratory, where greater control over the conditions of the experiment can be exerted.

A schematic diagram of the original design of the LCS experiment is shown in Figure 2-2. A number of sub-experiments were initially planned; each involved drilling 3 separate boreholes from the main access tunnel into the granite walls, intersecting the known shear zones. In each case a cementitious source would be placed in one borehole (the ‘emplacement’ borehole), and the extent of the resulting hyperalkaline plume determined from measurements taken from the other 2 boreholes (the ‘observation/monitoring’ and the ‘extraction/recovery’ boreholes).
Although three sub-experiments are shown in Figure 2-2, only two were taken forward at Grimsel. These new experiments would use static cement sources (both liquid and pre-hardened) and be conducted in the natural flow regime at Grimsel. The third planned experiment, using low-pH cement, was considered but was not implemented. The LCS in-situ experiments commenced in 2009 and were carried out as part of the wider LCS project.

The first experiment involved injection of fresh cement grout into the emplacement borehole (LCS Experiment 1); the second experiment used a solid (pre-hardened) cement source (LCS Experiment 2).

### 2.1 LCS Experiment 2

The remainder of this report is concerned with LCS Experiment 2, where pre-hardened cement was used as the source. LCS Experiment 1, in which fresh grout was injected as a source of alkalinity, was subsequently found to be located in a stagnant zone within the fracture and was therefore not considered further. Details of Experiment 2 can be found in Rüedi et al. (2009), Rüedi (2010) and Lanyon & Mäder (2020); readers should be aware that some of the information in the older reports has been superseded by the later ones. A summary of the experiment is presented below.
2.1.1 Summary of the LCS Experiment 2

Figure 2-3 shows an overview of the fractures and boreholes of interest for the LCS experiments; the pre-hardened cement was placed in emplacement/injection borehole (LCS 08.003; cf. Fig. 2-5 to 2-7) in the bottom interval (I1), which intersects fracture F16. Boreholes LCS07.002 (interval I3) and LCS08.001 (interval I2) intersect the fracture further along the flow path and are used to monitor responses and retrieve fluid samples (‘observation’ and ‘extraction’ boreholes).

The location of the emplacement, observation and extraction boreholes within the F16 fracture plane is shown in Figure 2-4. The observation borehole is just over half a metre from the emplacement borehole, and the extraction borehole is similarly just over half a metre away from the observation borehole. The distance between emplacement and extraction boreholes is thus a little over a metre.

Note: For LCS Experiment 2, fracture F16 is of interest; the cement sample is emplaced in borehole LCS 08.003 (red) at interval I1; the alkaline plume is monitored via borehole LCS 07.002 (purple) and samples are retrieved from borehole LCS 08.001 (black). The borehole LCS 07.001 was used to test injection techniques. The diagram also indicates the location of bands of lamprophyre (ultrapotassic igneous rocks) that are present in the Grimsel geology.
As described by Rüedi (2010), the cement source used in the experiment was pre-hardened into half-pipes using concentric plastic tubes as a mould. Eight of these half-pipes were then fitted around a tubular metal dummy core (60 mm in diameter) forming part of an emplacement tool, as shown in Figure 2-5. The cement half-pipes had a thickness of approximately 13 mm. Titanium wire was used to hold the cement in place (placed into grooves cut into the surface). Above the cement, an inflatable packer section on the emplacement tool ensured sealing of the borehole after emplacement. The cement mix used included Ultrafin 16 (UF16) Portland cement (OPC) mixed with 2.5 wt% ‘Mighty 150’ superplasticiser, with a water/cement ratio of 0.8 and 1% D2O water added as a tracer (Rüedi, 2010). The total mass of the cement pipe was 3.032 kg.

The metal emplacement tool contained integrated flow ports, which were used to inject/extract fluid into/out of the borehole during the experiment (this is discussed further below). One of these flow ports can be seen on the right in Figure 2-5(c). There were three flow ports in the tool, as described by Lanyon & Mäder (2020):

- **P** = lower injection port, also used for pressure measurement (85 mm from packer end)
- **Q** = upper extraction/circulation port (725 mm from packer end)
- **R** = lower injection/circulation port (85 mm from packer end, 180° from port P)

The location of the ports on the tool is shown in Figure 2-6. When the cement shells were attached to the tool, they were aligned so that ports Q and R were situated in one of the gaps between the shells. This can be seen in Figure 2-5(b). Although not recorded at the time, on dismantling the experiment it was confirmed that port P was also aligned with the gap on the reverse side of the emplacement tool.

The entire assemblage was placed into the pre-drilled borehole LCS08.003, with the cement section coinciding with the fracture intersection near the end of the borehole (the exact location of the fracture with respect to the cement shells was not recorded). The borehole has a diameter of 86 mm and is over 17 m long. Details of the tool assemblage are given in Figure 2-7; the cement section is marked as interval 1 in the diagram. After emplacement, water containing uranine tracer was injected through the ports to saturate the cement (tracer test 09-04a).
(a) Schematic diagram of a cross-section through the cement emplaced in the borehole

(b) Image of the cement half-pipes, showing titanium wires used for attachment and a flow port (circled)

(c) The metal core of the emplacement tool, prior to the cement elements being attached. The lower injection port P can be seen at the right-hand end of the tool (indicated by the arrow)

(d) The cement elements being attached to the emplacement tool

Fig. 2-5: Preparation of the pre-hardened cement elements before emplacement (from Rüedi, 2010)
Fig. 2-6: Locations of the flow ports on the emplacement tool (c.f. Fig. 2-5c)
Note: Not to scale

Fig. 2-7: Details of the borehole emplacement tool used (from Rüedi, 2010)
Note: The cement half-pipes were attached to the tool in Interval 1, with the mid-point of the shells located at 17.02 m along the borehole (highlighted in red).
The experiment commenced on 17 August 2009. A rapid decline in the concentration of the uranine tracer injected into the borehole with the saturating water was observed, suggesting a possible leak in the packer system. The emplacement tool was removed, the leak fixed and the tool re-emplaced on 30 September 2009. Water containing uranine tracer was again used to saturate the cement (tracer test TT09-04b). Although a high concentration of uranine was circulated (10 ppm), and the results indicated a higher flow through the interval than that observed prior to emplacement, no significant tracer signal was detected at the observation and extraction boreholes (Lanyon & Mäder, 2020).

When the tool was removed after the first emplacement in August 2009, it was noted that a greasy slime covered the surface of the cement elements. Rüedi (2010) suggests that this may have been a biofilm or an early, extremely reactive phase. Unfortunately, no analysis was performed on the substance, and it is not documented whether the cement was cleaned before re-emplacement in September 2009.

Throughout the whole of the experiment, water was extracted through the observation borehole (LCS07.002i3) at a constant low rate of 0.05 ml/min (approximately 1 litre over a 14-day period). A constant hydraulic head was applied at the extraction borehole (LCS08.001i2); flow was approximately 4 ml/min at the start of the experiment (e.g. during tracer test TT09-04b; see Lanyon & Mäder (2020) for details).

A further tracer test (TT10-01) was conducted in February 2010. A small amount of tracer was detected at the observation interval but there was no significant recovery at the extraction interval, similar to the tracer tests conducted after emplacement in 2009. Due to the lack of strong signals at the observation and extraction boreholes, a decision was made to force the experiment by pumping 0.25 ml/min of natural Grimsel groundwater (extracted from a shear zone) into the emplacement borehole through port P. This pumping began on 22 October 2010 and continued until early 2012 when the constant injection rate was replaced with an approximately constant hydraulic head. This switch to a constant head resulted in a decrease in flow into the emplacement borehole, eventually settling down to a rate of approximately 0.04 ml/min. A summary of the flow rates and heads at each of the three boreholes is shown in Figure 2-8.

Further tracer tests were conducted in i) April 2011 (test TT11-01) ii) April, June and August 2012 (tests TT12-01, TT12-02 and TT12-03) iii) October 2013 (test TT13-01) and iv) April 2015 (test TT15-01). These tests all produced detectable signals at both the observation and extraction boreholes – for further details see Lanyon & Mäder (2020). In July 2015, the experiment was stopped and overcoring of the emplacement borehole commenced. This was completed in November 2015, and subsequent analysis of the samples removed was undertaken, as described in section 2.1.2 below. A timeline of the experiment is shown in Figure 2-9.

The LCS experiment has overcome some challenging engineering issues, which were to be expected for any large-scale in-situ experiment, but after some teething troubles it began operating smoothly, producing useful data through an on-line monitoring system.
Fig. 2-8: Overview of head and flow from the LCS Experiment 2 fracture (F16) (from Lanyon & Mäder, 2020)

Note: Tracer test periods are indicated in yellow. Heads are calculated relative to the elevation of a survey point in the tunnel floor in the LCS area of Grimsel (see Lanyon & Mäder, 2020 for further details). Red lines indicate the injection borehole (08.003i1); magenta lines to the observation borehole (07.002i3) and black lines to the extraction borehole (08.001i2).

Fig. 2-9: Timeline of LCS Experiment 2 showing key events and tracer tests.

Note: The tracer tests (TT) are denoted according to the year of execution together with a continuous numbering of the tests in that year - ‘TT-xx-xx(x)’.
2.1.2 Summary of laboratory results from LCS Experiment 2

2.1.2.1 Emplacement borehole – cement shells

LCS Experiment 2 ended in July 2015, and the emplacement tool and cement shells were removed from the borehole. A visual inspection revealed precipitation of solids on the shells themselves (Fig. 2-10) and on the emplacement tool, both underneath the shells and on the end of the tool (Fig. 2-11 and Fig. 2-12). When the shells were cut, a clearly defined leached zone was apparent (Fig. 2-13 and Fig. 2-14), which often extended all around the perimeter of the cement, indicating that there was some water ingress between the shells and the emplacement tool as well as in gaps between individual shells and between the shells and the borehole wall. The leaching was not uniform throughout the samples, with some exhibiting a thicker leaching zone than others, but there did not appear to be a clear pattern with respect to position in the borehole. The most likely explanation is the thickness of the adjacent relevant gap, which is likely to have been extremely heterogeneous throughout the borehole. In particular, there did not appear to be a larger zone of leaching in samples 1L (labelled L1 in the figure) and 1RB on the side nearest the injection port (the left-hand side in the image of the former, the right for the latter). The fracture intersected the borehole in the region of the cement shells labelled 2X(X) and 3X(X), although the exact location was not known at the time of writing (the results from CT scans may be able to help pinpoint the intersection point with a greater degree of certainty). It is noted that sample 2RB showed greater amounts of alteration on its left-hand side than the other samples, but it is not possible to attribute this to the influence of groundwater entering the borehole via the fracture.

Computed tomography (CT) scans on the cement shell samples performed at the University of Bern indicated a significant porosity difference between the unleached and leached zones with sharp boundaries. However, it was not possible to quantify the difference in porosity using this technique.

A number of analyses on the cement samples were performed at EMPA (Swiss Federal Laboratories for Materials Science and Technology). Microscopy and Mercury Intrusion Porosimetry (MIP) were able to give values for the porosity, but a large range of values was determined from the different techniques. However, the results do seem to indicate a difference of approximately 10% between the leached and unleached regions. Results using X-Ray Diffraction (XRD) and Thermogravimetric Analysis (TGA) also indicated that portlandite is preferentially removed from the leached zone, with the other cement minerals remaining largely intact. Electron microscopy techniques also revealed decalcification of C-S-H gel at the surface in the leached zone, and also the possibility of calcite precipitation on the very surface of the cement samples. In addition, the precipitates sampled from the shells and emplacement tool were also analysed by TGA and XRD at EMPA. The material on top of the shells was found to be primarily calcite with some C-S-H gel and hydrogarnet, along with quartz, feldspar and mica. It is likely that these latter minerals arose from particles or dust from the surrounding granite finding their way onto the cement, rather than being precipitates that formed during the experiment. Portlandite and some calcite were also found on the emplacement tool with traces of vaterite (a calcium carbonate polymorph) and a little hydrotalcite and mica. The white precipitate on the foot of the tool was found to be comprised largely of calcite.
Fig. 2-10: Emplacement tool and cement shells after removal from the borehole

Note: The injection port P (circled) can be seen in the gap between the two half shells, near the metal packer edge. A white precipitate is also apparent on the surface of the shells.
Fig. 2-11: Emplacement tool after removal from the borehole with one of the cement shells removed
Note: The end of the tool on the right corresponded to the end of the borehole. White precipitate can be seen on the tool here.

Fig. 2-12: Emplacement tool after the cement shells were removed, showing the white precipitate that was scraped off for analysis
Note: Injection port P (circled) can be seen near the metal packer edge.
Fig. 2-13: Images of the cut surfaces of the cement shells, with the unleached zone highlighted in each case

Note: The red arrow points towards the deepest end of the borehole. See Figure 2-14 for the corresponding locations in the borehole.
2.1.2.2 Emplacement borehole - overcore

Following the removal of the equipment from the emplacement borehole, the borehole and surrounding granite were overcored. Two stabilising boreholes, slightly smaller in diameter than the original one, were drilled and can be seen in the extracted rock shown in Figure 2-15. The core was then cut into various samples for analysis in the laboratory at the British Geological Survey (BGS), as described by Field et al. (2016).

Field et al. (2016) found evidence of secondary mineral precipitation in most samples. On the borehole wall, C-S-H or C-A-S-H gels were prevalent; these precipitates were also identified lining the walls of fractures that intersected the borehole and found in pore spaces in the rock. This was exhibited even in samples taken from the furthest distance from the emplacement borehole (up to 85 mm away from the borehole wall).

Some calcite, minor amounts of aragonite and very small amounts of vaterite were also found within or replacing the C-S-H/C-A-S-H gels. These precipitates could have been caused by partial carbonation of the samples, but the most likely explanation is that they were a direct result of the hyperalkaline plume reacting with the natural groundwater. Although the number of samples analysed was relatively small, there was some indication that there was more C-S-H gel around the end of the overcore near the injection port, with a transition to calcite along the borehole towards the deepest end.

Smectite (swelling 2:1 clay) was also identified by XRD in some samples but, as this is known to be present in fault gouge (mineral naturally present in fractures), it is not possible to identify the origin with any certainty.

In addition, there was evidence of etching and dissolution of primary silicate mineral surfaces (mostly quartz and feldspar, with some mica) in some of the samples.
2.1.2.3 Extraction borehole

White precipitate was found on the equipment when it was removed from the extraction borehole during the dismantling of the experiment (Fig. 2-16). Analysis by EMPA using XRD and TGA techniques revealed that this was mostly calcite (with traces of quartz, mica and albite also being detected, presumably as traces of primary host rock minerals).

A camera was subsequently inserted into the extraction borehole; there is a suggestion of further precipitation in the region where the F16 fracture intersects the borehole, as shown in Figure 2-17. Unfortunately, it was not possible to retrieve a sample for analysis.
Fig. 2-16: Equipment removed from the extraction borehole at the end of the experiment
Note: A white precipitate was observed.

Fig. 2-17: Image of the extraction borehole after removal of the equipment
Note: Area of suspected precipitate circled.
3 SKB - Flow and transport modelling of pre-emplacement tracer test 09-03

During the in-situ experiment, before the cement source was inserted into the shear zone, a series of trace tests were performed. In tracer test 09-03 the concentration of the tracer uranine was held constant in the emplacement borehole for 43 days. The response concentrations were measured in the observation and extraction boreholes. Detailed information of the tracer tests (cf. Fig. 2-9) performed at the site can be found in Rüedi & Kontar (2012)

In this section the flow field is modelled by a two-dimensional, mostly homogeneous fracture plane with three boreholes using Darcy’s law. To verify the model, the tracer test 09-03 is reconstructed by adding a mass transport model and by coupling a one-dimensional transport model of the observation borehole to the two-dimensional model.

The importance of the size of the model is discussed as well as mesh convergence. The influence of the reported (Lanyon & Mäder, 2020) low transmissivity zones around the emplacement and observation boreholes is investigated. By adjusting parameters in the mass transport model, the measured tracer recovery and concentrations can be reproduced.

3.1 Flow and transport modelling

The models have all been implemented in the COMSOL Multiphysics software package (COMSOL 2015a), using the subsurface flow module (COMSOL 2015b). COMSOL is a general code for finite element analysis where some common mathematical models of physical phenomena are implemented in different modules that may be combined and solved together in the same model.

3.1.1 Flow modelling

The flow through the shear zone is modelled by a two-dimensional fracture with a spatially variable isotropic permeability. The boundary conditions are the flow through the boreholes as measured during the experiment and the hydraulic gradient of the natural flow field, measured before the pumping and tracer tests. The flow is described by Darcy’s law

\[ \mathbf{q} = -K \nabla h \]  

(3-1)

where \( \mathbf{q} \) is the Darcy velocity of the flow in the fracture, \( K \) is the hydraulic conductivity and \( h \) is the hydraulic head.

3.1.2 Transport

The mass transport of tracer in the model of the tracer test is governed by the conservation of mass and is calculated as

\[ \frac{\partial \phi c}{\partial t} = \nabla \cdot (\phi D \nabla c) - \nabla \cdot (\mathbf{q} c) \]  

(3-2)

where \( \phi \) is the porosity, \( c \) is the concentration (of tracer), \( D \) is the dispersion-diffusion tensor and \( \mathbf{q} \) is the Darcy velocity vector from the previous section. The dispersion-diffusion tensor is the sum of the mechanical dispersion and the (isotropic) pore diffusion coefficient (\( D_p \))
where $\alpha_L$ and $\alpha_T$ are the longitudinal and transverse dispersivities.

3.1.3 Solver sequence

The simulation first solves the stationary problem of determining the flow velocity field, given the boundary conditions of the borehole flows and the background hydraulic head. The flow velocity field is used as a parameter in the time-dependent transport model. The solution to the time-dependent two-dimensional model of the fracture is then used as boundary condition for the time-dependent one-dimensional transport model of the observation borehole.

Figure 3-1 shows the models and their connections. The blue field (and all the fields surrounded by it) is the model of the fracture plane where the stationary flow problem is solved. The boundary conditions are the background hydraulic head on the black frame of the blue field, and the flow through the three boreholes. The time-dependent mass transport problem is solved on a smaller model (green field in Fig. 3-1). The size of the green field is chosen so that the concentration of species from the emplacement borehole is negligible on the red border. The size of the flow model is chosen so that the direction and magnitude of the flow velocity on the red boundary of the transport model are invariant to changes in the size of the flow model. The yellow field is a low transmissivity zone around the emplacement borehole. The brown field is a corresponding zone around the observation borehole. Around the extraction borehole there is no indication that there should be a zone of reduced transmissivity (Rüedi & Kontar, 2012).

The concentration at the intersection of the observation borehole and the fracture is coupled to a one-dimensional model describing the flow through the interval of the observation borehole. The same could be done for the extraction borehole interval, but it is not needed since the volume of water in the extraction borehole interval is small compared to the flow through it. The concentration will be the same at the end of the interval as at the intersection almost instantly.
Fig. 3-1: Boundary conditions for the sequence of models

Note: The black frame around the blue area is where the background hydraulic head boundary conditions are applied. The red frame around the green area is where the flow velocity boundary conditions are applied to the mass transport model. The dotted line shows how the concentration at the observation borehole is transferred to the one-dimensional model.

3.2 Two-dimensional modelling of tracer test 09-03

In tracer test 09-03, the tracer uranine was circulated in the emplacement borehole, keeping the concentration constant at 3.46 mg/l (3000 ppb) for 43 days. The recirculation continued afterwards with water without tracer. The tracer concentration was measured in the water extracted from the observation and extraction boreholes. The flowrate was 4.5 ml/min in the extraction borehole and 0.05 ml/min in the observation borehole (Rüedi and Kontar, 2012).

3.2.1 Computational setup

The flow in the fracture zone was modelled by a stationary solution to Darcy’s law in a two-dimensional zone with varying dimensions. The boundary conditions are the borehole flowrates and the natural fracture flow, described by imposing a hydraulic head at the zone boundaries. In Figure 3-2 the natural flow in the fracture zone is shown together with the hydraulic head. The tracer transport was modelled by solving the advection-dispersion-diffusion equation in a smaller part of the fracture. The flow velocities were imported from the stationary solution to Darcy’s law in the previous step.
3.2.2 Convergence tests

To obtain the correct boundary conditions on the edges of the smaller model, it is important that the larger model is sufficiently large that the imposed boundary conditions of the natural hydraulic head do not alter the direction of the flow velocity on the boundary of the smaller model. In Figure 3-3 the height of the larger model is varied and the angle and size of the Darcy velocity on the boundary of the smaller model is plotted. Figure 3-4 shows the same, but with varying width of the larger model. The absolute value of the angle of the flow velocity with respect to the x-axis is calculated as

$$\alpha = \left| \arccos \left( \frac{\vec{v} \cdot \vec{u}}{\| \vec{u} \|} \right) \right|$$

(3-4)

It is clear from Figures 3-3 and 3-4 that it is important to apply the boundary conditions of the natural background flow far enough from the smaller model if the flow field in the vicinity of the boreholes is to be accurate.

From Figures 3-3 and 3-4 it is concluded that a model size of 7 m × 6 m (height × width) is sufficient to accurately describe the flow on the boundary of the mass transport model.
Fig. 3-3: Angle and size (colour) of the Darcy velocity at the boundary of the transport model zone for different heights of the larger model, imposing the natural flow hydraulic head boundary conditions

Note: The width of the model was 8 m. A height of 6 m is sufficient to not influence the flow in the smaller transport model zone.

Fig. 3-4: Angle and size (colour) of the Darcy velocity at the boundary of the transport model zone for different widths of the larger model, imposing the natural hydraulic head boundary conditions

Note: The height of the model was 8 m. A width of 7 m is sufficient to not influence the flow in the smaller transport model zone.
Another important convergence parameter is the mesh size. The models use quadratic shape functions, which influence the mesh convergence. The Darcy velocity is not so sensitive to mesh size, and in order to investigate the mesh convergence it is better to look at tracer concentrations. Figure 3-5 shows the tracer concentration around the observation borehole for a number of different mesh sizes.

![Figure 3-5: Tracer concentration around the observation borehole for different mesh sizes](image)

Note: With 80 elements around the edge of the borehole (which corresponds to an edge element length of about 3 mm), the concentration in the vicinity of the borehole can be accurately described.

### 3.3 Results

In tracer test 09-03, uranine dye was recirculated in the emplacement borehole and held at almost constant concentration (3000 ppb $\approx$ 3000 mg/m$^3$ $\approx$ 8·10^{-6} mol/l). Due to the pumping in the extraction and observation boreholes, some of the tracer was recovered in these boreholes. In Figure 3-6, the recovered tracer in the extraction borehole, as measured in the tracer test, as well as the modelled recovered tracer for different values of the lowered transmissivity in the zone around the observation borehole and the transverse dispersivity are shown.

In the tracer test, 0.57 mg of uranine were recovered in the extraction borehole, which seems to indicate that the lower values of transverse dispersivity are to be preferred in the model.

The recovery of tracer in the observation borehole is shown in Figure 3-7. The concentration and recovery of tracer in the observation borehole was measured in the experiment from day 21 onwards. Before this, the fluorometer was used to monitor the concentration at the emplacement borehole. The final recovery of tracer in the observation borehole in the experiment was 0.15 mg. By shifting the experimental values, the inclination of the curves (which is the concentration of
tracer in the borehole) can be compared to the experimental values. The model fits the experimental data best if the transverse dispersivity is set to 1 mm and the transmissivity of a zone around the observation borehole is reduced.

It is worth noting that, in the experiment, it was estimated that more than 1.5 mg of tracer was taken into the shear zone, yet only $0.57 \text{mg} + 0.15 \text{mg} = 0.72 \text{mg}$ were recovered in any of the boreholes. Half of the tracer was lost. It may be stuck in stagnant zones of the shear zone, or it may have left the vicinity of the boreholes. By increasing the hydraulic head gradient of the background flow in the model to 3.5 m/m, it was possible to make half of the tracer leave the model through the external boundary.

![Fig. 3-6: Recovery of tracer in the extraction borehole](image)

Note: The model prediction is reasonable, as long as the transverse dispersivity is lower than 1 cm. The reduced transmissivity around the observation borehole lowers the recovery in the extraction borehole, but it is only necessary if the transverse dispersivity is set too high in the model. $t_{\text{obs}}$ is the factor by which transmissivity is reduced in the calculation.
Note: The measurement started after 20 days. If the experimental values are shifted it is possible to compare the inclination of the recovery versus time. A transverse dispersivity of 1 mm in the model describes the experimental behaviour best. The lowered transmissivity does not alter the recovery in the observation borehole in any significant way, although it is curious that the recovery goes up with lowered transmissivity in the case of large $\alpha_T$. $t_{obs}$ is the factor by which transmissivity is reduced in the calculation.

If the transmissivity around the emplacement borehole were not reduced as much as in the model, the flow through the borehole intersection with the fracture would increase and more tracer would be taken into the shear zone. However, the increase in hydraulic head gradient is needed to bring the tracer away from the extraction borehole (Fig. 3-9). In the following simulations the missing tracer was ignored and the reported background hydraulic head gradient of 1 m/m (Lanyon & Mäder, 2020) was used.

Figure 3-9 shows the concentration of tracer at the tunnel end of the observation borehole, using a transmissivity reduction of 0.1 around the observation borehole and a transverse dispersivity of 1 mm. The background hydraulic head gradient is 1 m/m. The concentration at the extraction borehole is shown in Figure 3-10. The model can reproduce the concentration measured in tracer test 09-03 reasonably well, although the missing tracer reported in the experiment cannot be explained with this model.

With a reasonable choice of parameters, the model can describe the tracer recovery or concentration at the extraction and observation boreholes. All parameters used in the models are listed in Table 3-1.

### Table 3-1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Recovery [mg]</th>
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<tr>
<td>$\alpha_t$</td>
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<td>$t_{obs}$</td>
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</tr>
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<td>$t_{obs}$</td>
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<tr>
<td>$\alpha_t$</td>
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<td>$t_{obs}$</td>
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<td>0</td>
</tr>
<tr>
<td>$\alpha_t$</td>
<td>0.1 mm</td>
<td>0</td>
</tr>
<tr>
<td>$t_{obs}$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$\alpha_t$</td>
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<tr>
<td>$t_{obs}$</td>
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<tr>
<td>$t_{obs}$</td>
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<td>0</td>
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</table>

Fig. 3-7: Recovery of tracer in the observation borehole
Fig. 3-8: Flowlines describing the flow in the shear zone.

Note: If the hydraulic head gradient is kept at 1 m/m (a), all of the flow passing the emplacement borehole ends up in the extraction borehole. If the hydraulic head gradient is increased to 3.5 m/m (b), half of the flow passing the emplacement borehole escapes the vicinity of the boreholes and vanishes. The coloured surface shows the reduced transmissivity around the emplacement and observation boreholes.
Fig. 3-9: Measured and modelled tracer concentrations at the tunnel side of the observation borehole
Note: The transverse dispersivity is 1 mm and the transmissivity of the zone around the observation borehole is reduced to 0.1 of the fracture transmissivity.

Fig. 3-10: Measured and modelled tracer concentration at the extraction borehole
Note: The transverse dispersivity is 1 mm and the transmissivity of the zone around the observation borehole is reduced to 0.1 of the fracture transmissivity.
### Parameters used in the model (compiled from Lanyon & Mäder, 2020)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values used in models</th>
<th>Values used in the model that fit the measured data best</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance between boreholes</td>
<td>0.57 [m]</td>
<td>0.57 [m]</td>
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</tr>
<tr>
<td>Borehole radius</td>
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<td>0.043 [m]</td>
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</tr>
<tr>
<td>Flow model width</td>
<td>4-100 [m]</td>
<td>6 [m]</td>
<td>---</td>
</tr>
<tr>
<td>Flow model height</td>
<td>4-100 [m]</td>
<td>7 [m]</td>
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</tr>
<tr>
<td>Transport model width</td>
<td>1 [m]</td>
<td>1 [m]</td>
<td>---</td>
</tr>
<tr>
<td>Transport model height</td>
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<tr>
<td>Number of elements around the boreholes</td>
<td>8-200</td>
<td>80</td>
<td>---</td>
</tr>
<tr>
<td>Transmissivity of fracture</td>
<td>$3 \times 10^{-9}$ [m$^2$/s]</td>
<td>$3 \times 10^{-9}$ [m$^2$/s]</td>
<td>Corresponding to a hydraulic conductivity of $6 \times 10^{-6}$ [m/s] with a fracture width of $5 \times 10^{-4}$ [m]</td>
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<td>Reduction factor for transmissivity around observation borehole</td>
<td>0.001-1</td>
<td>0.1</td>
<td>---</td>
</tr>
<tr>
<td>Reduction factor for transmissivity around emplacement borehole</td>
<td>0.01-1</td>
<td>0.01</td>
<td>---</td>
</tr>
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<td>Fracture aperture</td>
<td>$5 \times 10^{-4}$ [m]</td>
<td>$5 \times 10^{-4}$ [m]</td>
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</tr>
<tr>
<td>Radius of reduced transmissivity zone</td>
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<td>0.2 [m]</td>
<td>Gaussian function with $\sigma = 0.2$ [m]</td>
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<tr>
<td>Background flow velocity angle with respect to the x-axis</td>
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<td>61.22 [°]</td>
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</tr>
<tr>
<td>Hydraulic head gradient of the background flow</td>
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</tr>
<tr>
<td>Recirculation time</td>
<td>43 [d]</td>
<td>43 [d]</td>
<td>---</td>
</tr>
<tr>
<td>Rise time of recirculation concentration</td>
<td>2 [d]</td>
<td>2 [d]</td>
<td>---</td>
</tr>
<tr>
<td>Concentration in emplacement borehole during tracer recirculation</td>
<td>3000 [ppb]</td>
<td>$8 \times 10^{-6}$ [mol/l]</td>
<td>The concentration is multiplied by a rectangular function with a smearing of ±1 day to avoid discontinuities in the concentration</td>
</tr>
<tr>
<td>Molecular diffusion coefficient</td>
<td>$2.5 \times 10^{-11}$ [m$^2$/s]</td>
<td>$2.5 \times 10^{-11}$ [m$^2$/s]</td>
<td>---</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>0.01 [m]</td>
<td>0.01 [m]</td>
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</tr>
<tr>
<td>Transverse dispersivity</td>
<td>$10^{-4}$ - $10^{-2}$ [m]</td>
<td>$1 \times 10^{-3}$ [m]</td>
<td>---</td>
</tr>
<tr>
<td>Volume of water in the observation interval</td>
<td>$1.55 \times 10^{-3}$ [m$^3$]</td>
<td>$1.55 \times 10^{-3}$ [m$^3$]</td>
<td>---</td>
</tr>
</tbody>
</table>
3.4 Summary and conclusions

The tracer test 09-03 of the LCS 2 Experiment at Grimsel has been modelled with a finite element model implemented in COMSOL. It was discovered that the model was sensitive to the size of the model domain. The boundary conditions representing the background flow have to be placed further from the boreholes than initially expected. The mass transport model was also quite sensitive to the mesh size.

Since the flow in the observation borehole is slow compared to the volume of water present in the interval of the borehole intersecting the fracture, the flow in the observation borehole interval had to be modelled in a one-dimensional model coupled to the two-dimensional fracture model in order to obtain the right shape of the measured tracer concentration at the end of the observation interval.

The model can produce a reasonable agreement with the measured values by adjusting the transverse dispersivity. The missing tracer reported from the tracer test cannot be accounted for in the model without increasing the background hydraulic head gradient.

In principle, this flow and transport model could be used as a basis for a model describing the reactive transport of the experiment after the cement core was inserted. This would require an implementation of a large number of chemical reactions in COMSOL, or a coupling to another code capable of handling the chemical reactions, for example PHREEQC.
Prior to the in-situ experiment, a tracer test was performed to characterise the initial flow and transport properties of the rock around the 3 experimental boreholes. This study reports on the model interpretation of tracer test 09-03 (uranine); it has already been reported by Manette et al. (2015). The calculations were performed by means of a two-dimensional model (fracture plane) including the three relevant boreholes (emplacement, observation, extraction).

4.1 Description of the flow and solute transport code

Flow and tracer transport calculations were performed using the Retraso-CodeBright software package (Olivella et al., 1996; Saaltink et al., 2004), which uses a finite element spatial discretisation.

Regarding flow, the code solves the total mass balance for water and air and the total energy balance. In the calculation presented here, fully saturated conditions and constant temperature were assumed. The flow of water was calculated using Darcy’s law ignoring the buoyancy term (eq. 4-1).

\[ q = -\frac{k}{\mu} \nabla P \]  \hspace{1cm} (4-1)

\( q \) is the Darcy velocity (m\(^3\)/m\(^2\)/s), \( k \) is permeability (m\(^2\)), \( \mu \) is the dynamic viscosity (8.9 × 10\(^{-4}\) Pa s at 25 °C) and \( P \) is pressure (Pa)

Concerning solute transport, the code solved the mass balance for solutes (advection-dispersion equation), which has the form

\[ \frac{\partial \phi C}{\partial t} = \nabla \cdot (\phi D \nabla C_i) - \nabla \cdot (qC_i) \]  \hspace{1cm} (4-2)

where \( \phi \) is porosity, \( C_i \) is the concentration of species \( i \) in solution (mol/m\(^3\)) and \( D \) is the combined dispersion-diffusion coefficient (m\(^2\)/s). \( D \) is defined as the sum of the mechanical or kinematic dispersion \( D_{\text{m}} \) and the pore diffusion coefficient \( D_p \).

\[ D = D_{\text{m}} + D_p \]  \hspace{1cm} (4-3)

The kinematic dispersion coefficient tensor is written in 2D as

\[ D_{\text{m}} = \begin{pmatrix} \alpha_L v_x^2 + \alpha_T v_y^2 & (\alpha_L - \alpha_T)v_x v_y \\ (\alpha_L - \alpha_T)v_x v_y & \alpha_L v_y^2 + \alpha_T v_x^2 \end{pmatrix} \]  \hspace{1cm} (4-4)

where \( \alpha_L \) and \( \alpha_T \) are longitudinal and transverse dispersivities (m), and \( v \) are linear velocities (\( v = q/\phi \)).
4.2 Two-dimensional modelling of tracer test 09-03

4.2.1 Concept and setup

In the tracer test, Grimsel groundwater containing the tracer (uranine, initial concentration $C_0 = 3.46 \text{ mg/l}$) was circulated in the emplacement borehole for 43 days (zero injection flow rate). Circulation continued without tracer thereafter. Water was extracted at the observation and extraction boreholes. Extraction flow rates were 0.05 ml/min and 4.5 ml/min at the observation and extraction boreholes, respectively (Rüedi & Kontar, 2012). The model considered a $5 \times 5 \text{ m}$ two-dimensional domain (the fracture) including the 3 boreholes (Fig. 4-1). Two fracture zones (inner and outer) were considered. The finite element mesh was finer in the inner fracture zone, where most of the solute transport took place. Regarding boundary conditions, all external boundaries had prescribed pressures for flow and considered purely advective fluxes of tracer into or out of the domain. The model did not address the effect of the heterogeneous nature of permeability in these types of fractures (Soler et al., 2006).

Fig. 4-1: Two-dimensional domain of the calculations ($5 \times 5 \text{ m}$), which includes the fracture and the 3 boreholes (emplacement – upper right; observation – middle, extraction – lower left)

Figures 4-2 to 4-4 show the borehole geometries implemented in the model. All borehole circulation and extraction intervals contained an inner dummy cylinder to reduce the open volume. Water only occupied the narrow gap between the inner dummy cylinder and the borehole wall.
Gap porosities were equal to 1 (open space), but they were upscaled in the 2D model to take into account the total amount of water in the circulation system (tank, tubing, gap). Model gap porosities were calculated according to

\[
\phi_{\text{gap, model}} = \phi_{\text{gap}} \times \frac{\text{total water volume}}{\text{gap volume}}
\]

where gap volume refers to the volume of gap intersected by the fracture. The fracture was assumed to have a thickness of 1 mm (Lanyon & Mäder, 2020). The model also assumed the presence of a skin (8 cm radius) around the boreholes, according to calculations reported by Lanyon & Mäder (2020). Figure 4-5 shows the details of the spatial discretisation near the boreholes.

The model considered that tracer was circulated in the emplacement borehole during the whole simulated period (69 days). However, tracer was actually only circulated for 43 days. Calculated tracer concentrations in the different boreholes were corrected after \( t = 43 \) days using

\[
C_{t, \text{corr}} = C_t - C_{t-43d}
\]

For similar corrections see e.g. Russo (2002) or Cihan & Tyner (2011).

**Emplacement Borehole**

- **Coordinates:** 0.16; 0.55 m
- **Interval length:** 136 cm
- **Radius:** 43 mm
- **Inner dummy:** \( r = 29.5 \) mm
- **Cement:** thickness = 11.5 mm
- **Gap:** thickness = 2 mm
- **Skin:** thickness = 37 mm
- **Volume of water:** 0.0205146 m³
- **Vol. water flux:** 0 m³/s
- **Gap volume:** 5.278e-7 m³

Fig. 4-2: Geometry and flow parameters for the emplacement borehole in the model

Note: The plot also shows the finite elements implemented in the cement and gap.
Observation Borehole

Coordinates: 0.0; 0.0 m
Interval length: 99.3 cm
Radius: 43 mm
Inner dummy: r = 40 mm
Gap: thickness = 3 mm
Skin: thickness = 37 mm
Volume of water: 1.07e-3 m³
Vol. water flux: 8.33e-10 m³/s
Gap volume: 7.823e-7 m³

Extraction Borehole

Coordinates: -0.16; -0.55 m
Interval length: 50.5 cm
Radius: 43 mm
Inner dummy: r = 41 mm
Gap: thickness = 2 mm
Skin: thickness = 37 mm
Volume of water: 0.000323 m³
Vol. water flux: 7.5e-8 m³/s
Gap volume: 5.278e-7 m³

Fig. 4-3: Geometry and flow parameters for the observation borehole in the model
Note: The plot also shows the finite elements implemented in the gap.

Fig. 4-4: Geometry and flow parameters for the extraction borehole in the model
Note: The plot also shows the finite elements implemented in the gap.
Fig. 4-5: Detail of the finite element mesh near the 3 boreholes

Note: All boreholes are surrounded by a circular skin with an external radius equal to 8 cm.

The pre-hardened cement was not yet present in the emplacement borehole at the time of the tracer test. The cement zone was included in the model (to be used in later modelling of the reaction phase), but it was assigned negligible porosity and permeability.

4.2.2 Results

A limited sensitivity analysis was performed by changing some of the relevant flow and transport parameters (magnitude of the background hydraulic gradient, permeabilities of the skin zones), starting from an initial reference case. In the reference case (Tab. 4-1), common values for the pore diffusion coefficients (Dp) were assigned, except for the cement zone (negligible porosity, zero diffusion). Dispersivities ($\alpha_L = \alpha_T$) were assigned according to the size of the finite element mesh, in order to comply with numerical requirements (grid Peclet-number condition). Fracture permeability was calculated from a transmissivity of $3 \times 10^{-9}$ m$^2$/s (Rüedi, 2010; Lanyon & Mäder, 2020) and a fracture aperture of 1 mm (Lanyon & Mäder, 2020). Permeabilities of the skin zones around the boreholes were based on the values adopted in preliminary modelling by QUINTESSA, based in turn on initial hydrogeological characterisation (Lanyon & Mäder, 2020). Fracture porosity was assumed to be 0.21, which was the value obtained from the modelling of a fracture-core infiltration experiment in the HPF project (Soler & Mäder, 2007). The background hydraulic gradient in the reference case was 1 m/m (from lower left to upper right in the 2D domain), according to previous calculations by Lanyon & Mäder (2020). This value was implemented by fixing pressures at the external boundaries of the domain.

4.2.2.1 Case 1 (reference case)

The results corresponding to case 1 are shown in Figs. 4-6 to 4-8. Flow and transport parameters are given in Table 4-1. The model reproduces tracer concentrations in the emplacement and extraction boreholes reasonably well (Fig. 4-8). Model concentrations at the emplacement borehole decrease slightly more slowly than the measured data. Concentrations are clearly underestimated for the observation borehole. Note that concentrations at the emplacement borehole were only measured up to $t = 17$ days. Concentration then started to be measured at the observation borehole.
Tab. 4-1: Case 1 - Flow and transport parameters for the different zones

Note: Background hydraulic gradient is 1 m/m.

<table>
<thead>
<tr>
<th></th>
<th>Dp (m²/s)</th>
<th>Dispersivities (m)</th>
<th>k (m²)</th>
<th>C₀ (empl. gap)</th>
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<tbody>
<tr>
<td>Cement</td>
<td>0.0</td>
<td>0.0</td>
<td>8.0 E-18</td>
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</tr>
<tr>
<td>Emplacement Gap</td>
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<td>0.00346 g/l</td>
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<tr>
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<td>3.0 E-10</td>
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<tr>
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<td>3.0 E-13</td>
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</tr>
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</table>

Fig. 4-6: Case 1 – Steady-state water pressures in the domain
Fig. 4-7: Case 1 – Tracer concentrations for C < 0.1 mg/L at t = 69 days

Note: Very high concentrations near the emplacement borehole not plotted. Concentrations are not corrected for zero tracer concentration at emplacement after t = 43 days.
4.2.2.2 Case 2

Flow and transport parameters are the same as in case 1 (Tab. 4-2), except for the magnitude of the background hydraulic gradient (0 m/m in case 2). The results corresponding to case 2 are shown in Figures 4-9 to 4-11. The model reproduces tracer concentrations in the emplacement and...
extraction boreholes reasonably well (Fig. 4-11). Model concentrations at the emplacement borehole decrease slightly more slowly than the measured data. Concentrations are clearly underestimated for the observation borehole. These results are very similar to those from case 1, showing the small effect of the background hydraulic gradient under the conditions of the tracer test.

Tab. 4-2:  Case 2 – Flow and transport parameters for the different zones

Note: Background hydraulic gradient is 0 m/m.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Dp (m²/s)</th>
<th>Dispersivities (m)</th>
<th>k (m²)</th>
<th>C₀ (empl. gap)</th>
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<tr>
<td>Cement</td>
<td>0.0</td>
<td>0.0</td>
<td>8.0 E-18</td>
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</tr>
<tr>
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<td>3.0 E-10</td>
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<tr>
<td>Emplacement Skin</td>
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<td>0.02</td>
<td>3.0 E-15</td>
<td>0.00346 g/l</td>
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<tr>
<td>Observation Gap</td>
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<td>10</td>
<td>3.0 E-10</td>
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<tr>
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<td>3.0 E-14</td>
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<tr>
<td>Extraction Gap</td>
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<td>3.0 E-10</td>
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<tr>
<td>Extraction Skin</td>
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<td>3.0 E-13</td>
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<tr>
<td>Fractura Inner</td>
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</tr>
<tr>
<td>Fractura Outer</td>
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<td>0.5</td>
<td>3.0 E-13</td>
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</tr>
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</table>

Fig. 4-9:  Case 2 – Steady-state water pressures in the domain
Fig. 4-10: Case 2 – Tracer concentrations for C < 0.1 mg/L at t = 69 days

Note: Very high concentrations near the emplacement borehole not plotted. Concentrations are not corrected for zero tracer concentration at emplacement after t = 43 days.
Fig. 4-11: Case 2 – Modelling results (model) vs. measured tracer concentrations (Grimsel data) in the 3 boreholes

Note: a) Emplacement borehole, b) Observation borehole, c) Extraction borehole.
4.2.2.3  Case 3

Flow and transport parameters are the same as in case 1, but the permeability of the skin around the emplacement borehole has been increased to $3 \times 10^{-14} \text{m}^2$ (Tab. 4-3). Results are shown in Figures 4-12 to 4-14. With this increase in permeability, a very good match is achieved for the concentrations at emplacement borehole (faster flow of water favouring the release of tracer), but concentrations at the observation and extraction boreholes are clearly overestimated (Fig. 4-14).

Tab. 4-3:  Case 3 – Flow and transport parameters for the different zones

<table>
<thead>
<tr>
<th>Zone</th>
<th>Dp (m$^2$/s)</th>
<th>Dispersivities (m)</th>
<th>k (m$^2$)</th>
<th>$C_0$ (empl. gap)</th>
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</thead>
<tbody>
<tr>
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<td>0.0</td>
<td>8.0 E-18</td>
<td></td>
</tr>
<tr>
<td>Emplacement Gap</td>
<td>2.0 E-10</td>
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<td>3.0 E-10</td>
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</tr>
<tr>
<td>Emplacement Skin</td>
<td>1.0 E-09</td>
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<td>3.0 E-14</td>
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</tr>
<tr>
<td>Observation Gap</td>
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<td>3.0 E-10</td>
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<tr>
<td>Observation Skin</td>
<td>1.0 E-09</td>
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</tr>
<tr>
<td>Extraction Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Extraction Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Inner</td>
<td>1.0 E-09</td>
<td>0.1</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Outer</td>
<td>1.0 E-09</td>
<td>0.5</td>
<td>3.0 E-13</td>
<td></td>
</tr>
</tbody>
</table>

Note: Background hydraulic gradient is 1 m/m.

Fig. 4-12:  Case 3 – Steady-state water pressures in the domain
Fig. 4-13: Case 3 – Tracer concentrations for C < 0.1 mg/L (top) and C < 1 mg/L (bottom) at t = 69 days

Note: Very high concentrations near the emplacement borehole not plotted. The plot at the bottom shows a detail of the emplacement borehole. Concentrations are not corrected for zero tracer concentration at emplacement after t = 43 days.
Fig. 4-14: Case 3 – Modelling results (model) vs. measured tracer concentrations (Grimsel data) in the 3 boreholes

Note: a) Emplacement borehole, b) Observation borehole, c) Extraction borehole.
4.2.2.4 Case 4

Flow and transport parameters are the same as in case 1, but the permeabilities of all skin zones have been increased by an order of magnitude (Tab. 4-4). Results are shown in Figures 4-15 to 4-17. A very good match is achieved for the concentrations at emplacement borehole, but concentrations at the observation and extraction boreholes are clearly overestimated (Fig. 4-17).

Tab. 4-4: Case 4 – Flow and transport parameters for the different zones

Note: Background hydraulic gradient is 1 m/m.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Dp (m²/s)</th>
<th>Dispersivities (m)</th>
<th>k (m²)</th>
<th>C₀ (empl. gap)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
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<td>0.0</td>
<td>8.0 E-18</td>
<td></td>
</tr>
<tr>
<td>Emplacement Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td>0.00346 g/l</td>
</tr>
<tr>
<td>Emplacement Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-14</td>
<td></td>
</tr>
<tr>
<td>Observation Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Observation Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-14</td>
<td></td>
</tr>
<tr>
<td>Extraction Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Extraction Skin</td>
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<td>0.02</td>
<td>3.0 E-12</td>
<td></td>
</tr>
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<td>1.0 E-09</td>
<td>0.1</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Outer</td>
<td>1.0 E-09</td>
<td>0.5</td>
<td>3.0 E-13</td>
<td></td>
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</tbody>
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Fig. 4-15: Case 4 – Steady-state water pressures in the domain
Fig. 4-16: Case 4 – Tracer concentrations for C < 0.1 mg/L (top) and C < 1 mg/L (bottom) at t = 69 days

Note: Very high concentrations near the emplacement borehole not plotted. The plot at the bottom shows a detail of the emplacement borehole. Concentrations are not corrected for zero tracer concentration at emplacement after t = 43 days.
Fig. 4-17: Case 4 – Modelling results (model) vs. measured tracer concentrations (Grimsel data) in the 3 boreholes

Note: a) Emplacement borehole, b) Observation borehole, c) Extraction borehole.
4.2.2.5 Case 5

Flow and transport parameters are the same as in case 1, but the permeability of the skin around the emplacement borehole has been decreased to $10^{-15} \text{ m}^2$. The permeability of the skin at observation has been increased to $3 \times 10^{-13} \text{ m}^2$ (Tab. 4-5). Results are shown in Figures 4-18 to 4-20. Tracer concentrations are underestimated at the observation and extraction boreholes (Fig. 4-20), due to the slower flow of water at the emplacement borehole.

Tab. 4-5: Case 5 – Flow and transport parameters for the different zones

<table>
<thead>
<tr>
<th></th>
<th>Dp (m$^2$/s)</th>
<th>Dispersivities (m)</th>
<th>k (m$^2$)</th>
<th>C$_0$ (empl. gap)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>0.0</td>
<td>0.0</td>
<td>8.0 E-18</td>
<td></td>
</tr>
<tr>
<td>Emplacement Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Emplacement Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>1.0 E-15</td>
<td></td>
</tr>
<tr>
<td>Observation Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td>0.00346 g/l</td>
</tr>
<tr>
<td>Observation Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Extraction Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Extraction Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Inner</td>
<td>1.0 E-09</td>
<td>0.1</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Outer</td>
<td>1.0 E-09</td>
<td>0.5</td>
<td>3.0 E-13</td>
<td></td>
</tr>
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Fig. 4-18: Case 5 – Steady-state water pressures in the domain
Fig. 4-19: Case 5 – Tracer concentrations for C < 0.1 mg/L (top) and C < 1 mg/L (bottom) at t = 69 days

Note: Very high concentrations near the emplacement borehole not plotted. The plot at the bottom shows a detail of the emplacement borehole. Concentrations are not corrected for zero tracer concentration at emplacement after t = 43 days.
Fig. 4-20: Case 5 – Modelling results (model) vs. measured tracer concentrations (Grimsel data) in the 3 boreholes

Note: a) Emplacement borehole, b) Observation borehole, c) Extraction borehole.
4.2.2.6 Case 6

Flow and transport parameters are the same as in case 5 (Tab. 4-6), except for the magnitude of the background hydraulic gradient (0 m/m in case 6). The results corresponding to case 6 are shown in Figures 4-21 to 4-23. Tracer concentrations are underestimated at the observation and extraction boreholes (Fig. 4-23). These results are very similar to those from case 5, showing the small effect of the background hydraulic gradient under the conditions of the tracer test.

Tab. 4-6: Case 6 – Flow and transport parameters for the different zones

Note: Background hydraulic gradient is 0 m/m.

<table>
<thead>
<tr>
<th></th>
<th>Dp (m²/s)</th>
<th>Dispersivities (m)</th>
<th>k (m²)</th>
<th>C₀ (empl. gap)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>0.0</td>
<td>0.0</td>
<td>8.0 E-18</td>
<td></td>
</tr>
<tr>
<td>Emplacement Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Emplacement Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>1.0 E-15</td>
<td></td>
</tr>
<tr>
<td>Observation Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td>0.00346 g/l</td>
</tr>
<tr>
<td>Observation Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Extraction Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Extraction Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Inner</td>
<td>1.0 E-09</td>
<td>0.1</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Outer</td>
<td>1.0 E-09</td>
<td>0.5</td>
<td>3.0 E-13</td>
<td></td>
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Fig. 4-21: Case 6 – Steady-state water pressures in the domain
Fig. 4-22: Case 6 – Tracer concentrations for C < 0.1 mg/L (top) and C < 1 mg/L (bottom) at t = 69 days

Note: Very high concentrations near the emplacement borehole not plotted. The plot at the bottom shows a detail of the emplacement borehole. Concentrations are not corrected for zero tracer concentration at emplacement after t = 43 days.
Fig. 4-23: Case 6 – Modelling results (model) vs. measured tracer concentrations (Grimsel data) in the 3 boreholes

Note: a) Emplacement borehole, b) Observation borehole, c) Extraction borehole.
4.2.2.7 Case 7

Flow and transport parameters are the same as in case 1, but the permeability of the skin around the emplacement borehole has been decreased to $10^{-15}$ m$^2$ (Tab. 4-7). Results are shown in Figures 4-25 to 4-27. As in case 5, tracer concentrations are underestimated at the observation and extraction boreholes (Fig. 4-27), due to the slower flow of water at the emplacement borehole. In case 5 the permeability of the skin at observation had been increased to $3 \times 10^{-13}$ m$^2$.

Tab. 4-7: Case 7 – Flow and transport parameters for the different zones

<table>
<thead>
<tr>
<th>Zone</th>
<th>Dp (m$^2$/s)</th>
<th>Dispersivities (m)</th>
<th>k (m$^2$)</th>
<th>$C_0$ (empl. gap)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>0.0</td>
<td>0.0</td>
<td>8.0 E-18</td>
<td></td>
</tr>
<tr>
<td>Emplacement Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Emplacement Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>1.0 E-15</td>
<td></td>
</tr>
<tr>
<td>Observation Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Observation Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-14</td>
<td></td>
</tr>
<tr>
<td>Extraction Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Extraction Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-13</td>
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<td>Fractura Inner</td>
<td>1.0 E-09</td>
<td>0.1</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Outer</td>
<td>1.0 E-09</td>
<td>0.5</td>
<td>3.0 E-13</td>
<td></td>
</tr>
</tbody>
</table>

Note: Background hydraulic gradient is 1 m/m.

Fig. 4-24: Case 7 – Steady-state water pressures in the domain
Fig. 4-25: Case 7 – Tracer concentrations for C < 0.1 mg/L (top) and C < 1 mg/L (bottom) at t = 69 days

Note: Very high concentrations near the emplacement borehole not plotted. The plot at the bottom shows a detail of the emplacement borehole. Concentrations are not corrected for zero tracer concentration at emplacement after t = 43 days.
Fig. 4-26: Case 7 – Modelling results (model) vs. measured tracer concentrations (Grimsel data) in the 3 boreholes

Note: a) Emplacement borehole, b) Observation borehole, c) Extraction borehole.
4.2.2.8 Case 8

Flow and transport parameters are the same as in case 7 (Tab. 4-8), except for the magnitude of the background hydraulic gradient (0 m/m in case 8). The results corresponding to case 8 are shown in Figures 4-27 to 4-29. Tracer concentrations are underestimated at the observation and extraction boreholes (Fig. 4-29). These results are very similar to those from case 7, showing the small effect of the background hydraulic gradient under the conditions of the tracer test.

Tab. 4-8: Case 8 – Flow and transport parameters for the different zones

Note: Background hydraulic gradient is 0 m/m.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Dp (m²/s)</th>
<th>Dispersivities (m)</th>
<th>k (m²)</th>
<th>C₀ (empl. gap)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>0.0</td>
<td>0.0</td>
<td>8.0E-18</td>
<td></td>
</tr>
<tr>
<td>Emplacement Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0E-10</td>
<td></td>
</tr>
<tr>
<td>Emplacement Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>1.0E-15</td>
<td>0.00346 g/l</td>
</tr>
<tr>
<td>Observation Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0E-10</td>
<td></td>
</tr>
<tr>
<td>Observation Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0E-14</td>
<td></td>
</tr>
<tr>
<td>Extraction Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0E-10</td>
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</tr>
<tr>
<td>Extraction Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0E-13</td>
<td></td>
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<tr>
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<td>3.0E-13</td>
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<tr>
<td>Fractura Outer</td>
<td>1.0 E-09</td>
<td>0.5</td>
<td>3.0E-13</td>
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</table>

Fig. 4-27: Case 8 – Steady-state water pressures in the domain
Fig. 4-28: Case 8 – Tracer concentrations for $C < 0.1$ mg/L (top) and $C < 1$ mg/L (bottom) at $t = 69$ days.

Note: Very high concentrations near the emplacement borehole not plotted. The plot at the bottom shows a detail of the emplacement borehole. Concentrations are not corrected for zero tracer concentration at emplacement after $t = 43$ days.
Fig. 4-29: Case 8 – Modelling results (model) vs. measured tracer concentrations (Grimsel data) in the 3 boreholes

Note: a) Emplacement borehole, b) Observation borehole, c) Extraction borehole.
4.2.2.9 Case 9

Flow and transport parameters are the same as in case 1, but the permeability of the skin around the emplacement borehole has been increased to $10^{-14}$ m$^2$ (Tab. 4-9; it was $3 \times 10^{-14}$ m$^2$ in case 3). Results are shown in Figures 4-30 to 4-32. A good match is achieved for the concentrations at emplacement borehole. Concentrations at observation are reproduced approximately, while concentrations at extraction are clearly overestimated (Fig. 4-32).

Tab. 4-9: Case 9 – Flow and transport parameters for the different zones

<table>
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<tr>
<th>Zone</th>
<th>Dp (m$^3$/s)</th>
<th>Dispersivities (m)</th>
<th>k (m$^2$)</th>
<th>C$_0$ (empl. gap)</th>
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<tbody>
<tr>
<td>Cement</td>
<td>0.0</td>
<td>0.0</td>
<td>8.0 E-18</td>
<td></td>
</tr>
<tr>
<td>Emplacement Gap</td>
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<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Emplacement Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>1.0 E-14</td>
<td></td>
</tr>
<tr>
<td>Observation Gap</td>
<td>2.0 E-10</td>
<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Observation Skin</td>
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<td>0.02</td>
<td>3.0 E-14</td>
<td></td>
</tr>
<tr>
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<td>10</td>
<td>3.0 E-10</td>
<td></td>
</tr>
<tr>
<td>Extraction Skin</td>
<td>1.0 E-09</td>
<td>0.02</td>
<td>3.0 E-13</td>
<td></td>
</tr>
<tr>
<td>Fractura Inner</td>
<td>1.0 E-09</td>
<td>0.1</td>
<td>3.0 E-13</td>
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<tr>
<td>Fractura Outer</td>
<td>1.0 E-09</td>
<td>0.5</td>
<td>3.0 E-13</td>
<td></td>
</tr>
</tbody>
</table>

0.00346 g/l

Fig. 4-30: Case 9 – Steady-state water pressures in the domain
Fig. 4-31: Case 9 – Tracer concentrations for C < 0.1 mg/L (top) and C < 1 mg/L (bottom) at t = 69 days.

Note: Very high concentrations near the emplacement borehole not plotted. The plot at the bottom shows a detail of the emplacement borehole. Concentrations are not corrected for zero tracer concentration at emplacement after t = 43 days.
Fig. 4-32: Case 9 – Modelling results (model) vs. measured tracer concentrations (Grimsel data) in the 3 boreholes

Note: a) Emplacement borehole, b) Observation borehole, c) Extraction borehole.
4.3 Summary and conclusions

Flow and solute transport modelling has been performed to interpret tracer test 09-03 (uranine) at Grimsel, which was performed before installation of the pre-hardened cement in the emplacement borehole. The 2D calculations assumed a homogeneous and isotropic fracture and explicitly included the emplacement, observation and extraction boreholes. These calculations did not address the effect of the heterogeneous nature of permeability in these types of fractures.

Results of the sensitivity analyses showed 3 cases where the evolution of tracer concentrations in the 3 different boreholes was satisfactory. These were cases 1, 2 and 9 (see Tabs. 4-1, 4-2 and 4-9). In all 3 cases, a low-permeability skin affected the emplacement and observation boreholes. No skin appears to affect the extraction borehole. The background hydraulic gradient appears to have no effect on the results of the tracer test. The goal after this exercise was to apply the results in the calculation of the initial flow field for the reactive transport phase of in-situ Experiment 2 (interaction between pre-hardened cement and fractured granite at Grimsel).
Prior to the reactive phase of the experiment, a tracer test was performed to characterise the initial flow and transport properties of the rock around the 3 experimental boreholes. The interpretation of this test using a two-dimensional homogeneous fracture model (see previous chapter) was reported by Manette et al. (2015). Solute transport was assumed to be controlled by diffusion in the cement and by advection-dispersion in the rock fracture.

In this chapter, reactive transport calculations corresponding to the formation of a high-pH plume and its interaction with the rock are reported. The model takes into account the total volumes of water at the different boreholes (1.16 L, 1.07 L, 0.32 L at emplacement, observation and extraction, respectively), and the changing injection (emplacement borehole) and extraction (observation and extraction boreholes) flow rates during the experiment. Monitoring data from the 3 different boreholes (pH and major element chemical composition) have been used to calibrate or otherwise check the performance of the model. This study has already been reported by Saaltink & Soler (2016). Further modelling was performed once the results of analyses of rock and cement after overcoring were available (see next chapter).

Initially, the flow model calculated from the results of the pre-emplacement tracer test, assuming a homogeneous fracture, was used to model reactive transport after emplacement of the cement. Since the small grid size from the flow model led to excessive computation times, the domain was divided into (a) a 1D radial model for the emplacement borehole and a small volume of rock around it, and (b) a 2D model for the rest of the domain. The results from (a) were used as input for (b).

5.1 Reactive transport code and mathematical formulation

Reactive transport calculations were performed using the Retraso-CodeBright software package (Olivella et al., 1996; Saaltink et al., 2004), which uses a finite element spatial discretisation. Regarding flow, the formulation presented here assumes fully saturated steady-state conditions and constant temperature.

The flow of water, \( q \), is calculated using Darcy’s law ignoring the buoyancy term

\[
q = -\frac{k}{\mu} \nabla P
\]  

where \( k \) is the intrinsic permeability tensor (m\(^2\)), \( \mu \) is the dynamic viscosity (8.9 \times 10^{-4} \text{ Pa s at } 25 \degree \text{C}) and \( P \) is the water pressure (Pa).

Concerning reactive transport, the transport of solutes is considered by means of advection, dispersion and diffusion and both complexation of aqueous species (at equilibrium) and precipitation/dissolution of minerals (kinetics). Then, the mass balance for chemical components has the form

\[
\frac{\partial \phi u_{a,i}}{\partial t} = -\nabla q u_{a,i} + \nabla \left( \phi D \nabla u_{a,i} \right) - R_i \quad i = 1, ..., n_c
\]  

where subscript \( i \) refers to the chemical component, \( u_{a,i} \) (mol m\(^{-3}\) water) is the total aqueous concentration of a component, \( \phi \) is the porosity, \( D \) is a tensor for both diffusion and dispersion (m\(^2\) s\(^{-1}\)), \( R \) is the precipitation-dissolution rate for a component (mol m\(^{-3}\) porous medium s\(^{-1}\)) and \( n_c \) is the number of chemical components.
The diffusion-dispersion coefficient is expressed by

\[ \mathbf{D} = D_p \mathbf{I} + \mathbf{D}_{\text{dis}} \]  

(5-3)

where \( \mathbf{I} \) is the identity matrix, \( D_p \) is the pore diffusion coefficient (m\(^2\) s\(^{-1}\)) and \( \mathbf{D}_{\text{dis}} \) is the dispersion tensor (m\(^2\) s\(^{-1}\)) which can be calculated from the velocities of the water \( (v = q/\phi) \) in 2D from

\[
\mathbf{D}_{\text{dis}} = \begin{pmatrix}
\alpha_L v_x^2 + \alpha_T v_y^2 & (\alpha_L - \alpha_T) v_x v_y \\
(\alpha_L - \alpha_T) v_y v_x & \alpha_L v_y^2 + \alpha_T v_x^2
\end{pmatrix}
\]  

(5-4)

where \( \alpha_L \) and \( \alpha_T \) are the longitudinal and transverse dispersivities (m).

Total aqueous concentrations of chemical components \( (u_a) \) are calculated from the concentrations of primary and secondary aqueous species \( (c_{a1} \text{ and } c_{a2}) \) and stoichiometric coefficients of complexation reactions \( (S_{ai}) \)

\[
u_{a,i} = c_{a1,i} + \sum_{j}^{n} S_{a,i,j} c_{a2,j} \quad i = 1, \ldots, n_c
\]  

(5-5)

where subscript \( j \) refers to the aqueous complexes or secondary species, and \( n_c \) is the number of aqueous complexation reactions. The concentrations of secondary species are calculated from the primary species through the mass action law

\[
\log c_{a2,i} + \log \gamma_{a2,i} = \sum_{j}^{n} S_{a,i,j} \left( \log c_{a1,j} + \log \gamma_{a1,j} \right) - \log K_{x,j} \quad j = 1, \ldots, n_x
\]  

(5-6)

where \( K_x \) is the equilibrium constant and \( \gamma \) is the activity coefficient which is calculated from the ionic strength \( (I \text{ in mol/kg H}_2\text{O}) \) through the extended Debye-Hückel equation

\[
\log \gamma_k = \frac{-AZ_k^2 \sqrt{I}}{1 + Bq_k \sqrt{I}} + bI
\]  

(5-7)

where subscript \( k \) refers to the aqueous species (both primary and secondary), \( A, B \) and \( b \) are constants that depend on the temperature and \( z \) and \( \bar{d} \) are the charge and ion size of the aqueous species.

Finally, \( R \) is calculated from the individual mineral precipitation-dissolution rates \( (r) \) using

\[
R_i = \sum_{m}^{n} S_{p,m} r_m \quad i = 1, \ldots, n_c
\]  

(5-8)

The precipitation-dissolution rates, \( r \), are calculated assuming a kinetic approach. For this a kinetic rate law is required, which is a function of all concentrations. In this work the rate law of Lasaga (1984) is used, given by

\[
r_m = \kappa_m \sigma_m \left( \Omega_m^a - 1 \right)^\eta \sum_{i}^{m} a_i \eta_i \quad m = 1, \ldots, n_p
\]  

(5-9)
where subscript \( l \) refers to a catalyzer, \( \kappa \) is the kinetic rate constant (mol m\(^{-2}\) s\(^{-1}\)), \( \sigma \) is the reactive surface of a mineral (m\(^2\) of mineral m\(^{-3}\) of porous medium), \( a \) is the activity of a species, \( p \) is the catalyzer coefficient and \( \Omega \) is the saturation index, which is calculated from

\[
\log \Omega_m = \sum_{i=1}^{n} S_{p,m} \left( \log \gamma_{a_{i,j}} + \log c_{a_{i,j}} \right) - \log K_{p,m} \quad m = 1, \ldots, n_p
\]  

where \( K_p \) is the equilibrium constant.

5.2 Conceptual model

5.2.1 Modelling approach

Initially a model was built that used the same setup (geometry, boundary conditions and finite element mesh) as the model used to interpret pre-emplacement tracer test 09-03 (Manette et al., 2015). It soon became clear that this setup could not be used for the modelling of reactive transport. A very fine mesh was required near the emplacement borehole, as minerals precipitate in narrow fringes, implying excessive CPU times. Therefore, it was decided to use two models.

A first model simulates the emplacement borehole together with the skin around it. It assumes that, during the period without injection, the permeability of the skin is low enough to avoid flow of water in it (see Fig. 5-1). It also assumes that when water is injected, the flow in the skin is only affected by this injection and not by other phenomena (e.g. injection/extraction in other boreholes and natural gradient). In both cases, a one-dimensional radial symmetry can be assumed. This significantly reduces the number of nodes and computational times.

A second model simulates the fracture at the scale of all three boreholes (emplacement, observation and extraction) in a two-dimensional domain. It uses as input the results calculated by the 1D radial model (solute concentrations at the outer boundary of the skin of the emplacement borehole).

Fig. 5-1: Illustration of the basic assumptions

Note: During the diffusion period, water flows around the skin and there is no water flow within the skin. During injection, flow spreads out radially from the borehole.
5.2.2 Chemical system

5.2.2.1 Cement and rock composition

Table 5-1 shows the initial composition of the cement in the emplacement borehole used in the model. This composition is based on that reported by Lothenbach & Winnefeld (2006) for OPC. The volume fractions of the different phases have been modified to account for the porosity of 0.5 estimated from the elevated water/cement ratio of this cement (w/c = 0.8).

Table 5-2 shows the initial composition of the rock fracture (fault gouge; Soler & Mäder, 2010). It also applies to the zones defined as skins around boreholes.

Tab. 5-1: Initial volume fractions and reactive surface areas for the cement in the emplacement borehole

<table>
<thead>
<tr>
<th></th>
<th>Vol %</th>
<th>A (m²/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>2.0</td>
<td>10⁶</td>
</tr>
<tr>
<td>Portlandite</td>
<td>11.7</td>
<td>10⁶</td>
</tr>
<tr>
<td>CSH-1.67</td>
<td>21.5</td>
<td>10⁶</td>
</tr>
<tr>
<td>Ettringite</td>
<td>12.6</td>
<td>10⁶</td>
</tr>
<tr>
<td>Monocarboaluminate</td>
<td>2.3</td>
<td>10⁶</td>
</tr>
<tr>
<td>Porosity</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 5-2: Initial volume fractions and reactive surface areas for the rock fracture (after Soler & Mäder, 2010)

<table>
<thead>
<tr>
<th></th>
<th>Vol %</th>
<th>A (m²/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>19</td>
<td>10730</td>
</tr>
<tr>
<td>Albite</td>
<td>14</td>
<td>7920</td>
</tr>
<tr>
<td>Microcline</td>
<td>15</td>
<td>8480</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>09</td>
<td>5100</td>
</tr>
<tr>
<td>Muscovite</td>
<td>22</td>
<td>12420</td>
</tr>
<tr>
<td>Porosity</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

The potential secondary phases that were considered (Soler & Mäder, 2010) were C-S-H solid solution (discretised as phases with Ca/Si 1.4, 1.2, 1.0 and 0.8), brucite, several zeolites (analcime, natrolite, scolecite, stilbite, gismondine, mordenite, wairakite), prehnite (analogue for C-A-S-H), hydrotalcite and several crystalline C-S-H phases (foshagite, gyrolite, hillebrandite, okenite, tobermorite-14A).

5.2.2.2 Solution composition

Table 5-3 shows the initial compositions of the cement porewater and the water in the rock fracture (Grimsel groundwater; T = 15 °C). The composition of the cement porewater is at equilibrium with the initial solid phases in the cement. Additionally, equilibrium with respect to phlogopite, limiting Mg concentration, has been imposed to avoid initial supersaturation with respect to
this phase. Na and K concentrations were taken from Lothenbach & Winnefeld (2006) but decreased to account for the larger porosity of 0.5 (porosity of the OPC used by Lothenbach & Winnefeld, 2006, was 0.42, as calculated by Savage et al., 2011, using CrunchFlow).

The initial composition of water in the rock fracture (Grimsel groundwater) is based on the composition reported by Soler & Mäder (2010), Mäder et al. (2006) and Eikenberg et al. (1994). Calcite equilbrium has been assumed to calculate the carbonate content. Equilibrium with respect to prehnite (analogue for C-A-S-H) and laumontite have been assumed to limit the concentrations of Al and Si and avoid initial supersaturation with respect to these phases.

Tab. 5-3: Initial compositions (total molalities and pH) for the cement porewater and the water in the rock fracture; T = 15 °C

<table>
<thead>
<tr>
<th></th>
<th>Cement porewater</th>
<th>Rock fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C&lt;sub&gt;ion&lt;/sub&gt; (molal)</td>
<td>Constraint</td>
</tr>
<tr>
<td>Al</td>
<td>3.67·10⁻⁵</td>
<td>monocarb.</td>
</tr>
<tr>
<td>CO₃</td>
<td>2.17·10⁻⁴</td>
<td>calcite</td>
</tr>
<tr>
<td>Ca</td>
<td>8.64·10⁻⁴</td>
<td>portlandite</td>
</tr>
<tr>
<td>Cl</td>
<td>1.00·10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>5.26·10¹</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>1.78·10⁻⁸</td>
<td>phlogopite</td>
</tr>
<tr>
<td>Na</td>
<td>5.05·10⁻²</td>
<td></td>
</tr>
<tr>
<td>SO₄</td>
<td>2.93·10⁻³</td>
<td>ettringite</td>
</tr>
<tr>
<td>SiO₂ (aq)</td>
<td>1.42·10⁻⁴</td>
<td>CSH-1.7</td>
</tr>
<tr>
<td>pH</td>
<td>13.84</td>
<td>charge</td>
</tr>
</tbody>
</table>

* The measured value for Cl in the Grimsel groundwater was 1.5·10⁻⁴ molal. The different value in the model is due to charge balance issues. The effects are discussed in the results section.

5.2.2.3 Thermodynamic data

All the chemical equilibria in solution at 15 °C (Tab. 5-4) were taken from the LLNL database included in the code, which is based on the EQ3/6 database (Wolery et al., 1990). The equilibrium constants for all the mineral reactions are given in Table 5-4. All the solid equilibrium constants at 15 °C were taken from the LLNL database, except for portlandite (Hummel et al., 2002), monocalciccarbonate, ettringite and hydrotalcite (cemdata07 database: Matschei et al., 2007; Lothenbach et al., 2008), and C-S-H (Kulik & Kersten, 2001). The C-S-H solid solution has been introduced in the model as several discrete compositions (different mol fractions of the end-members), with solubilities calculated from the original solid solution model.
Tab. 5-4: Equilibrium constants (log K at 15 °C) and stoichiometric coefficients of equilibria in solution

Note: Reactions are written as the destruction of 1 mole of the species in the first column.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
<th>Primary species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>al(oh)4-ca2+</td>
</tr>
<tr>
<td>al(oh)2+</td>
<td>16.0512</td>
<td>1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>al(oh)3(aq)</td>
<td>8.3143</td>
<td>1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>al(so4)2-</td>
<td>29.2892</td>
<td>1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>al+3</td>
<td>34.1086</td>
<td>1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>aloh+2</td>
<td>25.0999</td>
<td>1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>also4+</td>
<td>31.1653</td>
<td>1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>ca(h3sio4)2(aq)</td>
<td>-5.1323</td>
<td>0.000 1.000 0.000 0.000 0.000 2.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>cac1+</td>
<td>0.7044</td>
<td>0.000 1.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>cac12(aq)</td>
<td>0.6032</td>
<td>0.000 1.000 2.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>caco3(aq)</td>
<td>-3.2271</td>
<td>0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>cah2so4(aq)</td>
<td>-5.8692</td>
<td>0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>cah3so4+</td>
<td>-1.3012</td>
<td>0.000 1.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>cahco3+</td>
<td>2.8700</td>
<td>0.000 1.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>caco+</td>
<td>-1.0959</td>
<td>0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>caso4(aq)</td>
<td>-2.0746</td>
<td>0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>co2(aq)</td>
<td>11.8405</td>
<td>0.000 0.000 0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>h+</td>
<td>14.3380</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>h2so4-2</td>
<td>-1.1417</td>
<td>0.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>hco3-</td>
<td>3.9148</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>hso4-</td>
<td>12.4785</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>kc1(aq)</td>
<td>1.5848</td>
<td>0.000 0.000 1.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>khsso4(aq)</td>
<td>13.6985</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>koh(aq)</td>
<td>0.1220</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>koso4-</td>
<td>-0.8653</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>mg(h3sio4)2(aq)</td>
<td>-6.4623</td>
<td>0.000 0.000 0.000 0.000 2.000 0.000 1.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>mg4(oh)4+</td>
<td>-15.4903</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 4.000 0.000 4.000 0.000</td>
</tr>
<tr>
<td>mgc1+</td>
<td>0.1237</td>
<td>0.000 0.000 1.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>mgco3(aq)</td>
<td>-2.9210</td>
<td>0.000 0.000 0.000 1.000 0.000 0.000 1.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>mgh2so4(aq)</td>
<td>-6.9492</td>
<td>0.000 0.000 0.000 0.000 1.000 0.000 1.000 0.000 1.000 0.000</td>
</tr>
<tr>
<td>mgm3sio4+</td>
<td>-1.5512</td>
<td>0.000 0.000 0.000 0.000 1.000 0.000 1.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>Species</td>
<td>log K</td>
<td>coeff 1</td>
</tr>
<tr>
<td>--------------------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>mghco3+</td>
<td>2.8831</td>
<td>0.000</td>
</tr>
<tr>
<td>mgoh+</td>
<td>-2.2100</td>
<td>0.000</td>
</tr>
<tr>
<td>mgso4(aq)</td>
<td>-2.2681</td>
<td>0.000</td>
</tr>
<tr>
<td>nacl(aq)</td>
<td>0.8083</td>
<td>0.000</td>
</tr>
<tr>
<td>naco3-</td>
<td>-0.6302</td>
<td>0.000</td>
</tr>
<tr>
<td>nahco3(aq)</td>
<td>3.6620</td>
<td>0.000</td>
</tr>
<tr>
<td>nahsio3(aq)</td>
<td>-1.7357</td>
<td>0.000</td>
</tr>
<tr>
<td>naoh(aq)</td>
<td>0.1516</td>
<td>0.000</td>
</tr>
<tr>
<td>naso4-</td>
<td>-0.7869</td>
<td>0.000</td>
</tr>
<tr>
<td>sio2(aq)</td>
<td>4.2453</td>
<td>0.000</td>
</tr>
</tbody>
</table>
## Tab. 5-5: Equilibrium constants (log K at 15 °C) and stoichiometric coefficients for mineral reactions

Note: Reactions are written as the dissolution of 1 mole of mineral.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
<th>Primary species</th>
</tr>
</thead>
<tbody>
<tr>
<td>albite</td>
<td>-8.4207</td>
<td>(oh) 4-ca+2 1.00 0.000 0.000 0.000 3.000 0.000 0.000 0.000 0.000 1.000 -3.000 0.000</td>
</tr>
<tr>
<td>k-feldspar</td>
<td>-11.6313</td>
<td>1.00 0.000 0.000 0.000 3.000 1.000 0.000 0.000 -3.000 0.000</td>
</tr>
<tr>
<td>phlogopite</td>
<td>-58.2010</td>
<td>1.00 0.000 0.000 0.000 3.000 1.000 0.000 0.000 3.000 0.000</td>
</tr>
<tr>
<td>muscovite</td>
<td>-16.1003</td>
<td>3.00 0.000 0.000 0.000 3.000 1.000 0.000 0.000 -5.000 0.000</td>
</tr>
<tr>
<td>quartz</td>
<td>0.0231</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>calcite</td>
<td>-8.4182</td>
<td>0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>portlandite</td>
<td>-5.0755</td>
<td>0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000 2.000 0.000</td>
</tr>
<tr>
<td>brucite</td>
<td>-11.7000</td>
<td>0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>csh-08</td>
<td>-17.1207</td>
<td>0.000 1.820 0.000 0.000 2.270 0.000 0.000 0.000 0.000 0.000</td>
</tr>
<tr>
<td>csh-10</td>
<td>-9.3507</td>
<td>0.000 1.000 0.000 0.000 1.000 0.000 0.000 0.000 1.000 0.000</td>
</tr>
<tr>
<td>csh-12</td>
<td>-10.7076</td>
<td>0.000 1.200 0.000 0.000 1.000 0.000 0.000 0.000 1.400 0.000</td>
</tr>
<tr>
<td>csh-14</td>
<td>-11.9594</td>
<td>0.000 1.400 0.000 0.000 1.000 0.000 0.000 0.000 1.800 0.000</td>
</tr>
<tr>
<td>csh-1667</td>
<td>-13.4795</td>
<td>0.000 1.670 0.000 0.000 1.000 0.000 0.000 0.000 2.340 0.000</td>
</tr>
<tr>
<td>analcime</td>
<td>-7.9852</td>
<td>0.960 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 -2.040 0.000</td>
</tr>
<tr>
<td>laumontite</td>
<td>-16.6560</td>
<td>2.000 1.000 0.000 0.000 4.000 0.000 0.000 0.000 -4.000 0.000</td>
</tr>
<tr>
<td>mesolite</td>
<td>-20.6696</td>
<td>1.990 0.657 0.000 0.000 3.010 0.000 0.000 0.000 0.000 -3.010 0.000</td>
</tr>
<tr>
<td>natrolite</td>
<td>-16.0081</td>
<td>2.000 0.000 0.000 0.000 3.000 0.000 0.000 0.000 0.000 -3.000 0.000</td>
</tr>
<tr>
<td>scolecite</td>
<td>-18.5429</td>
<td>2.000 1.000 0.000 0.000 3.000 0.000 0.000 0.000 0.000 -3.000 0.000</td>
</tr>
<tr>
<td>stilbite</td>
<td>-22.3222</td>
<td>2.180 1.019 0.000 0.000 6.820 0.006 0.000 0.000 0.136 -6.820 0.000</td>
</tr>
<tr>
<td>gismondine</td>
<td>-37.6948</td>
<td>4.000 2.000 0.000 0.000 4.000 0.000 0.000 0.000 0.000 -4.000 0.000</td>
</tr>
<tr>
<td>mordenite</td>
<td>-6.6626</td>
<td>0.940 0.289 0.000 0.000 5.060 0.000 0.000 0.000 0.361 -5.060 0.000</td>
</tr>
<tr>
<td>wairakite</td>
<td>-11.9252</td>
<td>2.000 1.000 0.000 0.000 4.000 0.000 0.000 0.000 0.000 -4.000 0.000</td>
</tr>
<tr>
<td>prehnite</td>
<td>-29.5188</td>
<td>2.000 2.000 0.000 0.000 3.000 0.000 0.000 0.000 0.000 -1.000 0.000</td>
</tr>
<tr>
<td>foshagite</td>
<td>-33.9203</td>
<td>0.000 4.000 0.000 0.000 3.000 0.000 0.000 0.000 5.000 0.000</td>
</tr>
<tr>
<td>gyrolite</td>
<td>-21.2633</td>
<td>0.000 2.000 0.000 0.000 3.000 0.000 0.000 0.000 1.000 0.000</td>
</tr>
<tr>
<td>hillebrandite</td>
<td>-15.0717</td>
<td>0.000 2.000 0.000 0.000 1.000 0.000 0.000 0.000 3.000 0.000</td>
</tr>
<tr>
<td>okenite</td>
<td>-9.7110</td>
<td>0.000 1.000 0.000 0.000 2.000 0.000 0.000 0.000 3.000 0.000</td>
</tr>
<tr>
<td>tobermorite-14a</td>
<td>-52.7703</td>
<td>0.000 5.000 0.000 0.000 6.000 0.000 0.000 0.000 4.000 0.000</td>
</tr>
<tr>
<td>hydrotalcite-OH</td>
<td>-56.6656</td>
<td>2.000 0.000 0.000 0.000 0.000 0.000 0.000 4.000 0.000</td>
</tr>
<tr>
<td>ettring-All0</td>
<td>-46.1057</td>
<td>2.000 6.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 4.000 0.000</td>
</tr>
<tr>
<td>monocarb-All0</td>
<td>-31.8580</td>
<td>2.000 4.000 0.000 1.000 0.000 0.000 0.000 0.000 0.000 4.000 0.000</td>
</tr>
</tbody>
</table>
5.2.2.4 Reaction rates

The rate laws used for the primary minerals in the rock (quartz, albite, microcline, phlogopite, muscovite) are based on those used by Soler & Mäder (2010) for the modeling of the core infiltration experiment in the HPF project (Tab. 5-6). Values of $\theta$ and $\eta$ for albite and microcline are from Soler & Lasaga (1998). For all the other phases (cement and secondary phases), large values of the rate constants ($10^{-9}$ mol m$^{-2}$ s$^{-1}$) and of the surface areas have been used, leading to local equilibrium with respect to those phases.

Tab. 5-6: Rate parameters for the primary minerals in the rock

<table>
<thead>
<tr>
<th>MINERAL</th>
<th>$m_{\text{log}} \kappa_m$ (mol/m$^2$/s)</th>
<th>$P_{\alpha_\text{H}_+}$</th>
<th>$\theta$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>-13.92</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Albite</td>
<td>-12.92</td>
<td>0.2</td>
<td>0.4</td>
<td>14</td>
</tr>
<tr>
<td>Microcline</td>
<td>-20.22</td>
<td>-0.73</td>
<td>0.4</td>
<td>14</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>-13.52</td>
<td>-0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Muscovite</td>
<td>-13.12</td>
<td>-0.1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The initial composition of the Grimsel groundwater in the model was supersaturated with respect to mesolite, scolecite, stilbite and gismondine. Therefore, large supersaturation thresholds were imposed for those phases ($\Omega = 3900, 230, 1.8 \cdot 10^5, 190$, for mesolite, scolecite, stilbite and gismondine, respectively), preventing their precipitation.

5.2.3 One-dimensional radial model

The geometry of the 1D radial model is shown in Figure 5-2. The domain is discretised in 101 1D finite elements with sizes ranging from 0.1 mm near the gap between cement and rock to 1.5 mm near the skin-fracture interface. Like the model of Manette et al. (2015), the total volume of water in the circulation system (tank, tubing, gap) is taken into account by rescaling the porosity. The same is done for the cement which has a thickness larger than the fracture. This assumes that concentrations are the same in the direction of the borehole perpendicular to the fracture (well-mixed conditions).
Table 5-7 shows the transport parameters of the model with both the real and rescaled porosities. The gap is assumed to contain only water. Porosity for the fracture is taken from Soler et al. (2006) and Soler & Mäder (2007), corresponding to the porosity of the fault gouge in a granite core from Grimsel. Cement porosity was estimated to be 0.5, which is in agreement with reported porosities for cements with the same water/cement ratio of 0.8 (Walker, 2016). The diffusion coefficient for the skin (rock fracture) is based on common values in the literature. The diffusion coefficient of the cement was also based on previous values in the literature. For instance, Trapote-Barreira et al. (2016) found values of $D_p$ from $2 \cdot 10^{-13}$ to $9 \cdot 10^{-13} \text{m}^2\text{s}^{-1}$ for diffusion of cement components in mortar grains (mortar porosity $\phi = 0.125$) in column experiments. However, reported values from through-diffusion experiments in cement paste using HTO and Cl$^-$ are much higher ($D_p$ values about $6 \cdot 10^{-10}$ and $2 \cdot 10^{-10} \text{m}^2\text{s}^{-1}$ for HTO and Cl$^-$, respectively, for $\phi = 0.5$; capacity factors are about 1.5 and 1.7, respectively; Walker, 2016). Diffusion coefficient and dispersivity of the gap are sufficiently high to ensure perfect mixing within the gap. The dispersivity of the skin (0.02 m) is from Manette et al. (2015). The dispersivity assigned to the cement has no effect because there is no flow of water through the cement.

Table 5-7: Transport parameters for the 1D radial model

<table>
<thead>
<tr>
<th></th>
<th>$\phi_{\text{real}}$</th>
<th>$\phi_{\text{rescaled}}$</th>
<th>$D_p$ (m$^2$s$^{-1}$)</th>
<th>$\alpha$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>0.5</td>
<td>345.0</td>
<td>$2.0 \cdot 10^{-12}$</td>
<td>0.002</td>
</tr>
<tr>
<td>Gap</td>
<td>1.0</td>
<td>2205.0</td>
<td>$1.0 \cdot 10^{-5}$</td>
<td>10.0</td>
</tr>
<tr>
<td>Skin</td>
<td>0.21</td>
<td>0.21</td>
<td>$1.0 \cdot 10^{-9}$</td>
<td>0.02</td>
</tr>
</tbody>
</table>
In order to simulate the various flow regimes, the following boundary conditions were used. During the initial diffusion period (August 2009 to October 2010) there is no injection. However, there is flow of water around the skin-fracture interface. This is simulated as an inflow of water into the second node from the end of the domain and an outflow at the last node. This inflow-outflow is calculated from the flow rate at the extraction borehole using:

\[ q_{\text{skin}} \cdot 2 \pi d_{\text{empl-ext}} b = Q_{\text{ext}} \]  

and

\[ Q_{\text{skin}} = q_{\text{skin}} \cdot 2 \pi r_{\text{skin}} b = Q_{\text{ext}} \cdot \frac{r_{\text{skin}}}{d_{\text{empl-ext}}} \]

where \( q_{\text{skin}} \) (m\(^3\) m\(^{-2}\) s\(^{-1}\)) is the Darcy velocity at the skin-fracture interface, \( d_{\text{empl-ext}} \) (m) is the distance between the emplacement and extraction boreholes, \( b \) is the thickness of the fracture (10\(^{-3}\) m), \( Q_{\text{ext}} \) (m\(^3\) s\(^{-1}\)) is the extraction flow rate at extraction borehole, \( r_{\text{skin}} \) is the radius of the skin (0.08 m) and \( Q_{\text{skin}} \) is the flow rate at the skin-fracture interface (m\(^3\) s\(^{-1}\)). A value of 2.4\( \cdot 10^{-6} \) L s\(^{-1}\) is obtained.

After this, water is injected at the gap, first with a flow rate of 3.98\( \cdot 10^{-6} \) L s\(^{-1}\) (between October 2010 and June 2011) and later with a flow rate of 9.83\( \cdot 10^{-7} \) L s\(^{-1}\) (between June 2011 and September 2014). During the injection period there is no flow of water around the skin-fracture interface. The water injected at the gap simply leaves the system at this boundary.

### 5.2.4 Two-dimensional model

The 2D model assumes that the flow of water is only affected by the flow rates at the three boreholes (emplacement, observation and extraction). The initial diffusion period is not included in the 2D model. Only the period when water is injected into the emplacement borehole is taken into account. As in the conservative tracer test interpreted by Manette et al. (2015), the natural gradients can be ignored due to the high flow rates at these boreholes. This means that the system is symmetrical with respect to the line crossing the centre of the three boreholes and only half of the domain has to be modelled. Figure 5-3 shows the geometry and the finite element mesh which consists of triangular elements with a size of about 2 cm. This model also explicitly includes the volumes of water in the gaps of the boreholes by rescaling the porosities.

Table 5-8 shows the flow and transport parameters. Intrinsic permeabilities are taken from Manette et al. (2015). The gaps are assumed to contain only water. Porosities for the skin and fracture are taken from Soler et al. (2006) and Soler & Mäder (2007). Diffusion coefficients of the fracture and skins are the same as in the 1D model, although they do not greatly affect the results as dispersion dominates over diffusion. The dispersivities of the gaps of both boreholes are sufficiently high to ensure perfect mixing. The dispersivities of the skins and fracture have been calibrated to adjust the modelled to the measured pH values.
A prescribed flux is imposed at the outer boundary of the domain. The flux is calculated from the flow rates of the three boreholes using the equation

$$q_b = \frac{1}{2\pi b^2} \sum_i Q_i \frac{x_{b_i} - x_{i}}{|x_{b_i} - x_i|^2} = emp, obs, ext$$

(5-13)
where $Q_i$ ($\text{m}^3 \text{s}^{-1}$) is the flow rate at borehole $i$, $b$ is the fracture thickness ($10^{-3} \text{ m}$), $q_b$ ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$) is the Darcy flow vector at the boundary and $\mathbf{x}_b$ and $\mathbf{x}_i$ are the vectors of coordinates of a node at the boundary and of borehole $i$, respectively. Equation 5-13 assumes a homogeneous permeability and the flow rates to be located at the centre of the boreholes, which is a safe assumption for the model. Flow rates vary in time and are calculated by averaging measured flow rates for periods of 3 months (see Fig. 5-4). Flow rates for the emplacement and observation boreholes are prescribed using time-dependent values, and the values at extraction are calculated by the code (mass balance), matching the measured data well. At the extraction borehole the pressure is fixed at 0.1 MPa (atmospheric pressure).

Fig. 5-4: Measured and modelled flow rates for the three boreholes
Note: Positive values mean injection, negative values extraction.

5.3 Results and discussion
Before discussing the results of the model, we will first calculate some characteristic times over which transport processes take place. This is helpful for the interpretation of the results of the models. We will then discuss the results of the 1D radial model that simulates the domain in the vicinity of the emplacement borehole, followed by the results of the 2D model that simulates the domain with three boreholes: emplacement, observation and extraction.
5.3.1 Characteristic times

A characteristic time for diffusion, \( t_{\text{dif}} \), can be defined as

\[
  t_{\text{dif}} = \frac{(L_2 - L_1)^2}{2D_p}
\]

(5-14)

where \( D_p \) is the pore diffusion coefficient and \( L_1 \) and \( L_2 \) are the two boundaries between which diffusion takes place. This means that when there are no changes at the boundaries, a steady state is reached after a time of roughly \( t_{\text{dif}} \). Equation 5-14 only makes sense when diffusion is the dominant process, that is only in the cement and in the skin of the emplacement borehole, the latter only during the diffusion period.

A characteristic time for advection, \( t_{\text{adv}} \), can be defined in a radial system as

\[
  t_{\text{adv}} = \frac{\pi \phi b (L_2^2 - L_1^2)}{Q}
\]

(5-15)

where \( \phi \), \( b \) and \( Q \) are porosity, thickness of the system and injection flow rate, respectively. This means \( t_{\text{adv}} \) is the time it takes water and a dissolved solute to flow from \( L_1 \) to \( L_2 \).

A third characteristic time is the average transient time of a solute in an ideally mixed system, \( t_{\text{mix}} \)

\[
  t_{\text{mix}} = \frac{V}{Q}
\]

(5-16)

where \( V \) is the volume of the ideally mixed system. The model volume includes the gap between the dummy cylinder or cement and the borehole wall plus the volume of water circulating in tubes and reservoir tank.

Table 5-9 shows the calculated characteristic times for the various processes. It can be seen that diffusion in the cement is the slowest process and therefore may be the one that controls the system the most. Advection times are short, indicating that water probably will not change its chemistry very much due to precipitation/dissolution of minerals during its passage through the fracture and skins as there is not much time for reactions to occur.

Tab. 5-9: Characteristic times for the different processes

Note: Characteristic times for diffusion, advection and ideal mixing are calculated by equations 5-14, 5-15 and 5-16, respectively. Characteristic times with two values are calculated from minimum and maximum flow rates.

<table>
<thead>
<tr>
<th>Process (( t_{\text{( \cdot )}} ))</th>
<th>Location</th>
<th>Characteristic time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion (( t_{\text{dif}} ))</td>
<td>Cement</td>
<td>383</td>
</tr>
<tr>
<td></td>
<td>Skin of emplacement borehole</td>
<td>7.9</td>
</tr>
<tr>
<td>Advection (( t_{\text{adv}} ))</td>
<td>Skin of emplacement borehole</td>
<td>0.009 - 0.035</td>
</tr>
<tr>
<td></td>
<td>From emplacement to extraction borehole</td>
<td>0.27 - 0.57</td>
</tr>
<tr>
<td>Ideal mixing (( t_{\text{mix}} ))</td>
<td>Gap of emplacement borehole</td>
<td>3.4 - 13.7</td>
</tr>
<tr>
<td></td>
<td>Gap of observation borehole</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>Gap of extraction borehole</td>
<td>0.10 - 0.21</td>
</tr>
</tbody>
</table>
5.3.2 One-dimensional model

Figure 5-5 shows the modelled and measured aqueous chemistry versus time. The behaviour during the period of only diffusion (before October 2010) is quite different from the period when water is injected in the gap. During this diffusion period, the chemical composition at the skin-fracture interface shows only small changes. That is because the flux of water in the fracture maintains the chemical composition close to that of the natural Grimsel water and the diffusion of cement water is not fast enough to cause an important effect. During the diffusion period, the concentrations at the gap rise or fall due to diffusion from or to the cement, respectively. As the characteristic diffusion time in the cement (383 days) is more or less the same as the diffusion period (430 days), changes in concentrations in the gap can still be observed. During injection, the concentrations in the gap are practically identical to those at the skin-fracture interface (with the possible exception of A1). The water injected in the gap interacts with the cement and changes only slightly during its passage through the skin, which takes only between 0.009 and 0.035 days (13 and 51 minutes, Tab. 5-3). This does not necessarily mean that there is no dissolution or precipitation of minerals, as will be seen later. When the injection rate changes to a lower value (June 2011), diffusion from the cement with high pH and Ca concentration has a greater effect as there is less dilution by the injected natural Grimsel water. This results in a higher pH and Ca concentration in both the gap and the skin-fracture interface.

There are some differences between model results and measurements. There can be various reasons for these discrepancies:

- The chemical composition of the Grimsel and cement water as assumed in section 5.3.2 may be different from reality. This is clearly the case for Cl in Grimsel groundwater (measured and model concentrations are $1.5 \times 10^{-4}$ and $4.6 \times 10^{-4}$ mol/L, respectively).
- The volume of water in the gap may be larger than originally thought (up to about 1.7 L from the original 1.16 L).
- The pore diffusion coefficient of the cement is based on a guess from previous information. A proper calibration of the diffusion coefficient can improve the match between measurements and the model, since diffusion from the cement is the controlling step of the overall process.
- Cement and cement porewater composition was also assumed from values for a generic cement (Lothenbach & Winnefeld, 2006). These compositions may not be completely accurate.
- The actual injection flow rates show larger variations than the model flow rates. This can also cause higher variation in the model.
- The assumption that no water flow takes place in the skin during the diffusion period may not be entirely true.

Although the match between measurements and model can be improved by changing the model with respect to the above-mentioned items, the concept and dominant processes will probably not fundamentally change.

Figures 5-6 and 5-7 show the precipitated volume fractions of minerals. Portlandite in the cement dissolves at a sharp dissolution front near the gap (Fig. 5-6). Note that this front has advanced about only 1 mm in five years. C-S-H also dissolves and does so at an even lower rate. During the diffusion period, C-S-H, ettringite and some monocarboaluminate precipitate in the skin.

C-S-H precipitates near the gap with the same composition as originally found in the cement (Ca/Si = 1.67). After injecting Grimsel water at the gap, these minerals in the skin completely redissolve. Similarly, tobermorite and prehnite precipitate in the skin during the diffusion period.
When Grimsel water is injected, they first dissolve, but then precipitate again. Subtle changes in the chemical composition may sometimes under- and sometimes over-saturate the water in the skin with respect to these two minerals. Calcite precipitates in the skin near the gap and in the gap itself due to the mixing of Ca and alkalinity from dissolved portlandite and CO$_3$ from the injected Grimsel water. Calcite precipitation can also be observed at the skin-fracture interface. This is the result of the mixing of the injected water reacted with the cement (hence containing much Ca and alkalinity) and Grimsel water (hence containing much CO$_3$). In our model, these two waters mix completely directly at the skin-fracture interface. In reality, this mixing and ensuing calcite precipitation are probably distributed over a larger area; this large amount of calcite precipitation can be considered a boundary effect. A similar mechanism may be observed for phlogopite due to the mixing of Mg from the Grimsel water and OH$^-$ from dissolution of portlandite in the cement. The primary minerals of the skin except phlogopite (K-feldspar, albite, muscovite and quartz) dissolve due to the high-pH cement conditions.

Figure 5-8 shows the porosity change due to precipitation and dissolution of minerals. The porosity change in the cement is mainly due to portlandite dissolution and amounts to 0.12, which is the initial volume fraction of the portlandite in the cement. In the skin, there is a temporary porosity reduction of about 0.02 due to ettringite precipitation during the diffusion period. During injection, the porosity in the skin increases slightly at the end of the simulation due to dissolution of silicate minerals. Porosity decreases directly at the gap-rock interface, due mainly to the precipitation of phlogopite.
Fig. 5-5: Modelled and measured total aqueous concentrations and pH versus time for the 1D radial model
Fig. 5-6: Modelled precipitated/dissolved volume fractions of portlandite, C-S-H, ettringite and monocarboaluminate (volume of mineral per volume of medium) for the 1D radial model.

Note: Positive values indicate precipitation; negative values dissolution. Dashed lines indicate the location of the gap.
Fig. 5-7: Modelled change in volume fractions of calcite, tobermorite, prehnite, phlogopite, K-feldspar, albite, muscovite and quartz (volume of mineral per volume of medium) versus distance for the 1D radial model

Note: Positive values indicate precipitation; negative values dissolution. Dashed lines indicate the location of the gap.
Figure 5.8: Porosity change versus distance for the 1D radial model

Note: Dashed lines indicate the location of the gap.

Figure 5.9 shows the modelled aqueous chemistry versus distance. At the end of the diffusion period (or start of the injection), the gradients of concentrations indicate a diffusion of Cl towards the cement caused by the initially low concentration in the cement. In contrast, Na, K and OH⁻ (pH) diffuse out of the cement. The Ca concentration in the cement shows a peak at the gap, which indicates the dissolution of a mineral containing Ca (portlandite), whereas the CO₃ concentration indicates the precipitation of a mineral containing CO₃ (calcite). Also, we can observe the concentrations of Al and Si indicating dissolution of silicates (K-feldspar, albite, muscovite and quartz). The dissolution of K-feldspar, albite and muscovite also affects the concentrations of Na and K, but its effect is less visible because the overall concentrations of Na and K are much higher than those of Al and Si.
Fig. 5-9: Modelled total aqueous concentrations and pH versus distance for the 1D radial model.

Note: Dashed lines indicate the location of the gap.
5.3.3 Two-dimensional model

Table 5-10 shows the chemical composition of the water at the emplacement borehole skin boundary. This is the water that enters the 2D domain near the emplacement borehole (cement porewater already reacted with rock in the 1D model). From the results of the 1D model, 2 different water compositions have been used at different times ((1) $t = 0$ to $t = 10$ d; (2) $t > 10$ d).

Tab. 5-10: Composition of the water at the emplacement borehole skin boundary for the 2D model

<table>
<thead>
<tr>
<th></th>
<th>$0 &lt; t \leq 10$ d</th>
<th>$t &gt; 10$ d</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{tot}$ (molal)</td>
<td>Constraint</td>
<td>C$_{tot}$ (molal)</td>
</tr>
<tr>
<td>Al</td>
<td>$1.30 \cdot 10^{-5}$</td>
<td>$5.00 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>$4.00 \cdot 10^{-5}$</td>
<td>$9.00 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>Ca</td>
<td>$3.00 \cdot 10^{-3}$</td>
<td>$4.00 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>Cl</td>
<td>$3.80 \cdot 10^{-4}$</td>
<td>$1.14 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>K</td>
<td>$4.50 \cdot 10^{-2}$</td>
<td>$1.20 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>Mg</td>
<td>$3.40 \cdot 10^{-10}$</td>
<td>$1.66 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>Na</td>
<td>$1.00 \cdot 10^{-2}$</td>
<td>$7.00 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>$3.00 \cdot 10^{-4}$</td>
<td>$6.00 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>SiO$_2$ (aq)</td>
<td>$1.70 \cdot 10^{-4}$</td>
<td>$9.00 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>pH</td>
<td>13.00</td>
<td>12.20</td>
</tr>
</tbody>
</table>

Before discussing reactive transport, we will first look at flow of water and conservative transport. Figure 5-10 shows the head distribution. It reveals a pattern of more or less circular isohypses around the extraction borehole and, hence, radial flow, due to the relatively high extraction rates at this borehole. However, the injection of water in the emplacement borehole slightly disturbs the pattern in the vicinity of this borehole. In any case, the pattern shows that all water injected at the emplacement borehole will end up at either the observation or extraction boreholes.
Conservative transport can be characterised by a mixing ratio, $\lambda$, between the natural Grimsel water and water reacted with the cement that has been injected at the emplacement borehole. Its value can be calculated from the concentrations of a conservative tracer using

$$
\lambda = \frac{c - c_{gri}}{c_{emp} - c_{gri}}
$$

(5-17)

where subscripts $emp$ and $gri$ mean emplacement and Grimsel, respectively. A $\lambda$ of 0 means pure Grimsel water and a $\lambda$ of 1 means pure emplacement water reacted with cement. It is worth noting that, because all injected water ends up at either the observation or extraction boreholes, at steady state the following must hold:

$$
Q_{emp} = Q_{ext} \lambda_{ext} + Q_{obs} \lambda_{obs}
$$

(5-18)

where $Q$ means flow rate (magnitude) and subscripts $ext$ and $obs$ refer to extraction and observation borehole. As $Q_{ext}$ is about 20 to 40 times larger than $Q_{obs}$, equation 5-18 can be simplified to

$$
Q_{emp} \approx Q_{ext} \lambda_{ext}
$$

(5-19)

Figure 5-11 shows the mixing ratio versus time. Besides the standard model with dispersivities from Table 5-8 ($\alpha_L = 0.10\ m$; $\alpha_L = 0.05\ m$), we also studied the effect of lower dispersion ($\alpha_L = 0.05\ m$; $\alpha_L = 0.02\ m$). Obviously, the mixing ratio in the observation borehole is much larger than the extraction borehole, the latter being the furthest away from the emplacement borehole. The ups and downs in Figure 5-11 are caused by the change in the flow rates for the three boreholes. The mixing ratio in the extraction borehole is basically controlled by flow rates through equation 5-19, with parameters such as dispersivity having hardly any effect. The mixing ratio in the observation borehole is affected by both dispersivity and flow rates. Figure 5-11 also shows that it takes a bit more time for the observation borehole to reach a steady state after a change in flow rate than for the extraction borehole due to the larger characteristic time for mixing (Tab. 5-9). The distribution of the mixing ratio (Fig. 5-12) shows that, with higher injection rates at the emplacement borehole (October 2011), the size of the plume is larger than for lower injection rates (September 2014). It also shows that the plume is smoother (lines of equal mixing ratio are further away from each other) for higher dispersivities.

Figure 5-13 shows the modelled and measured aqueous chemistry versus time. There is some discrepancy between modelled and measured data. This can probably be attributed to the same reasons as mentioned for the 1D radial model. In any case, it can be observed that the modelled chemistry oscillates significantly because of the changing flow rates. The same oscillations can be observed for the measured chemistry. It can thus be concluded that the measured oscillations are not caused by analytical errors or some random external effect but by changes in the flow rates.
Fig. 5-11: Mixing ratio ($\lambda$) at the two boreholes for the 2D model with different dispersivities

Fig. 5-12: Mixing ratio distribution at two instants for the 2D model with different dispersivities
Fig. 5-13: Modelled and measured total aqueous concentrations and pH versus time for the 2D model
Figure 5-14 shows the precipitated/dissolved volume fractions of minerals. The primary silicate minerals in the fracture (albite, K-feldspar, muscovite, quartz) dissolve due to the increase in pH in the centre of the plume. Prehnite and tobermorite also precipitate in the centre of the plume. Phlogopite and especially calcite precipitate at the outer edge of the plume. It must be noted that, at the end of the simulation, calcite almost clogs the fracture near the extraction borehole (Fig. 5-15) with precipitated volume fractions of up to 0.2.

Note: Primary minerals are the sum of albite, K-feldspar, muscovite and quartz. Positive values indicate precipitation; negative values dissolution. For phlogopite and calcite the volume fraction change is particularly high near the extraction borehole. Therefore, that part of the domain is redrawn with a different volume fraction scale.
An interesting question is why calcite precipitates and consequently porosity is reduced at the edge of the plume and particularly near the extraction borehole. To analyse this we simplify the chemical system to only one chemical reaction: calcite precipitation-dissolution at equilibrium ($\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$). When two waters with a different chemical composition are mixed but both are in equilibrium with calcite, the mixed water tends to be oversaturated with respect to calcite. As a result, calcite precipitates, reducing Ca and CO$_3$ concentrations in equal amounts (because of the stoichiometry of the reaction) until equilibrium is reached. We can calculate the new concentrations from the mixing ratio ($\lambda$) and the chemical composition of the two end-members (emplacement borehole and Grimsel water):

$$
\begin{align*}
    u &= c_{Ca} - c_{CO_3} = \lambda (c_{Ca,emp} - c_{CO_3,emp}) + (1 - \lambda) (c_{Ca,gr} - c_{CO_3,gr}) \\
    c_{Ca} c_{CO_3} &= K_{cc} \\
    c_{Ca} &= \frac{1}{2} \left( u + \sqrt{u^2 + 4K_{cc}} \right) \\
    c_{CO_3} &= \frac{1}{2} \left( -u + \sqrt{u^2 + 4K_{cc}} \right)
\end{align*}
$$

(5-20)

where $K_{cc}$ is the equilibrium constant for calcite dissolution-precipitation. According to De Simoni et al. (2005), in the case of transport by advection and dispersion one can calculate the calcite precipitation rate, $r$, from

$$
    r = \phi \frac{\partial^2 c_{Ca}}{\partial \lambda^2} \nabla \lambda \tau D \nabla \lambda
$$

(5-21)

where $D$ is the dispersion-diffusion tensor explained in section 5.1 and $c_{Ca}$ is the Ca concentration. The rate depends on two factors: a chemical factor ($\partial^2 c_{Ca}/\partial \lambda^2$) that can be calculated from equation 5-20 and a transport factor ($\phi \nabla \lambda \tau D \nabla \lambda$) that can be calculated from the results of conservative transport. Figure 5-16 shows the calculations of calcite precipitation rate at the y-axis (axis cross-
ing the three boreholes). The end-member concentrations are taken from section 5.2.2.2 (Grimsel) and 5.3.3 (emplacement), shown in Figure 5-16a together with the calcite equilibrium \( c_{\text{CaCO}_3} = K_c \). From this, one can calculate the chemical factor \( \frac{\partial^2 c_{\text{CaCO}_3}}{\partial \lambda^2} \) as a function of mixing ratio (Fig. 5-16b). Our particular end-member concentrations give a high chemical factor for a low mixing ratio (i.e. much Grimsel water). Mixing ratios (Fig. 5-16c) are taken from the numerical model with \( a_L = 0.10 \) m and \( a_L = 0.05 \) m at the end of the simulation (Fig. 5-12). This gives high values for the transport factor near the emplacement and extraction boreholes (Fig. 5-16d) due to the high concentration gradients, \( \nabla \lambda \) (for the emplacement borehole) or high dispersion-diffusion coefficients, \( D \), due to high velocity of water (for the extraction borehole). The chemical factor is lower at the centre of the plume near the emplacement borehole where the mixing ratio is high (Fig. 5-16e). Multiplication of both factors gives a high value near the extraction borehole, because there both the chemical and transport factors are high (Fig. 5-16f).

![Fig. 5-16: Calculation of calcite precipitation rate at the y-axis (axis crossing the three boreholes) assuming equilibrium calcite precipitation is the only reaction](image)

Note: Emp, obs and ext refer to emplacement, observation and extraction boreholes.

Of course, the chemical system is in reality much more complicated than just one reaction and other reactions also have an impact. Nevertheless, equation 5-21 and Figure 5-16 can give a qualitative explanation of why such a high calcite precipitation was found near the extraction borehole.
5.4 Conclusions

Reactive transport modelling of Experiment 2 at Grimsel (pre-hardened cement in the emplace-ment borehole) has been performed using the Retraso-CodeBright software package. Due to the numerical complexity of the problem, modelling has been performed in 2 steps: (1) A 1D radial model simulating the emplacement borehole with the cement and a volume of rock fracture around it (skin, up to a radius of 8 cm). (2) A 2D model starting at the emplacement borehole skin and including the other two boreholes (observation and extraction). The solution composition at the outer boundary of the 1D model has been incorporated into the 2D model as a boundary condition. The changing flow conditions and the different volumes of water in the boreholes have been taken into account.

Results from the 1D model predict the dissolution of portlandite in a thin (1 mm) outer layer of the cement, with a corresponding increase in porosity. Porosity at the gap-fracture interface is reduced due mainly to the precipitation of phlogopite.

The results from the 2D model show dissolution of the primary silicates (except phlogopite) and precipitation of C-S-H, C-A-S-H and calcite in the fracture. Porosity is reduced in a belt around the 3 boreholes, converging at the extraction borehole (due to the magnitude of the extraction flow rate). The decrease in porosity, due mainly to the precipitation of calcite, is stronger directly adjacent to the extraction borehole, due to the more favourable mixing conditions between Grimsel groundwater and cement porewater. The changing water injection rate conditions in the emplacement borehole lead to changes in the flow field and in the position of the mineral reaction fronts.

There are some differences between model results and measurements (water composition at the different boreholes). Factors that can influence these discrepancies are:

- The chemical composition of the Grimsel and cement water used in the model may be different from reality. This is clearly the case for Cl in Grimsel groundwater (measured and model concentrations are $1.5 \times 10^{-4}$ and $4.6 \times 10^{-4}$ mol/L, respectively).
- The volume of water in the gap at the emplacement borehole may be larger than originally thought (up to about 1.7 L from the original 1.16 L).
- The pore diffusion coefficient of the cement is based on a guess from previous information. A proper calibration of the diffusion coefficient can improve the match between measurements and the model, since diffusion from the cement is the controlling step of the overall process.
- Cement and cement porewater composition was also assumed from values for a generic cement (Lothenbach & Winnefeld, 2006). These compositions may not be completely accurate.
- The actual injection and extraction flow rates at the different boreholes show larger variations than the model flow rates. This can also cause higher variation in the model results.
- The assumption that no water flow takes place in the emplacement borehole skin during the initial diffusion period (zero injection rate) may not be entirely true.
The objective of this modelling exercise was to develop a qualitative and partially quantitative understanding of the geochemical processes that take place during the experiment. To do so, a conceptual model with a relatively simple flow model based on an initially homogeneous fracture was considered. The results of the numerical model are compared with the available experimental data. We used the monitoring data for flow rates and solution composition at the emplacement, observation and extraction boreholes, the data from post-mortem analysis of the cement done by EMPA and the mineralogical analysis of samples next to the emplacement borehole done by BGS.

A preliminary reactive transport model corresponding to the formation of a high-pH plume and its interaction with the rock (see previous chapter) was reported by Saaltink & Soler (2016). The conceptual model considered a 1D radial model for the emplacement borehole and a small volume of surrounding rock (fault gouge), and a 2D model for the rest of the domain. The results of the 1D model were used as input for the 2D model. Following this conceptual model, new reactive transport modelling has been performed using new data for the composition of the cement used in the experiment, new thermodynamic data for C-A-S-H (calcium aluminium silicate hydrate) and M-A-S-H (magnesium aluminium silicate hydrate), updated water chemistry information from the different boreholes, and inclusion of illite as a potential secondary phase. Also, precipitation of primary minerals in the rock has now been excluded, effectively meaning that phlogopite cannot precipitate in the rock as it did in the previous modelling. A fracture thickness of 5 mm has now been considered, instead of the 1 mm previously taken into account.

First, we developed a numerical model where permeability was not updated following the porosity changes due to precipitation and dissolution of minerals. This model was characterised by a coarse temporal discretisation in the evolution of the flow rates and chemical composition of the input boundary water for the 2D model. We improved this by updating permeability and considering a finer temporal discretisation for the input water. Moreover, we performed a sensitivity analysis with respect to (1) the addition of zeolites and supplementary crystalline C-S-H phases and (2) the fracture thickness.

The results presented here have already been published by Chaparro et al. (2017).

6.1 Modelling approach

6.1.1 Conceptual model

Our conceptual model considers only one homogeneous fracture of 5 mm thickness, taking into account the reactions that may occur during the interaction between the cement, Grimsel groundwater and the fault gouge filling the fracture. Initially a model was constructed that used the same setup (geometry, boundary conditions and finite element mesh) as the model used to interpret pre-emplacement tracer test 09-03 (Manette et al., 2015). It soon became clear that this setup could not be used for the modelling of reactive transport. A very fine mesh was required near the emplacement borehole, as minerals precipitate in narrow fringes, implying excessive CPU times. Therefore, it was decided to use two separate models (1D radial and 2D). The simulations are carried out using Retraso-CodeBright software package (Saaltink et al., 2004).

First, a 1D radial model simulates the emplacement borehole (hardened cement) together with the surrounding skin (Fig. 6.1b). Then, the results of this model (solute concentrations at the outer boundary of the skin of the emplacement borehole) are used as input data for the 2D model that
simulates the fracture plane at the scale of all three boreholes (emplacement, observation and extraction). The conceptual model assumes that, during the initial test period without injection of water in the borehole, the permeability of the skin is low enough to avoid flow of water. It also assumes that, when water is injected, the flow in the skin is affected only by this injection (radial flow) and not by the extraction in the other boreholes.

Fig. 6-1: Conceptual model. a) Plan view of the fracture plane with the three boreholes; lines indicate the main direction of flow, b) Geometry of the 1D and 2D models.

6.1.2 Geometry and mesh

The geometry of the 1D radial model reflects the hardened cement, the existing gap between cement and rock and the skin with total length (radius) of 80 mm (Fig. 6-1b). The domain is discretised into 97 1D finite elements with sizes ranging from 0.1 mm near the gap between cement and skin to 1.5 mm near the outer boundary. The model considers the width of the fracture to be 5 mm, based on observations at the locations of several individual fractures with millimetre aperture.

The geometry of the 2D model represents the fault gouge filling the fracture and the three boreholes. Neither the cement in the emplacement borehole nor the skin of the emplacement borehole are considered explicitly. The concentrations at the outer end of the 1D model are used as a
time-dependent boundary condition for the 2D model (skin-fracture interface). For the observation and extraction boreholes, their gaps and skins are modelled. The mesh refinement has been studied, because results depend on the spatial discretisation (Marty et al., 2009). Nevertheless, we do not observe significant qualitative changes in our case with the implemented mesh. The finite element mesh consists of triangular elements with a size of about 2 cm. The possible natural background hydraulic gradients can be ignored due to the high flow rates at these boreholes. This means that the 2D model assumes that the flow of water is only affected by the injection or extraction flow rates at the three boreholes (emplacement, observation and extraction) and that the system is symmetrical with respect to the line crossing the centre of the three boreholes. Only half of the domain has to be modelled (Fig. 6-1b). Only the period when water is injected into the emplacement borehole is taken into account in this 2D model. The initial diffusion period is not considered, because this period has no measurable effect on the water chemistry at the observation and extraction boreholes.

6.1.3 Transport parameters

Table 6-1 shows the transport parameters of the materials used in the 1D and 2D models. Intrinsic permeabilities are taken from Manette et al. (2015). The porosity of the gaps is 1, i.e. they are assumed to contain only water. However, the total volume of water in the circulation system (tank, tubing, gap) is taken into account by rescaling the porosity of the gap by multiplying the real porosity by the total water volume divided by the model gap volume. The same is done for the cement which has a thickness larger than the model fracture. This procedure assumes that concentrations in the borehole are the same in the direction perpendicular to the fracture (well-mixed conditions). The porosity of cement is based on the results of the cement source characterisation at EMPA. The porosity for the fracture is taken from Soler & Mäder (2010) for a laboratory core infiltration experiment. The diffusion coefficient of the cement is calibrated based on the thickness of the alteration zone in the cement (portlandite dissolution and porosity increase). Diffusion coefficient and dispersivity of the gaps are sufficiently high to ensure perfect mixing within the gap. The dispersivity of the skin is from Manette et al. (2015). The dispersivity assigned to the cement has no effect because there is no flow of water through the cement.

For the models that update porosity and permeability, the porosity is calculated from the volumetric fractions of minerals at the previous time step according to

$$\varphi^{k+1} = \varphi^k - \sum_m (f_m^k - f_m^{k+1})$$

(6-1)

where superscript $k$ refers to time step and $f_m$ is the volume fraction of mineral $m$. The intrinsic permeability is calculated using Kozeny’s model

$$k = k_0 \frac{\varphi^3}{(1-\varphi)^2} \frac{(1-\varphi_0)^2}{\varphi_0^4}$$

(6-2)

where $\varphi_0$ and $\varphi$ are the initial and updated porosity, and $k$ and $k_0$ are the intrinsic permeability for $\varphi$ and $\varphi_0$, respectively.
6.1.4 Boundary conditions

In order to simulate the varying flow regime, we used the flow rates shown in Figure 6-2. Flow rates used in the numerical models were based on the monitored data. The 1D model assumed a time-dependent injection flow rate of the Grimsel groundwater at the gap of the emplacement borehole. During the initial diffusion period (August 2009 to October 2010), when there was no injection, the concentration at the skin-fracture interface (the last node of the 1D model) was fixed at that of the Grimsel groundwater. After the diffusion period, when water was injected into the gap, the 1D model assumed an outflowing mass flux boundary condition at the skin-fracture interface (mass flux equals flow rate times concentration at the boundary). The 2D model started after the initial diffusion period (October 2010). The 2D model considered the time-dependent flow rates at the three boreholes, shown in Figure 6-2. At the observation and extraction boreholes there was only extraction. The solute concentrations of the outflowing water of the 1D model were used for the inflowing water entering the 2D model (at the skin-fracture interface of the emplacement borehole). At the observation and extraction boreholes, the 2D model assumed an outflowing mass flux boundary condition.

<table>
<thead>
<tr>
<th>Tab. 6-1: Parameters of the materials used in the 1D and 2D models</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 D model</strong></td>
</tr>
<tr>
<td>Cement</td>
</tr>
<tr>
<td>$k_a$ ($m^2$)</td>
</tr>
<tr>
<td>$8.0 \cdot 10^{-18}$</td>
</tr>
<tr>
<td>Gap empl.</td>
</tr>
<tr>
<td>$3.0 \cdot 10^{-10}$</td>
</tr>
<tr>
<td>Skin empl.</td>
</tr>
<tr>
<td>$3.0 \cdot 10^{-15}$</td>
</tr>
<tr>
<td><strong>2 D model</strong></td>
</tr>
<tr>
<td>Gap obs.</td>
</tr>
<tr>
<td>$3.0 \cdot 10^{-10}$</td>
</tr>
<tr>
<td>Gap ext.</td>
</tr>
<tr>
<td>$3.0 \cdot 10^{-10}$</td>
</tr>
<tr>
<td>Skin obs.</td>
</tr>
<tr>
<td>$3.0 \cdot 10^{-14}$</td>
</tr>
<tr>
<td>Gap ext.</td>
</tr>
<tr>
<td>$3.0 \cdot 10^{-13}$</td>
</tr>
<tr>
<td>Fault gauge</td>
</tr>
<tr>
<td>$3.0 \cdot 10^{-13}$</td>
</tr>
</tbody>
</table>
6.1.5 Chemical system

6.1.5.1 Cement and rock composition

Table 6-2 gives the initial composition of the cement in the emplacement borehole considered by the numerical model. The cement composition is based on the results of a calculation using the GEM-Selektor (GEMS) software package (Wagner et al., 2012; Kulik et al., 2013) which can handle equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. In the numerical model, Fe has not been considered to simplify the chemical system. The primary phases that are taken into account are C-S-H gel (Ca/Si=1.667), portlandite, ettringite, siliceous hydrogarnet and hydrotalcite. C-S-H gel is modelled as 5 pure solid phases with Ca/Si ratios ranging from 0.83 to 1.67 (Trapote-Barreira et al., 2014). C-S-H gel with a Ca/Si of 1.667 is the primary phase and the others are secondary phases. The potential secondary phases considered are C-A-S-H, tobermorite, calcite, monosulfoaluminate, monocarboaluminate, illite and M-S-H. The model with zeolites and additional crystalline C-S-H phases also considered laumontite, analcime, natrolite, mordenite, wairakite, foshagite, gyrolite and okenite as secondary phases. C-A-S-H is also a solid solution, but in this case only 3 phases were considered with a Ca/Si ratio of 1 and Al/Si ratios equal to 0.05, 0.10 and 0.15 (Myers et al., 2015). M-S-H, another solid solution, has also been considered. We only used the end-member compositions (M$_3$Si$_4$H$_5$ and M$_4$Si$_5$H$_6$) with Mg/Si ratios of 0.7 and 1.5 (Nied et al., 2016). Table 6-3 shows the
initial composition of the fault gouge. The minerals considered are quartz, K-feldspar, albite, muscovite and phlogopite. The volumetric fractions of the minerals, the porosity and the surface areas are based on Soler & Mäder (2010).

Tab. 6-2: Cement composition

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Vol. frac. (m³/m³)</th>
<th>σ (m²/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-S-H-1667</td>
<td>0.275</td>
<td>1.0·10⁶</td>
</tr>
<tr>
<td>Portlandite</td>
<td>0.126</td>
<td>1.0·10⁹</td>
</tr>
<tr>
<td>Ettringite</td>
<td>4.66·10⁻²</td>
<td>1.0·10⁶</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>6.70·10⁻²</td>
<td>1.0·10⁶</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>9.66·10⁻³</td>
<td>1.0·10⁶</td>
</tr>
<tr>
<td>Porosity</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tab. 6-3: Fault gouge composition, based on Soler & Mäder (2010)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Vol. frac. (m³/m³)</th>
<th>σ (m²/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>0.19</td>
<td>1.07·10⁴</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>0.15</td>
<td>8.48·10³</td>
</tr>
<tr>
<td>Albite</td>
<td>0.14</td>
<td>7.92·10³</td>
</tr>
<tr>
<td>Muscovite</td>
<td>0.22</td>
<td>1.24·10⁴</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>0.09</td>
<td>5.1·10³</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>
6.1.5.2 Solution composition

Table 6-4 shows the initial compositions of the cement porewater and the Grimsel groundwater (the initial groundwater in the fault gouge). The temperature of both waters is 15 °C. The initial composition of the cement porewater is in equilibrium with the cement phases. The initial composition of the Grimsel groundwater is in equilibrium with the minerals of the fault gouge and also based on the monitoring data.

Tab. 6-4: Initial composition of the cement porewater and composition of the Grimsel groundwater

Note: Imposed constraints for calculating some of these values (equilibrium with solids or charge balance) are also indicated.

<table>
<thead>
<tr>
<th>Component</th>
<th>Cement porewater (mol L⁻¹)</th>
<th>Grimsel groundwater (mol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>5.20·10⁻³ Portlandite</td>
<td>1.10·10⁻⁴ Calcite</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>6.49·10⁻⁴ C-S-H-1667</td>
<td>8.31·10⁻⁴ Quartz</td>
</tr>
<tr>
<td>Al(OH)₆⁻</td>
<td>2.04·10⁻⁵ Hydrogarnet</td>
<td>1.24·10⁻⁷ Muscovite</td>
</tr>
<tr>
<td>K⁺</td>
<td>8.91·10⁻²</td>
<td>1.72·10⁻⁵ K-feldspar</td>
</tr>
<tr>
<td>Na⁺</td>
<td>9.95·10⁻¹</td>
<td>5.22·10⁻⁴</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3.98·10⁻⁴ Ettringite</td>
<td>5.20·10⁻⁴</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.5·10⁻⁹ Hydrogarnet</td>
<td>8.48·10⁻⁷ Phlogopite</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.0·10⁻¹⁵</td>
<td>7.62·10⁻⁴</td>
</tr>
<tr>
<td>F⁻</td>
<td>1.0·10⁻¹⁵</td>
<td>1.63·10⁻⁴</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>4.98·10⁻⁷</td>
<td>3.17·10⁻⁴ charge bal.</td>
</tr>
<tr>
<td>pH</td>
<td>13.23 charge bal.</td>
<td>9.65</td>
</tr>
</tbody>
</table>

6.1.5.3 Thermodynamic data

The thermodynamic data (at 15 °C) for all the mineral reactions are given in Table 6-5. The equilibrium constants (log K) for quartz, K-feldspar, albite, muscovite, phlogopite, tobermorite, illite, calite and laumontite are taken from the EQ3/6 database (Wolery et al., 1990); C-S-H gel phases from Kulik & Kersten (2001); portlandite, ettringite, hydrogarnet, hydrotalcite, monocarboaluminate and monosulfaluminate from the cemdata07 database (Matschei et al., 2007), C-A-S-H phases from Myers et al. (2015) and M-S-H phases from Nied et al. (2016). Table 6-6 shows the equilibrium constants (log K) for aqueous complexation reactions which are taken from the EQ3/6 database (Wolery et al., 1990).
Tab. 6-5: Equilibrium constants taken into account in the numerical model (log $K_{eq}$ at 15 °C)

Note: Reactions are written as the dissolution of 1 mol of mineral in terms of the primary species $\text{Ca}^{2+}$, $\text{HSiO}_3^-$, $\text{Al(OH)}_3^-$, $\text{OH}^-$, $\text{SO}_4^{2-}$, $\text{Mg}^{2+}$, $\text{CO}_3^{2-}$, $\text{K}^+$, $\text{Na}^+$, $\text{Cl}^-$, $\text{F}^-$. 

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>log $K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>0.02 (a)</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>KAlSi$_3$O$_8$</td>
<td>-11.63 (a)</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi$_3$O$_8$</td>
<td>-8.42 (a)</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl$_2$Si$<em>3$O$</em>{10}$(OH)$_2$</td>
<td>-16.10 (a)</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>KMg$_3$[(AlSi$_3$O$_10$)(OH)$_2$]</td>
<td>-58.20 (a)</td>
</tr>
<tr>
<td>C-S-H-08</td>
<td>2.27SiO$_2$·1.82Ca(OH)$_2$·1.82H$_2$O</td>
<td>-17.12 (b)</td>
</tr>
<tr>
<td>C-S-H-10</td>
<td>SiO$_2$·Ca(OH)$_2$·0.86H$_2$O</td>
<td>-9.35 (b)</td>
</tr>
<tr>
<td>C-S-H-12</td>
<td>SiO$_2$·1.2Ca(OH)$_2$·0.91H$_2$O</td>
<td>-10.70 (b)</td>
</tr>
<tr>
<td>C-S-H-14</td>
<td>SiO$_2$·1.4Ca(OH)$_2$·0.95H$_2$O</td>
<td>-11.95 (b)</td>
</tr>
<tr>
<td>C-S-H-1667</td>
<td>SiO$_2$·1.67Ca(OH)$_2$·1H$_2$O</td>
<td>-13.47 (b)</td>
</tr>
<tr>
<td>Portlandite</td>
<td>Ca(OH)$_2$</td>
<td>-5.07 (c)</td>
</tr>
<tr>
<td>Ettringite</td>
<td>Ca$_4$Al$_2$(SO$_4$)$<em>3$(OH)$</em>{12}$·26H$_2$O</td>
<td>-46.10 (c)</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>3CaO·Al$_2$O$_3$·0.84SiO$_2$·4.32H$_2$O</td>
<td>-26.82 (c)</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>Mg$_6$Al$<em>2$(OH)$</em>{14}$·3H$_2$O</td>
<td>-56.66 (c)</td>
</tr>
<tr>
<td>C-A-S-H-05</td>
<td>(CaO)$_4$(Al$_2$O$<em>3$)$</em>{0.025}$ (SiO$_2$) (H$<em>2$O)$</em>{1.2}$</td>
<td>-10.28 (c)</td>
</tr>
<tr>
<td>C-A-S-H-10</td>
<td>(CaO)$_4$(Al$_2$O$<em>3$)$</em>{0.05}$ (SiO$_2$) (H$<em>2$O)$</em>{1.2}$</td>
<td>-10.21 (c)</td>
</tr>
<tr>
<td>C-A-S-H-15</td>
<td>(CaO)$_4$(Al$_2$O$<em>3$)$</em>{0.075}$ (SiO$_2$) (H$<em>2$O)$</em>{1.2}$</td>
<td>-10.02 (c)</td>
</tr>
<tr>
<td>Monocarboaluminate</td>
<td>Ca$_4$Al$_2$(CO$<em>3$)(OH)$</em>{13}$·5H$_2$O</td>
<td>-31.85 (c)</td>
</tr>
<tr>
<td>Monosulfoaluminate</td>
<td>Ca$_4$Al$_2$(CO$<em>3$)(OH)$</em>{13}$·6H$_2$O</td>
<td>-29.50 (c)</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>Ca$_4$Si$_3$H$<em>2$O$</em>{2.5}$</td>
<td>-52.77 (c)</td>
</tr>
<tr>
<td>Illite</td>
<td>Mg$<em>{6.2}$K$</em>{0.6}$Al$<em>{3}$Si$</em>{3.5}$O$_{10}$(OH)$_2$</td>
<td>-13.53 (c)</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>-8.41 (c)</td>
</tr>
<tr>
<td>M-S-H-0,7</td>
<td>3MgO·4SiO$_2$·5H$_2$O</td>
<td>-40.61 (c)</td>
</tr>
<tr>
<td>M-S-H-1.5</td>
<td>3MgO·2SiO$_2$·5H$_2$O</td>
<td>-38.60 (c)</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg$_3$Si$<em>3$O$</em>{10}$(OH)$_2$</td>
<td>-47.09 (c)</td>
</tr>
<tr>
<td>Saponite</td>
<td>Ca$<em>{16.16}$Mg$</em>{0.16}$Al$<em>{0.33}$Si$</em>{3.6}$O$_{10}$(OH)$_2$</td>
<td>-50.94 (c)</td>
</tr>
<tr>
<td>Laumontite</td>
<td>Ca$_4$Si$<em>3$O$</em>{12}$·4H$_2$O</td>
<td>-16.65 (c)</td>
</tr>
<tr>
<td>Analcime</td>
<td>Na$<em>{3.86}$Al$</em>{0.98}$Si$<em>{3.04}$O$</em>{9.5}$·H$_2$O</td>
<td>-7.98 (c)</td>
</tr>
<tr>
<td>Natrolite</td>
<td>Na$<em>{3.16}$Al$</em>{0.5}$Si$<em>{5.2}$O$</em>{9.2}$·2H$_2$O</td>
<td>-16.00 (c)</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Ca$<em>{0.23}$Na$</em>{0.36}$Al$<em>{0.96}$Si$</em>{2.06}$O$_{12}$·3.46H$_2$O</td>
<td>-6.66 (c)</td>
</tr>
<tr>
<td>Wairakite</td>
<td>Ca$_4$Al$_2$Si$<em>3$O$</em>{10}$(OH)$_2$</td>
<td>-11.92 (c)</td>
</tr>
<tr>
<td>Foshagite</td>
<td>Ca$_3$Si$<em>3$O$</em>{14}$(OH)$_2$·0.5H$_2$O</td>
<td>-33.92 (c)</td>
</tr>
<tr>
<td>Gyrolite</td>
<td>Ca$_3$Si$<em>3$O$</em>{14}$(OH)$_2$·1.5H$_2$O</td>
<td>-21.26 (c)</td>
</tr>
<tr>
<td>Okenite</td>
<td>Ca$_3$Si$<em>3$O$</em>{14}$(OH)$_2$·H$_2$O</td>
<td>-9.71 (c)</td>
</tr>
</tbody>
</table>
Tab. 6-6: Secondary species with their equilibrium constants taken into account in the numerical model (log $K_{eq}$ at 15 °C)

Note: Reactions are written as the dissolution of 1 mol of mineral in terms of the primary species $Ca^{2+}$, $HSiO_3^-$, $Al(OH)_2^+$, $OH^-$, $SO_4^{2-}$, $Mg^{2+}$, $CO_3^{2-}$, $K^+$, $Na^+$, $Cl^-$, $F$.

<table>
<thead>
<tr>
<th>Formula</th>
<th>$log K_{eq}$</th>
<th>Formula</th>
<th>$log K_{eq}$</th>
<th>Formula</th>
<th>$log K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al(OH)_2$(aq)</td>
<td>8.31</td>
<td>$CaHCO_3^+$</td>
<td>2.87</td>
<td>$MgCl^+$</td>
<td>0.12</td>
</tr>
<tr>
<td>$AlOH^{2+}$</td>
<td>16.05</td>
<td>$CaOH^-$</td>
<td>-1.09</td>
<td>$MgCO_3$(aq)</td>
<td>-2.92</td>
</tr>
<tr>
<td>$AlSiO_4^{2-}$</td>
<td>29.28</td>
<td>$CaSO_4$(aq)</td>
<td>-2.07</td>
<td>$MgH_2SiO_4$(aq)</td>
<td>-6.94</td>
</tr>
<tr>
<td>$AlF_3$(aq)</td>
<td>17.52</td>
<td>$CaF^-$</td>
<td>-0.65</td>
<td>$MgH_2SiO_4^+$</td>
<td>-1.55</td>
</tr>
<tr>
<td>$AlF_2^+$</td>
<td>21.66</td>
<td>$CO_3$(aq)</td>
<td>11.84</td>
<td>$MgHCO_3^+$</td>
<td>2.88</td>
</tr>
<tr>
<td>$Al^+$</td>
<td>15.10</td>
<td>$H_2SiO_4^{2-}$</td>
<td>-1.14</td>
<td>$MgOH^+$</td>
<td>-2.21</td>
</tr>
<tr>
<td>$AlOH^{2+}$</td>
<td>25.09</td>
<td>$HCO_3^-$</td>
<td>3.91</td>
<td>$MgSO_4$(aq)</td>
<td>-2.26</td>
</tr>
<tr>
<td>$AlF_2^{2-}$</td>
<td>27.38</td>
<td>$HSO_4^-$</td>
<td>12.47</td>
<td>$MgF^+$</td>
<td>-1.34</td>
</tr>
<tr>
<td>$Al^3+$</td>
<td>34.10</td>
<td>$HF$(aq)</td>
<td>11.25</td>
<td>$NaCl$(aq)</td>
<td>0.80</td>
</tr>
<tr>
<td>$AlSiO_4^{3+}$</td>
<td>31.16</td>
<td>$HF_2^-$</td>
<td>11.91</td>
<td>$NaCO_3$(aq)</td>
<td>-0.63</td>
</tr>
<tr>
<td>$Ca(H_3SiO_4)_2$(aq)</td>
<td>-5.13</td>
<td>$KCl$(aq)</td>
<td>1.58</td>
<td>$NaHCO_3$(aq)</td>
<td>3.66</td>
</tr>
<tr>
<td>$CaCl^+$</td>
<td>0.70</td>
<td>$KHSO_4$(aq)</td>
<td>13.69</td>
<td>$NaHSiO_3$(aq)</td>
<td>-1.73</td>
</tr>
<tr>
<td>$CaCl_2$(aq)</td>
<td>-3.22</td>
<td>$KSO_4^-$</td>
<td>-0.86</td>
<td>$NaSiO_3^-$</td>
<td>-0.78</td>
</tr>
<tr>
<td>$CaH_2SiO_4$(aq)</td>
<td>-5.86</td>
<td>$Mg(H_2SiO_4)_2$(aq)</td>
<td>-6.46</td>
<td>$NaF$(aq)</td>
<td>1.04</td>
</tr>
<tr>
<td>$CaH_3SiO_4^{3+}$</td>
<td>-1.30</td>
<td>$Mg_4(OLH)_4^+$</td>
<td>-15.49</td>
<td>$SiO_2$(aq)</td>
<td>4.24</td>
</tr>
</tbody>
</table>

6.1.5.4 Reaction rates

A kinetic approach is used for the dissolution-precipitation of mineral phases (Eq. 6-3), although sometimes the reaction is fast enough to be at local equilibrium. The rate laws used for the primary minerals in the fault gouge (quartz, albite, K-feldspar, phlogopite, muscovite), based on those used by Soler & Mäder (2010), are given in Equation 6-3 and Table 6-7. The form of the rate law is from Lasaga (1984). Values of $\Theta$ and $\eta$ for albite and microcline are from Soler & Lasaga (1998). For all the other phases (cement and secondary phases), large values for the rate constants ($1x10^9$ mol m$^{-2}$s$^{-1}$) and for the surface areas ($1x10^6$ m$^{-2}$ m$^{-3}$) have been used, leading to local equilibrium with respect to those phases. The gap contains no minerals, but large surface areas have been implemented ($1x10^6$ m$^{-2}$ m$^{-3}$) to allow mineral precipitation.

$$r_m = k_m \sigma_m (\Omega_m^n - 1)^n a_{H^+}^m$$

$m = 1, ..., n_p$ (6-3)

$r_m$ is the mineral dissolution-precipitation rate (mol m$^{-2}$s$^{-1}$), $k_m$ is the kinetic rate constant (mol m$^{-2}$s$^{-1}$), $\sigma_m$ is the surface area (m$^{-2}$ m$^{-3}$), $a_{H^+}$ is the activity of protons and $p$ is a catalyst coefficient, $\Omega_m$ is IAP/K where IAP is the ionic activity product and $K$ is the equilibrium constant (ionic activity product at equilibrium).
Tab. 6-7: Rate parameters used for the primary minerals in the fault gouge

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$\log k_m$ (mol m$^{-2}$m$^{-1}$)</th>
<th>$p$</th>
<th>$\Theta$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>-13.92</td>
<td>-0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>-20.22</td>
<td>-0.73</td>
<td>0.4</td>
<td>14</td>
</tr>
<tr>
<td>Albite</td>
<td>-12.92</td>
<td>-0.2</td>
<td>0.4</td>
<td>14</td>
</tr>
<tr>
<td>Muscovite</td>
<td>-13.12</td>
<td>-0.1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>-13.52</td>
<td>-0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

6.1.6 Results and discussion

Before discussing the results of the model, we will first calculate some characteristic times over which transport processes take place. This is helpful for the interpretation of the results of the models. We will then discuss the results of the 1D radial model that simulates the domain in the vicinity of the emplacement borehole, followed by the results of the 2D model that simulates the domain with three boreholes: emplacement, observation and extraction.

6.1.6.1 Characteristic time

Table 6-8 shows the calculated characteristic times for the various processes (see section 5.3.1 for the definition of the characteristic times). It can be seen that diffusion is the slowest process and, therefore, may be the one that controls the system the most. Advection times are short, indicating that water probably will not change its chemistry very much due to precipitation/dissolution of minerals during its passage through the fracture and skins as there is not much time for reactions to occur.

Tab. 6-8: Characteristic times for the different processes

Note: Characteristic times for diffusion, advection and ideal mixing are calculated by Equations 5-14, 5-15 and 5-16, respectively. Characteristic times with two values are calculated from minimum and maximum flow rates.

<table>
<thead>
<tr>
<th>Process</th>
<th>Location</th>
<th>Characteristic time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion ($t_{d0}$)</td>
<td>Cement</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>Skin of emplacement borehole</td>
<td>15.8</td>
</tr>
<tr>
<td>Advection ($t_{adv}$)</td>
<td>Skin of emplacement borehole</td>
<td>0.0035 - 0.032</td>
</tr>
<tr>
<td></td>
<td>From emplacement to extraction borehole</td>
<td>0.69 - 2.14</td>
</tr>
<tr>
<td>Ideal mixing ($t_{mix}$)</td>
<td>Gap of emplacement borehole</td>
<td>13.6 - 124.6</td>
</tr>
<tr>
<td></td>
<td>Gap of observation borehole</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td>Gap of extraction borehole</td>
<td>0.07 - 0.21</td>
</tr>
</tbody>
</table>
6.1.6.2 1D model

Figure 6-3 shows the measured and modelled aqueous chemistry against time at the gap of the emplacement borehole. There are discrepancies between model results and the monitored data at the emplacement borehole. Generally, the measured data are more scattered than the model results. A possible explanation is the assumption of ideally mixed water in gap, tank and tubing of the emplacement borehole. This assumption is particularly doubtful for the periods without water injection (before October 2010 and at the end of 2013, see Fig. 6-2) during which, coincidentally, the majority of measurements were made. A smaller volume available for mixing would give less storage capacity, leading to more pronounced changes in concentrations. Another explanation is that the flow around the emplacement borehole may not be perfectly radial as assumed by the model. However, we can qualitatively compare the measured data with the model results in order to understand the reactions that may occur during the experiment.

The model shows that, at the beginning, there is a rapid increase of pH, Ca, K and Na concentrations because of out-diffusion from the cement. Si decreases due to diffusion towards the cement and SO₄ decreases because of precipitation in the rock (ettringite) plus diffusion from gap towards rock. Cl and F also decrease because cement porewater does not contain these components. During the diffusion period (before October 2010), the chemical composition remains constant. From the beginning of the injection onwards, Ca concentration varies according to the changes in the flow rates. Higher injection rates imply lower Ca concentrations. K and Na concentrations decrease until there is no high concentration left in the cement porewater. Si concentration remains approximately constant, as this is very similar to that in Grimsel groundwater and in the cement porewater. Small variations can be seen in concentration of SO₄ and Al. Cl and F concentrations increase at the beginning of the injection period until they reach the same concentration as in Grimsel groundwater. pH varies according to the variations in Ca concentration.
Fig. 6-3: Evolution of the measured concentrations (points) compared with those calculated by the numerical model (lines)
Fig. 6-4: Variation of volumetric fraction of minerals against distance

Note: Positive values mean precipitation and negative ones mean dissolution. Vertical dashed lines indicate the gap.
Figure 6-4 shows the variation of volumetric fraction of minerals versus distance calculated by the numerical model. Cement (from 0.035 to 0.041 m), gap (from 0.041 to 0.043 m) and skin (from 0.043 to 0.08 m) are represented on the x axis. These results can be compared with the post-mortem analyses carried out by EMPA (Lothenbach et al., 2016) and the mineralogical analyses done by BGS (Field et al., 2016). In the cement, model results show dissolution of portlandite, with a sharp dissolution front at 3 mm from the cement-gap interface after 5 years. This dissolution of portlandite, which was also observed in the postmortem analyses by EMPA, allowed the calibration of the pore diffusion coefficient with a value of $2 \cdot 10^{-11}$ m$^2$/s. C-S-H (Ca/Si = 1.6) also dissolves, though at a lower rate. Ettringite dissolves at the interface between the cement and gap only after injection of water is started. On the other hand, after injecting Grimsel groundwater, C-A-S-H (Al/Si = 0.05 and Ca/Si = 1) precipitates near the gap and calcite precipitates at the cement-gap interface and into the gap, due to the mixing of both waters. This calcite precipitation at the interface was also observed in the analysis by EMPA.

At the skin (rock), during both diffusion and injection periods, the primary minerals of the fault gouge (quartz, albite, K-feldspar, muscovite and phlogopite) dissolve due to the high-pH conditions. Also, there is significant precipitation of C-A-S-H, ettringite and hydrotalcite. Precipitation of smaller amounts of calcite, hydrogarnet and monocarboaluminate can also be observed. Precipitation of C-A-S-H and calcite is consistent with the results of mineralogical analyses of the overcore by BGS (Field et al., 2016). However, ettringite was not observed. Traces of gypsum were detected in scrapings from the borehole wall.

The variation of porosity due to precipitation and dissolution of minerals is shown in Figure 6-5. The porosity change in the cement is mainly due to portlandite dissolution. The porosity increase amounts to 0.12, which is the initial volume fraction of portlandite in the cement. The porosity reduces slightly in the skin next to the gap due to C-A-S-H, ettringite and hydrotalcite precipitation.

![Fig. 6-5: Variation of volumetric fraction of porosity against length](image)

Note: Vertical dashed lines indicate the gap.
6.1.6.3  2D model

As mentioned in the introduction, the first numerical models were developed with and without an update of permeability with changes in porosity. Hardly any difference was found between concentrations in water and mineral contents from both models. The only difference was in water pressure (Fig. 6-6). A gradient of water pressure due to the extraction can be observed. When permeability is updated with changes in porosity, this gradient is higher near the extraction borehole because mineral precipitation causes a reduction in porosity. Nevertheless, the flow pattern does not change, because it is controlled mainly by the flow rates imposed at the boreholes.

Before discussing the results of the 2D reactive transport model, we will first look at conservative transport. This can be characterised by a mixing ratio, $\lambda$, between the background Grimsel groundwater and water injected at the emplacement borehole reacted with the cement. Its value can be calculated from the concentrations of a conservative tracer with Equation 6-4

$$\lambda = \frac{c_{emp} - c_{gri}}{c_{emp} - c_{gri}}$$  \hspace{1cm} (6-4)

where subscripts $gri$ and $emp$ mean Grimsel groundwater and emplacement water, respectively. A $\lambda$ of 0 means pure Grimsel groundwater and a $\lambda$ of 1 means pure emplacement water reacted with cement.

Fig. 6-6: Comparison of water pressure (MPa) at the end of the experiment, for the cases where permeabilities are and are not updated

The distribution of the mixing ratio (Fig. 6-7) shows that the mixing ratio in the observation borehole is much larger than in the extraction borehole, the latter being the furthest away from the emplacement borehole. Also, with higher injection rates at the emplacement borehole (October 2010), the size of the plume is larger than for lower injection rates (September 2014).
Fig. 6-7: Mixing ratio distribution at two instants for the 2D model

Note: A $\lambda$ of 0 means pure Grimsel groundwater and a $\lambda$ of 1 means pure emplacement water reacted with cement.

Figure 6-8 shows the modelled and measured aqueous chemistry versus time. The oscillations of the modelled chemistry are due to the changing flow rates. These oscillations can also be observed for the measured chemistry. As was the case for the emplacement borehole, the observed data are more scattered than the modelled results. Moreover, the model seems to overestimate the effect of the alkaline plume at the observation borehole. Part of this may be due to simplifications in the 1D model, with results used as input for the 2D model. In addition, heterogeneity in both permeability and distribution of minerals can have an effect, which is not taken into account by the model (initially homogeneous fracture assumed). Bearing these limitations in mind, reasonable fits are obtained for both observation and extraction boreholes. However, modelled Si concentrations are lower than the measured ones. This is because of the assumption of local equilibrium with respect to quartz.

The variation of the volume fractions of minerals of the fault gouge is shown in Figure 6-9. All the minerals of the fault gouge (quartz, albite, K-feldspar, muscovite and phlogopite) dissolve in the centre of the plume, due to the increase of pH. Albite dissolves in larger amounts, followed by K-feldspar and phlogopite. There is less dissolution of quartz and muscovite. Note that the hyperalkaline plume has a concentric shape due the fact that the model considers a homogeneous fracture. In reality, the shape of the plume will depend on heterogeneities and preferential flow paths in the fracture.

Precipitation and dissolution of secondary minerals are shown in Figure 6-10. Ettringite precipitates at the edge of the emplacement borehole. C-A-S-H ($\text{Al/Si}=0.05$ and $\text{Ca/Si}=1$) precipitates in the centre of the plume, followed by the precipitation of tobermorite. Hydrotalcite precipitates at the centre of the plume and near the extraction borehole. Small amounts of monocarboaluminate and hydrogarnet also precipitate at the centre of the plume. Near the extraction borehole there is significant precipitation of calcite and, to a lesser extent, also of illite. This precipitation of calcite is because of the high flow rate near that borehole, causing extensive mixing between the alkaline water and Grimsel groundwater (see section 5.3.3 and Fig. 5-16 for further details).
Figure 6-11 shows the distribution of porosity and pH. Near the emplacement borehole there is a reduction in porosity of 0.02 due to ettringite precipitation. In the centre of the plume there is a similar reduction due to C-A-S-H (Al/Si=0.05 and Ca/Si=1) and hydrotalcite precipitation. Near the extraction borehole there is high reduction in porosity of 0.09, because illite and especially calcite precipitate at the outer edge of the plume. The pH plot shows the distribution of the alkaline plume, with higher pH close to the emplacement borehole because of the cement source and lower pH near the extraction borehole.
Fig. 6-9: Variation of volumetric fraction (m³/m³) of primary minerals of the rock at the end of the experiment

Note: Negative values mean dissolution. Dimensions are 1.7 m x 0.7 m.
Fig. 6-10: Variation of volumetric fraction ($\text{m}^3\text{m}^{-3}$) of secondary minerals at the end of the experiment

Note: Positive values mean precipitation. Dimensions are 1.7 m x 0.7 m.

Fig. 6-11: Variation of porosity and pH at the end of the experiment

Note: Dimensions are 1.7 m x 0.7 m.
6.1.7 Sensitivity analysis

In this section the effect of (1) adding zeolites and supplementary C-S-H crystalline phases as secondary minerals, and (2) the effect of fracture thickness have been studied. It is known that individual fracture thicknesses are millimetric, while a fracture thickness of 5 mm was used in the reference model to account for the presence of several fractures. However, new numerical models have also been developed considering a fracture thickness of only 1 mm, which was the value used in previous modelling (Saaltink & Soler, 2016; chapter 5).

6.1.7.1 Model with zeolites and additional crystalline C-S-H phases

A model with potential zeolite precipitation has been developed (Fig. 6-12). Only laumontite precipitates and the other zeolites considered (analcime, natrolite, mordenite, wairakite) do not. Some other crystalline C-S-H phases have also been taken into account (foshagite, gyrolite, okenite), but they also do not precipitate. There is less precipitation of illite when laumontite is considered.

Fig. 6-12: Variation of volumetric fraction of illite and laumontite (m$^3$ m$^{-3}$) at the end of the experiment

Note: Dimensions are 1.7 m x 0.7 m.

6.1.7.2 1D model with 1 mm fracture thickness

In this numerical model, the fracture thickness is 1 mm instead of 5 mm, hence the flow boundary conditions (kg/m/s) have changed. Note that the flow rate (Darcy velocity) is now a factor of 5 higher. The evolution of the chemical and mineralogical composition for the 2 models is practically identical. The changes in the fracture thickness do not affect the chemical composition measured at the emplacement borehole.
We can compare the variation of volumetric fraction of minerals versus distance, which is shown in Figure 6-13. Only minerals with some change with respect to the reference model are shown (portlandite, C-S-H, ettringite, C-A-S-H and calcite). The decrease in the fracture thickness does not change the dissolution of the primary minerals of the fault gouge. Changes are only small, with slightly less mineral reaction.

![Variation of volumetric fraction of minerals versus length](image)

**Fig. 6-13:** Variation of volumetric fraction of minerals versus length

Note: Positive values mean precipitation and negative ones mean dissolution. Vertical dashed lines indicate the gap.

### 6.1.7.3 2D model with 1 mm fracture thickness

The variation of the volumetric fraction of the minerals and the variation of porosity and pH are shown in Figures 6-14 and 6-15. The primary minerals of the fault gouge (albite, K-feldspar, phlogopite, muscovite, quartz) show a very slightly increased dissolution when the fracture thickness is 1 mm (Fig. 6-14). Near the emplacement borehole, ettringite precipitates slightly less than in the previous model. However, the higher dissolution of the primary minerals causes higher precipitation of C-A-S-H, illite and calcite, with practically no tobermorite and monocarboaluminate precipitation. This higher precipitation of calcite results in a higher reduction of porosity. The pH plume is very similar to that from the reference model.
Fig. 6-14: Variation of volumetric fraction (m$^3$ m$^{-3}$) of primary minerals of the rock at the end of the experiment

Note: Negative values mean dissolution. Dimensions are 1.7 m x 0.7 m.
Fig. 6-15: Variation of volumetric fraction (m$^{-3}$) of secondary minerals at the end of the experiment

Note: Positive values mean precipitation. Variation of porosity and pH are also plotted. Dimensions are 1.7 m x 0.7 m.

### 6.1.8 Conclusions

The interaction between Portland cement and rock at the Grimsel Test Site has been modelled. The conceptual model consists of a simple flow system considering a homogeneous fracture and taking into account the reactions that may occur during the interaction between the cement, groundwater and fault gouge filling the fracture. The modelling has been performed in 2 steps: firstly a 1D radial model simulating the emplacement borehole with the cement and the surrounding skin and secondly a 2D model starting at the emplacement borehole skin and including the other two boreholes (observation and extraction). The solution composition at the outer boundary of the 1D model has been incorporated into the 2D model as a time-dependent boundary condition. The changing flow conditions and the different volumes of water in the boreholes have also been taken into account.

In both models, results show that changes in flow rates (mainly emplacement) cause noticeable changes in concentrations in all boreholes, which is consistent with the observed oscillations in the measurements. Nevertheless, the monitored data show more scattering. In addition, the model seems to overestimate the effect of the alkaline plume at the observation borehole. These discrepancies can be attributed to simplifications in the models, such as perfect mixing of the water in the emplacement borehole and a homogeneous fracture. Here we focused on the complexity of the geochemical system rather than that of the flow pattern.
Results from the 1D model show dissolution of portlandite (3 mm), C-S-H gel and ettringite at the cement-gap interface, with a corresponding increase in porosity, mainly due to portlandite dissolution. There is also precipitation of calcite and C-A-S-H (Al/Si=0.05 and Ca/Si=1). At the gap there is precipitation of calcite due to the mixing between the Grimsel groundwater and the cement porewater. At the skin, primary minerals of the fault gouge (albite, K-feldspar, phlogopite, muscovite and quartz) dissolve. Ettringite, C-A-S-H, calcite, hydrotalcite and hydrogarnet precipitate, causing a reduction of porosity. Dissolution of portlandite in the cement and precipitation of calcite at the cement-gap interface were observed in the postmortem analyses made by EMPA. C-A-S-H and calcite precipitation in the skin was also observed in the mineralogical analyses of the overcore by BGS, both of which are consistent with our numerical model results. However, ettringite precipitation in the skin was not found. A model with a fracture thickness of 1 mm shows slightly lower dissolution of portlandite and C-S-H gel in the cement and lower precipitation of ettringite, C-A-S-H and calcite at the skin.

The results from the 2D model show dissolution of primary minerals (albite, K-feldspar, quartz, muscovite and phlogopite) due to the increase in pH at the centre of the plume. There is also precipitation of ettringite very close to the emplacement borehole. There is precipitation of C-A-S-H (Al/Si=0.05 and Ca/Si=1) in the centre of the plume, followed by a narrow zone of tobermorite precipitation. At the edge of the plume, calcite and illite precipitate. This precipitation of calcite next to the extraction borehole, due to the more favourable mixing conditions between Grimsel groundwater and cement porewater, causes a 40% reduction in porosity. Results of the numerical model where zeolites have been added show precipitation of laumontite, partially inhibiting the precipitation of illite. The model considering a fracture thickness of 1 mm gives slightly higher dissolution of the primary minerals. Near the emplacement borehole, there is less precipitation of ettringite. At the centre of the plume, there is slightly higher precipitation of C-A-S-H, hydrotalcite and illite, but there is no precipitation of tobermorite. At the edge of the plume, there is higher precipitation of hydrotalcite, illite and mainly calcite, the latter almost clogging the porosity.
7 QUINTESSA (RWM) - Blind geochemical modelling of the evolution of the cement source

‘Blind’ modelling (using only data related to the setting up of the experiment, e.g. physical dimensions, chemical compositions, transport parameters, results of tracer tests conducted prior to the experiment, but not data produced by the experiment) was undertaken by the LCS modelling teams in parallel with the experiment. This was partly for practical reasons - while the groundwater composition in the observation borehole is monitored in “real time”, detailed information on mineralogical changes will only be obtained once the experiment has concluded and the boreholes are overcored (i.e. a larger core over-drilled and removed) for analysis – but there are numerous other merits in blind modelling exercises:

- Without knowledge of the outcome of the experiment, the exercise is a test of the general understanding (conceptual models) of the system as a whole.
- The robustness and predictive powers of numerical models can be tested, without falling into the trap of “overfitting” model parameters simply to match experimental data.
- The “big picture” is considered, focusing on the general behaviour of similar systems rather than minute details of one particular experiment which may be subject to experimental artefacts.
- The model can be used to inform the experiment; interesting results produced by the model can be investigated while the experiment is still running, whereas in non-blind modelling it is often the case that there is no chance to collect extra data once the experiment has concluded.
- The experiment can also be used to inform the model, with the reasons for any differences investigated and, if understood, fed back to improve the model for future applications.

This report describes the modelling work undertaken by the RWM team participating in the LCS project; other modelling groups reported their work separately (e.g. Manette et al., 2015; Saaltink & Soler, 2016). Here the focus is on the evolution of the cement placed in contact with the water-conducting fracture; work on the larger system, incorporating the other monitoring boreholes and surrounding rock, and focusing on the extent of the alkaline plume, will be reported separately. This study has already been reported by Watson et al. (2016a). The results supersede those of Watson et al. (2014).

The remainder of this report is structured as follows:

- In section 7.1 a model of the LCS experiment is described, and input parameters specified.
- In section 7.2 the modelling results are presented.
- In section 7.3 the results are discussed, and conclusions drawn.
7.1 Model description and inputs

7.1.1 Modelling aims

As discussed in the introduction, the modelling described in this section was conducted ‘blind’. This means that no results from LCS Experiment 2 were used to fit model parameters or tune the model in other ways. Details from the experimental setup, such as the geometric arrangement of boreholes, physical properties of the various materials used and so on, were used to construct the model. Information from pre-emplacement tracer tests was also used to help quantify the physical nature of the undisturbed fracture system and flow field. However, no information gathered while the experiment was in progress or subsequent to its completion was used. In this way, it is possible to test the predictive capability of the models and ascertain how complete our understanding is of cement interactions in the environment of a geological disposal facility (GDF).

The modelling described in this report concentrates on the chemical evolution of the cement source inserted into the fracture via the emplacement borehole. Leaching and alteration of the cement were modelled over a six-year period. Modelling of the movement of the alkaline plume through the fracture, and the chemical reactions that may occur as it interacts with the host rock and mixes with the natural Grimsel porewater, was also carried out and is reported separately.

The aims of the current modelling study were to:

- Demonstrate an ability to predict the geochemical evolution of the cement source and water composition within the emplacement borehole, which can ultimately be compared with the experimental results.
- Conduct sensitivity studies to ascertain which uncertainties are important in the model, and therefore identify areas for further research.
- Direct the experimental work where required, for example by requesting certain types of analysis or removal of samples from particular locations of interest.
- Provide input to a larger model of the whole (three boreholes, fracture plane and rock) system by indicating which minerals are important to include and the amount of alteration expected.
- Consider the implications of the model results for the performance of the GDF as a whole, in particular any consequences for performance assessment (PA) calculations.

7.1.2 Software

The modelling requires use of software that can be used to numerically simulate coupled processes, in this case hydrological (H) and chemical (C). In this case, the general purpose modelling tool QPAC (Quintessa, 2013) was selected for this purpose, as it provides a fully coupled modelling capability. QPAC has been used successfully in numerous other studies concerned with geochemical alteration, including previous LCS modelling tasks (see for example Savage et al. (2010), Watson et al. (2013), Wilson et al. (2015), Watson et al. (2016b)) and is highly flexible and adaptable.
7.1.3 Geometry and discretisation

7.1.3.1 Two-dimensional model

In the first instance, a 2D model representing a slice through the borehole where the fracture intersects was constructed, as illustrated in Figure 7-1.

Note: The right-hand figure shows the cross section that is modelled in 2D.

It was assumed, in the absence of detailed information from the experiment, that the borehole intersects the fracture plane at right-angles\(^1\), and that the intersection occurs on the same plane as the ports, P and R\(^2\). It is also assumed that a small gap runs between the edge of the cement shells and the rock of the borehole wall, and that there is similarly a gap on each side of the emplacement tool where the two cement shells meet (one such gap can be seen in the pre-emplacement photograph shown in Figure 2-5, but it is not known if gaps were present on both sides of the tool).

The model domain and the discretisation used in the 2D case are shown in Figure 7-2. Only the cement and gaps are explicitly included; the steel emplacement tool is considered to be an impermeable inner boundary, while a constant head, constant water composition boundary condition

---

\(^1\) This is almost certainly not the case; see, for example, Fig. 1.4 of Lanyon (2015a) which shows a photograph of the granite core extracted from the emplacement borehole. Fractures can clearly be seen at around 17 mah (metres along hole), coinciding with the ultimate placement of the cement shells, and are at an angle of at least 45° from the perpendicular. However, geometry such as this is difficult to model. The main effect would be a slightly greater fracture-borehole surface area but, given that the fracture aperture is already uncertain, there is not much to be gained from including this explicitly within the model.

\(^2\) Again, this is almost certainly not the case. However, it can be thought of as representing a “worst case” scenario as it combines the effects of inflow of fresh water from two sources in a single location.
applied to the outside of the gap represents the fracture. Pumping of water into the borehole through port P during the experiment is represented by specifying a fixed flow, constant water composition boundary condition to the bottom right innermost cell.

As shown in Figure 7-2, a cylindrical grid is employed with angular and radial discretisation. Due to the symmetrical nature of the system, only a 180° section of the borehole is included in the model (note that this is only valid because of the position chosen for the injection port). A 15° angular resolution is used in most of the model, except in the gap between the cement halfpipes and the cement cells immediately adjacent to that gap. Radially, the gap between the cement and borehole wall is not discretised and is modelled as a single cell; the cement is split into 5 radial cells, with the outermost cells having the same dimensions in the radial direction as the adjacent single-cell gap. The cement cells become progressively wider in the radial direction closer to the emplacement tool (where less alteration is expected).

Geometric parameters used in the 2D model are given in Table 7-1. The assumption that the gap between the cement and borehole wall is 1 mm results in the cement in the halfpipes being 12 mm thick – the exact thickness was not recorded prior to emplacement. Also included in this table is the fracture aperture used in the permeability calculation described in section 7.1.5.

Fig. 7-2: The 2D model, showing the boundary conditions and discretisation employed
Tab. 7-1: Geometric parameters used in the 2D model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of borehole</td>
<td>43 mm</td>
<td>Lanyon (2015a; Tab. D.3)</td>
</tr>
<tr>
<td>Radius of emplacement tool</td>
<td>30 mm</td>
<td>Lanyon (2015a; Appendix D)</td>
</tr>
<tr>
<td>Width of gap between cement and borehole wall</td>
<td>1 mm</td>
<td>Modelling assumption</td>
</tr>
<tr>
<td>Width of gap between cement halfpipes</td>
<td>5 mm</td>
<td>Modelling assumption, based on photographs (see Fig. 2-15)</td>
</tr>
<tr>
<td>Fracture aperture</td>
<td>0.5 mm</td>
<td>J. Rüedi (pers. comm. 23 August 2012), consistent with Lanyon &amp; Mäder (2020)</td>
</tr>
</tbody>
</table>

7.1.3.2 Three-dimensional model

In order to model the spatial alteration of the cement more accurately, a 3D model is required. Modelling chemical reactions in 3D is not often attempted because the large number of cells required, combined with the large number of variables to be solved for (one per chemical species – typically 30 to 40 per cell), results in models that require a great deal of computational resources and take a very long time to run (of the order of weeks rather than hours or days). Despite this, a 3D model of the LCS experiment has been developed.

The 3D model is comprised of the whole borehole rather than a slice through it (see Fig. 7-1). The model domain and discretisation employed are shown in Figure 7-3. The angular resolution is decreased from the 2D case, but the radial resolution remains the same. A coarse discretisation is applied in the longitudinal direction (along the borehole), with greater resolution around the intersection with the fracture plane and near the injection port P.
During overcoring of the borehole, it was discovered that there was some additional volume in the borehole beyond the end of the interval that had not been recorded (Lanyon & Mäder, 2020). Although, as discussed previously, the modelling was to be carried out “blind”, this information has been incorporated into the model as it is considered to fall into the category of experimental setup data, and the influence of the extra volume could affect the model results. This extra volume has been included as a cylinder, rather than the annulus and wedge that it is in reality, because these shapes are rather difficult to model. The shape of the extra volume is not considered to be an important factor in the model because it is completely open and well-connected.

Similarly to the 2D model, the steel emplacement tool that runs through the centre of the cement halfpipes is not included explicitly in the model but is included as a no flow boundary condition. The fracture plane is also included as a constant head, fixed water composition boundary condition as in the 2D model. The host rock is considered to be impermeable in this case. While there will be some diffusion between the rock matrix and the borehole, over the timescale of the experiment this is a very minor secondary effect compared to the advection along the borehole and through the fracture. Finally, the 3D nature of the model allows the injection port P to be located towards the end of the borehole, away from the fracture. The orientation of the port in relation to
the natural head gradient across the fracture plane was not recorded; here it is assumed to lie in a position that allows a symmetry argument to be applied, so only one cement shell is included in the model.

Geometric parameters used in the 3D model are given in Table 7-2, some of which have been replicated from Table 7-1 for completeness. The length of the borehole interval quoted is the originally recorded length, which does not account for the void discovered during overcoring. This is assumed to be the total length of the cement shells.

Tab. 7-2: Geometric parameters used in the 3D model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of borehole</td>
<td>43 mm</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Radius of emplacement tool</td>
<td>30 mm</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Width of gap between cement and borehole wall</td>
<td>1 mm</td>
<td>Modelling assumption</td>
</tr>
<tr>
<td>Width of gap between cement halfpipes</td>
<td>5 mm</td>
<td>Modelling assumption, based on photographs (see Fig. 2-5)</td>
</tr>
<tr>
<td>Fracture aperture</td>
<td>0.5 mm</td>
<td>J. Rüedi (pers. comm. 23 August 2012), consistent with Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Length of borehole interval (as originally recorded)</td>
<td>69 cm</td>
<td>Rüedi (2010; see Fig. A-4)</td>
</tr>
<tr>
<td>Volume of unrecorded void space at end of borehole</td>
<td>733.5 ml</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
</tbody>
</table>

7.1.4 Geochemistry

7.1.4.1 Theory

In geochemical modelling, a set of aqueous species is usually adopted as a “basis” (also known as master species). One basis species exists for each dissolved ion included in the model, e.g. SiO$_2$(aq) is generally used as the basis for Si, Ca$^{2+}$ is used for Ca and so on. The basis species provide building blocks from which other chemical species (“aqueous complexes”, for example CaHCO$_3^-$ or CaCO$_3$(aq) in the case of Ca) and minerals can be formed.

Consider a system containing $N_b$ basis aqueous species, $N_c$ complex aqueous species and $N_m$ minerals. Assuming a constant water density, the transport and reaction of basis species $i$ in a saturated porous medium is described by the following equation for $b_i$ (mol kg$^{-1}$), the concentration of the basis species in solution (e.g. Bear, 1972; Zhu & Anderson, 2002):

$$
\rho_w \frac{\partial}{\partial t} (\phi b_i) = \rho_w \nabla \cdot (D_e + \Lambda |q(t)|) \nabla b_i - q(t) b_i - \sum_{j=1}^{N_c} v_{ij} R_j^C - \sum_{k=1}^{N_M} \mu_{ik} R_k^M
$$

(7-1)

where $\rho_w$ is the density of water (kg m$^{-3}$), $\phi$ is the porosity (-), $D_e$ is the effective diffusion coefficient$^3$ (m$^2$ s$^{-1}$), $\Lambda$ is the longitudinal dispersion length (m) and $q(t)$ is the Darcy velocity (m s$^{-1}$). The first sum appearing on the right hand side describes the consumption (or creation) of the basis

---

$^3$ The effective diffusion coefficient could, in theory, differ for each species $i$ in solution. This may be used to represent processes such as anion exclusion, which are important in some contexts, for example when modelling transport through clays. In the modelling described in this report, a single value of the diffusion coefficient is used for all species, avoiding problems with charge imbalances in solution. Further complexity could be added to the model in future if results from the in-situ experiment indicate that diffusion of individual species is important.
species in reactions with complex aqueous species; here $v_{ij}$ is the stoichiometry of basis species $i$ in the reaction for complex species $j$, and $R_j^C$ is the rate at which this reaction proceeds in the bulk volume (mol m\(^{-3}\) s\(^{-1}\)). Similarly, the second summation represents the consumption (or creation) of the basis species by solid minerals; here $\mu_{ik}$ is the stoichiometry of basis species $i$ in the reaction for mineral $k$ (-), and $R_k^M$ is the rate at which this reaction proceeds (mol m\(^{-3}\) s\(^{-1}\)).

The governing equation for the transport and reaction of complex species (which, due to the structure of the thermodynamic database, do not partake in mineral reactions) is similarly given by

$$\rho_w \frac{\partial}{\partial t} (\phi c_j) = \rho_w \nabla \cdot ([D_e + \Lambda|\mathbf{q}(t)|] \nabla c_j - \mathbf{q}(t) c_j) + R_j^C$$

(7-2)

where $c_j$ is the concentration of complex species $j$ in solution (mol kg\(^{-1}\)).

Finally, the governing equation for the reaction of minerals is

$$\frac{\partial m_k}{\partial t} = R_k^M$$

(7-3)

where $m_k$ is the volumetric concentration of mineral $k$ (mol m\(^{-3}\)) and $R_k^M$ is the rate of change of mineral $k$ (mol m\(^{-3}\) s\(^{-1}\)).

It is usually assumed that the chemical reactions for complex species occur instantaneously, i.e. the complex species are always in equilibrium with the basis species. In this case, the complex species reaction rates $R_j^C$ are eliminated by combining equations (7-1) and (7-2) and the concentration of an individual complex species $c_j$ is determined from the mass action equation (e.g. Appelo & Postma, 2007):

$$\prod_{i=1}^{NB} (y_i^P b_i)^{v_{ij}} = y_j^C c_j K_j^C$$

(7-4)

where $\gamma$ denotes an activity coefficient for the relevant basis or complex species (kg mol\(^{-1}\)) and $K_j^C$ is the equilibrium constant for the reaction (-) which can be determined experimentally and is available from thermodynamic databases that are prepared for use with geochemical modelling codes.

Usually, the activity coefficients $\gamma$ are expressed as a function of the ionic strength of the solution and an activity model. The ionic strength $I$ (kg mol\(^{-1}\)) is given by (e.g. Zhu & Anderson, 2002)

$$I = \frac{1}{2} \left( \sum_{i=1}^{NB} b_i z_i^2 + \sum_{j=1}^{NC} c_j z_j^2 \right)$$

(7-5)

where $z$ is the charge number of the basis or complex species (-).

The activity model for aqueous species used in the simulations presented here is the Davies Equation (e.g. Zhu & Anderson, 2002) which is suitable for ionic strengths to a few tenths molal and gives the activity coefficient as

$$\log_{10} \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + \sqrt{I}} + 0.2Az_i^2 I$$

(7-6)

where $A$ is a constant that varies slightly with temperature, which is again available from compilations of thermodynamic data.
7.1.4.2 Mineralogy

Cement

The cement mixture used in the experiments is Ultrafin 16 (UF16) Portland cement (OPC), with a water/cement mass ratio (w/c) of 0.8 and no silica fume (Lanyon and Mäder, 2017). It is assumed that the cement mix was fully hydrated on emplacement. Unfortunately, the cement was not analysed prior to emplacement (nor was a sample retained in suitable conditions) in order to determine its mineralogy or porosity, thus expert judgement must be used.

Modelling of the hydration of a similar cement blend undertaken by Lothenbach et al. (2011) suggests the cement will include the phases: portlandite, C-S-H gel, monocarbonate (also referred to as monocarboaluminate), hydrotalcite, calcite and ettringite. The relative proportions of these phases are given in Table 7-3. The C-S-H gel is modelled as an ideal solid solution, with jennite-like (high Ca/Si ratio) and tobermorite-like (low Ca/Si ratio) end-members (note that the terms “CSH-jennite”, “jennite end-member”, “CSH-tobermorite” and “tobermorite end-member” will be used as shorthand in the rest of this document, but these names simply represent high and low Ca compositional end-members of the idea solid solution and are not necessarily closely linked to the crystalline forms of jennite and tobermorite). A comprehensive study by Walker (2016), which brings together measured porosities for various w/c ratios, suggests that a porosity of 0.5 (± 0.17) is appropriate for hydrated OPC with a w/c ratio of 0.8.

Gaps and void spaces

The gaps and voids included in the model (between the cement and borehole walls, between the two cement halfpipes, and the extra volume at the end of the borehole) are assigned an initial porosity of 1.0. No minerals are present in these regions at the start of the simulation.

Tab. 7-3: Hydrated cement composition (based on modelling by Lothenbach et al., 2011)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>0.715</td>
</tr>
<tr>
<td>Portlandite</td>
<td>13.215</td>
</tr>
<tr>
<td>CSH-jennite</td>
<td>19.645</td>
</tr>
<tr>
<td>CSH-tobermorite</td>
<td>2.145</td>
</tr>
<tr>
<td>Ettringite</td>
<td>5.715</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>2.145</td>
</tr>
<tr>
<td>Monocarbonate</td>
<td>6.43</td>
</tr>
<tr>
<td>Porosity</td>
<td>50.0</td>
</tr>
</tbody>
</table>

7.1.4.3 Fluid compositions

Grimsel groundwater

The groundwater at Grimsel is extremely dilute, alkaline and has a low ambient \( p\text{CO}_2 \) (\( \log p\text{CO}_2 = -6 \) bars). The composition is thus very weakly buffered. A representative composition (from Soler et al., 2006) is presented in Tab. 7-4. The concentrations of Al and Mg were reduced from those quoted in Soler et al. (2006) because aluminosilicates were found to be supersaturated with respect to the groundwater in the model.
Tab. 7-4: “GIMRT” groundwater composition at Grimsel (after Soler et al., 2006)

Note: The concentration of Al has been reduced from $8 \times 10^{-6}$ to $10^{-7}$ mol kg$^{-1}$ and Mg from $6.2 \times 10^{-7}$ to $10^{-7}$ mol kg$^{-1}$ (the original values in Soler et al., 2006; pgs 8, 28) to exclude aluminosilicate mineral supersaturations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Molality (mol kg$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>$1.00 \times 10^{-7}$</td>
<td>9.81</td>
</tr>
<tr>
<td>Si</td>
<td>$7.55 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>$3.61 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>$1.96 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$1.40 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>$1.00 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>$2.00 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>$6.10 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>$2.20 \times 10^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

Cement porewater

The initial cement porewater composition is given in Table 7-5 (this is the composition of the water initially present in the modelled cement; as soon as the solve begins, this water will change in composition with its evolution controlled by the leaching model). The composition was produced by equilibrating the Grimsel groundwater composition (Tab. 7-4) with the cement phases (Tab. 7-3) at 15°C, the ambient temperature at Grimsel. These calculations were undertaken with PHREEQC (Parkhurst & Appelo, 1999). Here it is assumed that alkalis associated with the C-S-H phases have been leached out and washed away, a common assumption that is made when modelling cement dissolution in the context of radioactive waste disposal. Because the current study is largely concerned with short-term behaviour, preliminary modelling reported by Watson et al. (2014) considered the impact of including alkali leaching explicitly. However, this was found to have a very short-term (<1 year) impact on the aqueous chemistry and did not have any large effects on the mineralogical alteration, so has not been considered in the present model.

Tab. 7-5: The initial cement porewater composition, calculated using PHREEQC (Parkhurst & Appelo, 1999)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molality (mol kg$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>$7.14 \times 10^{-4}$</td>
<td>13.16</td>
</tr>
<tr>
<td>Si</td>
<td>$1.18 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>$3.61 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>$1.96 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$6.02 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>$1.78 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>$7.49 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>$3.73 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>$2.20 \times 10^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>
7.1.4.4 Thermodynamic data for aqueous species

The basis aqueous species incorporated in the modelling were Al\(^{3+}\), HCO\(_3^-\), Ca\(^{2+}\), K\(^+\), Mg\(^{2+}\), Na\(^+\), SiO\(_2\)\(_{aq}\), and H\(^+\). Aqueous complexes are listed in Table 7-6, together with thermodynamic data for the reactions. These data are taken from the Geochemist’s Workbench (Bethke, 2008) version of the Lawrence Livermore (LLNL) database \textit{“thermo.com.V8.R6+”}, and computed at the ambient Grimsel temperature of 15 °C using a linear interpolation.

Tab. 7-6: Equilibrium data for aqueous complexes at 15 °C

Note: All data are from the Geochemist’s Workbench version of the LLNL database \textit{“thermo.com.V8.R6+”}.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
<th>(\log_{10} K_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlO(_2^-)</td>
<td>AlO(_2^-) + 4H(^+) = Al(^{3+}) + 2H(_2)O</td>
<td>24.0479</td>
</tr>
<tr>
<td>CO(_3^{2-})</td>
<td>CO(_3^{2-}) + H(^+) = HCO(_3^-)</td>
<td>10.4469</td>
</tr>
<tr>
<td>CO(<em>2)(</em>{aq})</td>
<td>CO(<em>2)(</em>{aq}) + H(_2)O = H(^+) + HCO(_3^-)</td>
<td>-6.4390</td>
</tr>
<tr>
<td>CaOH(^+)</td>
<td>CaOH(^+) + H(^+) = Ca(^{2+}) + H(_2)O</td>
<td>12.8500</td>
</tr>
<tr>
<td>CaSO(<em>4)(</em>{aq})</td>
<td>CaSO(<em>4)(</em>{aq}) = Ca(^{2+}) + SO(_4^{2-})</td>
<td>-2.0952</td>
</tr>
<tr>
<td>CaHCO(_3)(^+)</td>
<td>CaHCO(_3)(^+) = Ca(^{2+}) + HCO(_3^-)</td>
<td>-1.0661</td>
</tr>
<tr>
<td>CaCO(<em>3)(</em>{aq})</td>
<td>CaCO(<em>3)(</em>{aq}) + H(^+) = Ca(^{2+}) + HCO(_3^-)</td>
<td>7.2019</td>
</tr>
<tr>
<td>KSO(_4)(^-)</td>
<td>KSO(_4)(^-) = K(^+) + SO(_4^{2-})</td>
<td>-0.8819</td>
</tr>
<tr>
<td>MgSO(<em>4)(</em>{aq})</td>
<td>MgSO(<em>4)(</em>{aq}) = Mg(^{2+}) + SO(_4^{2-})</td>
<td>-2.3025</td>
</tr>
<tr>
<td>MgHCO(_3)(^+)</td>
<td>MgHCO(_3)(^+) = Mg(^{2+}) + HCO(_3^-)</td>
<td>-1.0533</td>
</tr>
<tr>
<td>MgCl(^-)</td>
<td>MgCl(^-) = Mg(^{2+}) + Cl(^-)</td>
<td>0.1007</td>
</tr>
<tr>
<td>MgCO(<em>3)(</em>{aq})</td>
<td>MgCO(<em>3)(</em>{aq}) + H(^+) = Mg(^{2+}) + HCO(_3^-)</td>
<td>7.5059</td>
</tr>
<tr>
<td>NaHCO(<em>3)(</em>{aq})</td>
<td>NaHCO(<em>3)(</em>{aq}) = Na(^+) + HCO(_3^-)</td>
<td>-0.2418</td>
</tr>
<tr>
<td>NaSO(_4)(^-)</td>
<td>NaSO(_4)(^-) = Na(^+) + SO(_4^{2-})</td>
<td>-0.8200</td>
</tr>
<tr>
<td>NaCl(_{aq})</td>
<td>NaCl(_{aq}) = Na(^+) + Cl(^-)</td>
<td>0.7976</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>OH(^-) + H(^+) = H(_2)O</td>
<td>14.3730</td>
</tr>
<tr>
<td>HSiO(_3)(^-)</td>
<td>HSiO(_3)(^-) = SiO(<em>2)(</em>{aq}) + H(_2)O</td>
<td>10.1007</td>
</tr>
<tr>
<td>H(_2)SiO(_3)(^2-)</td>
<td>H(_2)SiO(_3)(^2-) + 2H(^+) = SiO(<em>2)(</em>{aq}) + 2H(_2)O</td>
<td>22.96</td>
</tr>
</tbody>
</table>

7.1.4.5 Mineral dissolution and precipitation

Mineral kinetics

As discussed in section 7.1.4.1 (equation 7-3), a kinetic approach is used to represent the precipitation and dissolution of minerals. All minerals are therefore assumed to dissolve/grow at a volumetric rate \(R\) (mol m\(^{-3}\) s\(^{-1}\)) governed by the following equation (e.g. Lasaga, 1998)

\[
R = A k_0 (a_{H^+})^p (\Omega - 1)
\]  

\(^{(7-7)}\)

\(^4\) The LLNL database was chosen over alternatives (such as HATCHES or Thermoddem) because it has a larger range of data for zeolite-type minerals and is widely used and trusted. In addition, it is available in formats compatible with all computer codes used in the modelling, including QPAC and Geochemist’s Workbench.
where $A$ is the mineral reactive surface area (m$^2$ m$^{-3}$); $k_0$ is the rate constant for dissolution or growth (mol m$^2$ s$^{-1}$); $a_{H^+}$ is the activity of H$^+$ in solution (-); $p$ is a constant (-); and $\Omega$ is the saturation of the mineral (the ratio of the ion activity product to the equilibrium constant, $k_{eq}$, for the mineral).

A positive rate ($\Omega > 1$) represents precipitation, while a negative rate ($\Omega < 1$) represents dissolution. Note that this leads to asymmetric precipitation/dissolution rates (the range for $\Omega - 1$ is unbounded at the upper end for the former case, while the latter case is bounded in the range [-1, 0] mol m$^{-3}$ s$^{-1}$, as $\Omega$ is always positive), but a lack of data in the literature precludes the confident use of any other form for the majority of minerals. In addition, in interactions in natural systems such as this, with the exception of times close to initial disequilibrium (e.g. shortly after emplacement), minerals are often close to saturation (mildly under- or over-saturated), and the bias will have little effect.

The issues associated with the upscaling of laboratory-derived kinetic data to models at the natural system scale have been discussed in previous LCS modelling exercises (e.g. Savage et al., 2011). For example, during the evaluation of weathering in groundwater catchments in granitic rocks (e.g. White & Brantley, 1995; White & Brantley, 2003), it has become well-established that mineral dissolution rates calculated from mass fluxes in groundwater are generally 2-3 orders of magnitude less than those measured in the laboratory. This is largely due to the time-dependence of reaction rates, with the depletion of energetically reactive surfaces and accumulation of leached layers in weathered samples.

With the exception of calcite, in the base case of the present model the primary cement minerals are assigned a “fast” rate constant for dissolution, i.e. $\log_{10} k_0 = -5.0$ (where $k_0$ has units of mol m$^{-3}$ s$^{-1}$) and $p = 0$. This is in agreement with adoption of local equilibrium in other cement modelling studies (e.g. Grandia et al., 2010). However, Baur et al. (2004) measured much slower rates for ettringite and C-S-H, thus a variant case is also considered using $\log_{10} k_0 = -12.0$. The kinetic data for calcite are given in Table 7-7.

It is likely that precipitation of secondary minerals will be limited due to the restricted timescales of the experiment. Nevertheless, a range of potential secondary solids is considered in the modelling (which can then be consistently carried forward to the future full-scale model of all three boreholes), and these are also required for the longer-term study which is included as a variant case. Phases are selected from those considered most likely to form, bearing in mind both thermodynamic and kinetic data (e.g. Arthur et al., 2005, Savage et al., 2007). Kinetic data for the secondary minerals are given in Table 7.7; these data are estimated using the Arrhenius expression (e.g. Zhu & Anderson, 2002) at 15 °C.

The reaction of cement pore fluids with aluminosilicate minerals leads to rapid precipitation of calcium (aluminium) silicate hydrate (C-A-S-H) gels/solids (Savage et al., 1992). Here the zeolites stilbite, mordenite, scolecite and gismondine are included as proxies for C-A-S-H.

The solid products of the interaction of groundwater with granitic rocks can include a wide range of minerals, such as clays, oxides, carbonates, feldspars, and zeolites, depending upon groundwater composition, host rock type, and geological history. The reaction of hyperalkaline cement pore fluids with these fracture fillings and host rock minerals will tend to stabilise minerals such as zeolites and feldspars (Savage, 1997). Although these minerals may be kinetically inhibited from forming in the in-situ experiments, they will be of relevance to modelling long-term cement-rock interactions. Consequently, laumontite and analcime have been selected as potential Ca- and Na-bearing zeolites, respectively. Laumontite can occur with clay, quartz, and calcite as a low-temperature (<100 °C) filling in fractures in granite (e.g. Savage et al., 1987), although it is stabilised relative to analcime by higher temperature and/or a low Na/Ca ratio in a coexisting fluid. From a theoretical perspective, analcime and laumontite are stabilised by pH > 8, with their relative pre-
dominance controlled by the Na+/Ca²⁺ ratio of the fluid. Higher temperature stabilises laumontite relative to analcime and both these minerals are stabilised relative to stilbite, mordenite, scolecite and gismondine by higher temperature (e.g. Walker, 1960).

Montmorillonite can occur with laumontite, quartz, and calcite in low-temperature veins in granite (e.g. Savage et al., 1987). Gibbsite and kaolinite may be sinks for Al prior to the stabilisation of smectite. Brucite and sepiolite have been included as potential ‘sinks’ for Mg.

Tab. 7-7: Kinetic data for calcite and secondary minerals (at 15 °C except where indicated)

Note: For rates assigned to other primary minerals, see text.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>( \log_{10} k_0 ) (mol m²s⁻¹)</th>
<th>( p )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>-3.7</td>
<td>0.9</td>
<td>Busenberg &amp; Plummer (1986)</td>
</tr>
<tr>
<td>Tobermorite-11Å</td>
<td>-10.0</td>
<td></td>
<td>Estimated</td>
</tr>
<tr>
<td>Laumontite</td>
<td>-14.5</td>
<td></td>
<td>Savage et al. (1993)</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>-17.1</td>
<td>-0.8</td>
<td>Nagy (1995)</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-17.2</td>
<td>-0.472</td>
<td>Palandri &amp; Kharaka (2004)</td>
</tr>
<tr>
<td>Gismondine</td>
<td>-14.6</td>
<td></td>
<td>As for scolecite</td>
</tr>
<tr>
<td>Scolecite</td>
<td>-14.6</td>
<td></td>
<td>As for scolecite</td>
</tr>
<tr>
<td>Mordenite</td>
<td>-14.6</td>
<td></td>
<td>As for scolecite</td>
</tr>
<tr>
<td>Stilbite</td>
<td>-14.6</td>
<td></td>
<td>As for scolecite</td>
</tr>
<tr>
<td>Analcime</td>
<td>-13.9</td>
<td>-0.4</td>
<td>Savage et al. (2001)</td>
</tr>
<tr>
<td>Chalcedony</td>
<td>-14.5</td>
<td>-0.5</td>
<td>Plettinck et al. (1994) (at 25°C)</td>
</tr>
<tr>
<td>Brucite</td>
<td>-8.5</td>
<td></td>
<td>Nagy (1995)</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>-8.5</td>
<td></td>
<td>As for brucite</td>
</tr>
<tr>
<td>Montmor-Na</td>
<td>-13.6</td>
<td>-0.15</td>
<td>Sato et al. (2004) (at 25°C)</td>
</tr>
<tr>
<td>Montmor-K</td>
<td>-13.6</td>
<td>-0.15</td>
<td>As for montmor-Na</td>
</tr>
<tr>
<td>Montmor-Ca</td>
<td>-13.6</td>
<td>-0.15</td>
<td>As for montmor-Na</td>
</tr>
<tr>
<td>Montmor-Mg</td>
<td>-13.6</td>
<td>-0.15</td>
<td>As for montmor-Na</td>
</tr>
<tr>
<td>Saponite-Na</td>
<td>-13.6</td>
<td>-0.15</td>
<td>As for montmor-Na</td>
</tr>
<tr>
<td>Saponite-K</td>
<td>-13.6</td>
<td>-0.15</td>
<td>As for montmor-Na</td>
</tr>
<tr>
<td>Saponite-Ca</td>
<td>-13.6</td>
<td>-0.15</td>
<td>As for montmor-Na</td>
</tr>
<tr>
<td>Saponite-Mg</td>
<td>-13.6</td>
<td>-0.15</td>
<td>As for montmor-Na</td>
</tr>
</tbody>
</table>

Reactive surface areas

In the absence of other data, the reactive surface area (\( A \) in equation 7-7) of all minerals is calculated by making an assumption of small (sand-sized) grains with a radius of 0.5 μm. Very low crystallinity phases often have surface areas of a few tens of square metres per gram, which implies a smaller grain radius.

Assigning alternative reactive surface areas would alter the rate at which reactions occur; as it is difficult in a model with a large number of minerals to predict what impact varying the reactive surface area would have on the results, this is often the focus of a sensitivity study or variant case (e.g. Steefel & Lichtner, 1998) or, in non blind modelling, is one of the parameters used to fit the
model to the data (e.g. Savage et al., 2011). In the present model, the reactive surface area has not been included in a sensitivity study because varying it has the same effect as changing the kinetic rate, which is included as a sensitivity study.

**Thermodynamic data**

Molar volume, weight and solubility data for primary cement and secondary minerals are presented in Tables 7-8 and 7-9, respectively. These data were taken from the Geochemist’s Workbench (Bethke, 2008) version of the Lawrence Livermore (LLNL) database “thermo.com.V8.R6+” and computed at the ambient Grimsel temperature of 15 °C using a linear interpolation. Molar volumes of minerals were also taken from this database; given the lack of data for the molar volumes of smectite minerals, these were calculated using the analogue algorithm model described by Ransom & Helgeson (1994). The molar volumes are important when determining porosity (and hence permeability) changes in the modelled system due to the precipitation or dissolution of minerals. If a significant amount of smectite precipitation is observed in the model, this assumption may be revisited in further work.

**Tab. 7-8:** Molar volume, weight and equilibrium data for the cement minerals (at 15 °C)

Note: Data are from the LLNL database “thermo.com.V8.R6+”, except for those minerals marked with an asterisk which are from Matschei et al. (2007).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Molar Volume (cc mol⁻¹)</th>
<th>Molar Weight (g mol⁻¹)</th>
<th>Reaction</th>
<th>( \log_{10} K_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>36.934</td>
<td>100.0872</td>
<td>( \text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^- )</td>
<td>1.9995</td>
</tr>
<tr>
<td>Portlandite</td>
<td>33.056</td>
<td>74.0927</td>
<td>( \text{Ca(OH)}_2 + 2\text{H}^+ = \text{Ca}^{2+} + 2\text{H}_2\text{O} )</td>
<td>23.3828</td>
</tr>
<tr>
<td>CSH-jennite°</td>
<td>78.40</td>
<td>191.341</td>
<td>((\text{CaO})_{0.6666}\text{SiO}_2:2.1\text{H}_2\text{O} + 3.3332\text{H}^+ = 1.6666\text{Ca}^{2+} + \text{SiO}_2 + 3.7666\text{H}_2\text{O})</td>
<td>30.8209</td>
</tr>
<tr>
<td>CSH tobermorite°</td>
<td>58.7000</td>
<td>130.8350</td>
<td>((\text{CaO})_{0.9333}\text{SiO}_2:1.3333\text{H}_2\text{O} + 1.6666\text{H}^+ = 0.8333\text{Ca}^{2+} + \text{SiO}_2 + 2.1666\text{H}_2\text{O})</td>
<td>11.3534</td>
</tr>
<tr>
<td>Ettringite</td>
<td>710.3200</td>
<td>1255.1072</td>
<td>(\text{Ca}_6\text{Al}_2(\text{SO}_4)\text{(OH)}_4:26\text{H}_2\text{O} + 12\text{H}^+ = 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 6\text{Ca}^{2+} + 38\text{H}_2\text{O})</td>
<td>65.1121</td>
</tr>
<tr>
<td>Hydrotalcite°</td>
<td>220.2000</td>
<td>443.3308</td>
<td>(\text{Mg}_3\text{Al}_2(\text{OH})_4:3\text{H}_2\text{O} + 14\text{H}^+ = 2\text{Al}^{3+} + 4\text{Mg}^{2+} + 17\text{H}_2\text{O})</td>
<td>75.8046</td>
</tr>
<tr>
<td>Monocarbonate°</td>
<td>261.9580</td>
<td>568.4478</td>
<td>(\text{Ca}_6\text{Al}_2(\text{CO}_3)(\text{OH})_4:5\text{H}_2\text{O} + 13\text{H}^+ = 2\text{Al}^{3+} + 4\text{Ca}^{2+} + \text{HCO}_3^- + 17\text{H}_2\text{O})</td>
<td>82.2216</td>
</tr>
</tbody>
</table>
Tab. 7-9: Molar volume, weight and equilibrium data for the secondary minerals (at 15 °C)
Note: All data are from the LLNL database “thermo.com.V8.R6+”, except for the molar volumes of smectite minerals which are calculated, see text for details.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Molar Volume (cc mol⁻¹)</th>
<th>Molar Weight (g mol⁻¹)</th>
<th>Reaction</th>
<th>log⁹ Kₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tobermorite-11Å</td>
<td>286.81</td>
<td>739.976</td>
<td>Ca₉Si₆O₁₄(OH)₆·4.5H₂O + 10H⁺ = 5Ca²⁺ + 6SiO₂(aq) + 10.5H₂O</td>
<td>67.2179</td>
</tr>
<tr>
<td>Laumontite</td>
<td>207.55</td>
<td>470.437</td>
<td>CaAl₂Si₂O₅·4H₂O + 8H⁺ = Ca²⁺ + 2Al³⁺ + 4SiO₂(aq) + 8H₂O</td>
<td>14.6784</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>31.956</td>
<td>78.0036</td>
<td>Al(OH)₃ + 3H⁺ = Al³⁺ + 3H₂O</td>
<td>8.4051</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>99.52</td>
<td>258.1604</td>
<td>Al₂Si₅O₁₄(H)₄ + 2Al³⁺ + 2SiO₂(aq) + 5H₂O</td>
<td>7.6933</td>
</tr>
<tr>
<td>Analcime</td>
<td>96.800</td>
<td>219.2786</td>
<td>Na₂₉Al₆Si₁₈O₅₂H₁₂O + 3.84H⁺ = 0.96Na⁺ + 0.96Al³⁺ + 2.04SiO₂(aq) + 2.92H₂O</td>
<td>6.5398</td>
</tr>
<tr>
<td>Gismondine</td>
<td>152.0</td>
<td>718.5521</td>
<td>Ca₂Al₂Si₅O₁₄·9H₂O + 16H⁺ = 2Ca²⁺ + 4Al³⁺ + 4SiO₂(aq) + 17H₂O</td>
<td>41.7170</td>
</tr>
<tr>
<td>Scolecite</td>
<td>172.29</td>
<td>392.3374</td>
<td>CaAl₂Si₅O₁₄·3H₂O + 8H⁺ = Ca²⁺ + 2Al³⁺ + 3SiO₂(aq) + 7H₂O</td>
<td>17.0619</td>
</tr>
<tr>
<td>Mordenite</td>
<td>209.9</td>
<td>441.8470</td>
<td>Ca₁₉MelNa₁₉₂Al₂₁₆Si₆₀O₁₄·3·468H₂O + 3·76H⁺ = 0.2895Ca²⁺ + 0.361Na⁺ + 0.94Al³⁺ + 5·06SiO₂(aq) + 5·348H₂O</td>
<td>-5.5134</td>
</tr>
<tr>
<td>Stilbite</td>
<td>333.5</td>
<td>714.6048</td>
<td>Ca₁₉₂Na₆₆Al₆₆Si₆₆O₃₆H₁₂·7·33MgOH₂ + 8·72H⁺ = .136Na⁺ + .006K⁺ + 1·019Ca²⁺</td>
<td>1.3065</td>
</tr>
<tr>
<td>Chaledony</td>
<td>22.688</td>
<td>60.0843</td>
<td>SiO₂ = SiO₂(aq)</td>
<td>-3.9712</td>
</tr>
<tr>
<td>Brucite</td>
<td>24.630</td>
<td>58.3197</td>
<td>Mg(OH)₂ + 2H⁺ = Mg²⁺ + 2H₂O</td>
<td>17.0147</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>285.600</td>
<td>647.8304</td>
<td>Mg₉Si₁₄O₅(OH)₆·6H₂O + 8H⁺ = 4Mg²⁺ + 6SiO₂(aq) + 11H₂O</td>
<td>31.2214</td>
</tr>
<tr>
<td>Montmor-Na</td>
<td>141.377</td>
<td>367.0171</td>
<td>Na₉₃Mg₆₃Al₆₃Si₆₃O₃₆(OH)₆ + 6H⁺ = .33Na⁺ + .33Mg²⁺ + 1.67Al³⁺ + 4SiO₂(aq) + 4H₂O</td>
<td>2.9090</td>
</tr>
<tr>
<td>Montmor-K</td>
<td>149.0671</td>
<td>372.3329</td>
<td>K₉₂Mg₉₆Al₉₆Si₉₆O₉₆(OH)₉ + 6H⁺ = .33K⁺ + .33Mg²⁺ + 1.67Al³⁺ + 4SiO₂(aq) + 4H₂O</td>
<td>2.5326</td>
</tr>
<tr>
<td>Montmor-Ca</td>
<td>137.259</td>
<td>366.0434</td>
<td>Ca₁₆₅Mg₃Al₃₅Si₅₅Si₅₅O₅₅(OH)₂ + 6H⁺ = .165Ca²⁺ + .33Mg²⁺ + 1.67Al³⁺ + 4SiO₂(aq) + 4H₂O</td>
<td>2.9633</td>
</tr>
<tr>
<td>Montmor-Mg</td>
<td>134.501</td>
<td>363.4408</td>
<td>Mg₉₃Al₉₃Si₉₃O₉₃(OH)₉ + 6H⁺ = .495Mg²⁺ + 1.67Al³⁺ + 4SiO₂(aq) + 4H₂O</td>
<td>2.8718</td>
</tr>
<tr>
<td>Saponite-Na</td>
<td>146.787</td>
<td>386.488</td>
<td>Na₉₃Mg₆₃Al₆₃Si₆₃O₃₆(OH)₆ + 7·32H⁺ = .33Na⁺ + .33Al³⁺ + 3·37Mg²⁺ + 3·67SiO₂(aq) + 4·66H₂O</td>
<td>27.4863</td>
</tr>
<tr>
<td>Saponite-K</td>
<td>154.477</td>
<td>391.8038</td>
<td>K₉₂Mg₉₆Al₉₆Si₉₆O₉₆(OH)₉ + 7·32H⁺ = .33K⁺ + .33Al³⁺ + 3·37Mg²⁺ + 3·67SiO₂(aq) + 4·66H₂O</td>
<td>27.1149</td>
</tr>
<tr>
<td>Saponite-Ca</td>
<td>142.669</td>
<td>385.5142</td>
<td>Ca₁₆₅Mg₃Al₃₅Si₅₅Si₅₅O₅₅(OH)₂ + 7·32H⁺ = .165Ca²⁺ + .33Al³⁺ + 3·37Mg²⁺ + 3·67SiO₂(aq) + 4·66H₂O</td>
<td>27.4716</td>
</tr>
<tr>
<td>Saponite-Mg</td>
<td>139.911</td>
<td>382.9117</td>
<td>Mg₉₃Al₉₃Si₉₃O₉₃(OH)₉ + 7·32H⁺ = .165Mg²⁺ + .33Al³⁺ + 3·37Mg²⁺ + 3·67SiO₂(aq) + 4·66H₂O</td>
<td>27.4522</td>
</tr>
</tbody>
</table>
7.1.5  Transport

7.1.5.1  Theory

The dominant transport process in this system is advection. The hydraulic conductivity, $K$ (m s$^{-1}$), is specified as (e.g. Phillips, 2009)

$$K = \frac{\rho g k}{\nu}$$  \hspace{1cm} (7-8)

where $\rho$ is the density of water (kg m$^{-3}$), $g$ is the acceleration due to gravity (m s$^{-2}$), $k$ is the permeability (m$^2$) and $\nu$ is the viscosity of water (Pa s). The hydraulic conductivity is related to the fracture transmissivity, $T$ (m$^2$ s$^{-1}$), by

$$K = \frac{T}{a}$$  \hspace{1cm} (7-9)

where $a$ (m) is the fracture aperture.

The permeability is related to the porosity in the model via a Kozeny-Carman type relationship (e.g. de Marsily, 1986)

$$k = k_0 \frac{(1 - \theta_0)^2}{\theta_0^3} \frac{\theta^3}{(1 - \theta)^2}$$  \hspace{1cm} (7-10)

Here $k_0$ is the initial permeability (m$^2$), $\theta_0$ is the initial porosity (-) and $\theta$ is the porosity at time $t$ (-). The initial permeability is chosen to give an initial hydraulic conductivity (or transmissivity) equal to that measured for the unaltered media (at the initial porosity).

Diffusion is coupled to the porosity in the model by Archie’s Law (e.g. Appelo & Postma, 2007)

$$D_e = \theta^m D_0$$  \hspace{1cm} (7-11)

where $D_e$ is the effective diffusion coefficient (m$^2$ s$^{-1}$), $D_0$ is a diffusion coefficient in water (m$^2$ s$^{-1}$) and $m$ is a constant, here taken to be 2.

Within QPAC, geochemistry and transport are fully coupled (i.e. the equations are solved together rather than sequentially), allowing feedback between porosity changes and transport to be modelled more accurately.

7.1.5.2  Input parameters

The average fracture transmissivity was determined from the pre-emplacement tracer tests (Lanyon & Mäder, 2020). It is noted that shear zone structures can be highly heterogeneous at a range of scales, and thus transmissivity varies with location even at the centimetre scale. Modelling reported by Lanyon & Mäder (2020) suggests that the transmissivity in fracture F16 is $3.0 \times 10^9$ m$^2$ s$^{-1}$, with a range of $1.5 \times 10^9$ m$^2$ s$^{-1}$. The modelling also suggests that, prior to emplacement, there were local “skins” around the boreholes with lower transmissivities. Around the emplacement borehole, transmissivity was calculated to be 100 times lower than the value estimated for F16, and around the observation borehole it was calculated to be 10 times lower. A model variant has been included to investigate sensitivity to the transmissivity.
The fracture plane is not included explicitly in the model. The natural head gradient (1 m m$^{-1}$; rounded down from the value of 1.5 m m$^{-1}$ given by Lanyon & Mäder, 2020), deduced from modelling of the pre-emplacement tracer tests, is applied across the borehole as a boundary condition; an ‘apparent’ transmissivity has been set for the gap between the cement and the borehole wall (in fact, all void spaces) to that of the fracture so that flow rates through the borehole are correct.

Walker (2016) has collated data from experimental studies on cement with various water/cement (w/c) ratios to determine an expression for the effective diffusion coefficient ($D_e$) as a function of porosity. For a hydrated OPC of initial w/c = 0.8 and porosity of 0.5 (see section 7.1.4.2), this gives $D_e = (3.1 \pm 0.8) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ for HTO and $D_e = (1.0 \pm 0.5) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ for Cl$^-$. An initial effective diffusion coefficient of $1.0 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ for all species is thus selected for use in the model. Previous studies (e.g. Soler, 2010) have assumed a smaller effective diffusion coefficient, thus a variant case is considered with an effective diffusion coefficient an order of magnitude smaller than the base case to investigate the importance of this parameter.

The form of Archie’s Law used within QPAC is given by equation (7.11), where the diffusion coefficient in water $D_o$ is a model input and used with the calculated porosity to give an effective diffusion coefficient, $D_e$. The initial value of $D_e$ given above is used in this equation to determine a consistent value of $D_o$, given an initial porosity. This value of $D_o$ is then used throughout the simulation to calculate $D_e$ as the porosity evolves.

Dispersion is also included in the model but is difficult to quantify. Here a dispersion length (dispersivity) of 0.01 m is adopted, following the approach for the HPF experiment (Soler et al., 2006).

Input parameters used in the transport calculations are summarised in Table 7-10.

**Tab. 7-10: Transport parameters used in the modelling**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity of cement</td>
<td>$1.0 \times 10^{-11} \text{ m s}^{-1}$</td>
<td>Kim et al. (2011)</td>
</tr>
<tr>
<td>Hydraulic conductivity of gap</td>
<td>$6.0 \times 10^{-6} \text{ m s}^{-1}$</td>
<td>Fitted (see text)</td>
</tr>
<tr>
<td>Average fracture (F16) transmissivity</td>
<td>$3.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Head gradient in fracture (F16)</td>
<td>1 m/m</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Dispersion length</td>
<td>0.01 m</td>
<td>Soler et al. (2006)</td>
</tr>
<tr>
<td>Effective diffusion coefficient of cement</td>
<td>$1.0 \times 10^{-10} \text{ m}^2\text{s}^{-1}$</td>
<td>Walker (2016)</td>
</tr>
</tbody>
</table>

### 7.1.6 Boundary conditions

Only two permeable boundaries are considered in the model. The first is the intersection between the borehole and the fracture (see Figs. 7-1 and 7-2). Here, a temporally constant head condition is applied, using the head gradient specified in Table 7-10 so that water flows across the borehole.

The second boundary is the injection port P, where a fixed flow into the adjacent cell (marked in Figs. 7-2 and 7-3) is imposed. The rate of injection varied throughout the experiment; the rates and times used in the model are given in Table 7-11. These are derived from information provided by Lanyon & Mäder (2020); in particular the times at which the injection rate changed have been read from graphs and will therefore not be entirely accurate (but are considered accurate enough for the purposes of the modelling).
Tab. 7-11: Rate of injection through port P used in the model (derived from Lanyon & Mäder, 2020)

<table>
<thead>
<tr>
<th>Time</th>
<th>Rate of Injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 436 days</td>
<td>0.00 ml min⁻¹</td>
</tr>
<tr>
<td>436 - 862 days</td>
<td>0.25 ml min⁻¹</td>
</tr>
<tr>
<td>862 days onwards</td>
<td>0.04 ml min⁻¹</td>
</tr>
</tbody>
</table>

The Grimsel groundwater specified in Table 7-4 is used as a constant water composition boundary condition at both boundaries.

Note that the imposed flow rate into the borehole through the injection port P will perturb the head gradient in the region of the borehole, therefore the fixed head condition imposed around the outside of the model is a simplification. This will result in larger heads in the borehole than might realistically be expected, which could result in greater penetration of alteration into the cement.

7.2 Model results

7.2.1 Description of variant cases considered

For the 2D modelling, four variants are considered in addition to the base case, as shown in Table 7-12. These include a case with an effective diffusion coefficient an order of magnitude smaller than the base case to reflect values adopted in previous modelling studies (see section 7.1.5.2); a case with much slower kinetic rates for the primary cement minerals (with the exception of calcite) to include values reported in the literature (see section 7.1.4.5) and a case with fracture transmissivity reduced by two orders of magnitude to reflect the possibility that the emplacement borehole is situated in a low permeability region of the fracture (see section 7.1.5.2). Finally, a variant case with the slower cement mineral kinetic rates is run to 10,000 years (rather than 6 years, the lifetime of the experiment). The aim of this case is to investigate the evolution of the cement over timescales that are more relevant to radioactive waste disposal (the choice of 10,000 years is arbitrary, but considerably more relevant than 6 years); slower kinetic rates were selected as they are considered most relevant for the longer-term system.

The 3D model takes much longer to run than the 2D model (of the order of weeks rather than hours), so only a single variant case has been considered, with slower kinetic rates for the primary cement minerals (except calcite). This is summarised in Table 7-13.

In addition to the variant cases discussed above, during the preliminary modelling phase other variants and model sensitivities were investigated. These have not been carried forward to the current modelling phase because they were not found to have a large impact on the model results. These variants included:

- Finer discretisation (2D case)
- Explicit representation of alkali leaching
- Positioning of injection port on opposite side of borehole
- Larger (5 μm) grain radii used to calculate mineral surface areas

The results of the modelling study are discussed in the remainder of this section.
7.2.2 Case 1a – 2D base case

The plot in Figure 7-4 shows the initial composition of the cement in the borehole, being dominated by the jennite end-member of the C-S-H gel solid-solution and portlandite. After 1.2 years of the simulation (Fig. 7-5; during this period there is no injection of water into the borehole, only a background head gradient is applied across the fracture), there was significant removal of portlandite, ettringite and the jennite C-S-H gel end-member in the cells nearest the gap between cement and borehole wall (these cells are 1 mm thick in the radial direction) and significant production of the tobermorite end member of the C-S-H gel solid solution on the left-hand side of the cement halfpipe (flow is from left to right in all figures).

At 2.4 years (Fig. 7-6) is the point where the injection into the borehole, which started at 1.2 years, slowed down and, at 6 years (Fig. 7-7), this trend is continued, but with additional removal of all cement minerals on the right-hand side (adjacent to the injection port) and the precipitation of small amounts of both Ca-saponite (smectite clay) and gismondine (zeolite). At the left-hand margin, where water from the fracture flows into the borehole, CSH-jennite, portlandite and ettringite are dissolved and replaced by CSH tobermorite and minor amounts of Ca-saponite and gismondine.

The volume fraction plot of minerals in the cells representing the gap between the cement and the borehole wall at the end of the simulation (6 years; Fig. 7-8) shows minor amounts of residual monocarbonate and C-S-H gel, together with smaller amounts of neoformed Ca-saponite, and 11Å-tobermorite.

Figure 7-9 shows the volumes of minerals at the end of the simulation in the cement cells nearest the emplacement tool (these cells are ~4.5 mm thick), showing less dissolution than in the outer cement after 6 years (Fig. 7-7), although portlandite is still lost in the region 0-90° (the inflowing side) and there is a conversion of the jennite C-S-H end-member to the tobermorite end-member in the same area. This is consistent with expectations, as the cement near the emplacement tool is protected by the outer layers and not exposed to the advective flow in the same way as the outer.

Tab. 7-12: 2D model variants

<table>
<thead>
<tr>
<th>Case</th>
<th>Diffusion Coefficient De</th>
<th>Cement Mineral Kinetic Rates $k_0$</th>
<th>Fracture Transmissivity $t_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a Base Case</td>
<td>$1.0 \times 10^{-10}$ m$^2$s$^{-1}$</td>
<td>$1.0 \times 10^{-5}$ mol m$^2$s$^{-1}$</td>
<td>$3.0 \times 10^{-9}$ m$^2$s$^{-1}$</td>
</tr>
<tr>
<td>1b Slow Diffusion</td>
<td>$1.0 \times 10^{-11}$ m$^2$s$^{-1}$</td>
<td>As base case</td>
<td>As base case</td>
</tr>
<tr>
<td>1c Slow Kinetics</td>
<td>As base case</td>
<td>$1.0 \times 10^{-12}$ mol m$^2$s$^{-1}$</td>
<td>As base case</td>
</tr>
<tr>
<td>1d Reduced Transmissivity</td>
<td>As base case</td>
<td>As base case</td>
<td>$3.0 \times 10^{-11}$ m$^2$s$^{-1}$</td>
</tr>
<tr>
<td>1e Slow Kinetics, Long-term Evolution</td>
<td>As base case</td>
<td>$1.0 \times 10^{-12}$ mol m$^2$s$^{-1}$</td>
<td>As base case</td>
</tr>
</tbody>
</table>

Tab. 7-13: 3D model variants

<table>
<thead>
<tr>
<th>Case</th>
<th>Cement Mineral Kinetic Rates $k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a Base Case</td>
<td>$1.0 \times 10^{-4}$ mol m$^2$s$^{-1}$</td>
</tr>
<tr>
<td>2b Slow Kinetics</td>
<td>$1.0 \times 10^{-12}$ mol m$^2$s$^{-1}$</td>
</tr>
</tbody>
</table>
region is in the model. However, the conversion of jennite to tobermorite (lower Ca/Si ratio) end member in the C-S-H gel throughout the cement on the inflowing side indicates that the water composition within the cement is indeed altered.

Fig. 7-4: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 0 years (Case 1a: Base Case)

Note: Flow around the borehole is orientated left to right in the figure.
Fig. 7-5: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 1.2 years, just after injection into the borehole at the high rate begins (Case 1a: Base Case)

Fig. 7-6: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 2.4 years, just after injection into the borehole reduces to the lower rate (Case 1a: Base Case)
Fig. 7-7: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 6 years, the end of the simulation (Case 1a: Base Case).

Fig. 7-8: Volume fraction plot of minerals in the cells representing the gap between the cement and the borehole wall at 6 years, the end of the simulation (Case 1a: Base Case). Note: Scale of the y-axis is reduced.
The porosity distribution is shown in Figure 7-10, indicating increased porosity (dissolution) in the 0-90° upstream section and near the injection port (~170°, in the downstream section of the halfpipe).

The distribution of secondary minerals in the cement is shown in Figure 7-11. There are sparse amounts of 11Å-tobermorite (top Fig. 7.11), with more abundant gismondine (middle Fig. 7-11) and Ca-saponite (bottom Fig. 7-11), mainly in the 0-90° upstream half and near the injection port. This highlights a reduction in pH (~160°).

Figure 7-12 shows the evolution of the molality of H⁺ in the whole model from near 13 (dark blue areas) to approximately 10 (red areas) where dissolution of the cement has been modelled to occur.

The evolution of pH at four locations around the gap between the cement and the borehole wall is shown in Figure 7-13. This figure highlights the lowering of pH to ~10.5 at the upstream 1.8 and 82.6 degree positions after a relatively brief period of time (~<< 1 year), and a rapid reduction to ~9.8 at the downstream location near the port when injection begins, whereas pH is maintained at ~12.5 at the 97.5 degree position at all time periods. This position is located furthest from all sources of inflowing water; dissolution of the cement minerals is able to buffer the effects of the inflowing lower-pH water from the fracture and the injection into the borehole.

The evolution of a number of major elements (Ca, C, K, Mg, Na, Si, S and Al) in the aqueous phase at the gap between the cement and the borehole wall at four different positions (1.8, 82.6, 97.5 and 178.3 degrees) is a shown in Figure 7.14. Notable features in this diagram are that Ca broadly follows the pattern of pH shown in Figure 7.13 and that Mg concentrations are suppressed by high pH.
Fig. 7-10: Porosity distribution after 6 years
Note: The initial porosity of the cement was 0.5 (Case 1a: Base Case).
Fig. 7-11: Distribution of secondary minerals after 6 years (Case 1a: Base Case)
Fig. 7-12: Molality of H⁺ ions in the model at (a) 1.2 years, just after injection begins; (b) after 2.4 years, just after the injection rate is decreased; and (c) after 6 years, the end of the simulation.

Note: Dark blue indicates a pH of approximately 13, dark red a pH of approximately 10 (Case 1a: Base Case).
Fig. 7-13: Evolution of pH at four locations around the gap between the cement and borehole wall (Case 1a: Base Case)
Fig. 7-14: Evolution of ion concentrations in gap between cement and borehole wall (Case 1a: Base Case)
7.2.3 Case 1b - 2D slow diffusion

Figure 7-15 shows the volume fraction of minerals in the outer 1 mm ring of cement at the end of this simulation (6 years). Portlandite and ettringite have been totally removed, leading to an approximate halving of solid volume throughout this thin ring, but C-S-H gel end-members and monocarbonate are better preserved than in the analogous base case version (see Fig. 7-7), except at the injection location where alteration is similar to the base case.

Figure 7-16 shows mineral volume fractions in the gap between the cement and the borehole wall at the end of the simulation (6 years), revealing less precipitation of neoformed minerals than in the base case (Fig. 7-8), but proportionally more 11Å-tobermorite.

Figure 7-17 shows the volume fraction of minerals in the cement cells nearest the emplacement tool (these cells are approximately 4.5 mm thick) at the end of the simulation (6 years) and reveals much less alteration than the base case (Fig. 7-9).

Fig. 7-15: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 6 years, the end of the simulation (Case 1b: Slow Diffusion)
Fig. 7-16: Volume fraction plot of minerals in the cells representing the gap between the cement and the borehole wall at 6 years, the end of the simulation (Case 1b: Slow Diffusion)

Note: The scale of the y-axis is reduced.

Fig. 7-17: Volume fraction plot of minerals in the cement cells nearest the emplacement tool (cells are ~4.5 mm thick) at 6 years, the end of the simulation (Case 1b: Slow Diffusion)
Less alteration than in the base case is also mirrored in the porosity distribution after six years (compare Figs. 7-18 and 7-20), again except for the injection location, where the porosity reduction in both cases is similar.

The minor precipitation of secondary minerals (principally gismondine, a zeolite) for this slow diffusion case is mainly around the injection port (Fig. 7-19).

Figure 7-20 shows \( \text{H}^+ \) molality (pH) distribution in the halfpipe at 3 different simulation durations. The high pH in the gap is restricted to higher (downstream) angles compared to the base case since lower diffusion reduces the effects of diffusion out of the cement into the flowing gap. This explains why secondary minerals are more concentrated around the injection port. Similarly, the lower pH Grimsel water does not penetrate quite as far into the cement due to less diffusion and this is the reason for the reduced dissolution in the cement.

Figure 7-21 shows the evolution of pH around the gap. The slower diffusion conditions of this simulation mean a slower increase in pH, such that higher pH is now confined to a smaller part of the gap (cf. Fig. 7-13 for the base case).

Figure 7-22 shows the evolution of element concentrations in the gap between cement and the borehole wall with similar features to that for pH, i.e. slower build-up in concentrations as compared with the base case (Fig. 7-14).
Fig. 7-19: Distribution of secondary minerals after 6 years (Case 1b: Slow Diffusion)
a) **1.2 years**

Molality of H$^+$ ions in the model at (a) 1.2 years, just after injection begins; (b) after 2.4 years, just after the injection rate is decreased; and (c) after 6 years, the end of the simulation.

Note: Dark blue indicates a pH of approximately 13, dark red a pH of approximately 10 (Case 1b: Slow Diffusion).
Fig. 7-21: Evolution of pH at four locations around the gap between the cement and borehole wall (Case 1b: Slow Diffusion)
a) Ca

b) C

c) K
d) Mg

e) Na
f) Si

g) S
h) Al

Fig. 7-22: Evolution of ion concentrations in gap between cement and borehole wall (Case 1b: Slow Diffusion)
7.2.4  Case 1c - 2D slow kinetics

This simulation produces much less dissolution than the base case (compare Figs. 7-23 and 7-7). Some ettringite and portlandite dissolution leads to a small increase in porosity uniformly around the cells neighbouring the gap, which have a thickness of 1 mm. Small amounts of Ca-saponite and gismondine precipitates occur throughout the cement, but not in the gap itself.

Figure 7-24 shows the volume fraction of minerals in the cement cells nearest the emplacement tool at the end of the simulation (after 6 years), emphasising the reduced amount of dissolution of primary minerals and precipitation of neoformed minerals (mainly gismondine). The extent of dissolution is greatest near the gaps between the halfpipes.

Little dissolution is seen to be caused by the injected water in this case, in comparison to previous cases.

Fig. 7-23:  Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 6 years, the end of the simulation (Case 1c: Slow Kinetics)
The secondary mineral distribution for this simulation is shown in Figure 7-25; amounts are much less than the base case. Gismondine is evenly distributed, however.

Figure 7-26 shows the molality of H⁺ ions at three different times. pH is lower than the base case across the system (pH ~11), showing a more uniform distribution and little change with time. This is due to the slower buffering of the in-diffusing Grimsel water, caused by the slower mineral dissolution rates.

The evolution of pH at four locations around the gap between the cement and the borehole wall is shown in Figure 7-27. pH is generally lower than the base case, reflecting less dissolution of the cement phases.

Figure 7-28 shows the evolution of element concentrations in the aqueous phase in the gap between the cement and the borehole wall. Concentrations are lower than the base case, reflecting smaller amounts of dissolution in this simulation.
Fig. 7-25: Distribution of secondary minerals after 6 years (Case 1c: Slow Kinetics)
Fig. 7-26: Molality of H⁺ ions in the model at (a) 1.2 years, just after injection begins; (b) after 2.4 years, just after the injection rate is decreased; and (c) after 6 years, the end of the simulation.

Note: Light blue/cyan indicates a pH of approximately 12, dark red a pH of approximately 10 (Case 1c: Slow Kinetics).
Fig. 7-27: Evolution of pH at four locations around the gap between the cement and borehole wall (Case 1c: Slow Kinetics)
Fig. 7-28: Evolution of ion concentrations in gap between cement and borehole wall (Case 1c: Slow Kinetics)
7.2.5 Case 1d - 2D reduced fracture transmissivity

The results of this simulation show features characterised by greater dissolution of the cement minerals due primarily to flow being dominated by the injection process. The lower transmissivity of the fracture reduces the flux of injected water into the gap and out of the borehole and causes more injected fluid to flow through the cement, thus increasing dissolution (Fig. 7-29; cf. Fig. 7-7).

Due to the greater amount of cement dissolution, there is more Ca in solution, leading to precipitation of larger amounts of 11Å-tobermorite in the gap between the cement and borehole wall compared to the base case, as shown in Figure 7-30 (cf. Fig. 7-8).

The alteration extends deeper into the cement than in the base case, as demonstrated by the complete loss of portlandite in the cells nearest the emplacement tool, and the replacement of portlandite and C-S-H gel by Ca-saponite and gismondine near the emplacement tool (Fig. 7-31; cf. Fig. 7-9). The increase in porosity throughout the cement is shown in Figure 7-32 (cf. Fig. 7-10).

While 11Å-tobermorite precipitates in the gap between the cement and the borehole wall, gismondine and Ca-saponite appear throughout the downstream half of the cement and at the surface in the upstream half (Fig. 7-33). Both of these minerals appear in larger amounts than in the base case (Fig. 7-11).

The distribution of H$^+$ ions is shown in Figure 7-34 for three key points in time (just after injection begins, just after the injection rate is reduced, and at the end of the simulation). The lowering of pH to ~10 occurs in most of the downstream portion of the cement (cf. Fig. 7-12), reflecting the loss of cement minerals in this region. This is echoed in Figure 7-35 which shows the evolution of pH at four locations around the gap between the cement and the borehole wall; the pH at 97.5° was maintained at around 12.5 at this location in the base case (Fig. 7-13), but in this variant it has fallen to ~11 by the end of the simulation. However, the pH at 1.8° and 82.6° stays slightly higher than in the base case (where it is around 10.5 for most of the simulation); this is because of the higher heads in the borehole created by the injection, which act to slow the natural flow of water into this side of the borehole.

The evolution of the concentrations of elements in aqueous solution for this variant is shown in Figure 7-36 (cf. Fig. 7-14). At 178°, nearest the injection point, the results are very similar to the base case. In the upstream half of the gap (< 90°) there is more Ca and less Mg and S than in the base case, due to the reduced influence of the natural background water on this region than in the base case. At 98° there is less Ca, Mg and S and more Si and Al than in the base case, reflecting the loss of cement minerals here and the greater influence on the composition of the injected water.
Fig. 7-29: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 6 years, the end of the simulation (Case 1d: Reduced Transmissivity).

Fig. 7-30: Volume fraction plot of minerals in the cells representing the gap between the cement and the borehole wall at 6 years, the end of the simulation (Case 1d: Reduced Transmissivity).

Note: The scale of the y-axis is reduced.
Fig. 7-31: Volume fraction plot of minerals in the cement cells nearest the emplacement tool (cells are ~4.5 mm thick) at 6 years, the end of the simulation (Case 1d: Reduced Transmissivity)

Fig. 7-32: Porosity distribution after 6 years (Case 1d: Reduced Transmissivity)
a) **Tobermorite-11Å**

b) **Gismondine**

c) **Ca-Saponite**

Fig. 7-33: Porosity distribution after 6 years (Case 1d: Reduced Transmissivity)
a) **1.2 years**

Direction of natural flow

![Diagram showing molality of H+ ions after 1.2 years](image)

![Color legend](image)

Chem::Molality_Basis [mol/kg]

- 1.55e-010
- 3.27e-012
- 6.92e-014

b) **2.4 years**

Direction of natural flow

![Diagram showing molality of H+ ions after 2.4 years](image)

![Color legend](image)

Chem::Molality_Basis [mol/kg]

- 1.55e-010
- 3.27e-012
- 6.92e-014

c) **6 years**

Direction of natural flow

![Diagram showing molality of H+ ions after 6 years](image)

![Color legend](image)

Chem::Molality_Basis [mol/kg]

- 1.55e-010
- 3.27e-012
- 6.92e-014

**Fig. 7-34:** Molality of H+ ions in the model at (a) 1.2 years, just after injection begins; (b) after 2.4 years, just after the injection rate is decreased; and (c) after 6 years, the end of the simulation.

Note: Dark blue indicates a pH of approximately 13, dark red a pH of approximately 10 (Case 1d: Reduced Transmissivity).
Fig. 7-35: Evolution of pH at four locations around the gap between the cement and borehole wall (Case 1d: Reduced Transmissivity)
a) Ca  

b) C  

c) K  

d) Mg  

e) Na  

f) Si  

g) S  

h) Al  

Fig. 7-36: Evolution of ion concentrations in gap between cement and borehole wall (Case 1d: Reduced Transmissivity)
7.2.6 Case 1e - 2D slow kinetics and long-term evolution

This simulation addresses time periods longer than that investigated experimentally (up to 10 000 years) with the slow kinetics option. Injection at the slower rate (0.04 ml/min) is continued until the end of the simulation.

Figures 7-37 and 7-38 show that initially cement minerals dissolve and gismondine and Ca-saponite precipitate uniformly on the cement surface. After about 500 years, all the cement in this thin layer (1 mm) is removed and the Ca-saponite starts to dissolve, with gismondine and calcite precipitating. Stilbite (Na-Ca zeolite) precipitates in the gap between the halfpipes, coinciding with the point of injection. This reduces the porosity and hence the permeability; however, as a fixed rate of injection is imposed on the model, the same volume of water must flow through this restricted pore space. In reality, it would become more and more difficult to inject water at this rate into the borehole and injection would probably have to be halted.

After 10 000 years, gismondine, stilbite and calcite collectively occupy almost all the volume available from 140 to 180 degrees (note that a small amount of porosity, resp. 0.5 % is held open in the model, which allows the simulation to continue running and represents a small region of pore space that precipitating minerals do not fill, which may be particularly relevant if they are crystalline in nature due to the imperfect tessellation of crystals). The plot of porosity evolution in the cell adjacent to the injection point (Fig. 7-39) shows that this porosity clogging occurs at around 4 500 years.

All of the cement sees a similar pattern of alteration, thus plots for cells adjacent to the emplacement tool have not been included.

Figure 7-40 shows the evolution of minerals within the outer 1 mm of cement, at ~160°. This shows the timescales of dissolution of the primary cement minerals, and precipitation of calcite and gismondine throughout the simulation. Ca-saponite precipitates but subsequently dissolves, and stilbite only appears late in the simulation.
Fig. 7-37: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 100 years (Case 1e: Slow Kinetics and Long-Term Evolution)

Fig. 7-38: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick) at 10 000 years (Case 1e: Slow Kinetics and Long-Term Evolution)
Fig. 7-39: Evolution of porosity in the cell adjacent to the injection point (Case 1e: Slow Kinetics and Long-Term Evolution)

Fig. 7-40: Evolution of mineral concentration in cement located at ~160°, in outer ring
Stilbite also precipitates between the cement and the borehole wall, starting at about 4500 years, again occupying almost all of the volume around the injection point, between 140 and 180 degrees (Fig. 7-41 – as noted above, 0.5% of the volume is enforced as open porosity in the model). Large quantities also precipitate in the upstream half of the gap, 0-90°. In the downstream region far from the injection point, 90-140°, the pH is higher and the water composition not conducive to stilbite precipitation. The evolution of all minerals in the gap (at ~160°) is shown in Figure 7-42; as was seen in the cement itself, Ca-saponite initially precipitates but then dissolves in favour of stilbite.

pH is generally less than 10.5 throughout (Fig. 7-43), emphasising the short timescales over which the cement is dissolved in this model.

Fig. 7-41: Volume fraction plot of minerals in the cells representing the gap between the cement and borehole wall at 10 000 years (Case 1e: Slow Kinetics and Long-Term Evolution)
Fig. 7-42: Evolution of mineral concentration in gap located at ~160°

Fig. 7-43: Evolution of pH at four locations around the gap between the cement and borehole wall (Case 1e: Slow Kinetics and Long-Term Evolution)
7.2.7 Case 2a - 3D base case

The simulations in 3D emphasise the spatial sensitivity of the results much more than those carried out in 2D and suggest that the location of sampling (both the extraction of water samples during the experiment, and sampling of cement for analysis after overcoring) may have a significant impact on the ability to gain meaningful results from the experiment and facilitate comparisons with numerical models. The 3D simulations were run to 5 years, rather than the 6 years of the 2D cases, as they are significantly more expensive computationally, and 5 years was the original planned timescale of the LCS experiment.

Figure 7-3 shows the layout of the 3D model; note that the system has been rotated through 180° so that the gap at the foot of the borehole appears at the top, and the intersection with the fracture at the bottom, in the figures in this section. This allows the alteration near the fracture intersection to be viewed.

Figure 7-44 shows the distribution of $\text{H}^+$ molality along the halfpipe at the end of the simulation (5 years) and reveals a broadly uniform high pH ($\geq 13$), but with a lower pH (~10) adjacent to the injection port. This is consistent with the 2D model (see Fig. 7-12).

This heterogeneity of chemical conditions is also highlighted by the 3D representation of secondary minerals (Fig. 7-45 – 11Å-töbermorite; Fig. 7-46 – gismondine; Fig. 7-47 – Ca-saponite). 11Å-töbermorite is concentrated along the longitudinal edges of the halfpipe, whereas gismondine and Ca-saponite form adjacent to the borehole wall near the fracture. These minerals are the same as those predicted by the 2D model (cf. Fig. 7-11), but here the 3D model is more informative about the spatial distribution of the precipitation. The porosity evolution is also heterogeneous (Fig. 7-48), increasing to 0.7 in much of the cement adjacent to the various gaps, and approaching 1 in the outer upstream cells at the fracture intersection. These results indicate that the 2D model over-predicts the increase in porosity in the cement (Fig. 7-10), as the 3D model shows much of the cement that is not adjacent to a gap is largely unaltered. This would be expected, since the 2D model constrains all reaction caused by the inflowing and injected waters to occur in a narrower band of the cement.
Fig. 7-44: Molality of H$^+$ ions in the model at 5 years, the end of the simulation
Note: Dark blue indicates a pH of approximately 13, dark red a pH of approximately 10 (Case 2a: Base Case).

Fig. 7-45: Distribution of tobermorite-11Å after 5 years (cells representing gap between cement and borehole wall are included in left-hand plot; Case 2a: Base Case)
Fig. 7-46: Distribution of gismondine after 5 years (cells representing gap between cement and borehole wall are NOT included in left-hand plot; Case 2a: Base Case)

Fig. 7-47: Distribution of Ca-saponite after 5 years (cells representing gap between cement and borehole wall are NOT included in left-hand plot; Case 2a: Base Case)
Dissolution features across the halfpipe vary slightly, showing removal of portlandite and most of the jennite C-S-H gel end-member (Figs. 7-49, 7-50, 7-51) in the outer cement cells (1 mm thick), but both these minerals are preserved in varying amounts in the cement cells nearest the emplacement tool (Figs. 7-55, 7-56, 7-57; these cells are approximately 4.5 mm thick).

However, secondary mineral distributions vary more:

- minor amounts of Ca-saponite, gismondine and 11Å-tobermorite occur in the cement at the end nearest the fracture (Fig. 7-51);

- 11Å-tobermorite dominates the assemblage in the cells representing the gap between the cement and the borehole, at the end nearest the void space (Fig. 7-52) and at the same borehole location as the injection point (Fig. 7-53), although the actual precipitated amounts are small (<2% volume);

- Ca-saponite dominates in the cells representing the gap between the cement and the borehole, at the end nearest the fracture (Fig. 7-54). Here the precipitated amount is greater than at the end near the void space (up to 10% volume).

Significant variation is shown in pH according to the online sampling location (Fig. 7-58), with pH low (10 - 10.5) but increasing with time at the upstream location (1.8°) near the fracture, whereas pH is high (12.5 - 13.0) at other locations and generally decreases when injection begins, although the drop varies greatly, with pH being 10.5 to 12.5 during this period. There is a slight rise in pH at most locations when injection is slowed, but again a large spread in values (11 to 12.5 and higher). The highest pH is generally retained along the centre position, i.e. 104.9°. Concentrations of ions (Fig. 7-59) also vary greatly with sampling location in many cases. This spatial variation is not captured by the 2D model (see Fig. 7-14) but the range of concentrations is similar in both models.
Fig. 7-49: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick), at the end nearest the void space, at 5 years, the end of the simulation (Case 2a: Base Case)

Fig. 7-50: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick), at the same borehole location as the injection point, at 5 years, the end of the simulation (Case 2a: Base Case)
Fig. 7-51: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick), at the end nearest the fracture, at 5 years, the end of the simulation (Case 2a: Base Case)

Fig. 7-52: Volume fraction plot of minerals in the cells representing the gap between the cement and the borehole, at the end nearest the void space, at 5 years, the end of the simulation (Case 2a: Base Case)

Note: The scale of the y-axis is reduced
Fig. 7-53: Volume fraction plot of minerals in the cells representing the gap between the cement and the borehole, at the same borehole location as the injection point, at 5 years, the end of the simulation (Case 2a: Base Case)

Note: The y-axis scale is reduced.

Fig. 7-54: Volume fraction plot of minerals in the cells representing the gap between the cement and the borehole, at end nearest the fracture, at 5 years, the end of the simulation (Case 2a: Base Case)

Note: The y-axis scale is reduced.
Fig. 7-55: Volume fraction plot of minerals in the cement cells nearest the emplacement tool (cells are ~4.5 mm thick), at end nearest the void space, at 5 years, the end of the simulation (Case 2a: Base Case)

Fig. 7-56: Volume fraction plot of minerals in the cement cells nearest the emplacement tool (cells are ~4.5 mm thick), at the same location as the injection point, at 5 years, the end of the simulation (Case 2a: Base Case)
Fig. 7-57: Volume fraction plot of minerals in the cement cells nearest the emplacement tool (cells are ~4.5 mm thick), at end nearest the fracture, at 5 years, the end of the simulation (Case 2a: Base Case)

Fig. 7-58: Evolution of pH in the gap between the cement and borehole wall, at 3 locations along the borehole (near the fracture, near the injection point, and near the void), and 3 angular points at each location (Case 2a: Base Case)
Fig. 7-59: Evolution of ion concentrations in the gap between the cement and borehole wall, at 3 locations along the borehole (near the fracture, near the injection point, and near the void), and 3 angular points at each location (Case 2a: Base Case)
7.2.8 Case 2b - 3D slow kinetics

As with the 2D case, this simulation with slower cement mineral kinetics results in less dissolution. The molality of H$^+$ ions at 5 years is shown in Figure 7-60. Comparing this to the 3D base case (Fig. 7-44), it is clear that the pH in this case is lower due to the decreased dissolution. This echoes the findings of the 2D modelling (see section 7.2.4).

Figure 7-61 shows the distribution of gismondine after 5 years; Figure 7-62 shows Ca-saponite (note the difference in the scales used on the legends compared to the equivalent plots for the base case, Figs. 7-46 and 7-47). Tobermorite is not shown because there is barely any at 5 years; prior to injection, small amounts precipitate in the gap between the cement and borehole wall but it subsequently dissolves. The spatial extent of gismondine and Ca-saponite is greater in this case than in the base case, although they do not precipitate in such quantities. Because of the small quantity of secondary minerals, changes to porosity in this case are much more uniform than in the 3D base case. Porosity in the outer cement cells increases but remains less than 0.6.

Fig. 7-60: Molality of H$^+$ ions in the model at 5 years, the end of the simulation
Note: Dark blue indicates a pH of approximately 13, dark red a pH of approximately 10 (Case 2b: Slow Kinetics)
Fig. 7-61: Distribution of gismondine after 5 years (cells representing gap between cement and borehole wall are NOT included in left-hand plot; Case 2b: Slow Kinetics)

Fig. 7-62: Distribution of Ca-saponite after 5 years (cells representing gap between cement and borehole wall are NOT included in left-hand plot; Case 2b: Slow Kinetics)
A volume fraction plot of the minerals in the cement cells nearest the gap (thickness 1 mm), at the end nearest the fracture is shown in Figure 7-63; the mineral assemblages at the void end and the point where the injection port is located look more or less identical and are not shown. There is little dissolution of the cement minerals, and some precipitation of gismondine. This is also the case in the cement nearest the emplacement tool, although there is of course less dissolution there and consequently even smaller amounts of gismondine. There is no precipitation in the gap between the cement and the borehole wall in this case.

The pH evolution is shown in Figure 7-64, and total concentrations of ions in Figure 7-65. As with the base case, there is great variation in the results for many of the species depending on the sampling location.

Fig. 7-63: Volume fraction plot of minerals in the cement cells nearest the gap (cells are 1 mm thick), at the end nearest the fracture, at 5 years, the end of the simulation (Case 2b: Slow Kinetics)
Fig. 7-64: Evolution of pH in the gap between the cement and borehole wall, at 3 locations along the borehole (near the fracture, near the injection point, and near the void), and 3 angular points at each location (Case 2b: Slow Kinetics)
Fig. 7-65: Evolution of ion concentrations in the gap between the cement and borehole wall, at 3 locations along the borehole (near the fracture, near the injection point, and near the void), and 3 angular points at each location (Case 2b: Slow Kinetics)
### 7.2.9 Summary of model results

Tab. 7-14: Summary of model results

<table>
<thead>
<tr>
<th>Model Variant</th>
<th>Key Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a: 2D Base Case</td>
<td>• Increase in porosity in cement (final porosity &gt; 0.6; maximum ~ 0.95)</td>
</tr>
<tr>
<td></td>
<td>• Dissolution of portlandite, ettringite, C-S-H</td>
</tr>
<tr>
<td></td>
<td>• Conversion of CSH-jennite to CSH tobermorite</td>
</tr>
<tr>
<td></td>
<td>• Precipitation of gismondine and Ca-saponite (C-A-S-H) on outer surface of cement and near injection port. Small amounts of tobermorite (C-S-H).</td>
</tr>
<tr>
<td></td>
<td>• pH varies by location; between ~12.5 and ~10</td>
</tr>
<tr>
<td>1b: 2D Slow Diffusion</td>
<td>• Increase in porosity in cement (profile into cement; ~ 0.7 in outer region)</td>
</tr>
<tr>
<td></td>
<td>• Dissolution of portlandite, ettringite, C-S-H in outer cement (2–3 mm)</td>
</tr>
<tr>
<td></td>
<td>• Conversion of CSH-jennite to CSH tobermorite in outer cement (1–2 mm)</td>
</tr>
<tr>
<td></td>
<td>• Precipitation of gismondine and Ca-saponite (C-A-S-H) near injection port. Small amounts of tobermorite (C-S-H).</td>
</tr>
<tr>
<td></td>
<td>• pH varies by location; between ~ 11.5 and ~ 10</td>
</tr>
<tr>
<td>1c: 2D Slow Kinetics</td>
<td>• Small increase in porosity in cement (to ~ 0.55)</td>
</tr>
<tr>
<td></td>
<td>• Small amount of dissolution of portlandite, ettringite, C-S-H throughout cement</td>
</tr>
<tr>
<td></td>
<td>• Precipitation of gismondine and Ca-saponite (C-A-S-H) throughout and near injection port</td>
</tr>
<tr>
<td></td>
<td>• pH varies only slightly by location; between ~10.5 and ~10</td>
</tr>
<tr>
<td>1d: 2D Reduced Transmissivity</td>
<td>• Large increase in porosity in cement (&gt; 0.7; maximum ~ 0.95)</td>
</tr>
<tr>
<td></td>
<td>• Dissolution of portlandite, ettringite, C-S-H</td>
</tr>
<tr>
<td></td>
<td>• Conversion of CSH-jennite to CSH tobermorite</td>
</tr>
<tr>
<td></td>
<td>• Precipitation of gismondine and Ca-saponite (C-A-S-H) on outer cement surfaces and throughout near injection port. Small amounts of tobermorite (C-S-H) on surface.</td>
</tr>
<tr>
<td></td>
<td>• pH varies by location; between ~12.5 and ~ 10</td>
</tr>
<tr>
<td>1e: 2D Slow Kinetics and Long-Term Evolution</td>
<td>• Stilbite (Na-Ca zeolite) precipitates in gap and near injection point; pore clogging at the injection point occurred after ~4500 years.</td>
</tr>
<tr>
<td></td>
<td>• Gismondine and calcite precipitation on surface of cement</td>
</tr>
</tbody>
</table>
Tab. 7-14: Summary of model results (continued)

<table>
<thead>
<tr>
<th>Model Variant</th>
<th>Key Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a: 3D Base Case</td>
<td>• Large spatial variations in porosity, secondary minerals, cement dissolution and porewater chemistry</td>
</tr>
<tr>
<td></td>
<td>• Increase in porosity in cement (profile into cement; ~0.7 in outer region)</td>
</tr>
<tr>
<td></td>
<td>• Dissolution of portlandite, ettringite, C-S-H in outer cement (up to ~4 mm) and in deeper layers near fracture and void space</td>
</tr>
<tr>
<td></td>
<td>• Conversion of CSH-jennite to CSH tobermorite in outer cement layers (~1 mm) and near fracture, particularly at fastest inflow and</td>
</tr>
<tr>
<td></td>
<td>outflow regions</td>
</tr>
<tr>
<td></td>
<td>• Precipitation of gismondine and Ca-saponite (C-A-S-H) near fracture intersection</td>
</tr>
<tr>
<td></td>
<td>• Tobermorite (C-S-H) precipitation near fracture intersection, gaps between halfpipes and void space</td>
</tr>
<tr>
<td></td>
<td>• pH varies greatly by location; between ~12.5 and ~11</td>
</tr>
<tr>
<td>2b: 3D Slow Kinetics</td>
<td>• Large spatial variations in secondary minerals and porewater chemistry</td>
</tr>
<tr>
<td></td>
<td>• Increase in porosity in cement (profile into cement; &lt;0.6 in outer region)</td>
</tr>
<tr>
<td></td>
<td>• Small amounts of dissolution of portlandite, ettringite, C-S-H throughout; more dissolution near fracture and void space</td>
</tr>
<tr>
<td></td>
<td>• Precipitation of gismondine and Ca-saponite (C-A-S-H); gismondine in small quantities throughout cement and particularly on surface;</td>
</tr>
<tr>
<td></td>
<td>Ca-saponite near fracture intersection and void space</td>
</tr>
<tr>
<td></td>
<td>• pH varies greatly by location; between ~12 and ~10</td>
</tr>
</tbody>
</table>

7.3 Conclusions

During this study carried out as part of the LCS project, ‘blind’ reactive transport models of LCS Experiment 2 have been developed. The experiment, which ran for 6 years at the Grimsel Test Site, involved insertion of pre-hardened cement into a borehole, drilled to intersect a fracture plane. The aim of the experiment was to obtain information on how the alkaline plume resulting from interaction between the cement and natural groundwater moved through the fracture. The models were developed using only data from the experimental setup and tracer tests; no chemical analysis data were used to fit parameters or guide selection of species. This blind modelling is a test of both the geochemical models and general understanding of cement interactions and rock transport pathways that informs such models. At a later date, the intention is to compare the model results with data obtained from the experiment, and, if differences exist, to use the experimental data to further improve and refine the models.

The modelling described in this report aimed only to consider alteration of the cement source; modelling of the movement of the alkaline plume through the fracture is reported separately. The results of the present study will be used to inform the larger model, having provided information
on the amount and types of secondary minerals expected to precipitate. The modelling demonstrates a capability to simulate the fine details of in-situ experiments at a high spatial resolution, with complex geometry and chemistry (including aqueous species and mineral kinetics).

A two-dimensional model was considered first, representing the area of cement nearest to the fracture intersection. A 2D model such as this is not a realistic representation of the system, as the water injected into the borehole has less volume to pass into and a lot less cement to interact with; however it could be considered conservative in that it would represent areas of the cement where the most alteration might be expected in the worst case scenarios. The advantage of the 2D model is that it runs fairly quickly (within a matter of hours) and can therefore be used to explore model sensitivities. Model variants were run considering alternative diffusion coefficients, kinetic rates and fracture transmissivity.

While the 2D simulations capture the broad trends of chemical evolution, they do not allow investigation of the spatial distribution of changes. A more realistic 3D model was therefore subsequently developed. This provides the most relevant results but is computationally expensive (running for the order of weeks) and therefore only the base case and one variant, with slower kinetic rates, were considered.

Some general features were apparent across all the models:

- Dissolution effects saw the preferential removal of portlandite, ettringite and the jennite C-S-H gel end-member (with conversion to the tobermorite C-S-H end member).
- Alteration minerals were principally 11Å­tobermorite (a low solubility crystalline C-S-H mineral), gismondine (Ca-zeolite; a proxy for C-A-S-H) and Ca saponite (smectite clay).
- 3D simulations demonstrated that the secondary minerals form in different locations:
  - Tobermorite forms between the longitudinal arms of the cement halfpipes, at the base of the borehole and near the point where the fracture intersects.
  - Gismondine and Ca-saponite form mainly at the edges of the intersection with the fracture.
- The base cases emphasise dissolution of the cement minerals and increase in pH in the borehole, except around the injection port where a lower pH is maintained.

One of the 2D simulations was run for an extended period, up to 10 000 years, a time period more relevant to the disposal of radioactive waste. At these longer timescales, stilbite (Na-Ca zeolite) precipitated abundantly, along with calcite and gismondine (C-A-S-H). Pore blocking was seen to occur within 5000 years at points where the natural groundwater flowed into the borehole.

The following observations were made from the variant cases considered:

- The slower diffusion case produced more secondary minerals around the injection port.
- The slower kinetic rate case produced less alteration and consequently the pH was lower; this precluded the precipitation of 11Å­tobermorite (C-S-H).
- The reduced transmissivity case resulted in greater dissolution, due to the dominance of the injection of water into the borehole compared to the natural flow through the fracture.

Comparison with the experimental results should hopefully give indications of which scenarios are the most realistic.

The 3D models indicated that there may be a great deal of spatial variability in the experiment. However, the real system may be better mixed than the model due to the number of tracer tests that were carried out during the lifetime of the experiment, which involve circulation of water
within the emplacement borehole and were not taken into account in the modelling presented here. This will be an interesting comparison to make once data from the lab analysis are available. Unfortunately, the orientation of the emplacement tool was not recorded at the start of the experiment, and this could be an important factor in predicting the spatial variability. If future experiments of a similar type are conducted, it would be helpful if the conditions could be recorded with greater rigour. This also extends to characterisation of the cement itself; retention of a sample for analysis to provide “virgin” conditions would have been of great help to the modelling.

In summary, in order to make comparisons with the present modelling, it would be helpful if the following information could be made available from the dismantling of the experiment and its subsequent analysis (which is just beginning at the time of writing):

- Porewater compositions over time – these data have been collected over the lifetime of the experiment. The position of the sampling point might be important.
- Porosity changes in the cement at several locations (primarily near the fracture intersection, near the injection port, and at a location away from these features).
- Analysis of mineralogical changes within the cement, again at several locations as described above.
- Orientation of the emplacement tool in the borehole, relative to the natural flow.
- Clarification of the alignment of the cement halfpipes relative to the injection ports, particularly the port used for long-term injection (port P).
- Information about flow in the fracture, particularly whether it appears to be channelled rather than uniformly planar.

The final bullet point relates to the possibility of channelled flow within the fracture, which has not been investigated in the present modelling study but is expected to play an important role in the modelling of the whole fracture system. If flow is confined to channels, it may result in more localised alteration in the emplacement borehole, and, in the longer term, mineral precipitation may cause the channel to become blocked; in the wider fracture, it may be important in understanding the spatial extent of the hyperalkaline plume and determining the strength of signal expected at the monitoring points in the fracture system. In particular, the hyperalkaline plume might be expected to extend further into the fracture if the degree of channelling is significant.
8 QUINTESSA (RWM) - Geochemical modelling of the LCS experiment

The blind modelling of the cement source in the emplacement borehole undertaken by the RWM team has been previously reported in Watson et al. (2016a; Section 7). Here, the results of that modelling are compared against available data produced by the analysis of samples taken from the experiment. The changes made to the model in light of the experimental results are discussed and the updated modelling results reported and compared again to the data from the experiment. A model of the wider fracture plane, aiming to simulate the movement of the high-pH plume through the host rock, is also described and compared against the available data. The aim of the modelling described here is to replicate the main characteristics and broad trends of the experiments, in order to demonstrate a predictive capability that could be transferred to other similar systems. There is little truly quantitative information from the experiment, making a detailed critique of the modelling impossible, but a more general quantitative comparison is possible.

The remainder of this chapter is structured as follows:
- In section 8.1, modelling of the cement source in the emplacement borehole is described.
- In section 8.2, modelling of the movement of the hyperalkaline plume through the fracture plane is presented and conclusions are drawn.
- In section 8.3, a discussion of the modelling approach and results is presented.
- In section 8.4, the Hong & Glasser model of alkali release is presented.

This study has already been reported by Watson et al. (2017).

8.1 Evolution of the cement source

8.1.1 Previous modelling

Blind modelling of the evolution of the cement source is described by Watson et al. (2016a; Section 7). The model concentrated on the chemical evolution of the cement source inserted into the fracture via the emplacement borehole over a five-year time period (the initial planned duration of the experiment). Details from the experimental setup, such as the geometric arrangement of boreholes, physical properties of the various materials used and so on, were used to construct the blind model. Information from pre-emplacement tracer tests was also used to help quantify the physical nature of the undisturbed fracture system and flow field. However, no information gathered while the experiment was in progress or subsequent to its completion was used to parameterise or calibrate the model in other ways. In this way, the predictive capability of the model could be tested, and current understanding of cement interactions in a geological disposal facility can be evaluated.

Watson et al. (2016a) considered both two- and three-dimensional models. Here only the 3D model is summarised, as it gives information about the spatial distribution of alteration that cannot be obtained from the 2D model, and it is the 3D model that has been carried forward in the additional modelling work described here. The modelling domain and discretisation are shown in Figure 7-3. The cement shells and the gaps between adjacent shells and between the shells and the fracture wall are explicitly included in the model. The metal emplacement tool, to which the shells were attached, is modelled with an impermeable boundary condition, as is the rock surrounding the borehole, except for the intersection point with the fracture, where a constant head gradient is
applied. In reality, the rock is slightly permeable (albeit with a very small porosity <1%), and reactions with the surface will occur, but it is assumed that these will be minor compared to the cement reactions.

The model is discretised rather coarsely, although greater refinement is included on the outer edge of the cement and around the injection point and the fracture intersection. This coarseness is a constraint of the 3D model, which is extremely expensive computationally (a model run taking in the order of weeks to complete; it is noted that 3D models of complicated chemical systems are not often attempted for this very reason), but is deemed sufficient for the purposes of the modelling undertaken here. Indeed, the samples of cement taken for analysis were not on a particularly fine scale, so more refinement in the model would not provide information that could be compared to real data.

During overcoring of the borehole, it was discovered that there was some additional volume in the borehole beyond the end of the interval that had not been recorded (Lanyon & Mäder, 2020). Although, as discussed previously, the modelling was to be carried out ‘blind’, this information was incorporated into the model as it was considered to fall into the category of experimental setup data, and the influence of the extra volume could strongly affect the model results. This extra volume has been included as a cylinder, rather than the annulus and wedge that it is in reality, because these shapes are rather difficult to model. The shape of the extra volume is not considered to be an important factor in the model because it is completely open and well-connected.

The blind model included aqueous reactions and kinetics were used to represent mineral dissolution and precipitation. A Kozeny-Carman type relationship between porosity and permeability was adopted, and Archie’s Law used to couple changes in porosity to diffusion.

Full results of the blind modelling work can be found in Watson et al. (2016a; Section 7), but the main conclusions were as follows:

- Dissolution effects saw the preferential removal of portlandite, ettringite and the jennite C-S-H gel end-member (with conversion to the tobermorite C-S-H end member) from the cement, with greater dissolution on the outer edge of the cement adjacent to the gap (Fig. 8-1). (Note that the C-S-H gel was modelled as an ideal solid-solution comprising compositional ‘jennite-like’ and ‘tobermorite like’ end-members).

- Alteration minerals were principally 11Å-tobermorite (a low solubility crystalline C-S-H mineral), gismondine (a Ca-zeolite mineral, included as a proxy for solid C-A-S-H), and Ca-saponite (a smectite clay).

- The alteration minerals formed in distinct locations and were not uniformly distributed:
  - Tobermorite formed in the gaps between the two cement halfpipes, at the base of the borehole and near the point where the fracture intersects (Fig. 7-45);
  - Gismondine (Fig. 7-46) and Ca-saponite (Fig. 7-47) formed mainly at the edges of the intersection with the fracture.

- There was an increase in pH in the borehole (>12), except around the injection port where a lower pH was maintained (11–11.5)
a) **Porosity** (initial value 0.5)

![Porosity Distribution Diagram]

b) **Portlandite**

![Portlandite Distribution Diagram]

Fig. 8-1: Section through the centre of the cement shell showing porosity (top) and portlandite (bottom) distribution after 5 years (cells representing gap between cement and borehole wall NOT shown) – Base Case of Watson et al. (2016a; chapter 7)

### 8.1.2 Comparison of blind model with laboratory analysis

A qualitative comparison between the key findings of the laboratory analysis (see section 2.2.2 for further details) and the results of the blind modelling reported by Watson et al. (2016a; Section 7) is given in Table 8-1. In general, the results of the model match the observations well, considering that the exercise was carried out ‘blind’. Characteristics such as a leached zone where all portlandite was removed, C-S-H gel was decalcified and porosity increased were replicated qualitatively. It is clear from this comparison that the model where a slower dissolution rate for the cement minerals was assumed (seven orders of magnitude smaller than the base case) did not produce a good fit to the observations.
One large difference between the models and the observations is the presence of calcite. No calcite precipitation occurred in any of the model variants, but this was the main precipitate observed in the laboratory analysis. Interrogation of the models reveals that calcite was oversaturated but kinetically limited due to a non-linear dependence on the pH (see section 7.1.4.5 for details of the kinetic rate adopted for calcite).

Another smaller difference is the spatial distribution of alteration in the borehole. The 3D model provides the opportunity to investigate this aspect in detail. While some attempt was made to take samples from the cement shells from various locations (see section 2.2.2), there was not much emphasis on this aspect, and the distribution of samples was rather rough. In particular, no information was recorded about the spatial distribution of precipitates. However, it is possible that the model is less well mixed than reality because no attempt was made to account for recirculation that occurred during the numerous tracer tests that were conducted during the lifetime of the experiment.

In addition to the qualitative comparisons made in Table 8-1, a more quantitative comparison can be made against the porewater compositions measured in the emplacement borehole during the experiment. This comparison is complicated by the inhomogeneous nature of the porewater composition in the model; for example, the pH can be 12.5 in one location (e.g. at the outflowing fracture) and 11 in another (e.g. near the injection point) at the same time (see Watson et al., 2016a; Section 7). Here, the comparison point is taken to be at the point where the water flows out of the borehole via the fracture. This point is selected because it is furthest away from both the injection port and the inflowing fracture in the model, and is thus less influenced by fresh Grimsel water, in addition to being the only extraction point in the model. The pH comparison is shown in Figure 8-2, and the other aqueous species in Figure 8-3. Crucially, measured values from the borehole are not available from the period when the highest injection rates occurred (between approximately 1.2 and 2.4 years), corresponding to the period when the models simulating fast and slow kinetics respectively tend to diverge by the greatest amount.

Noting that there is uncertainty in the measured data, which is not indicated on the plots included in this report, the fit between the blind model and the measured data is reasonable in some cases (e.g. pH, dissolved Ca, Al, Si concentrations). Here a ‘reasonable fit’ means that the general trends are captured by the model and the concentrations are of the same order of magnitude. The ‘alkalis’ (Na and K) stay at the Grimsel background level in the model, but observations show a sharp increase at the start of the experiment followed by a gradual fall-off back to the background level. This is not captured by the model because an assumption is made that alkalis are released rapidly from the cement and washed away quickly. On the long timescales of interest to performance assessment modelling, this is an appropriate assumption, but on the comparatively short timescales relevant to the LCS experiment clearly this is an important effect missed by the model.

Other species where a poor fit occurs are Mg, Cl, and S. The poor fit could either be caused by an incorrect assumption about the background Grimsel porewater, or by a mismatch in mineral precipitation/dissolution.
Tab. 8.1: Comparison of the key findings from the laboratory analysis of LCS Experiment 2 and the results of the blind modelling exercise reported by Watson et al. (2016a; chapter 7)

<table>
<thead>
<tr>
<th>Key Findings from Laboratory Analysis</th>
<th>Results of Blind Modelling</th>
<th>Comments</th>
</tr>
</thead>
</table>
| Leached zone in cement adjacent to any surface exposed to water, characterised by total loss of portlandite. | **Fast Cement Kinetics**
Portlandite totally removed from outer cement layers. Thickness of leached layer greater than observation suggests. | **Slow Cement Kinetics**
Very little loss of portlandite. | The model did not include a gap between the emplacement tool and the cement shells. Including this gap would have allowed the portlandite to be removed from both sides of the shell. |
| Higher porosity in leached zone (possibly 10% higher than unleached zone, but difficult to quantify); sharp interface between leached/unleached zones. | Increase in porosity in outer cement layers (difference between initial/unleached porosity of up to 20%). | Increase in porosity in outer cement layers (difference up to 10%). | The sharp interface between leached/unleached zones represents a reaction front travelling into the cement. |
| Decalcification of C-S-H at the surface of the leached zone. | Conversion of jennite-like C-S-H end-member (high Ca/Si ratio) to tobermorite-like C-S-H end-member (low Ca/Si ratio) in outer cement layers. | Little conversion between C-S-H end-members. |
| Amount of leaching throughout borehole is heterogeneous but cannot be attributed to proximity to injection port or fracture intersection. Overriding factor appears to be thickness of adjacent gap between cement and borehole wall. | Large spatial variation in porosity and cement dissolution, according to proximity to injection port and fracture inflow (which promote dissolution). | Little spatial variation in porosity and cement dissolution, due to lack of reaction. | The amount of mixing may have been greater in reality than in the model, in part due to recirculation that occurred during the tracer tests. |
| Precipitation on shell surfaces and emplacement tool primarily calcite with some C-S-H gel and vaterite. Quartz, feldspar and mica also identified. | Tobermorite (C-S-H) precipitation at fracture intersection, near injection port and in gaps between shells. Gismondine (C-A-S-H proxy mineral) and Ca saponite precipitation near fracture intersection. | Gismondine (C-A-S-H proxy mineral) precipitates in small amounts on shell surface. Ca-saponite precipitates near fracture intersection. | No spatial variation in the precipitates was recorded in the laboratory analysis, but no information on where on the shells or the tool the samples were taken from can be found. It is likely that samples were only collected from a single location. Calcite did not precipitate in any of the model variants, despite being the most abundant secondary mineral observed by the laboratory analysis. |

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Tab. 8.1: Comparison of the key findings from the laboratory analysis of LCS Experiment 2 and the results of the blind modelling exercise reported by Watson et al. (2016a; chapter 7)
Fig. 8-2: Evolution of pH in the emplacement borehole, comparing the results of the blind modelling reported by Watson et al. (2016a) with the measured values.  

Note: The model cases are as follows: (a) fast cement kinetics; and (b) slow cement kinetics (see Tab. 8-4 for rates used). The assumed background Grimsel pH for the model is also shown for reference.
Fig. 8-3: Evolution of aqueous species in the emplacement borehole, comparing the results of the blind modelling reported by Watson et al. (2016a) with the measured values (these figures are new for this report)

Note: The model cases are as follows: (a) fast cement kinetics; and (b) slow cement kinetics. The assumed background Grimsel concentration for the model is also shown for reference.
8.1.3 Updates of the model following analysis

Following the comparison between the blind model of Watson et al. (2016a; Section 7) and the results of the LCS experiment, some changes were made to the model and new results generated. The multi-purpose modelling tool QPAC (Quintessa, 2013) was used for this exercise, as in previous modelling.

Firstly, the variant with fast cement kinetics was retained as the base case as it was demonstrated that this produced the best qualitative fit to the data (in particular the mineralogical alterations within the cement). The simulation time was extended to 6 years to correspond to the final timescales of the LCS experiment.

Next, the Grimsel groundwater composition was reassessed and some changes made. These are given in Table 8-2. The potassium (K) and bicarbonate (HCO$_3^-$) concentrations were increased to better reflect the groundwater composition measured at Grimsel during the LCS experiment (in the case of K, the increase was by two orders of magnitude). As a consequence, the sodium (Na) concentration was also increased to allow for charge balance, and calcium (Ca) and pH were decreased slightly to avoid supersaturation of aluminosilicates/carbonates. This new composition was used in the base case and all variants considered. A representative measured composition of Grimsel porewater (derived from Schneeberger et al., 2017) is given for comparison in Table 8-2. Note that this is unrelated to the LCS experiment but illustrates the validity of the modelling assumptions.

The initial cement porewater was also updated, based on the updated Grimsel groundwater composition and updating the original PHREEQC calculation, which meant the C-S-H solid solutions were inaccurately simulated during the equilibration process. However, the initial cement porewater is soon displaced in an advective system such as the one modelled here, so the exact composition assumed has very little bearing on the results of the model and does not change the conclusions of Watson et al. (2016a; Section 7). The original and updated compositions are given in Table 8-3. Again, the new composition is used in the base case and all variants considered.

In order to address the issue of calcite precipitation (or lack thereof), a variant case was considered where the non-linear dependence on pH was removed in the expression for the kinetic rate of calcite, essentially modelling precipitation and dissolution of this mineral as an approximately equilibrium process. As this had the potential to accelerate dissolution of other cement minerals, notably portlandite, the slow cement kinetics variant of Watson et al. (2016a; Section 7) was retained and combined with the calcite equilibrium assumption to produce a third variant.

Finally, the release of alkalis from the cement was addressed by a variant case in which the Hong & Glasser (1999) model of alkali release was implemented (see section 8.4 for details). This was combined with the calcite equilibrium assumption.

Other changes that could have been made included incorporating a gap between the cement shells and the emplacement tool. However, this would add additional complexity to the model in terms of requiring additional cells and potentially increased cell refinement within the cement, which would increase run times even further. As run times are already very long (approximately 4 weeks), this modification was not made. Making this change to the model would not bring any more understanding to the problem in terms of the mineralogical changes expected, as the chemical alteration on both sides of the cement appears to be identical (see section 2.2.2).
Tab. 8-2: Grimsel groundwater composition assumed by Watson et al. (2016a) in the blind modelling exercise and the updated composition assumed here

Note: A representative measured composition (not related to the LCS experiment) is given for comparison.

<table>
<thead>
<tr>
<th>Species</th>
<th>Old Value (mol kg⁻¹)</th>
<th>New Value (mol kg⁻¹)</th>
<th>Schneeberger et al. (2017) Derived Composition (mol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.81</td>
<td>9.75</td>
<td>9.4 – 9.78</td>
</tr>
<tr>
<td>Al</td>
<td>1.00 × 10⁻⁷</td>
<td>1.00 × 10⁻⁷</td>
<td>2.96 × 10⁻⁷ – 5.93 × 10⁻⁷</td>
</tr>
<tr>
<td>Ca</td>
<td>1.40 × 10⁻⁴</td>
<td>1.01 × 10⁻⁴</td>
<td>1.36 × 10⁻⁴ – 1.69 × 10⁻⁴</td>
</tr>
<tr>
<td>Cl</td>
<td>2.20 × 10⁻⁴</td>
<td>5.00 × 10⁻⁵</td>
<td>4.26 × 10⁻⁵ – 5.64 × 10⁻⁵</td>
</tr>
<tr>
<td>C</td>
<td>2.00 × 10⁻⁴</td>
<td>4.00 × 10⁻⁴</td>
<td>6.41 × 10⁻⁴ – 1.03 × 10⁻⁴</td>
</tr>
<tr>
<td>K</td>
<td>1.96 × 10⁻⁷</td>
<td>1.00 × 10⁻⁵</td>
<td>7.67 × 10⁻⁵ – 1.46 × 10⁻⁵</td>
</tr>
<tr>
<td>Mg</td>
<td>1.00 × 10⁻⁷</td>
<td>1.00 × 10⁻⁷</td>
<td>7.41 × 10⁻⁵ – 1.48 × 10⁻⁵</td>
</tr>
<tr>
<td>Na</td>
<td>3.61 × 10⁻⁴</td>
<td>4.91 × 10⁻⁴</td>
<td>4.81 × 10⁻⁴ – 5.15 × 10⁻⁴</td>
</tr>
<tr>
<td>Si</td>
<td>7.55 × 10⁻⁵</td>
<td>7.55 × 10⁻⁵</td>
<td>4.78 × 10⁻⁵ – 8.95 × 10⁻⁵</td>
</tr>
<tr>
<td>S</td>
<td>6.10 × 10⁻⁵</td>
<td>6.10 × 10⁻⁵</td>
<td>4.68 × 10⁻⁵ – 7.65 × 10⁻⁵</td>
</tr>
</tbody>
</table>

Tab. 8-3: Initial cement porewater composition assumed by Watson et al. (2016a) in the blind modelling exercise and the updated composition assumed here

<table>
<thead>
<tr>
<th>Species</th>
<th>Old Value (mol kg⁻¹)</th>
<th>New Value (mol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>13.16</td>
<td>12.77</td>
</tr>
<tr>
<td>Al</td>
<td>7.14 × 10⁻⁸</td>
<td>8.05 × 10⁻⁷</td>
</tr>
<tr>
<td>Ca</td>
<td>6.02 × 10⁻²</td>
<td>2.34 × 10⁻²</td>
</tr>
<tr>
<td>Cl</td>
<td>2.20 × 10⁻⁴</td>
<td>5.00 × 10⁻⁵</td>
</tr>
<tr>
<td>C</td>
<td>7.49 × 10⁻⁶</td>
<td>7.70 × 10⁻⁵</td>
</tr>
<tr>
<td>K</td>
<td>1.96 × 10⁻⁷</td>
<td>1.00 × 10⁻⁵</td>
</tr>
<tr>
<td>Mg</td>
<td>1.78 × 10⁻⁹</td>
<td>1.78 × 10⁻⁹</td>
</tr>
<tr>
<td>Na</td>
<td>3.61 × 10⁻⁴</td>
<td>4.91 × 10⁻⁴</td>
</tr>
<tr>
<td>Si</td>
<td>1.18 × 10⁻⁶</td>
<td>1.02 × 10⁻⁵</td>
</tr>
<tr>
<td>S</td>
<td>3.73 × 10⁻³</td>
<td>4.22 × 10⁻³</td>
</tr>
</tbody>
</table>

Table 8-4 summarises the variant cases considered in the new round of modelling.

A further variant case was also considered where aragonite was considered as a potential secondary mineral in place of calcite. However, this proved problematic to run, taking considerably longer than the other variants to make progress, and was abandoned. The reasons for the increased difficulty in solution are not immediately apparent, particularly as preliminary results suggested that the simulation proceeds in a very similar manner to the variant case (b), with the exception that calcite precipitation is replaced by aragonite, as might be expected. However reactive transport simulations are complex with a large number of variables and a slight perturbation to the system can often lead to differences in solver performance.
Tab. 8-4: Model variants considered in the updated modelling

Note: “Instantaneous and removed” alkali release means the alkalis are assumed to have been released immediately and removed from the modelled domain.

<table>
<thead>
<tr>
<th>Model Variant</th>
<th>Description</th>
<th>Calcite Kinetics</th>
<th>Cement Kinetics</th>
<th>Alkali Release</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Calcite kinetics</td>
<td>As Watson et al. (2016a)</td>
<td>Fast ($k_0 = 1.0 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$)</td>
<td>Instantaneous and removed</td>
</tr>
<tr>
<td>b</td>
<td>Calcite equilibrium</td>
<td>Fast (equilibrium)</td>
<td>Fast ($k_0 = 1.0 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$)</td>
<td>Instantaneous and removed</td>
</tr>
<tr>
<td>c</td>
<td>Calcite equilibrium</td>
<td>Fast (equilibrium)</td>
<td>Slow ($k_0 = 1.0 \times 10^{-12}$ mol m$^{-2}$ s$^{-1}$)</td>
<td>Instantaneous and removed</td>
</tr>
<tr>
<td>d</td>
<td>Calcite equilibrium, alkali release</td>
<td>Fast (equilibrium)</td>
<td>Fast ($k_0 = 1.0 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$)</td>
<td>Hong &amp; Glasser (1999) model used</td>
</tr>
</tbody>
</table>

For a detailed description of all other model parameters, see Watson et al. (2016a; Section 7). In particular, it should be noted that the model includes both a solid solution C-S-H gel, with end-members referred to as ‘jennite-like’ and ‘tobermorite-like’, and a C-S-H mineral (11Å tobermorite). The former is a constituent part of the initial cement composition, while the latter is included as a secondary mineral precipitate.

8.1.4 Results of updated model and comparison to laboratory analysis

8.1.4.1 Porosity and primary mineral dissolution

The porosity in a section through the mid-point of the cement shells after 6 years of simulation in each of the variant cases is shown in Figure 8-4, which should be compared to the equivalent results from the blind modelling of Watson et al. (2016a; Section 7) shown in Figure 8-1, and the photographs of samples from the experiment shown in Figure 2-13. Even accounting for the extra year simulated (Fig. 8-4 shows the results after 6 years, Fig. 8-1 after 5 years), the amount of dissolution in the updated model variant (a) with calcite kinetics is slightly greater. This can also be seen in the concentration of portlandite shown in a similar cross-section (Fig. 8-5). The only difference between this model and the blind model is the Grimsel groundwater composition, which has a slightly lower pH and thus promotes portlandite dissolution.

In model variant (b), calcite is assumed to precipitate rapidly (equilibrium assumption) and this causes even greater amounts of dissolution of portlandite and a corresponding increase in porosity, to the extent that there is very little portlandite left in the cement at all. Conversely, if this assumption is coupled with slower cement dissolution as in variant (c), there is very little portlandite dissolution or corresponding change in porosity.

Note that the results of model variant (d), calcite equilibrium and alkali release, are not shown as they are identical to those of (b) in terms of the mineralogical changes.

Other primary minerals within the cement remain largely intact, although ettringite dissolves in a similar manner to portlandite, and the jennite-like C-S-H end-member (high Ca/Si ratio) is converted to a tobermorite-like C-S-H end-member (lower Ca/Si ratio), as in the blind modelling.
a) Calcite kinetics

b) Calcite equilibrium

c) Calcite equilibrium, slow cement kinetics

Fig. 8-4: Section through the centre of the modelled cement showing the porosity after 6 years
Note: The initial cement porosity was 0.5. The inner gap (between the cement and emplacement tool) was not modelled.

a) Calcite kinetics

b) Calcite equilibrium

c) Calcite equilibrium, slow cement kinetics

Fig. 8-5: Section through the centre of the modelled cement showing the concentration of portlandite after 6 years
Note: The initial concentration was $4.0 \times 10^3$ mol/m$^3$. Note that the inner gap (between the cement and emplacement tool) was not modelled.
8.1.4.2 Mineral precipitation

All model variants show a small decrease in porosity in the gap between the cement shell and the borehole wall at the end of the borehole closest to the injection port (Fig. 8-6). There is also a decrease in porosity in the gap close to the fracture inlet in all cases. The variants with calcite equilibrium (b) and (c) show the greatest alteration in porosity, with blocking of the pore space near the fracture inlet and, in the case of the faster cement kinetics (b), blocking around the injection port. Note that any reduction in porosity has a feedback on flow as porosity and permeability are coupled in the model. A small minimum porosity (0.005) is enforced within the model which allows the simulation to continue past “clogging” events.

This reduction in porosity is largely caused by the precipitation of 11Å-tobermorite (a C-S-H mineral) and, in the variants assuming calcite equilibrium, calcite, as shown in Figures 8-7 and 8-8. The precipitation of these minerals is caused by the Ca released by the dissolving portlandite reacting with the inflowing Grimsel groundwater. If calcite precipitation is modelled using a kinetic approach, as in variant (a), some Ca-saponite also precipitates in the gaps around the fracture inlet (Fig. 8-9), but this does not occur in the other variants, presumably because calcite removes Ca from the water faster than Ca-saponite can precipitate.

**Porosity (cement + gaps)**

![Diagram showing porosity of the modelled cement and surrounding gaps at 6 years](image-url)

Fig. 8-6: Porosity of the modelled cement and surrounding gaps at 6 years
11Å-Tobermorite (cement + gaps)

a) Calcite kinetics

b) Calcite equilibrium

Fig. 8-7: Concentration of 11Å-tobermorite (C-S-H mineral) in the modelled cement and surrounding gaps at 6 years

c) Calcite equilibrium, slow cement kinetics
Calcite (cement + gaps)

a) Calcite kinetics

b) Calcite equilibrium

c) Calcite equilibrium, slow cement kinetics

Fig. 8-8: Concentration of calcite in the modelled cement and surrounding gaps at 6 years
Sa-Saponite (cement + gaps)

a) Calcite kinetics

b) Calcite equilibrium

c) Calcite equilibrium, slow cement kinetics

Fig. 8-9: Concentration of Ca-saponite in the modelled cement and surrounding gaps at 6 years.

Within the cement itself, an increase in porosity can be seen in all locations in the variants with faster cement kinetics ((a) and (b)), as shown in Figure 8-10. In the variant with slow cement kinetics (c), there is very little change in porosity within the cement itself. In variant (a), with calcite kinetics, the greatest porosity changes are localised around the fracture inlet and the injection port. In variant (b), with calcite equilibrium, porosity changes are more widespread in the cement at the end of the borehole nearest the injection port, but the fracture inlet has a reduced effect.

Figure 8-11 shows that most of the changes to porosity are caused by calcite precipitation in the variants where calcite equilibrium is assumed ((b) and (c)), particularly around the injection port. Gismondine (included as a C-A-S-H proxy mineral) also precipitates in quite large quantities in these variants (Fig. 8-12), in particular in the case with faster cement kinetics (b) at the end of the cement near the injection port. In the case with calcite kinetics (a), gismondine is much more localised and is found around the fracture inlet only. Although Ca-saponite only precipitated in the gaps in the case with cement kinetics (a), in the cement it appears in all cases as shown in Figure 8-13, at the fracture inlet in variant (a), with calcite kinetics, and at the injection port end in the other variants, with calcite equilibrium.
As before, the results of variant (d), calcite equilibrium with alkali release, are not shown as they are identical to variant (b).

**Porosity (cement only)**

a) **Calcite kinetics**  

b) **Calcite equilibrium**

c) **Calcite equilibrium, slow cement kinetics**

Fig. 8-10: Porosity in the modelled cement (gap cells hidden) at 6 years (initial value 0.5)
Calcite (cement only)

a) Calcite kinetics

b) Calcite equilibrium

c) Calcite equilibrium, slow cement kinetics

Fig. 8-11: Concentration of calcite in the modelled cement (gap cells hidden) at 6 years
**Gismondine** (cement only)

a) **Calcite kinetics**

b) **Calcite equilibrium**

c) **Calcite equilibrium, slow cement kinetics**

Fig. 8-12: Concentration of gismondine in the modelled cement (gap cells hidden) at 6 years
Sa-Saponite (cement only)

a) Calcite kinetics

b) Calcite equilibrium

c) Calcite equilibrium, slow cement kinetics

Fig. 8-13: Concentration of Ca-saponite in the modelled cement (gap cells hidden) at 6 years

8.1.4.3 Porewater composition

A comparison between the modelled pH of the porewater in the emplacement borehole and the measurements taken during the experiment is shown in Figure 8-14. Concentrations of other major ions are shown in Figure 8-15. As noted in section 8.1.2, the model is heterogeneous in nature and therefore the results are greatly affected by the sampling point chosen. Here, as before, the point where the water flows out of the borehole via the fracture is selected for comparison.

As with the blind modelling (Figs. 8-2 and 8-3), the pH is a reasonable fit for the data, as are the concentrations of Ca, Al and Si. The Hong & Glasser (1999) approach to alkali release included in variant (d) produces a better fit to Na and K than the other variants, but the fall-off in concentration is not as quick in the model as in reality. The model could be re-parameterised to better fit the experimental data. The change to the assumed background Grimsel groundwater has improved the long-term fits to K and Cl (cf. Fig. 8-3).
All variant cases produce a poor fit for Mg, producing concentrations a number of orders of magnitude too low. The fact that the concentrations are below the background Grimsel level of Mg suggests that there is a precipitating mineral in the model consuming Mg at a rate which is too fast. Of the Mg-bearing minerals included in the model, only the saponites (primarily Ca-saponite) precipitate at all.

Similarly, the fit for S is poor across all the variants, with concentrations at least an order of magnitude too high. Ettringite is the only primary mineral containing S, and no S-bearing secondary minerals were included in the model. Thus, there is no mineral sink for the S that is released as ettringite dissolves in the cement.

![Fig. 8-14: Evolution of pH in the emplacement borehole.](image)

Note: The model cases are as follows: (a) calcite kinetics; (b) calcite equilibrium; (c) calcite equilibrium, slow cement kinetics; and (d) calcite equilibrium, alkali release. “Measured (lab)” indicates results from samples that were taken away and analysed in a laboratory environment, while “Measured (field)” indicates results from samples that were analysed in-situ.
Fig. 8-15: Evolution of aqueous species in the emplacement borehole

Note: The model cases are as follows: (a) calcite kinetics; (b) calcite equilibrium; (c) calcite equilibrium, slow cement kinetics; and (d) calcite equilibrium, alkali release.
8.1.5 **Summary and conclusions**

A summary of the comparison between the models and the observations is given in Table 8-5. The key difference in the updated model compared to the blind modelling is the inclusion of variants assuming calcite equilibrium, which allows calcite to precipitate, better matching the observations from the LCS experiment. Modifications to the assumed Grimsel groundwater have also improved the fit to the measured porewater composition, as shown in section 8.1.4.3. In addition, the variant including a model for short-term alkali release demonstrates that it should be possible to replicate the early-time behaviour of Na and K with some additional fitting of parameters.

Although the leaching of the portlandite from the cement is captured by the model, it tends to over-predict both this and the increase in porosity, particularly if the calcite equilibrium assumption is made. The results reaffirm that the slower cement kinetics used in variant (c) are not appropriate, but a better fit to the observations could be achieved using kinetic rates/reactive surface areas somewhere between the two model variants.

The decalcification of C-S-H in the outer cement is also captured well by the model, but there are no quantitative data to compare to, so it is not clear whether the degree of conversion predicted by the models is appropriate or not.

The model predicts a strong spatial variation in both dissolution and secondary mineral precipitation. There is little evidence from the observations to support this, perhaps suggesting that the borehole water was better mixed than assumed in the model, possibly due to the number of tracer tests conducted during the lifetime of the experiment.

A comparison with the measured porewater concentration in the borehole shows a good match for pH, dissolved Ca, Al and Si concentrations, in that the absolute values are of the same order of magnitude and the main trends through time are captured, as well as for Na and K concentrations at longer times (with potential for matching early times with appropriate parameterisation of the alkali release model). A poor match is shown for Mg and S, in that the absolute values differ by an order of magnitude or more; in the former case it is likely that the saponites are taking Mg up from the water too quickly; in the latter case there may either be a secondary mineral missing or ettringite dissolves too quickly.
<table>
<thead>
<tr>
<th>Key Findings from Laboratory Analysis</th>
<th>Results of updated Modelling</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Calcite Kinetics</td>
<td>(b) Calcite Equilibrium</td>
<td>(c) Calcite Equilibrium, Slow Cement Kinetics</td>
</tr>
<tr>
<td>Leached zone in cement adjacent to any surface exposed to water, characterised by total loss of portlandite.</td>
<td>Portlandite totally removed from outer cement layers. Thickness of leached layer greater than observation suggests.</td>
<td>Very little loss of portlandite.</td>
</tr>
<tr>
<td>Higher porosity in leached zone (possibly 10% higher than unleached zone, but difficult to quantify); sharp interface between leached/ unleached zones.</td>
<td>Increase in porosity in outer cement layers (difference between initial/ unleached porosity of approximately 17%).</td>
<td>Increase in porosity in outer cement layers (difference between initial/unleached porosity of approximately 5%).</td>
</tr>
<tr>
<td>Decalcification of C-S-H at the surface of the leached zone.</td>
<td>Conversion of jennite-like C-S-H end-member (high Ca/Si ratio) to tobermorite-like C-S-H end-member (low Ca/Si ratio) in outer cement layers.</td>
<td>Conversion of jennite-like C-S-H end-member (high Ca/Si ratio) to tobermorite-like C-S-H end-member (low Ca/Si ratio) in outer cement layers.</td>
</tr>
<tr>
<td>Key Findings from Laboratory Analysis</td>
<td>Results of updated Modelling</td>
<td>Comments</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>-----------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>(a) Calcite Kinetics</td>
<td>(b) Calcite Equilibrium</td>
<td>(c) Calcite Equilibrium, Slow Cement Kinetics</td>
</tr>
<tr>
<td>Amount of leaching throughout borehole is heterogeneous but cannot be attributed to proximity to injection port or fracture intersection. Overriding factor appears to be thickness of adjacent gap.</td>
<td>Large spatial variation in porosity and cement dissolution, according to proximity to injection port and fracture inflow (which promote dissolution).</td>
<td>Large spatial variation in porosity and cement dissolution, according to proximity to injection port and fracture inflow (which promote dissolution).</td>
</tr>
<tr>
<td>As variant (b)</td>
<td>The amount of mixing may have been greater in reality than in the model, in part due to recirculation that occurred during the tracer tests.</td>
<td></td>
</tr>
<tr>
<td>Precipitation on shell surfaces and emplacement tool primarily calcite with some C-S-H gel and vaterite. Quartz, feldspar and mica also identified.</td>
<td>Tobermorite (C-S-H mineral) precipitation at fracture intersection, near injection and in gaps between shells. Gismondine (C-A-S-H proxy) and Ca saponite precipitation near fracture intersection.</td>
<td>Large amounts of calcite precipitation around injection port and at fracture inflow. Some tobermorite (C-S-H mineral) precipitation at fracture intersection, near injection and in gaps between shells. Some Ca saponite and gismondine (C-A-S-H proxy) precipitation in cement near injection port.</td>
</tr>
<tr>
<td>As variant (b)</td>
<td>No spatial variation in the precipitates was recorded in the laboratory analysis, but no information on where on the shells or the tool the samples were taken from can be found. It is likely that samples were only collected from a single location.</td>
<td></td>
</tr>
</tbody>
</table>
8.2 Reactive transport in the fracture plane

8.2.1 Previous modelling

The result of the dissolution of the cement source, described in section 8.1, is a high-pH plume that travels through the fracture plane to the other two intersecting boreholes, as shown in Figure 8-16.

Modelling of the plume in the fracture has been carried out in parallel to the modelling of the emplacement borehole. Here a description of the model evolution, and the conceptual thinking behind it, is given.

Often, when modelling fractures in 2D, the simplifying ‘parallel plate’ assumption is made (e.g. Arcos et al., 2006; Benbow et al., 2011). This conceptual model represents the walls of the fracture as two flat plates, giving the whole fracture a constant aperture. The fracture may be assumed to be open (100% porosity) or uniformly partially filled with fault gouge material. Thus, in the absence of features such as boreholes or deposition holes, flow is considered to be uniform throughout the entire fracture plane. This is a useful modelling assumption when the pattern of flow in the fracture is not of importance and the main concern is the interaction of the water when it reaches its destination, e.g. a deposition hole in a GDF.

However, evidence suggests that this parallel plate model is not representative of most real systems (e.g. Abelin et al., 1994; Crawford, 2008; Alexander et al., 2009). Fracture walls are naturally rough and may have been displaced horizontally, creating a larger aperture in some places and a smaller (or zero) aperture in others. This leads to the potential removal of mineral fillings and erosion of fracture walls along preferential pathways through the fracture, intensifying the channelling effect. Indeed, large parts of the fracture will experience sufficiently low flows that they can be regarded as being stagnant for all practical purposes (e.g. Appendix A of SKB, 2010).
A classic example of this channelling effect is reported by Abelin et al. (1994), where a single fracture tracer test was conducted at the Stripa Mine site in Sweden. An injection borehole was drilled in the plane of a fracture, perpendicular to the expected flow field, and a receiver borehole was likewise drilled in the same orientation a short distance away downstream. At intervals along the injection borehole, non-sorbing tracers were injected, with five different types of tracer used\(^5\), and only one type of tracer injected at each interval. If flow in the fracture was uniform, as in the parallel plate approximation, it would be expected that each type of tracer would be picked up in the receiver borehole, roughly in the same position along the borehole as it was injected upstream. However, this was not found to be the case; only two of the five tracer types were detected at the receiver borehole. In addition, the concentration profiles of these tracers were not smooth but irregular, showing at least 2 main peaks, and the maximum amount of tracer recovered was < 13 %. It was concluded that the explanation for these observations was channelling in the fracture plane; some of the tracers were injected into ‘dead-end’ channels that never extended as far as the receiver borehole, while others followed a path that did not intersect the receiver. Of those tracers that were recovered, the multiple peaks in the concentration profile indicated multiple pathways with differing travel times.

At larger scales this channelling in individual fractures may result in reduced connectivity of fracture networks (Black et al., 2016), as an intersection of fractures may not necessarily be equated to an intersection of channels within those fractures. This may be of importance in understanding the large-scale evolution of flow in the environment surrounding a GDF constructed in higher-strength rock, but the LCS experiment is concerned only with flow in a single fracture plane so we mention this only in passing.

Quantifying the channels within the fracture plane is also difficult. In laboratory experiments (e.g. Yasuhara et al., 2006), it is possible to map the fracture surfaces quite precisely using lasers or casting techniques, but this is not possible in the field. However, some more generalised fracture characterisation has been attempted; see for example the Excavation Project (EP) component of the Radionuclide Migration Programme (RMP), undertaken at Grimsel in the 1990s (Alexander et al., 2009). Excavation and subsequent analysis showed that fractures were either filled with a fracture-filling material, such as fault gouge or breccia components, or were empty. About 43 % of the fractures by area were filled with fracture-filling material. Flow was found to take place mainly in channel-type fractures, with a mean width of 4.2 mm and aperture of 2.4 mm. The distribution of fracture-filling material was found to be highly heterogeneous, resulting in a pattern of flow paths between the fracture walls that could be compared to a branching river system with ‘islands’ of fault gouge between. Another important finding of this project, which may be relevant to the LCS project, was the presence of washed-out fault gouge, indicating that some of the open channels may have been produced by the preceding radiotracer experiment.

Similarly, Abelin et al. (1994) photographed 50 m of fractures at Stripa and found that channels range from millimetres to centimetres in width, with a few rare cases extending to tens of centimetres. They generally occurred in clusters with widths of 0.05 to 1 m, with two to four clusters over a length of 2.5 m; the channels occupied at most 50% of the width of an individual cluster and usually much less than this.

---

\(^5\) Uranine (Na-Fluorescein), Eosin Yellowish, Elbenyl Brilliant Flavine, Duasyn Acid Green V and Phloxine B. All were tested and found to be stable and non-sorbing on the granite (Abelin et al., 1994).
These general observations from individual fractures can be used to stochastically generate profiles of fractures (e.g. Cacas et al., 1990a; 1990b), but as such a stochastic representation of the fracture of relevance at Grimsel would not be an exact match for the real system, any reactive transport model based on it would generate detailed results that are likely to be of little similarity to the results obtained from the experiment.

Thus, attempts to model the LCS experiment eschewed the classical parallel plate model in favour of a model which represented the channels within the fracture plane. In the context of performance assessment (PA) modelling of a GDF, this distinction is quite important, as the amount of precipitation required to block a few channels is rather small compared to the amount required to block off a region in a parallel plate fracture (this also applies to pore blocking in the adjacent rock matrix).

The initial modelling attempt was based on an approach where multiple realisations of a channelled fracture plane were generated, with the channels created randomly by assigning either a high or low permeability to each cell in the grid (the probability of a cell being high permeability was increased if its neighbours were also high permeability, causing the channels and islands to be created). The pre emplacement tracer test TT09-03 was then modelled using each of the fracture realisations. The realisation which produced the best match to the tracer test results was selected and carried forward as the grid for the reactive transport model.

Some preliminary results from this modelling are shown in Figure 8-17, which depicts the porosity after 2.3 years, during the period of the fastest injection in the emplacement borehole. The black lines show the edges of the channels; the emplacement and extraction boreholes are linked by a channel while the observation borehole sits in a low permeability zone between the two. The distance that the hyperalkaline plume must travel to reach the extraction borehole is much further than the straight line distance between the two boreholes, and the direction of the natural head gradient sends much of the high-pH fluid out into the wider fracture plane, yet a response in pH at the extraction borehole was seen in the model when injection was carried out in the emplacement borehole.

![Fig. 8-17: Preliminary model of the fracture plane, depicting porosity at 2.3 years](image)

Note: Black lines indicate the edges of the channels; the emplacement and extraction boreholes are located within channels, the observation borehole is located in a low permeability zone. The straight-line distance between the emplacement and extraction boreholes is approximately 1 m. The legend depicts porosity expressed as a fraction, with a range of 0.25 to 0.30 to highlight changes.
The model also predicted the reduction of porosity around the emplacement borehole as ettringite and C-S-H gel precipitated. Further away, monocalcicarbonate and gismondine (C-A-S-H proxy) were the main precipitates.

However, convergence testing on the grid used revealed that the model boundaries need to be placed a long way away (much further than depicted in Figure 8-17 – tens of metres rather than a few metres) and very fine resolution is required in the region around the boreholes. Even if modelling of the chemical reactions is confined to the area of interest, the combination of the two requirements makes this 2.5D model (which includes the rock matrix as well as the fracture plane) computationally very expensive, even more so than the 3D model of the emplacement borehole described in section 7.2.7. Such a model was unviable to carry forward.

8.2.2 Description of current model

8.2.2.1 Conceptual model

The current model is still based on the conceptual idea of channels within the fracture plane, but is implemented in a more simplistic manner based on mass conservation. The entire system can be simplified down to nine distinct volumetric flows of water, as depicted in Figure 8-18:

- $Q_{\text{Emp}}$, $Q_{\text{Obs}}$ and $Q_{\text{Ext}}$, the artificial flow rates into the emplacement and out of the observation and extraction boreholes, caused by injection and extraction during the experiment
- $Q_{\text{EmpObs}}$ and $Q_{\text{EmpExt}}$, the flow along channels from the emplacement to the observation and extraction boreholes respectively
- $Q_{\text{EmpFrac}}$, the flow from the emplacement borehole to the wider fracture
- $Q_{\text{FracEmp}}$, $Q_{\text{FracObs}}$ and $Q_{\text{FracExt}}$, flow from the wider fracture into each of the three boreholes

Fig. 8-18: Conceptual model for the channel-based approach representing flow into, out of, and between, the three boreholes
The assumptions made here are that:

- Potential multiple pathways between boreholes are lumped together into a single route.
- Loss along pathways between boreholes, and at the observation and extraction boreholes, to the wider fracture and rock matrix are included in $Q_{\text{EmpFrac}}$.
- Any potential pathways linking the observation and extraction boreholes to each other are encompassed within the emplacement-extraction pathway.
- The mass of water in the system must be conserved, and as such the governing conservation equations are:

\[
\begin{align*}
Q_{\text{Emp}} &= Q_{\text{EmpObs}} + Q_{\text{EmpExt}} + Q_{\text{EmpFrac}} - Q_{\text{FracEmp}} \\
Q_{\text{Obs}} &= Q_{\text{EmpObs}} + Q_{\text{FracObs}} \\
Q_{\text{Ext}} &= Q_{\text{EmpExt}} + Q_{\text{FracExt}}
\end{align*}
\]

The borehole injection and extraction rates $Q_{\text{Emp}}, Q_{\text{Obs}}$, and $Q_{\text{Ext}}$ are known, giving a system of three equations with six unknowns. To reduce this to a solvable set of three unknowns, the model is fitted to the tracer tests to give values for $Q_{\text{EmpFrac}}$, the flow from the emplacement borehole to the wider fracture, and $Q_{\text{FracObs}}$ and $Q_{\text{FracExt}}$, the flow from the wider fracture into the observation and extraction boreholes respectively. This leaves $Q_{\text{FracEmp}}$, the flow from the wider fracture into the emplacement borehole, and $Q_{\text{EmpObs}}$ and $Q_{\text{EmpExt}}$, the flows between the emplacement and observation and extraction boreholes respectively, to be solved for. Once all of the flow rates are known they can be used in the reactive transport model to deduce the potential chemical and mineralogical changes along the flow path.

### 8.2.3 Fitting to the tracer tests

This section describes the fitting of the mass conservation channel model detailed in section 8.2.2.1 above to the tracer tests conducted throughout the duration of the LCS experiment (see section 2.2.1). The results of the tracer tests were taken from Lanyon & Mäder (2020), with the data (tracer concentrations and recovery vs. time for each borehole) extracted from graphs using GraphGrabber (Dedross & Boardley, 2009). The model was implemented in the general-purpose modelling tool QPAC (Quintessa, 2013), using the tracer transport (Robinson, 2009) and Darcy flow (Bond, 2015) modules. Model inputs common across all the tracer tests are given in Table 8-6.

Each of the tracer tests is considered in turn below. In each case, values for the flow rate into the observation and extraction boreholes from the fracture, $Q_{\text{FracObs}}$ and $Q_{\text{FracExt}}$, are sought by varying these parameters until a good fit to the tracer concentrations in each borehole is found. The net flow into the emplacement borehole, $Q_{\text{Emp}} - Q_{\text{FracEmp}}$, is found by enforcing a fixed head boundary condition and varying the volume of the flow paths between the emplacement borehole and the observation and extraction boreholes ($V_{\text{FracObs}}$ and $V_{\text{Ext}}$). In practice, the volumes were deduced from the first tracer test and then only the flow rates varied for subsequent tests to reflect the different conditions under which each test was carried out.
Tab. 8-6: Input parameters for the tracer test model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borehole radius</td>
<td>0.043 m</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Length of emplacement borehole interval</td>
<td>0.76 m</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Length of observation borehole interval</td>
<td>0.993 m</td>
<td>Rüedi (2010) Fig. A-2</td>
</tr>
<tr>
<td>Length of extraction borehole interval</td>
<td>0.505 m</td>
<td>Rüedi (2010) Fig. A-3</td>
</tr>
<tr>
<td>Observation borehole volume</td>
<td>1.174 L</td>
<td>Rüedi (2010) Fig. A-2</td>
</tr>
<tr>
<td>Extraction borehole volume</td>
<td>0.323 L</td>
<td>Rüedi (2010) Fig. A-3</td>
</tr>
<tr>
<td>Fracture aperture</td>
<td>0.5 mm</td>
<td>Rüedi (pers. comm.)</td>
</tr>
<tr>
<td>Transmissivity of fracture</td>
<td>$3.0 \times 10^{-9}$ m$^2$s$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Dispersion length</td>
<td>0.01 m</td>
<td>Soler et al. (2006)</td>
</tr>
<tr>
<td>Porewater diffusion coefficient</td>
<td>$2.44 \times 10^{-9}$ m$^2$s$^{-1}$</td>
<td>Walker (2016)</td>
</tr>
</tbody>
</table>

**8.2.3.1 Tracer Test - TT09-03**

Model input parameters specific to this tracer test (the only reliable one carried out prior to emplacement) are given in Table 8-7. A good fit to the tracer concentrations in each of the three boreholes was found by using the parameters given in Table 8-8, as shown in Figures 8-19 (emplacement borehole), 8-20 (observation) and 8-21 (extraction). These parameters mean that, in the model, 97.8% of the water extracted from the observation borehole, and 99.9% of the water extracted from the extraction borehole, is drawn from the wider fracture (i.e. was not in the emplacement borehole). In fact this is entirely consistent with the preliminary modelling described in section 8.2.1, where it was found that the boundaries had to be pushed far away from the boreholes to obtain a convergent solution – in other words, the boreholes affect the flow field across a large area (of the order of a few metres) in comparison to the size of the boreholes. The channel volumes that are determined are in the order of $5 \times 10^{-6}$ to $10^{-5}$ m$^3$. Given that the pathways are known to be longer than the straight-line distances of approximately 0.5 m, this would suggest that the average cross-sectional area of the pathways is less than $2 \times 10^{-3}$ m$^2$. For example, a candidate fracture channel could have an aperture and a net width of less than 1 mm and 10 mm respectively (i.e. could be comprised of ten fracture pathways with cross-sectional area less than 1 mm by 1 mm).

Tab. 8-7: Model input parameters specific to tracer test TT09-03

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement borehole volume</td>
<td>21.248 L</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Duration of test</td>
<td>1026.8 h</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Circulated concentration in emplacement borehole ($Q_{emp}$)</td>
<td>3464 ppb</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Injection rate in emplacement borehole ($Q_{inj}$)</td>
<td>0.02 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from observation borehole ($Q_{obs}$)</td>
<td>0.05 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from extraction borehole ($Q_{ext}$)</td>
<td>4.4 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
</tbody>
</table>
Sensitivity tests were also carried out to determine what effect other model inputs have upon the results: the diffusion coefficient was found to have virtually no effect, particularly at the extraction borehole; the dispersion length had a larger effect, particularly at the observation borehole, but was found to be insignificant compared to the flow rates and channel volumes. In general, the flow rate controls the magnitude, and the channel volume controls the timing, of the peak tracer concentration.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of channel between emplacement and observation boreholes, $V_{\text{Obs}}$</td>
<td>$1.12 \times 10^{-5}$ m$^3$</td>
</tr>
<tr>
<td>Volume of channel between emplacement and extraction boreholes, $V_{\text{Ext}}$</td>
<td>$5.60 \times 10^{-6}$ m$^3$</td>
</tr>
<tr>
<td>Flow rate from wider fracture into observation borehole, $Q_{\text{FracObs}}$</td>
<td>0.0489 ml min$^{-1}$</td>
</tr>
<tr>
<td>Flow rate from wider fracture into extraction borehole, $Q_{\text{FracExt}}$</td>
<td>4.39714 ml min$^{-1}$</td>
</tr>
</tbody>
</table>

Fig. 8-19: Concentration of tracer in the emplacement borehole (measured vs. modelled) for tracer test TT09-03
Note: The fluorometer was moved to the observation borehole at ~400 hours.
Fig. 8-20: Concentration of tracer and recovery in the observation borehole (measured vs. modelled) for tracer test TT09-03

Note: The fluorometer was not connected to this borehole until ~400 hours had elapsed.

Fig. 8-21: Concentration of tracer and recovery in the extraction borehole (measured vs. modelled) for tracer test TT09-03
8.2.3.2 Tracer Test - TT10-01

The model input parameters for this tracer test are given in Table 8-9, and the fitted values in Table 8-10 (note that the channel pathway volumes used were the same as for TT09-03).

In this case a good fit can be made to the tracer concentration in the emplacement borehole (Fig. 8-22), and the shape of the modelled concentration in the observation borehole is good, but the timing of the peak is a few hours off (Fig. 8-23). However, the timing of the peak concentration in the extraction borehole fits the measured data well (Fig. 8-24). The model predicts that, in this tracer test, 99.0% of the water extracted from the observation borehole, and 99.97% of the water extracted from the extraction borehole, is drawn from the wider fracture.

Tab. 8-9: Model input parameters specific to tracer test TT10-01

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement borehole volume</td>
<td>1.898 L</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Duration of circulation</td>
<td>398.9 h</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Circulated concentration in emplacement borehole</td>
<td>5000 ppb</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Time injection in emplacement borehole started</td>
<td>856 h</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Time injection in emplacement borehole stopped</td>
<td>1026 h</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Injection rate in emplacement borehole ( (Q_{Emp}) )</td>
<td>0.25 ml min(^{-1} )</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from observation borehole ( (Q_{Obs}) )</td>
<td>0.05 ml min(^{-1} )</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from extraction borehole ( (Q_{Ext}) )</td>
<td>3.0 ml min(^{-1} )</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
</tbody>
</table>

Tab. 8-10: Values of parameters used to fit the model to the results of TT10-01

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate from wider fracture into observation borehole, ( Q_{TracObs} )</td>
<td>0.0495 ml min(^{-1} )</td>
</tr>
<tr>
<td>Flow rate from wider fracture into extraction borehole, ( Q_{TracExt} )</td>
<td>2.9991 ml min(^{-1} )</td>
</tr>
</tbody>
</table>
Fig. 8-22: Concentration of tracer in the emplacement borehole (measured vs. modelled) for tracer test TT10-01
Note: The fluorometer was moved to the observation borehole at ~400 hours

Fig. 8-23: Concentration of tracer and recovery in the observation borehole (measured vs. modelled) for tracer test TT10-01
Note: The fluorometer was not connected to this borehole until ~400 hours had elapsed
8.2.3.3 Tracer Test - TT11-01

The model input parameters for this tracer test are given in Table 8-11, and the fitted values in Table 8-12 (note that the channel pathway volumes used were the same as for TT09-03).

The fits to the experimental data are not as good in this case (Figs. 8-25, 8-26 and 8-27); in particular, the amount of recovery of tracer in the extraction borehole is too high in the model. This is due to the fact that there were problems with the extraction fluorometer during the test, leading to the loss of data until about 700 hours of elapsed time. Because of the problems encountered during this test, some variants of the main reactive transport model will be included that disregard the data from this period (see section 8.2.4.1).

The model predicts that, in this tracer test, 80.0% of the water extracted from the observation borehole, and 96.0% of the water extracted from the extraction borehole, is drawn from the wider fracture.

Tab. 8-11: Model input parameters specific to tracer test TT11-01

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement borehole volume</td>
<td>19.569 L</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Duration of circulation</td>
<td>328 h</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Circulated concentration in emplacement borehole</td>
<td>2810.6 ppb</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Injection rate in emplacement borehole ($Q_{emp}$)</td>
<td>0.25 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from observation borehole ($Q_{obs}$)</td>
<td>0.05 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from extraction borehole ($Q_{ext}$)</td>
<td>1.7 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
</tbody>
</table>
Tab. 8-12: Values of parameters used to fit the model to the results of TT11-01

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate from wider fracture into observation borehole, $Q_{\text{FracObs}}$</td>
<td>0.04 ml min$^{-1}$</td>
</tr>
<tr>
<td>Flow rate from wider fracture into extraction borehole, $Q_{\text{FracExt}}$</td>
<td>1.632 ml min$^{-1}$</td>
</tr>
</tbody>
</table>

Fig. 8-25: Concentration of tracer in the emplacement borehole (measured vs. modelled) for tracer test TT11-01

Note: The fluorometer was moved to the observation borehole at ~400 hours.
Fig. 8-26: Concentration of tracer and recovery in the observation borehole (measured vs. modelled) for tracer test TT11-01

Note: The fluorometer was not connected to this borehole until ~400 hours had elapsed.

Fig. 8-27: Concentration of tracer and recovery in the extraction borehole (measured vs. modelled) for tracer test TT11-01

Note: There were no data from the fluorometer until ~700 hours had been reached.
8.2.3.4 Tracer Test - TT12-01

The model input parameters for this tracer test are given in Table 8-13, and the fitted values in Table 8-14 (note that the channel pathway volumes used were the same as for TT09-03).

The tracer concentrations are shown in Figures 8-28, 8-29 and 8-30 for this test. The results are reasonable, although the concentrations in the observation and extraction boreholes fall off too quickly following the arrival of the peak.

The model predicts that, in this tracer test, 94.5% of the water extracted from the observation borehole, and 99.4% of the water extracted from the extraction borehole, is drawn from the wider fracture.

Tab. 8-13: Model input parameters specific to tracer test TT12-01

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement borehole volume</td>
<td>13.898 L</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Duration of circulation</td>
<td>70 h</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Circulated concentration in emplacement borehole</td>
<td>3597.6 ppb</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Injection rate in emplacement borehole until 937 h ((Q_{\text{Emp}}))</td>
<td>0.08 ml min(^{-1})</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Injection rate in emplacement borehole after 937 h ((Q_{\text{Emp}}))</td>
<td>0.04 ml min(^{-1})</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from observation borehole ((Q_{\text{Obs}}))</td>
<td>0.05 ml min(^{-1})</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from extraction borehole ((Q_{\text{Ext}}))</td>
<td>1.6 ml min(^{-1})</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
</tbody>
</table>

Tab. 8-14: Values of parameters used to fit the model to the results of TT12-01

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate from wider fracture into observation borehole, (Q_{\text{FracObs}})</td>
<td>0.04725 ml min(^{-1})</td>
</tr>
<tr>
<td>Flow rate from wider fracture into extraction borehole, (Q_{\text{FracExt}})</td>
<td>1.5904 ml min(^{-1})</td>
</tr>
</tbody>
</table>
Fig. 8-28: Concentration of tracer in the emplacement borehole (measured vs. modelled) for tracer test TT12-01
Note: The fluorometer was moved to the observation borehole at ~ 100 hours.

Fig. 8-29: Concentration of tracer and recovery in the observation borehole (measured vs. modelled) for tracer test TT12-01
Note: The fluorometer was not connected to this borehole until ~ 100 hours had elapsed.
8.2.3.5 Tracer Test - TT12-02

The model input parameters for this tracer test are given in Table 8-15, and the fitted values in Table 8-16 (note that the channel pathway volumes used were the same as for TT09-03).

The tracer concentrations are shown in Figures 8-31, 8-32 and 8-33 for this test. Again, the results are reasonable, but the concentration tends to fall off too quickly in each of the boreholes.

The model predicts that, in this tracer test, 92.0% of the water extracted from the observation borehole, and 98.9% of the water extracted from the extraction borehole, is drawn from the wider fracture.

Tab. 8-15: Model input parameters specific to tracer test TT12-02

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement borehole volume</td>
<td>13.898 L</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Duration of circulation</td>
<td>138 h</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Circulated concentration in emplacement borehole ($Q_{e}$)</td>
<td>3000 ppb</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Injection rate in emplacement borehole ($Q_{e}$)</td>
<td>0.04 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from observation borehole ($Q_{o}$)</td>
<td>0.05 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from extraction borehole ($Q_{e}$)</td>
<td>1.6 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
</tbody>
</table>
Tab. 8-16: Values of parameters used to fit the model to the results of TT12-02

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate from wider fracture into observation borehole, ( Q_{\text{FracObs}} )</td>
<td>0.046 ml min(^{-1})</td>
</tr>
<tr>
<td>Flow rate from wider fracture into extraction borehole, ( Q_{\text{FracExt}} )</td>
<td>1.5824 ml min(^{-1})</td>
</tr>
</tbody>
</table>

Fig. 8-31: Concentration of tracer in the emplacement borehole (measured vs. modelled) for tracer test TT12-02

Note: The fluorometer was moved to the observation borehole at ~100 hours.
Fig. 8-32: Concentration of tracer and recovery in the observation borehole (measured vs. modelled) for tracer test TT12-02

Note: The fluorometer was not connected to this borehole until ~100 hours had elapsed.

Fig. 8-33: Concentration of tracer and recovery in the extraction borehole (measured vs. modelled) for tracer test TT12-02
8.2.3.6 Tracer Test – TT13-01

The model input parameters for this tracer test are given in Table 8-17, and the fitted values in Table 8-18 (note that the channel pathway volumes used were the same as for TT09-03). The tracer concentrations are shown in Figures 8-34, 8-35 and 8-36 for this test. Again, the concentration tends to fall off too quickly in each of the boreholes.

The model predicts that, in this tracer test, 92.0% of the water extracted from the observation borehole, and 98.0% of the water extracted from the extraction borehole, is drawn from the wider fracture.

Tab. 8-17: Model input parameters specific to tracer test TT13-01

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement borehole volume</td>
<td>13.898 L</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Duration of circulation</td>
<td>113 h</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Circulated concentration in emplacement borehole</td>
<td>2050 ppb</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Injection rate in emplacement borehole ($Q_{emp}$)</td>
<td>0.07 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from observation borehole ($Q_{obs}$)</td>
<td>0.05 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
<tr>
<td>Extraction rate from extraction borehole ($Q_{ext}$)</td>
<td>1.4 ml min$^{-1}$</td>
<td>Lanyon &amp; Mäder (2020)</td>
</tr>
</tbody>
</table>

Tab. 8-18: Values of parameters used to fit the model to the results of TT13-01

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate from wider fracture into observation borehole, $Q_{FracObs}$</td>
<td>0.046 ml min$^{-1}$</td>
</tr>
<tr>
<td>Flow rate from wider fracture into extraction borehole, $Q_{FracExt}$</td>
<td>1.372 ml min$^{-1}$</td>
</tr>
</tbody>
</table>
Fig. 8-34: Concentration of tracer in the emplacement borehole (measured vs. modelled) for tracer test TT13-01
Note: The fluorometer was moved to the observation borehole at ~ 100 hours.

Fig. 8-35: Concentration of tracer and recovery in the observation borehole (measured vs. modelled) for tracer test TT13-01
Note: The fluorometer was not connected to this borehole until ~100 hours had elapsed.
8.2.4 Reactive transport model

Having deduced plausible flow rates and pathway volumes using the tracer test results, a reactive transport model was then produced. The model includes advective flow along the channel pathway, linking the emplacement borehole to either the observation or extraction borehole, and sideways diffusion from the channel into the adjoining rock matrix and stagnant zone, as shown in Figure 8-37. Using symmetry, only one quarter of the channel is modelled, reducing the number of cells required.

![Schematic diagram of the reactive transport model](image)

Note: Flow is advective along the channel (blue); diffusion occurs sideways into the rock matrix (green) and stagnant zone (orange). The cells in these two directions are only connected in the direction perpendicular to the channel, making the model 2.5D, rather than 3D. Additional 1D discretisation in the rock matrix and stagnant zone is not shown.
At one end of the channel a time-varying flow rate and porewater concentration are applied. The porewater concentration is taken directly from the 3D model of the cement source in the emplacement borehole, described in section 8.1. The flow rate is taken from the tracer test fitting exercise described above in section 8.2.3; Figures 8-38 and 8-39 show the imposed flow rates for the observation and extraction pathways respectively. The results from tracer tests TT10-01 and TT11-01 do not give consistent flow rates, considering that both occurred during the high injection rate regime; a variant will be considered where the result from TT11-01 is discarded.

At the point where the water from the channel enters the observation/extraction boreholes, it is mixed with Grimsel groundwater (in the ratios calculated by fitting the tracer tests, as described above). It is noted that this advective mixing could (and indeed is likely to) occur at junctions between channels at various locations along the pathway, rather than just at the end. However, testing of the model indicates that mixing the waters earlier in the pathway causes the same minerals to precipitate but moves the precipitation point to coincide with the mixing location. Naturally, by only mixing at the end of the channel (where it joins the observation or extraction borehole), the model is likely to predict larger amounts of precipitation there than might otherwise be seen, but as this has not been quantified from the results of the LCS experiment it is impossible to say how this far from reality this assumption moves the model results.

Finally, boundary conditions are applied to the extremities of the rock matrix and the stagnant zone to allow diffusion of fresh Grimsel water into these cells. These boundaries are both placed 1 m away from the centre of the channel.

---

**Fig. 8-38:** The flow rate boundary condition assumed for the emplacement observation channel reactive transport model

**Note:** The shading and numbers at the top of the plot indicate the different injection rates into the emplacement borehole.
Fig. 8.39: The flow rate boundary condition assumed for the emplacement extraction channel reactive transport model.

Note: The shading and numbers at the top of the plot indicate the different injection rates into the emplacement borehole.

The governing equations are described by Watson et al. (2016a; Section 7), and the geochemical input parameters are the same as described therein, with the exception of the update to the Grimsel groundwater composition discussed in section 8.1.3 above. In addition, the model described by Watson et al. (2016a) did not include the rock matrix or fault gouge; the composition of these is given in Table 8-19. Here, plagioclase feldspar is assumed to consist of two-thirds albite and one-third anorthite, which is typical of plagioclase compositions in granitic (sensu lato) rocks. The biotite present in the fault gouge is most likely iron-rich, i.e. broadly of annite composition (KFe₃AlSi₃O₁₀(OH)₂). In order to exclude redox processes in the modelled system, which are more challenging to model and are not considered important in this system, the biotite is assumed here to be of phlogopitic composition (KAlMg₃Si₃O₁₀(OH)₂). The dissolution rates of these minerals are similar (e.g. Nagy, 1995) so that this simplifying assumption is not expected to dramatically affect the scale of water-rock interaction.

The minor minerals epidote, chlorite, and smectite have been excluded from the simplified composition since their abundances and (slow) reaction rates are unlikely to affect major element exchange between rock and groundwater.
Tab. 8-19: Compositions of fault gouge and rock matrix assumed in reactive transport modelling, after Mäder et al. (2006)

Note: Porosity of fault gouge from Lanyon & Mäder (2020); porosity of rock matrix rounded up from the value of 0.65% used by Soler et al. (2015).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Fault Gouge</th>
<th>Rock Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>16.1</td>
<td>30.7</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi₃O₈</td>
<td>7.7</td>
<td>16.8</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl₂(SiO₄)₂</td>
<td>4.2</td>
<td>6.9</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>KAlSi₃O₈</td>
<td>13.3</td>
<td>27.7</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>KAlMg₃Si₃O₁₀(OH)₂</td>
<td>7.7</td>
<td>7.9</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₃Si₂O₁₀(OH)₂</td>
<td>17.5</td>
<td>5.9</td>
</tr>
<tr>
<td>Inert</td>
<td>—</td>
<td>3.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Porosity</td>
<td>—</td>
<td>30.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The kinetic approach of Watson et al. (2016a; Section 7) is also adopted here to represent the precipitation and dissolution of minerals.

All minerals are assumed to dissolve/grow at a volumetric rate \( R \) (mol m\(^{-3}\) s\(^{-1}\)) governed by the following equation (e.g. Lasaga, 1998)

\[
R = A k_0 (a_{\text{H}^+})^p (\Omega - 1)
\]  

(8-1)

where \( A \) is the mineral reactive surface area (m\(^2\) m\(^{-3}\)); \( k_0 \) is the rate constant for dissolution or growth (mol m\(^{-2}\) s\(^{-1}\)); \( a_{\text{H}^+} \) is the activity of H\(^+\) in solution (-); the exponent \( p \) is a constant for a given mineral (-); and \( \Omega \) is the saturation of the mineral (the ratio of the ion activity product to the equilibrium constant, \( K_{eq} \), for the mineral).

A positive rate (\( \Omega > 1 \)) represents precipitation, while a negative rate (\( \Omega < 1 \)) represents dissolution. Note that this leads to asymmetric precipitation/dissolution rates (the range for \( \Omega - 1 \) is unbounded at the upper end for the former case, while the latter case is bounded in the range \([-1,0]\) mol m\(^{-3}\) s\(^{-1}\), as \( \Omega \) is always positive), but a lack of data in the literature precludes the confident use of any other form for the majority of minerals. In addition, in interactions in natural systems such as this, with the exception of times close to initial disequilibrium (e.g. shortly after emplacement), minerals are often close to saturation (mildly under- or over-saturated), and the bias will have little effect.

The kinetic data used for the primary rock and fault gouge minerals are given in Table 8-20; see chapter 7 for details of the data for the secondary (potentially precipitating) minerals. In the absence of other data, the reactive surface area (\( A \)) of all minerals is calculated by making an assumption of small (sand-sized) grains with a radius of 0.5 µm. In the case of anorthite, the slower dissolution rate (\( k_0 \)) of bytownite and the exponent (\( p \) in equation (1)) for albite from Palandri & Kharaka (2004) were used as preliminary results gave too much anorthite dissolution using the suggested values for anorthite itself.
Tab. 8-20: Kinetic data for primary minerals (at 15 °C except where indicated)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$\log_{10} k_0$ (mol m$^{-2}$m$^{-1}$)</th>
<th>$p$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>-17.0</td>
<td>-0.5</td>
<td>Knauss &amp; Wolery (1988)</td>
</tr>
<tr>
<td>Albite</td>
<td>-16.0</td>
<td>-0.572</td>
<td>Palandri &amp; Kharaka (2004)</td>
</tr>
<tr>
<td>Anorthite</td>
<td>-18.8</td>
<td>-0.572</td>
<td>Palandri &amp; Kharaka (2004)</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>-21.3</td>
<td>-0.823</td>
<td>Palandri &amp; Kharaka (2004)</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>-12.6</td>
<td>0</td>
<td>Palandri &amp; Kharaka (2004)</td>
</tr>
</tbody>
</table>

Molar volume, weight and solubility data are presented in Table 8-21. These data are taken from the Geochemist’s Workbench (Bethke, 2008) version of the Lawrence Livermore (LLNL) database ‘thermo.com.V8.R6+’, and computed at the ambient Grimsel temperature of 15 °C using a linear interpolation. Molar volumes and weights of minerals were also taken from this database.

Tab. 8-21: Molar volume, weight and equilibrium data for the primary minerals (at 15 °C)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Molar Volume</th>
<th>Molar Weight</th>
<th>Reaction</th>
<th>$\log_{10} K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>22.688</td>
<td>60.0843</td>
<td>$\text{SiO}_2 = \text{SiO}_2^{2(\text{aq})}$</td>
<td>-4.2524</td>
</tr>
<tr>
<td>Albite</td>
<td>100.250</td>
<td>262.2230</td>
<td>$\text{NaAlSi}_{2.0}\text{O}_6 = 3\text{SiO}_2^{2(\text{aq})} + \text{Na}^+ + \text{AlO}_2^-$</td>
<td>-21.0805</td>
</tr>
<tr>
<td>Anorthite</td>
<td>100.790</td>
<td>278.2073</td>
<td>$\text{CaAl}_2(\text{SiO}_4)_2 = \text{Ca}^{2+} + 2\text{SiO}_2^{2(\text{aq})} + 2\text{AlO}_2^-$</td>
<td>-19.672</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>108.870</td>
<td>278.3315</td>
<td>$\text{KAlSi}_3\text{O}_8 = 3\text{SiO}_2^{2(\text{aq})} + \text{K}^+ + \text{AlO}_2^-$</td>
<td>-24.3005</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>149.660</td>
<td>417.2600</td>
<td>$\text{KAlMg}_3\text{Si}<em>3\text{O}</em>{10}(\text{OH})_2 + 6\text{H}^+ = 4\text{H}_2\text{O} + \text{K}^+ + 3\text{Mg}^{2+} + 3\text{SiO}_2^{2(\text{aq})} + \text{AlO}_2^-$</td>
<td>15.2535</td>
</tr>
<tr>
<td>Muscovite</td>
<td>140.710</td>
<td>398.3081</td>
<td>$\text{KAl}_3\text{Si}<em>3\text{O}</em>{10}(\text{OH})_2 = 2\text{H}^+ + \text{K}^+ + 3\text{SiO}_2^{2(\text{aq})} + 3\text{AlO}_2^-$</td>
<td>-57.141</td>
</tr>
</tbody>
</table>

8.2.4.1 Variant cases

A number of variant cases were considered in the modelling, as shown in Table 8-22. As the 3D cement source model (section 8.1) is used to provide the porewater boundary condition, these model variants (calcite kinetics, calcite equilibrium, and calcite equilibrium with alkali release) are also considered here, with the exception of the variant where the slow cement kinetics were used as this did not match well with the experimental data.

In addition, since the tracer test fits (section 8.2.3) can only give information about the volume of the channels, and not specifically the length or width, variants are considered of the two extreme cases (i.e. a long, narrow channel and a short, wide channel).

Finally, variants are also included where the flow rates deduced from tracer test TT11 01 are removed, as they do not appear to be consistent with those derived from tracer test TT10 01. There were issues with the extraction fluorometer during this test (see section 8.2.3), which could have led to the inconsistent results.
Tab. 8-22: Model variants considered in the full fracture modelling

Note: “Calcite kinetics” and “Calcite equilibrium” indicate the approach taken to precipitation of calcite. “Long and narrow” and “Short and wide” indicate the assumption used about the channel dimensions. “Alkali release” indicates that the release of alkalis from the cement was modelled explicitly (rather than assuming they had already been removed). “TT11-01 ignored” indicates the results of tracer test TT11-01 were disregarded when calculating the flow rates along the channels.

<table>
<thead>
<tr>
<th>Model Variant</th>
<th>Short Description</th>
<th>3D Model Variant Supplying High-pH Water (Tab. 8-4)</th>
<th>Channel Length</th>
<th>Channel Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(a)</td>
<td>Calcite kinetics, long and narrow</td>
<td>(a)</td>
<td>44.8 m (Obs) 22.4 m (Ext)</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>2(a)</td>
<td>Calcite kinetics, short and wide</td>
<td>(a)</td>
<td>0.56 m (Obs) 1.12 m (Ext)</td>
<td>40 mm (Obs) 10 mm (Ext)</td>
</tr>
<tr>
<td>1(b)</td>
<td>Calcite equilibrium, long and narrow</td>
<td>(b)</td>
<td>44.8 m (Obs) 22.4 m (Ext)</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>2(b)</td>
<td>Calcite equilibrium, short and wide</td>
<td>(b)</td>
<td>0.56 m (Obs) 1.12 m (Ext)</td>
<td>40 mm (Obs) 10 mm (Ext)</td>
</tr>
<tr>
<td>1(d)</td>
<td>Calcite equilibrium, alkali release, long and narrow</td>
<td>(d)</td>
<td>44.8 m (Obs) 22.4 m (Ext)</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>2(d)</td>
<td>Calcite equilibrium, alkali release, short and wide</td>
<td>(d)</td>
<td>0.56 m (Obs) 1.12 m (Ext)</td>
<td>40 mm (Obs) 10 mm (Ext)</td>
</tr>
<tr>
<td>3(b)</td>
<td>Calcite equilibrium, TT11-01 ignored, long and narrow</td>
<td>(b)</td>
<td>44.8 m (Obs) 22.4 m (Ext)</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>4(b)</td>
<td>Calcite equilibrium, TT11-01 ignored, short and wide</td>
<td>(b)</td>
<td>0.56 m (Obs) 1.12 m (Ext)</td>
<td>40 mm (Obs) 10 mm (Ext)</td>
</tr>
</tbody>
</table>

8.2.5 Model results

8.2.5.1 Precipitation in the channel

In terms of the minerals that precipitate in the emplacement-extraction channel, all of the model variants produce similar results.

In the period prior to injection in the emplacement borehole, ettringite (hydrous calcium aluminium sulphate) precipitates at the emplacement borehole end, extending up to 5 m along the channel, along with smaller amounts of 11Å-tobermorite, as shown in Figure 8-40. When injection commences after approximately a year and a quarter, the pH in the channel is raised and ettringite consequently dissolves again. However, 11Å-tobermorite continues to precipitate along the channel, reaching up to just over 12 m. At the same time, calcite starts to precipitate at the end of the channel nearest to the extraction borehole (Fig. 8-41).
Fig. 8-40: Volume fraction plot of the emplacement-extraction channel after 1.2 years of simulation (Variant 1(b) – calcite equilibrium, long and narrow channel)

Fig. 8-41: Volume fraction plot of the emplacement-extraction channel after 6 years of simulation (Variant 1(b) – calcite equilibrium, long and narrow channel)
In the variants where calcite kinetics are assumed (1(a) and 2(a)), calcite also precipitates in large quantities at the end of the channel nearest the emplacement borehole (Fig. 8-42). While calcite is kinetically limited within the borehole due to the high pH (given the implemented rate law), in the channel the diffusive mixing with the Grimsel groundwater causes the pH to be lower (not rising far above 11), enabling the oversaturated calcite to precipitate. In these cases, the channel becomes blocked at the emplacement borehole end (noting that a zero porosity is not possible in the model; a minimum porosity of 0.005 is enforced to allow very small amounts of flow (and transport) to continue).

The minerals that precipitate are not influenced by the length of the channel; the only difference between the variants is the proportion of the channel that sees precipitate appear.

Fig. 8-42: Volume fraction plot of the emplacement-extraction channel after 6 years of simulation (Variant 1(a) – calcite kinetics, long and narrow channel)

In the emplacement-observation channel, the precipitating minerals are similar to those described above but there are some subtle differences caused by the lower flow rates. Here, the length of the channel does affect the minerals that are seen; ettringite does not appear in the long and narrow case, nor does calcite precipitate at the observation borehole end of the channel in these variants. Instead, calcite precipitates in small quantities about a quarter of the way along the channel from the emplacement borehole. In general, there is less calcite precipitation in this channel, and no blocking occurs in the variants where calcite kinetics are assumed, unlike the emplacement-extraction channel.

One of the main differences in this channel compared to the extraction channel is that, in the short and wide channel variant with calcite equilibrium (variant 2(b)), small amounts of gismondine (a C-A-S-H proxy) form, predominantly at the end of the channel nearest the observation borehole, as shown in Figure 8-43.
Fig. 8-43: Volume fraction plot of the emplacement-observation channel after 6 years of simulation (Variant 2(d) – calcite equilibrium, alkali release, short and wide channel)

It is noted that the blocking of cells in simulations such as this is very much dependent on the size of the cells used. Here a rather coarse discretisation has been adopted; tests with finer discretisation show that the precipitating minerals are the same but the impact on porosity may differ (i.e. smaller cells clog more quickly). In particular, calcite will precipitate in the final cell in the channel, at the point where the most mixing occurs as the high-pH plume enters the borehole; if this cell is small the impact on porosity will be great and blocking may occur.

8.2.5.2 Mineral alteration in the rock matrix and stagnant zone

Within the stagnant zone, alteration is confined to approximately 15 cm from the centre of the channel, as shown by the porosity profiles in Figure 8-44. Immediately adjacent to the channel, porosity is found to decrease (a change of ~0.012) near to the emplacement borehole and increase (a change of ~0.005) at the other end of the channel. Further into the stagnant zone, porosity is slightly decreased from its initial value, by about 0.003. This change in porosity is caused by the dissolution of albite (plagioclase feldspar) and some muscovite (mica) from the fault gouge and precipitation of 11Å-tobermorite (C-S-H mineral), some gismondine (C-A-S-H proxy) and small amounts of calcite (much more calcite precipitates in the variants with calcite kinetics, as discussed in section 8.2.5.1). All variants and both channels show broadly the same alteration characteristics.
Within the rock matrix, alteration is confined to a smaller zone close to the channel due to the much smaller porosity of the granite compared to the fault gouge. Here, porosity changes are only seen up to ~5 cm from the channel centre, as shown in Figure 8-45. In all locations along the channel there is an increase in porosity immediately adjacent to the channel (a change of ~0.019), with a decrease in the zone up to ~2.5 cm, and a small increase in the zone 2.5 - 5.0 cm. Again, albite dissolves from the rock matrix nearest the channel, although unlike the fault gouge there is very little muscovite dissolution. 11Å-tobermorite (C-S-H mineral) is the main precipitate, particularly near the channel; slightly deeper into the rock gismondine (C-A-S-H proxy) increases in abundance. There is little calcite precipitation predicted by the model in the rock matrix, except in variants where calcite kinetics are assumed, as discussed above. Again, apart from this difference, there is little diversity between the variant cases, with the length of the channel having little or no impact.

A summary of the modelled changes in the channel, stagnant zone and rock matrix is given in Figure 8-46. It should be stressed that, due to the limited timescales involved, the amounts of precipitation and dissolution predicted by the model are very small indeed.
Fig. 8-45: Porosity profiles into the rock matrix at different positions along the emplacement-extraction channel (Variant 1(b), calcite equilibrium, long and narrow channel). (Initial porosity = 0.01)

Fig. 8-46: Summary of mineral alteration in and around channel predicted by models

Note: The calcite only precipitates at the emplacement end if kinetics are employed, rather than adopting an equilibrium assumption.
### 8.2.5.3 Porewater composition

A comparison between the modelled pH of the porewater in the observation borehole and the measurements taken during the experiment is shown in Figure 8-47. Concentrations of other major ions in this borehole are shown in Figure 8-48. Only results from the variants with the long, narrow channel are shown; those from the short, wide channel were very similar, with the main difference being in the variants including alkali release (1(d) and 2(d), green line). In the short channel case, the early peaks in Na and K seen in the emplacement borehole (Fig. 8-15) are transmitted to the observation borehole, but in the long channel case there is not enough time for this to occur prior to the injection rate increasing.

There are two sets of pH measurements from the experiment, ‘lab’ and ‘field’, with the former analysed off-site in a laboratory environment and the latter analysed in-situ. Clearly the ‘lab’ data include unexpectedly low values of the pH during the early stages of the experiment (as indicated by the grey dashed line in Figure 8-47, the background pH at Grimsel is around 9.7). The ‘field’ data appear to be more reliable but are much sparser; in particular data are missing from the period of increased injection into the emplacement borehole.

In all cases the measured data are rather flat (i.e. the concentrations do not vary much with time), with the exception of Ca, pH and possibly Al. The simulations also show little change from the background concentrations in most species apart from when the highest injection rate was used in the emplacement borehole. However, there is a long-term slight increase in Al, Si and Na as the granitic minerals dissolve. The simulated peaks in pH and Ca caused by the increased injection rate are possibly a little earlier than the measured peaks, although it is hard to make a comparison with the sparse data, particularly around this episode.

It was noted previously (section 8.1.4.3) that the modelled values of Mg and S were poor in the emplacement borehole, and this effect carries through here to the observation borehole comparison for Mg. This may mean that the Mg concentration in the modelled Grimsel groundwater was not representative of the natural concentration experienced during the LCS experiment. On the other hand, the fit for S is quite good (the same order of magnitude as the measured concentrations), although there are few data points to match against the response during the high injection period.

The same comparisons between the modelled pH and aqueous species and the measurement are made for the extraction borehole in Figures 8-49 and 8-50. Again, only results for the long, narrow case are shown; the results for the short, wide channel are very similar. In this case there is also little difference between the two channel lengths for the variant including alkali release.

Most of the species show little response to the high-pH plume, in either the modelled or measured data, with the exception of Ca, Al, pH and K (the latter only at early times).

The model matches the pH relatively well, in particular variant 3(b) (calcite equilibrium and dubious flow rates from tracer test TT11-01 discarded). This variant is also a reasonable match for the Ca profile. The variant including alkali release (1(d)) is able to capture an early increase in the concentration of K which is not seen in the other models.
Fig. 8-47: Evolution of pH in the observation borehole

Note: The model cases are as follows: 1(a) calcite kinetics; 1(b) calcite equilibrium; 1(d) calcite equilibrium, alkali release; and 3(b) calcite equilibrium, TT11-01 ignored. All variants shown are for the long, narrow channel.
Fig. 8-48: Evolution of aqueous species in the emplacement borehole

Note: The model cases are as follows: 1(a) calcite kinetics; 1(b) calcite equilibrium; 1(d) calcite equilibrium, alkali release; and 3(b) calcite equilibrium, TT11-01 ignored. All variants shown are for the long, narrow channel.
Fig. 8-49: Evolution of pH in the observation borehole

Note: The model cases are as follows: 1(a) calcite kinetics; 1(b) calcite equilibrium; 1(d) calcite equilibrium, alkali release; and 3(b) calcite equilibrium, TT11-01 ignored. All variants shown are for the long, narrow channel. Note that the vertical axis range chosen hides some early ‘lab’ data which are at unfeasibly low pH values.
Fig. 8-50: Evolution of aqueous species in the extraction borehole

Note: The model cases are as follows: 1(a) calcite kinetics; 1(b) calcite equilibrium; 1(d) calcite equilibrium, alkali release; and 3(b) calcite equilibrium, TT11-01 ignored. All variants shown are for the long, narrow channel.
8.2.5.4 Summary and conclusions

A comparison between the key findings of the laboratory analysis and the results of the modelling is given in Table 8-23. According to this qualitative comparison, the model performs quite well; the main characteristics of C-S-H and C-A-S-H precipitation in the fracture and calcite at the extraction borehole are matched. However, the timescales of the experiment are such that not much alteration happens at all at any distance from the emplacement borehole, and thus it is rather difficult to truly assess the predictive capability of any model.

In addition, there is no evidence from LCS Experiment 2 that confirms or refutes the hypothesis that flow between the boreholes is channelled. The model predicts that large amounts of calcite will precipitate at any point where the high-pH plume mixes with the Grimsel groundwater; if the flow is channelled, this could potentially lead to the blocking of flow paths. Of course, there may be other flow paths that become active or more dominant once this blocking occurs, but again there is no evidence from the LCS experiment to help determine whether this is the case or not.

The model also predicts precipitation of C-S-H and, to a lesser degree, C-A-S-H along the length of the fracture and in the adjacent rock and fault gouge. Although not attempted here, consideration of armouring of the fracture could be undertaken, in the manner of Watson et al. (2016b).
<table>
<thead>
<tr>
<th>Key Findings from Laboratory Analysis</th>
<th>Results of Modelling</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-S-H and C-A-S-H found to line fractures and borehole walls; found in all samples, even those taken furthest from borehole.</td>
<td>C-S-H precipitates along most of the fracture in all variants. Some variants also predicted lesser amounts of C-A-S-H within the fracture, although this was more abundant in the adjacent rock and fault gouge.</td>
<td></td>
</tr>
<tr>
<td>Some calcite, minor amounts of aragonite and small amounts of vaterite found in or replacing the C-S-H/C-A-S-H gels in the fractures.</td>
<td>Some variants (those including calcite kinetics) predicted calcite precipitation near the emplacement borehole.</td>
<td>In these variants, calcite was oversaturated in the borehole but did not precipitate there because of the high pH. On entering the lower-pH environment of the channel, calcite precipitated in quantity.</td>
</tr>
<tr>
<td>Etching and dissolution of primary silicate mineral surfaces (mostly quartz and feldspar, some mica).</td>
<td>Very little quartz and K-feldspar dissolution; however, albite (plagioclase feldspar) dissolved in both the rock matrix and fault gouge, and muscovite (mica) dissolved in the fault gouge.</td>
<td></td>
</tr>
<tr>
<td>Calcite precipitation in extraction borehole.</td>
<td>In most variants, calcite precipitated at the end of the channel.</td>
<td>In the model, advective mixing only occurred at the end of the channel, where it entered the borehole. If the mixing point is moved, the calcite precipitation moves with it.</td>
</tr>
</tbody>
</table>
8.3 Discussion

During this study, carried out as part of the LCS project, two reactive transport models of LCS Experiment 2 have been developed. The experiment, which ran for 6 years at the Grimsel Test Site, involved insertion of pre-hardened cement into a borehole drilled to intersect a fracture plane. The aim of the experiment was to obtain information on how the alkaline plume resulting from interaction between the cement and natural groundwater migrated through the fracture. The first reactive transport model was concerned with the evolution of the cement source in the emplacement borehole; this work built on some earlier blind modelling reported by Watson et al. (2016a). The second model considered the wider fracture system, aiming to replicate the movement of the high-pH plume and its effect on the geochemistry at two sampling points also located in the same fracture. The output of the first model was used as input to the second, thus the two are intrinsically linked.

In each case, the results of the models have been compared against available data from laboratory analysis of the dismantled experiment. Quantitative information is somewhat lacking (at the time of writing) but qualitatively the models perform well.

The 3D model of the cement source in the emplacement borehole demonstrated a capability to simulate the fine details of in-situ experiments at a high spatial resolution, including complex geometry and chemistry (including aqueous speciation and mineral dissolution/precipitation kinetics). The results of the blind modelling carried out by Watson et al. (2016a) were first compared to the results of the laboratory analysis of the dismantled experiment. Characteristics such as a leached zone in the cement where all portlandite was removed, C-S-H was decalcified and porosity increased were replicated successfully. Crucially, however, no calcite precipitation was predicted by the model, although analysis showed that it was present on the cement shells. The model of Watson et al. (2016a) was updated, therefore, by allowing calcite to precipitate in equilibrium with the surrounding fluid. A variant case was also added which included a model of alkali release from the cement, in order to better match early-time concentrations of Na and K in the porewater. This updated model was shown to better match the data from the laboratory analysis, with calcite now precipitating in many areas of the borehole, and a better match for the measured porewater concentrations produced.

The cement porewater produced by the emplacement borehole model was then taken and used as input in a second reactive transport model, this time of the wider fracture system. A great deal of evidence points towards channelling of flow in fracture planes, and this conceptual model was used as the basis of the work. A relatively simple flow model was produced based on a mass conservation approach and tuned using the various tracer tests that were conducted throughout the lifetime of the LCS experiment. Although a number of variant cases were considered, including channels of different widths and lengths, in general each model produced results with similar characteristics. These included:

- precipitation of C-S-H and lesser amounts of C-A-S-H along the length of the channel and a few centimetres into the rock matrix and stagnant zone, causing a small reduction in porosity;
- precipitation of calcite at the end of the channel, where advective mixing with the Grimsel groundwater occurred, with the possibility of completely blocking the channel pathway; and
- minor amounts of dissolution of albite (plagioclase feldspar) and muscovite (mica) from the adjacent fault gouge and rock matrix.

All of these observations were entirely consistent with the qualitative findings of the laboratory analysis on samples taken from the overcored LCS experiment. However, the timescales of the experiment are such that not much alteration happens at all at any distance from the emplacement borehole, and thus it is rather difficult to truly assess the predictive capability of any model.
Modelling of the LCS experiment has provided an opportunity for modellers and experimentalists to work closely together. This allows liaison between the two disciplines, so that the modellers can understand better the experimental setup and the intrinsic limitations of various techniques, whilst the experimentalists can target their analysis in areas that are of particular use for the validation of models. While some early aspects of the experiment could, with hindsight, have been conducted more precisely, such as retaining a sample of the cement for chemical analysis and attempting to better characterise the flow system prior to emplacement (points to note when preparing another similar, experiment, or when constructing a GDF), the collaboration aspects of the project worked particularly well in the latter stages when the experiment was being dismantled and samples sent to laboratories for analysis. For example, the spatial distribution of mineral alteration suggested by the modelling work led to samples being taken from various locations around the cement shells, and a camera was used to investigate the extraction borehole because the models suggested precipitation there. Similarly, the modellers benefited from the input of the experimentalists when the results of the analysis were presented, leading to an enhanced understanding of what was seen in the experiment.

In particular, the modelling work described in this report has demonstrated that current state-of-the-art understanding of cement leaching processes is able to accurately replicate the observed leaching of cement in natural in-situ conditions, at least in a qualitative sense, such that the main mineralogical and porosity changes are captured. This is important for modelling that could contribute to performance assessment/safety case studies of GDFs, as an accurate representation of the source term (in terms of how it evolves with time and the main chemical features) is required in order to be able to model any subsequent movement of a resultant high-pH plume. Unfortunately, the LCS experiment may have revealed relatively little about the movement of the plume through the fracture itself, other than perhaps demonstrating that obtaining a good understanding of the flow fields is key. However, a modelling capability has been developed that is based on the conceptualisation of flow in channels and has been shown to match the observations at Grimsel relatively well. This model has the potential to be developed further in future, including the possibility of adding fracture armouring by precipitates, which has the potential to limit diffusion into the rock matrix and enhance transport distances along fractures, a matter which is of concern in safety case studies and the performance assessment modelling that contributes to those studies.

8.4 Hong & Glasser model of alkali release

8.4.1 Background

Hong & Glasser (1999) present a theory for determining the relative amounts of sodium and potassium bound into cement paste and dissolved in the pore fluid. They show, using experimental data, that a simple distribution ratio, $R_d$ (ml g$^{-1}$), can be used to determine the relative amounts:

\[ R_d = \frac{s}{l} \]  \hspace{1cm} (8-2)

where $s$ is the concentration of the alkali bound to the C-S-H gel in the paste (mmol g$^{-1}$) and $l$ is the concentration of the alkali in solution (mmol ml$^{-1}$). The value of the distribution ratio depends on the Ca/Si ratio of cement, with larger values of $R_d$ corresponding to smaller Ca/Si ratios.
8.4.2 Implementation in QPAC

This mechanism of alkali release can be managed in the standard QPAC reactive transport module using appropriate kinetic rates. The bound alkanis are represented by adding two mineral species to the database (which uses the Geochemist’s Workbench format), for example:

NaMineral
type=
formula= Na
mole vol.= 1.000 cc mole wt.= 1.0 g
1 species in reaction
1.0000 Na+
999 999 999 999
999 999 999 999

KMineral
type=
formula= K
mole vol.= 1.000 cc mole wt.= 1.0 g
1 species in reaction
1.0000 K+
999 999 999 999
999 999 999 999

Here, the log K values (the 999 values) are arbitrary as they will not be used in the calculation. Similarly, the molar volume and weight have been given small arbitrary (non-zero) values.

In general, kinetic rates are implemented in QPAC in the form

\[ r = kA \left( \frac{Q}{K} - 1 \right) \]  

(8-3)

where \( r \) is the rate of mineral precipitation (mol m\(^{-3}\) s\(^{-1}\)), \( k \) is the kinetic rate constant (mol m\(^{2}\) s\(^{-1}\)), \( A \) is the mineral reactive surface area (m\(^{2}\) m\(^{-3}\)), \( Q \) is the ion activity product (-) and \( K \) is the equilibrium constant (-). Thus, equilibrium is attained when \( Q/K = 1 \), i.e., \( Q = K \).

In the case of bound alkanis, however, equilibrium is attained when equation (8-2) is satisfied. Thus, for the alkali ‘minerals’ (8-3) is replaced by

\[ r_{alkali} = kA \left( R_d - \frac{S}{l} \right) \]  

(8-4)

To model this as a near instantaneous process, the kinetic rate constant \( k \) can be set to a large value. The mineral surface area \( A \) is fairly arbitrary here but can be retained (rather than choosing a value of \( k \) to cancel it out) so that the overall rate will tend to zero as the amount of bound alkali diminishes.

The concentration of bound alkali, \( s \) (mmol g\(^{-1}\)), is the number of moles of the alkali per unit mass of C-S-H gel in the cement and is given in QPAC syntax by:

\[ s = \frac{10^3 \times \text{Chem∷Conc_MINERAL}[\text{ALK}]}{\text{Chem∷Conc_MINERAL}[\text{C-S-H}] \times \text{Chem∷MolarWeight_MINERAL}[\text{C-S-H}]} \]  

(8-5)

where ALK is either ‘NaMineral’ or ‘KMineral’ and the scaling factor is needed because mineral concentrations have units of mol m\(^{-3}\) in QPAC. Similarly, the concentration of alkali in solution, \( l \) (mmol l\(^{-1}\)), is given by:

\[ l = 10^3 \times \text{Chem∷Molality_Basis}[b] \times 1 \text{ [kg l^{-1}]} \]  

(8-6)

where \( b \) is Na\(^+\) or K\(^+\) accordingly, and it has been assumed that 1 litre of water weights 1 kilogram.
8.4.3 Testing of the model

8.4.3.1 Comparison with experimental results

Hong & Glasser (1999) present results from a series of experiments where they either place fresh C-S-H gel in NaOH or KOH solutions, or place C-S-H gel ‘loaded’ with alkalis in distilled water. In each case they derive a value for $R_d$ by measuring the relative amounts of sorbed and dissolved alkali.

The experiments were conducted at a temperature of 20 °C, using 0.6 g of solid C-S-H and 9 ml of solution. This was simulated in QPAC in a compartment of size 9 ml, with porosity of 1 but an initial concentration of C-S-H gel that corresponds to 0.6 g.

Figures 8-51 and 8-52 show a comparison for the sorption results between Hong & Glasser and the model, for sodium and potassium respectively. In both cases, the model is able to replicate the experimental results almost perfectly, with the correct amount of alkali taken up by the solid. One notable exception is the C/S ratio of 1.2 for an initial potassium concentration of 4.95 mmol/l, where the model results show a slightly lower solid concentration than the experimental data. This appears to be a mistake in the original paper; with a final dissolved concentration of 4.36 mmol/l and a solid phase concentration of 0.0088 mmol/g, the value of $R_d$ should be 2.01, not 1.78 as reported. Using this value in the model gives a perfect fit to the experimental data.

![Graph showing comparison between Hong & Glasser and model results for sodium and potassium.](image)

**Fig. 8-51:** Sodium steady-state concentrations in solid C-S-H of varying C/S ratios as a function of aqueous Na⁺ concentration (sorption experiments)
Fig. 8-52: Potassium steady-state concentrations in solid C-S-H of varying C/S ratios as a function of aqueous K⁺ concentration (sorption experiments)

Note: It appears to be an error in Hong & Glasser (1999) for the value of $R_d$ at a C/S ratio of 1.2 and an initial concentration of K⁺ of 4.95 mmol/l.

The fit between the model and the experimental data is not so good for the desorption experiments, as shown in Figures 8-53 and 8-54 which compare the solid to dissolved phase concentrations for sodium and potassium respectively. Only the results for one C/S ratio were reported by Hong & Glasser (1999). Each point on the plots shows the results from an experiment with a different initial amount of alkali loading. Hong & Glasser (1999) state that they do not have complete confidence in the experimental data; the process of removing the aqueous phase from the alkali-loaded C-S-H samples before commencing the experiment is not straightforward. A correction was applied to the data to account for the mass of remaining water, but the accuracy of this procedure decreases as the alkali content of the solution increases, or as the Na:Ca ratio in the solid decreases. The inaccuracy in this procedure could account for the consistent difference between model and data (note that the model points seem to lie on the same curve as the data, possibly indicating inaccuracies in determining the initial alkali loading in the samples).

It is also noted that the value of $R_d$ for an initial Na loading of 0.0188 mmol/g is incorrect for the final solid/liquid ratio given, and should be 5.08 not 4.90 as stated in Hong & Glasser (1999). Changing this value does not improve the fit with the QPAC model.
Fig. 8-53: Sodium steady-state concentrations in solid C-S-H as a function of aqueous Na\(^+\) concentration (desorption experiments)

Fig. 8-54: Potassium steady-state concentrations in solid C-S-H as a function of aqueous Na\(^+\) concentration (desorption experiments)
8.4.3.2 Dissolution of C-S-H

As a final test of the model, the C-S-H is allowed to dissolve. This should force the sorbed alkalis to be released into solution. There are no experimental data to compare against, so this is a simple check that the model performs as expected.

In the QPAC model the initial quantities of sorbed and dissolved sodium and potassium were set as shown in Table 8-24. These were chosen from the previous runs, so that with prescribed values of $R_d$ and no dissolution of C-S-H the system would be in equilibrium.

Tab. 8-24: Starting conditions for the dissolution test

<table>
<thead>
<tr>
<th></th>
<th>Sodium</th>
<th>Potassium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_d$</td>
<td>7.89 ml/g</td>
<td>8.89 ml/g</td>
</tr>
<tr>
<td>Initial conc.</td>
<td>0.306 mmol/g</td>
<td>0.319 mmol/g</td>
</tr>
<tr>
<td>Initial conc.</td>
<td>0.0388 mmol/l</td>
<td>0.0360 mmol/l</td>
</tr>
</tbody>
</table>

As shown in Figures 8-55 and 8-56, as the C-S-H gel dissolves the concentrations of the bound alkalis in the solid decrease and reach zero at the same time as all the C-S-H gel disappears. Correspondingly, the concentrations of Na$^+$ and K$^+$ in solution increase over the same timescales, before levelling off when no more dissolution can occur.

Fig. 8-55: Concentrations of C-S-H and bound Na and K over time in the dissolution test
Fig. 8-56: Concentrations of Na\(^+\) and K\(^+\) in solution over time in the dissolution test

8.4.4 Conclusions

It has been shown that the Hong & Glasser (1999) model of alkali binding in cement pastes can be implemented simply in QPAC models using a fast kinetic rate. The implementation has been tested by comparing against the experimental data presented in Hong & Glasser (1999); an excellent fit was obtained for the sorption experiments but a poorer fit was obtained for the desorption experiments, although the model results seem to lie on the same curve as the data. Hong & Glasser (1999) were not entirely confident in their results for the desorption experiments, due to the difficulties in drying the samples and applying a correction for the remaining solution, hence the disparity between model and experiment might not be unexpected. A final check was applied to ensure that dissolution of C-S-H gel in the model does indeed lead to release of alkalis from the solid phase, and this was confirmed to be the case.
9 Summary of the modelling exercises

Flow, tracer transport and reactive transport modelling of the LCS situ Experiment 2 at Grimsel has been performed by different teams (SKB, IDAEA-CSIC/UPC (POSIVA), QUINTESSA (RWM)).

9.1 SKB

SKB modelled the results of tracer test 09-03, which was performed before emplacement of the pre-hardened cement shells in borehole LCS 08.003. Tracer (uranine) was circulated at the emplacement borehole and actively extracted at the observation (LCS 07.002) and extraction (LCS 08.001) boreholes. 2D modelling (fracture plane including the 3 boreholes) was performed using COMSOL Multiphysics. A homogeneous fracture was assumed (T = 3e-9 m²/s, fracture aperture = 0.5 mm, K = 6e-6 m/s), together with the presence of low-permeability skins around the emplacement and observation boreholes (no previous indication of such a skin around the extraction borehole). The radius of the skins was assumed to be 20 cm. Tracer transport calculations were performed based on a steady-state flow field. A large domain (7 m × 6 m) was used for the flow calculations (constant hydraulic head boundary conditions), while transport was solved in a smaller domain including the 3 boreholes. A constant concentration was prescribed at the emplacement borehole during the tracer circulation period. The effects of domain and mesh size on the results were also investigated. For the fitting procedure, the magnitudes of transverse dispersivities and of the reduced transmissivities around the boreholes (skins) were adjusted. The transmissivities of the skins around the emplacement and observation boreholes were reduced by factors of 0.01 (emplacement) and 0.1 (observation) with respect to the transmissivity of the fracture. It is argued (through a calculation) that the amount of tracer that migrated out of the emplacement borehole but was not recovered at either the observation or extraction boreholes could be explained by a higher background hydraulic gradient (larger than the assumed 1 m/m), pushing tracer out of the model domain. However, the amount of tracer still remaining in the fracture plane in the calculations at the end of the tracer test has not been quantified.

9.2 IDAEA-CSIC/UPC

IDAEA-CSIC/UPC also performed 2D modelling of tracer test 09-03 assuming a homogeneous fracture including the 3 boreholes. The calculations were performed using Retraso-CodeBright. In this case, the fracture was assumed to be filled with fault gouge (porosity equal to 0.21) and to have an aperture of 1 mm (T = 3e-9 m²/s, K =3e-6 m/s). Given the intended goal of applying the flow and transport parameters to the experiment after the emplacement of the cement, it was considered that mass fluxes into the wall rock (matrix diffusion) would be very small given the very small porosity (<1%) and diffusion coefficients in the rock matrix. The expected effect on rock alteration in the fracture would be small. This concept had previously been applied in the modelling of the HPF laboratory core infiltration experiment, including the modelling of tracer (NaCl) transport (Soler et al., 2006; Soler & Mäder, 2007).

Low-permeability skins (radius 8 cm) were assumed around the emplacement and observation boreholes. The size of the domain was 5 m × 5 m. Constant pressure was assumed at the external boundaries of the domain for the calculation of the steady-state flow field. Advection flux into or out of the domain was assumed for tracer transport. Values of (isotropic) dispersivity were assigned according to mesh size. Different calculations were performed (sensitivity analysis), with 3 cases reproducing approximately the observed breakthrough curves. Transmissivities of
the skins around the emplacement and observation boreholes were reduced by factors of 0.01 – 0.03 (emplacement) and 0.1 (observation) with respect to the transmissivity of the fracture. The magnitude of the background hydraulic gradient was shown to have no effect of the results (checked for values of 0 m/m and 1 m/m); the flow field was controlled by the large extraction rate at the extraction borehole.

Following the modelling of tracer test 09-03, IDAEA-CSIC/UPC performed preliminary reactive transport modelling of the experiment (after emplacement of the pre-hardened cement shells), before any characterisation of the solid phases was available. Calculations were performed using Retraso-CodeBright. Initially, implementation of the concept and model domain from the tracer transport model was attempted. However, since the small grid size led to excessive computation times, 2 separate models were implemented: (a) a 1D radial model for the emplacement borehole and a small volume of rock around it (skin), and (b) a 2D model for the rest of the domain. The results from the 1D radial model (solute concentrations at the outer boundary of the skin at emplacement) were used as a time-dependent boundary condition for the 2D model. Transport in the cement at emplacement was assumed to be only by diffusion, due to its low permeability. The variable flow rates at the emplacement (injection), observation and extraction boreholes were taken into account. The total volumes of water in the circulation systems of the 3 boreholes were also taken into account through upscaled porosity values (perfect mixing assumed). Dispersivities in the 2D model (fracture and skins) were calibrated to the measured pH data. Mineral reaction was calculated using reaction rate laws. Rate constants and reactive surface areas for primary minerals in the fault gouge were taken directly from the modelling of the HPF laboratory core infiltration experiment. For all cement and secondary phases, fast kinetics (local equilibrium) was assumed.

Results from the 1D model predicted the dissolution of portlandite in a thin (1 mm) outer layer of the cement, with a corresponding increase in porosity. There was also minor dissolution of C-S-H at the cement/gap interface. Porosity at the gap-fracture interface was reduced due mainly to the precipitation of phlogopite. The results from the 2D model showed dissolution of the primary silicates (except phlogopite) and precipitation of C-S-H, C-A-S-H (prehnite) and calcite in the fracture. Porosity was reduced in a belt around the 3 boreholes, converging at the extraction borehole (due to the magnitude of the extraction flow rate). The decrease in porosity, due mainly to the precipitation of calcite, was stronger right next to the extraction borehole, due to the more favourable mixing conditions between Grimsel groundwater and cement porewater. The changing water injection rate conditions in the emplacement borehole led to changes in the flow field and in the position of the mineral reaction fronts.

Overall, calculated solute concentrations in the different boreholes approximated the measured values. Factors that could influence the observed differences were:

- The chemical composition of the Grimsel and cement water used in the model could be different from reality. This was clearly the case for Cl in Grimsel groundwater.
- The volume of water in the gap at the emplacement borehole could be larger than originally thought (up to about 1.7 L from the original 1.16 L).
- The pore diffusion coefficient of the cement was based on a guess from previous information. A proper calibration of the diffusion coefficient could improve the match.
- Cement and cement porewater composition were also assumed from values for a generic cement.
• The actual injection and extraction flow rates at the different boreholes showed larger variations than the model flow rates. This could also cause higher variation in the model results.

• The assumption that no water flow took place in the emplacement borehole skin during the initial diffusion period (zero injection rate) may not be entirely true.

After the end of the experiment, final reactive transport modelling was performed. The concept was the same as in the preliminary modelling, with the following changes:


• Updated water chemistry information from the different boreholes.

• Illite included as a potential secondary phase.

• Precipitation of primary minerals in the rock excluded, effectively meaning that phlogopite cannot precipitate in the rock as it did in the previous modelling.

• A fracture thickness of 5 mm has now been considered, instead of the 1 mm previously taken into account.

• Initial diffusion coefficient of cement calibrated to experimental results (thickness of the altered cement zone at the end of the experiment); \( D_p = 2 \times 10^{-11} \text{ m}^2/\text{s}, D_e \approx 1 \times 10^{-11} \text{ m}^2/\text{s} \).

• Update in permeability due to changes in porosity included in the calculations (but very small effect on results; only changes in pressure field). Large control by flow rates at boreholes.

• Sensitivity cases - (i) model including zeolites and crystalline C-S-H phases, (ii) 1-mm fracture thickness (instead of 5 mm).

Results from the 1D model show dissolution of portlandite (3 mm), C-S-H gel and ettringite at the cement-gap interface, with a corresponding increase in porosity, mainly due to portlandite dissolution. There is also precipitation of calcite and C-A-S-H (Al/Si=0.05 and Ca/Si=1). At the gap there is precipitation of calcite due to the mixing between the Grimsel groundwater and the cement porewater. At the skin, primary minerals of the fault gouge (albite, K-feldspar, phlogopite, muscovite and quartz) dissolve. Ettringite, C-A-S-H, calcite, hydrotalcite and hydrogarnet precipitate, causing a reduction of porosity. Dissolution of portlandite in the cement and precipitation of calcite at the cement-gap interface were observed in the postmortem analyses performed by EMPA. Also, C-A-S-H and calcite precipitation in the skin was observed in the mineralogical analyses of the overcore by BGS, both of which are consistent with the numerical model results. However, ettringite precipitation in the skin was not found. A model with a fracture thickness of 1 mm shows slightly lower dissolution of portlandite and C-S-H gel in the cement and lower precipitation of ettringite, C-A-S-H and calcite at the skin.

The results from the 2D model show dissolution of primary minerals (albite, K-feldspar, quartz, muscovite and phlogopite) due to the increase of pH at the centre of the plume. There is also precipitation of ettringite very close to the emplacement borehole and precipitation of C-A-S-H (Al/Si=0.05 and Ca/Si=1) in the centre of the plume, followed by a narrow zone of tobermorite precipitation. At the edge of the plume, calcite and illite precipitate. This precipitation of calcite next to the extraction borehole, due to the more favourable mixing conditions between Grimsel groundwater and cement porewater, causes a 40% reduction in porosity. Results of the numerical model where zeolites have been added showed precipitation of laumontite, partially inhibiting the precipitation of illite.
The model considering a fracture thickness of 1 mm gives slightly higher dissolution of the primary minerals. Near the emplacement borehole there is less precipitation of ettringite. At the centre of the plume, there is slightly higher precipitation of C-A-S-H, hydrotalcite and illite, but there is no precipitation of tobermorite. At the edge of the plume, there is higher precipitation of hydrotalcite, illite and mainly calcite, the latter almost clogging the porosity.

9.3 QUINTESSA

QUINTESSA performed first blind reactive transport modelling of the cement source system. This model was updated after results from solid phase characterisation at the end of the experiment were available. A separate model of the fracture plane (channel concept) was also developed.

In the initial blind modelling exercise of the cement source system, 2D and 3D models were developed using QPAC. The model only considered the cement and the gap between cement and rock. Advective transport could, in principle, affect the cement (especially in the reduced rock transmissivity case). Fast kinetics (local equilibrium) was assumed for all primary cement phases, except for calcite. For all minerals, reactive surface areas were calculated assuming spherical grains with a radius of 0.5 µm. Several variant cases were calculated for the 2D and 3D models.

The 2D model was considered first, representing the area of cement nearest to the fracture intersection. Model variants were run considering alternative diffusion coefficients, kinetic rates and fracture transmissivity. While the 2D simulations capture the broad trends of chemical evolution, they do not allow investigation of the spatial distribution of changes. Therefore, a more realistic 3D model was subsequently developed. This provides the most relevant results but is computationally expensive (running for the order of weeks) and therefore only the base case and one variant, with slower kinetic rates, were considered.

Some general features were apparent across all the models:

- Dissolution effects saw the preferential removal of portlandite, ettringite and the jennite C-S-H gel end-member (with conversion to the tobermorite C-S-H end-member).
- Alteration minerals were principally 11Å-tobermorite (a low solubility crystalline C-S-H mineral), gismondine (Ca zeolite; a proxy for C-A-S-H) and Ca saponite (smectite clay).
- 3D simulations demonstrated that the secondary minerals form in different locations:
  - Tobermorite forms between the longitudinal arms of the cement halfpipes, at the base of the borehole and near the point where the fracture intersects.
  - Gismondine and Ca saponite form mainly at the edges of the intersection with the fracture.
- The base cases emphasise dissolution of the cement minerals and an increase in pH in the borehole, except around the injection port where a lower pH is maintained.

One of the 2D simulations was run for an extended period, up to 10000 years, a time period more relevant to the disposal of radioactive waste. At these longer timescales, stilbite (Na-Ca zeolite) precipitated abundantly, along with calcite and gismondine (C-A-S-H). Pore blocking was seen to occur within 5000 years at points where the natural groundwater flowed into the borehole.
The following observations were made from the variant cases considered:

- The slower diffusion case produced more secondary minerals around the injection port.
- The slower kinetic rate case produced less alteration and consequently the pH was lower; this precluded the precipitation of 11Å-tobermorite (C-S-H).
- The reduced transmissivity case resulted in greater dissolution, due to the dominance of the injection of water into the borehole compared to the natural flow through the fracture.

Comparison with the experimental results should hopefully give indications of which scenarios are the most realistic.

The 3D models indicated that there may be a great deal of spatial variability in the experiment. However, the real system may be better mixed than the model due to the number of tracer tests conducted during the experiment.

For the updated model after solid phase characterisation, the following changes were included:

- Change in the composition of Grimsel groundwater and cement porewater.
- Variant case – Change in the kinetic rate law for calcite (pH dependence removed; faster kinetics).
- Variant case with alkali retention by C-S-H using a K_d approach.
- 4 cases considered – calcite kinetics, calcite equilibrium, calcite equilibrium with slow cement kinetics, calcite equilibrium with alkali release.

Although the leaching of the portlandite from the cement is captured by the model, it tends to overpredict both this and the increase in porosity, particularly if the calcite equilibrium assumption is made. The results reaffirm that the slower cement kinetics used in variant (c) are not appropriate, but a better fit to the observations could be achieved using kinetic rates/reactive surface areas somewhere between the two model variants. The decalcification of C-S-H in the outer cement is captured well by the model, but there are no quantitative data for comparison, so it is not clear whether the degree of conversion predicted by the models is appropriate or not.

The model predicts a strong spatial variation in both dissolution and secondary mineral precipitation. There is little evidence from the observations to support this, perhaps suggesting that the borehole water was better mixed than assumed in the model, possibly due to the number of tracer tests conducted during the duration of the experiment.

A comparison with the measured porewater concentration in the borehole shows a good match for pH, dissolved Ca, Al and Si concentrations, in that the absolute values are of the same order of magnitude and the main trends through time are captured; this applies also for Na and K concentrations at longer times (with potential for matching early times with appropriate parameterisation of the alkali release model). A poor match is shown for Mg and S, in that the absolute values differed by an order of magnitude or more; in the former case it is likely that the saponites are taking Mg up from the water too quickly; in the latter case there may either be a secondary mineral missing or ettringite dissolves too quickly.

Concerning the reactive transport model of the fracture, the concept here is based on flow and transport through open channels in the fracture. This is a 2.5D model (advective flow in channels plus diffusion into stagnant zones – fault gouge – and rock matrix). The evolution of the flow through the system is based on the fitting of the model to the results of tracer tests conducted dur-
ing the experiment. Reaction rate laws for the primary minerals (fault gouge) are from the literature, with surface areas calculated assuming spherical grains with a radius of 0.5 µm. Solute concentrations from the cement source model are used as a time-dependent boundary condition.

Eight variant cases were considered, including channels of different widths and lengths. In general, each model produced results with similar characteristics. These included:

- Precipitation of C-S-H and lesser amounts of C-A-S-H (gismondine) along the length of the channel and a few centimetres into the rock matrix and stagnant zone, causing a small reduction in porosity.
- Precipitation of calcite at the end of the channel, where advective mixing with the Grimsel groundwater occurred, with the possibility of completely blocking the channel pathway.
- Minor amounts of dissolution of albite (plagioclase feldspar) and muscovite (mica) from the adjacent fault gouge and rock matrix.

Qualitatively, the main characteristics of C-S-H and C-A-S-H precipitation in the fracture and calcite at the extraction borehole are matched. However, the timescales of the experiment are such that not much alteration happens at all at any distance from the emplacement borehole, and thus it is rather difficult to truly assess the predictive capability of any model. In addition, there is no evidence from LCS Experiment 2 that confirms or refutes the hypothesis that flow between the boreholes is channelled. The model predicts that large amounts of calcite will precipitate at any point where the high-pH plume mixes with the Grimsel groundwater; if the flow is channelled, this could potentially lead to the blocking of flow paths. Of course, there may be other flow paths that become active or more dominant once this blocking occurs, but again there is no evidence from the LCS experiment to help determine whether this is the case or not. The model also predicts precipitation of C-S-H and, to a lesser degree, C-A-S-H along the length of the fracture and in the adjacent rock and fault gouge.
10 Discussion and conclusions

The results from the modelling exercises by the different teams (tracer transport and reactive transport) have shown that it is possible to model and interpret the results of the in-situ experiment assuming either a homogeneous fracture or a fracture where flow is along preferential flow paths or channels. Emphasis was put on the geochemical aspects of cement-groundwater-rock interaction and the main characteristics of the observed alteration of both cement and rock could be reproduced with the use of current thermodynamic and kinetic data (e.g. portlandite dissolution in the cement, calcite precipitation at the cement-gap and gap-rock interfaces, primary mineral dissolution in the rock, C-S-H/C-A-S-H precipitation in the rock), with improved results being obtained when using the most recent data for phases such as C-A-S-H. Finer details, such as the observed range in compositions of C-S-H/C-A-S-H in the rock or the presence of minor amounts of CaCO$_3$ precursor phases (aragonite, vaterite) could not be confirmed in the modelling approaches used here. In all cases, calcite precipitation was controlled by the mixing of Grimsel groundwater and cement-reacted groundwater (e.g. at the emplacement and extraction boreholes), while the other secondary phases in the rock are the result of the interaction between high-pH water and the primary minerals in the rock. Overall, the understanding of the geochemical processes involved seems sound.

It should be noted that the setup of the experiment was such that most information was obtained from the monitoring of solution composition at the 3 boreholes during the experiment, together with characterisation of the cement source and rock at the emplacement borehole at the end of the experiment. Therefore, while the main mineralogical and geochemical aspects of the alteration could be qualitatively reproduced, the calculated spatial extent and distribution pattern of alteration in the fracture was controlled by the implemented model concept (homogeneous fracture vs. discrete channels). Discrimination and further formulation of the concepts would depend on the characterisation of the flow field and of the mineralogical alteration in the fracture plane beyond the boreholes. Results from the modelling of tracer tests during the HPF experiment pointed to very heterogeneous fractures (Soler et al., 2006).

Concerning calcite precipitation, results from HPF, where a high-pH solution was injected directly into a fracture (dipole flow field with active injection and passive extraction; Mäder et al., 2006), also showed a progressive isolation and further channelling of the dipole-flow region during the experiment (earlier first arrival and tracer peak times, increase in peak concentrations, reduced mixing with Grimsel groundwater with time). This evolution would be consistent with calcite precipitation induced by the mixing of the high-pH solution and Grimsel groundwater at the edges of the dipole flow field.

It should be noted that the initial concept for the experiment called for realistic flow conditions, i.e. no active water injection at the emplacement borehole promoting faster leaching of the cement. However, after about 1 year from the start of the experiment, no high-pH signal could be detected at the observation and extraction boreholes. The natural background flow field was not sufficient to allow any measurements of the expected high-pH plume within the planned project duration, given the setup of the experiment. Therefore, it was decided to start injection of Grimsel groundwater into the emplacement borehole, which allowed the detection of the high-pH plume at the observation and extraction boreholes.

In this experiment, fluid flow and chemical reaction affected a fractured rock. Besides the issue of flow and solute transport being homogeneous along the fracture plane or dominated by preferential flow paths or channels, there is also diffusion into the wall rock (matrix diffusion). Ideally, any modelling would include all these processes, meaning that 3D models would be necessary.
Additionally, a fine spatial discretisation into the rock matrix would be necessary, especially if the rock is very tight (small porosities and diffusion coefficients). However, such 3D reactive transport models are computationally extremely demanding and therefore very rare. The translation of the experimental setup into a numerical model relies therefore on simplification regarding the dimensionality of the problem. Here, two different approaches were used: (1) 2D modelling along the fracture plane, ignoring matrix diffusion, and (2) a 2.5D model of the fracture plane. This second approach involved 1D channels and diffusion into stagnant zones and rock matrix. Alteration of the rock matrix was calculated, although limited (diffusion into the stagnant zones was more important in absolute terms). The mass fluxes in this type of diffusion-dominated domain will be controlled by their porosities and diffusion coefficients, being more relevant for rocks (or zones) with higher values of these parameters. In addition, the results from the experiment did not provide information regarding this process, although it is well known that the rock matrix at Grimsel is rather tight (e.g. Soler et al., 2015, and references within).

Some additional comments regarding the treatment of specific processes in the experiment are listed below:

- Alteration of the cement source, although somewhat irregular, was distributed all along both the external and internal faces of the cement shells. This observation points to rather uniform mixing of the solution in the circulation system of the emplacement borehole. It should be noted that solution was continuously circulated during the experiment (not only during tracer tests).
- The thickness of the altered cement zone, characterised mainly by the dissolution of portlandite with the resulting increase in porosity, depends mainly on the magnitude of solute transport through the cement, which is controlled to a large extent by the diffusion coefficients in the cement. A good match (on average) of the thickness of the altered zone could be obtained by calibration of this parameter. Values from the literature seem to predict too much alteration through the cement.
- Cation exchange processes in the fault gouge are expected to have some effect on the breakthrough curves of Na, K and Ca. Cation exchange was not included in any of the models. It is possible that cation exchange does have an effect, but it is not evident from the comparison of measurements and calculations that it plays any significant role. Observed differences seem to be more related to the overall magnitude of transport and dilution of the cement signal (high pH, Ca, Na, K) in the models.

Concerning recommendations for future experiments, improvements could be made with regard to the spatial characterisation of the alteration zone. As mentioned above, the spatial extent of alteration in the rock (fracture plane) is controlled by the flow field. Additional boreholes could be used to monitor the evolution of water composition in a larger section of the fracture and have a better constraint on the propagation of the high-pH plume. One of the conclusions from the HPF project at Grimsel was that fractures were very heterogeneous. A deterministic description of the flow field in such a domain is probably not possible, but a better constraint on its extension could certainly improve the concepts for the flow field used in the model calculations. Tracer tests using strongly sorbing tracers could also provide information regarding channelling (fast breakthroughs would be predicted for open channels, compared to more homogeneous fault gouge-filled fractures). Additional overcoring, for instance in selected boreholes where high-pH conditions were observed, could also provide valuable mineralogical information.
11 References


