Technical Report 16-06

Grimsel Test Site
Investigation Phase VI

Colloid Formation and Migration Project:

Modelling of tracer, colloid and radionuclide/homologue transport for dipole CFM 06.002 – Pinkel surface packer

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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 hydro-power company.

The tunnels of the GTS were excavated in 1983 and 1984 using both a tunnel boring machine and drill and blast techniques. Expansions of the site in 1995 and 1998 provided space for two large-scale demonstration tests. The branching tunnel system of more than 1 km in length is located at an elevation of 1730 m a.s.l., about 400 to 450 m beneath the Juchlistock, in the granite and granodiorite of the Aar Massif that was formed some 300 million years ago. The local geology is ideal for the investigation of a wide range of experimental concepts and scientific issues with both tectonically overprinted and fractured areas as well as zones of homogeneous intact rock. More than 5000 m of cored boreholes has 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 15-year 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) projects 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 emerged from its first three decades as an internationally renowned research laboratory in the field of safe disposal of radioactive waste in deep geological repositories. It has firmly established its roles as a strong driving force for scientific and technological progress, as an effective platform for international cooperation, as a hands-on training stage for knowledge transfer to the younger generation, and as a host for transparent dialogue with decision-makers and the public.
The CFM project

The Colloid Formation and Migration (CFM) project is designed to study bentonite colloid and colloid-associated radionuclide transport and to examine the colloid formation process under close to repository-like conditions at relatively low hydraulic gradients and flow velocities. The CFM experiment began in 2004 and is the current contribution to a series of experiments conducted within the Radionuclide Retardation Programme at the GTS since 1984. At this time, activities are scheduled until 2018.

Vital support has been provided as in-kind and financial contributions by the following past and present CFM project partners: Central Research Institute of the Electric Power Industry (CRIEPI, Japan), Department of Energy/Los Alamos National Laboratory (DOE/LANL, United States of America), Federal Ministry of Economics and Technology/Karlsruhe Institute of Technology – Institute for Nuclear Waste Disposal (BMWi/KIT-INE, Germany), French National Radioactive Waste Management Agency (Andra, France), Japan Atomic Energy Agency (JAEA, Japan), Korea Atomic Energy Research Institute (KAERI, Korea), National Cooperative for the Disposal of Radioactive Waste (Nagra, Switzerland), National Institute of Advanced Industrial Science and Technology (AIST, Japan), Nuclear Waste Management Organization of Japan (NUMO, Japan), Posiva Oy (Finland), Radioactive Waste Management Limited (RWM, United Kingdom), and Svensk Kärnbränslehantering AB (SKB, Sweden). The Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT, Spain) and the Paul Scherrer Institute (PSI, Switzerland) have contributed substantially through their active participation as experiment associates. The overall project lead and coordination is with Nagra.

The achievements to date would not have been possible without the development and maintenance work performed by the local GTS staff and specialist contractors from Baski Inc. (United States of America), Edi Meier + Partner AG (Switzerland), Gilson (Schweiz) AG (Switzerland), Golder Associates GmbH (Germany), SikaBau AG (Switzerland), and Solexprts AG (Switzerland). Special thanks are due to Michel DeCombarieu (Andra) who had the idea of the CFM tunnel packer concept.
Location of Nagra’s underground test facility at the Grimsel Pass in the Central Alps (Bernese Alps) of Switzerland
Grimsel area (view to the west)
Grimsel Test Site
GTS

- KWO-Access tunnel
- Laboratory tunnel
- Central Aaregranite (CAGR)
- High biotite content CAGR
- Grimsel-Granodiorite
- Shear zone
- Lamprophyre
- Main investigation borehole
- Central facilities

GTS Phase VI 2003-2018

- CFM Colloid Formation and Migration
- C-FRS Criepi Fractured Rock Studies
- CIM C-14 / I-129 Migration through aged cement
- ESDRED/TEM Test and Evaluation of Monitoring Systems
- FEBEX Full-scale Engineered Barriers Experiment
- FORGE Fate of Repository Gases
- GAST Gas-permeable Seal Test
- GMT Gas Migration Test in the EBS
- HotBENT High Temperature Bentonite project
- HPF Hyperalkaline Plume
- ISC In-situ Stimulation and Circulation Project
- JGP JAEA Grouting Project
- LASMO Large Scale Monitoring
- LCS Long-Term Cement Studies
- LTD Long Term Diffusion
- MACOTE Material Corrosion Test
- MODERN2020 Development and Demonstration of Monitoring Strategies and Technologies
- PSG Pore Space Geometry
Abstract

The Colloid Formation and Migration (CFM) project involves one of a series of experiments performed within the GTS Investigation Phase VI, which focuses on repository-relevant boundary conditions. CFM is dedicated to the study of colloid formation/bentonite erosion, the groundwater-porewater mixing zone, colloid migration and filtration, and colloid associated radionuclide transport.

The CFM field experiments are conducted within a permeable shear zone structure that has been the subject of previous tracer migration experiments (Frick et al. 1992, Smith et al. 2001, Möri 2004). The Colloid and Radionuclide Retardation Experiment (CRR; Möri 2004) focused on bentonite colloid and colloid-associated radionuclide transport. In CRR, colloid tracer tests were performed using borehole dipoles with a spacing of about 2 m and high extraction flow rates resulting in travel times of about 1 hour for conservative species. The aim of CFM has been to extend these results to longer timescales and to examine the colloid formation process under close to repository-like conditions at relatively low hydraulic gradients and flow velocities. In order to create the required flow conditions it was necessary to engineer one or more low-gradient but high-recovery controlled dipoles. This has been achieved with a novel tunnel packer system. The tunnel packer system currently in operation at the CFM site is fully described in Schlickenrieder et al. (2017).

The free outflow from the shear zone into the tunnel is approximately 600 ml/min (Tracer Test Runs 05-01 and 06-01). Reducing the outflow from the shear zone resulted in a significantly lowered hydraulic gradient in the shear zone. Since the first tunnel sealing work, 27 tracer tests have been performed under a range of shear zone outflows and hydraulic gradients. This report describes the modelling of colloid/homologue and colloid/radionuclide tracer migration tests performed in the shear zone between the borehole CFM 06.002 and the Pinkel surface packer (main shear zone outflow point). The tests considered here are:

- Tracer Test Runs 08-01 (colloid/homologue) and 08-02 (dye): outflow 160 ml/min
- Tracer Test Run 10-01 (colloid/homologue/dye): outflow 48 ml/min
- Tracer Test Run 10-03 (colloid/homologue/dye): outflow 10 ml/min
- Tracer Test Run 12-02 (colloid/radionuclide/dye): outflow 25 ml/min

This "dipole" is also that used in the CFM Long-term In situ Test (LIT) (Schlickenrieder et al. 2017) where a solid bentonite source traced with radionuclides has been emplaced in borehole CFM 06.002 while maintaining outflow from the Pinkel surface packer. The flow boundary conditions for the LIT (25 ml/min extraction from the Pinkel surface packer) are similar to those maintained during the colloid/radionuclide Tracer Test Run 12-02. Additional colloid/radionuclide tracer tests within CFM have now been performed in the CRR Dipole D-1 (shear zone between CRR 99.002 and BOMI 87.010) and will be described in a future report.

The modelling presented here focuses on colloid transport and filtration and associated transport of trivalent and tetravalent homologues or radionuclides. The work was performed by three different groups using different approaches but with a similar conceptual framework and a common dataset. The groups were:

- GRS: 2D model using the d3f and r3t codes
- LANL: 1D solution in space using finite difference models and RELAP (Laplace transform solution and numerical inversion to time domain)
- KTH: 1D time-transformed solution
All groups modelled Tracer Test Runs 10-01, 10-03 and 12-02. The modelling included both blind-prediction (by GRS) and back-analysis of the test results.

The different modelling approaches all yielded qualitatively similar results in that colloid transport in the field tracer tests could be described reasonably well as a first-order filtration process, and homologue or radionuclide transport was described as being controlled by the desorption rate of solutes from the colloids.

Somewhat better fits to the colloid breakthrough curves were obtained by assuming some additional reversible filtration of the colloids. For the homologue/radionuclide desorption process, GRS considered only a single first-order desorption reaction, and the deduced rate constants were in good agreement with the other models when only a single desorption reaction was considered. However, the LANL and KTH models achieved better fits to the homologue or radionuclide breakthrough curves in several cases in which desorption from the colloids was described using a two-site adsorption model and/or when an aging reaction was allowed that results in a decreasing desorption rate with time.

A limited comparison of laboratory and field-derived desorption rate constants found that the Am and Pu rate constants estimated for Tracer Test Run 12-02 were in reasonably good agreement with the estimates obtained by Huber et al. (2011) in batch laboratory experiments involving bentonite colloids, radionuclides and fracture filling materials from the GTS shear zone.

Inconsistencies between the best-fitting descriptions of homologue or radionuclide desorption processes from colloids were identified between the different tests but the reasons are unclear. While there was a general trend of a decreasing desorption rate constant with time scale of the tests when only a one-site adsorption model was considered, the rate constant for a second site exhibited no clear pattern or trend with test time scale or other test parameters.

The desorption rate constants of the tri- and tetravalent homologues and radionuclides in the CFM tracer tests suggest that all of the homologues or radionuclides should desorb from colloids within a few months or at most a few years. This implies that colloid-facilitated transport should not be a problem over safety assessment time and distance scales. Possible approaches to better interrogating the relevant slow filtration rate constants and slow desorption rate constants are given in the report.
Zusammenfassung

Das Projekt Colloid Formation and Migration (CFM, Bildung und Migration von Kolloiden) trägt zu einer Reihe von Experimenten bei, die im Rahmen der GTS Untersuchungsphase VI mit Blick auf endlagerrelevante Randbedingungen durchgeführt werden. Es widmet sich der Untersuchung der Kolloidbildung/Bentoniterosion, der Mischungszone von Grundwasser und Porenwasser, der Kolloidmigration und -filtration sowie dem kolloidgetragenen Radionuklidtransport.


- Tracerversuch Run 08-01 (Kolloid/Homolog) und 08-02 (konservativer Tracer): Ausstrom 160 ml/min
- Tracerversuch Run 10-01 (Kolloid/Homolog/konservativer Tracer): Ausstrom 48 ml/min
- Tracerversuch Run 10-03 (Kolloid/Radionuklid/konservativer Tracer): Ausstrom 10 ml/min
- Tracerversuch Run 12-02 (Kolloid/Radionuklid/konservativer Tracer): Ausstrom 25 ml/min


- **GRS**: 2D Modell unter Verwendung der Rechenprogramme d3f und r3t
- **LANL**: 1D Lösung im Raum unter Verwendung von Finite Differenzen Modellen und RELAP (Lösung über Laplace Transformation und numerische Inversion in der Zeit)
- **KTH**: 1D Lösung über Zeit-Transformation

Alle Gruppen haben die Tracerversuche Run 10-01, Run 10-03 und Run 12-02 modelliert. Die Modellierung beinhaltete sowohl Vorhersagerechnungen (Blind Prediction, GRS) als auch eine modellhafte Analyse der Versuche nach Erhalt der Ergebnisse (Back Analysis).


Die Desorptionsraten, die aus dem Tracerversuch Run 12-02 für Am und Pu bestimmt wurden, stimmen gut mit entsprechenden Daten aus Batch-Experimenten mit Bentonitkolloiden, Radionukliden und Kluftfüllmaterial aus der GTS-Scherzone (Huber et al. 2011) überein.


**Résumé**

Le projet Colloid Formation and Migration (CFM, Formation et migration des colloïdes) fait partie d'une série d'expériences menées dans le cadre de la phase d'investigation VI du LSG (Laboratoire souterrain du Grimsel) et consacrées à l'étude des conditions spécifiques prévalant dans les dépôts en couches géologiques profondes. Les études menées dans le cadre du projet CFM concernent la formation de colloïdes consécutive à l'érosion de la bentonite, la zone d'échange entre l'eau interstitielle et les eaux souterraines, la migration des colloïdes (percolation), ainsi que la migration des radionucléides par le biais des colloïdes.

Les expériences in situ du projet CFM ont lieu dans une zone de cisaillement de perméabilité élevée, qui a déjà été utilisée pour plusieurs expériences de migration utilisant des traceurs (Frick et al. 1992, Smith et al. 2001, Möri 2004). Le projet Colloid and Radionuclide Retardation (CRR; Möri 2004) s'est concentré sur l'étude du transport des colloïdes de bentonite et des radionucléides associés aux colloïdes. Les essais de traçage de colloïdes dans le cadre du projet CRR ont été réalisés entre des forages en dipôles distants d'environ 2 m, avec des débits relativement élevés. Pour des espèces conservatives, on obtenait ainsi des temps de transport d'environ une heure. L'objectif des expériences in situ du projet CFM était de transposer les résultats du projet CRR sur une durée plus longue et d'étudier les processus de génération des colloïdes dans un environnement comparable à celui d'un dépôt profond, à savoir avec des débits et des gradients hydrauliques relativement faibles. Pour obtenir ce type de débit, il a été nécessaire de créer un ou plusieurs dipôles ayant à la fois un gradient hydraulique faible et des taux de récupération élevés. Ceci a été possible grâce à la mise en œuvre d'un système d'isolation de tunnel ("tunnel packer system") d'un type nouveau. Le système d'isolation de tunnel actuellement en exploitation sur le site du projet CFM est décrit de manière détaillée dans Schlickenrieder et al. (2017).

Le débit d'écoulement libre entre la zone de cisaillement et le tunnel s'élève à environ 600 ml/min (tests au traceur 05-01 et 06-01). La réduction de l'écoulement provenant de la zone de cisaillement a provoqué une réduction significative du gradient hydraulique au niveau de la zone de cisaillement. Depuis les premiers travaux d'étanchéification du tunnel, 27 tests au traceur ont été réalisés à différents débits d'écoulement et gradients hydrauliques. Le présent rapport décrit la modélisation des tests de migration des traceurs colloïde/homologue et colloïde/radionucléide réalisés dans la zone de cisaillement, entre le forage CFM 06.002 et le collecteur au point d'extraction "Pinkel" (point d'écoulement principal de la zone de cisaillement). Les tests étudiés sont les suivants:

- Test au traceur 08-01 (colloïde/homologue) et 08-02 (colorant): débit d'écoulement de 160 ml/min
- Test au traceur 10-01 (colloïde/homologue/colorant): débit d'écoulement de 48 ml/min
- Test au traceur 10-03 (colloïde/homologue/colorant): débit d'écoulement de 10 ml/min
- Test au traceur 12-02 (colloïde/radionucléide/colorant): débit d'écoulement de 25 ml/min

Le même "dipôle" est utilisé dans le test au long terme in situ du projet CFM (LIT, Schlickenrieder et al. 2017), lequel consiste à stocker une source de bentonite solide tracée avec des radionucléides dans le trou de forage CFM 06.002 tout en maintenant un débit d'écoulement constant au niveau du collecteur du point Pinkel. Les conditions limites d'écoulement du LIT (extraction à 25 ml/min depuis le collecteur du point Pinkel) sont similaires à celles entretenues au cours du test au traceur 12-02 (colloïde/radionucléide). Des tests supplémentaires au traceur colloïde/radionucléide ont depuis été effectués dans le cadre du projet CFM au niveau du Dipôle CRR 1 (zone de cisaillement située entre les points CRR 99.002 et BOMI 87.010). Ils seront décrits dans un rapport ultérieur.
La modélisation présentée ici se concentre sur la migration et la filtration des colloïdes, ainsi que sur la migration d'homologues ou radionucléides trivalents et tétravalents qui leur sont associés. Les travaux ont été exécutés par trois équipes différentes et suivant différentes approches, quoique respectant une structure conceptuelle similaire et partageant un ensemble de données commun. Les équipes étaient les suivantes:

- **GRS**: modèle 2D basé sur les codes d'ét et r't
- **LANL**: solution 1D dans l'espace reposant sur des modèles aux différences finies et RELAP (Transformation de Laplace et inversion numérique appliquée au domaine temporel)
- **KTH**: solution 1D à transformation temporelle

Toutes les équipes ont travaillé sur la modélisation des tests au traceur 10-01, 10-03 et 12-02. La modélisation incluait à la fois une prédiction en aveugle (par GRS) et une analyse régressive des résultats du test.

Les différentes approches de modélisation ont fourni des résultats similaires sur le plan qualitatif: la migration des colloïdes observée au cours du test au traceur sur site peut être décrite de façon satisfaisante comme un processus de filtration du premier ordre. La migration des radionucléides et des homologues, quant à elle, a été décrite comme étant contrôlée par le taux de désorption des substances à partir des colloïdes.

Le postulat d'une filtration réversible supplémentaire des colloïdes a par ailleurs permis d'améliorer la concordance des simulations avec les courbes de restitution des colloïdes. Quant au processus de désorption des radionucléides/homologues, GRS a étudié une seule réaction de désorption du premier ordre. Les vitesses de désorption déduites de cette réaction étaient en accord avec les autres modèles lorsque l'on ne prenait en compte qu'une seule réaction de désorption. Cependant, les modèles du LANL et de KTH ont conduit à une meilleure correspondance avec les courbes de restitution des radionucléides et homologues dans plusieurs cas impliquant une désorption reposant sur un modèle d'adsorption sur deux sites et/ou une atténuation des taux de désorption avec le temps.

Une comparaison superficielle des taux de désorption observés en laboratoire et sur site montre une relativement bonne cohérence entre les taux d'Am et de Pu estimés pour le test au traceur 12-02 et les estimations de Huber et al. (2011) obtenues en laboratoire lors d'expériences en batch impliquant des colloïdes de bentonite, des radionucléides et des échantillons de remplissage de fracture extraits de la zone de cisaillement du LSG.

On a constaté, sans pouvoir les expliquer, des incohérences entre les meilleures calibrations des modèles de description des processus de désorption des radionucléides/homologues des colloïdes. Lors de l'étude d'un modèle à un seul site d'adsorption, le taux de désorption présentait une tendance généralement décroissante en fonction de l'échelle de temps. A contrario, pour le taux d'un second site d'adsorption, aucune tendance ou aucun schéma clairement défini en fonction du temps ou d'autres paramètres du test n'a pu être déterminé.

Pour les homologues et radionucléides trivalents et tétravalents, les taux de désorption observés au cours des tests au traceur du projet CFM suggèrent qu'une désorption des colloïdes devrait, pour tous les homologues ou radionucléides, s'effectuer en l'espace de quelques mois ou, au plus, quelques années. Ces résultats indiquent par conséquent que la migration par les colloïdes ne devrait pas poser de problème sur les périodes et les distances envisagées par les analyses de sûreté. Le rapport détaille les possibles approches permettant une meilleure estimation des faibles taux de filtration et de désorption.
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1 Introduction

Long-term safety assessments of radioactive waste repositories require a comprehensive system understanding of radionuclide release and transport processes and robust models to simulate these processes during the future evolution of the repository systems. While the dominant mechanisms for radionuclide transport in crystalline rock are likely to be solute advection, molecular diffusion, and sorption on fracture surfaces and within the rock matrix, this report is confined to consideration of colloid-associated radionuclide transport.

Many designs of engineered barrier systems (EBS) for deep geological repositories for high-level nuclear waste in crystalline rock formations include bentonite as buffer and backfill material, e.g. Nagra (1994), SKB (2011), and Posiva (2012). Bentonite clay has been found to be an appropriate material for the geotechnical barrier due to its ability to:

1. Inhibit groundwater access to the waste canister owing to its swelling properties (Pusch 1983)
2. Stabilise near field geochemical conditions
3. Retard radionuclide transport away from the repository near field (Liu & Neretnieks 2006)

However, depending on the physico-chemical conditions (e.g. gas and water pressure, groundwater flow velocity and water composition) the bentonite barrier may also be eroded by formation of colloids at the outer rim of the buffer (Gallé 2000, Missana et al. 2003, Yoshida et al. 2005, Alonso et al. 2006, Baik et al. 2007). This process could be exacerbated by an influx of low ionic strength groundwater due to the melting of thick inland ice sheets during or after future glacial periods (SKB 2011). The process is also of interest in relation to prolonged influx of meteoric water at the Swedish and Finnish sites during the present temperate climate phase, especially if this is prolonged due to the greenhouse effect. For scenarios in which radionuclides have been released from the waste container, the transport of radionuclides through the host rock formation might be strongly enhanced by sorption onto the bentonite colloids, particularly if the colloids are stable/mobile and the sorption is strong.

To assess the impact of bentonite colloids on the long-term safety of a repository in granite, a series of field experiments in the underground laboratory at the Grimsel Test Site (GTS, Nagra, www.grimsel.com) has been performed within the Colloid Formation and Migration (CFM) project (Blechschmidt & Lanyon 2008). The past and present CFM project partners have been: Central Research Institute of the Electric Power Industry (CRIEPI, Japan), Department of Energy/Los Alamos National Laboratory (DOE/LANL, United States of America), Federal Ministry of Economics and Technology/Karlsruhe Institute of Technology – Institute for Nuclear Waste Disposal (BMWi/KIT-INE, Germany), French National Radioactive Waste Management Agency (Andra, France), Japan Atomic Energy Agency (JAEA, Japan), Korea Atomic Energy Research Institute (KAERI, Korea), National Cooperative for the Disposal of Radioactive Waste (Nagra, Switzerland), National Institute of Advanced Industrial Science and Technology (AIST, Japan), Nuclear Waste Management Organization of Japan (NUMO, Japan), Posiva Oy (Finland), Radioactive Waste Management Limited (RWM, United Kingdom), and Svensk Kärnbränslehantering AB (SKB, Sweden). The Centro de Investigaciones Energéticas Medioambientales y Tecnológicas (CIEMAT, Spain) and the Paul Scherrer Institute (PSI, Switzerland) have been experiment associates.
CFM follows on from previous colloid studies at GTS within the Grimsel Colloid Exercise (Degueldre et al. 1990) and the Colloid and Radionuclide Retardation (CRR) Experiment (Möri 2004). The findings from CRR led to a recommendation to perform migration tests at larger spatial and longer temporal scales.

The CFM field experiments have been conducted in a low-gradient flow field within the Migration (MI) shear zone at GTS with the objectives of investigating processes related to bentonite erosion, colloid formation and colloid-associated radionuclide transport (Schäfer et al. 2009). The low-gradient flow field was made possible by the installation of a "megapacker" in the AU tunnel to seal off high inflow rates from the shear zone and thus achieve flow conditions more relevant for a nuclear waste repository in fractured crystalline rock than in the CRR experiments in the shear zone, where flow velocities were much higher (Möri 2004). The field programme has been supported by many laboratory investigations designed to understand bentonite erosion, colloid formation and radionuclide migration under more controlled conditions than in the field experiments, e.g. Jansson (2009), Matsumuto et al. (2009), and Huber et al. (2011).

The majority of the CFM field experiments to date have been migration (tracer) tests conducted in the shear zone using CFM 06.002-i2 (interval 2 of borehole CFM 06.002) as the injection point and the Pinkel surface packer on the tunnel wall as the extraction point. This dipole is sometimes referred to as CFM Dipole 1 and has a linear distance between the main water-conducting feature in CFM 06.002-i2 and the Pinkel surface packer of about 6 m. An earlier estimate of the dipole distance was 6.2 m and this was used in the modelling reported here, but subsequent surveys and a redefinition of the best-fit shear zone plane suggest the straight-line length between the main water-conducting feature in CFM 06.002-i2 and the Pinkel surface packer is 5.70 – 5.71 m. With respect to modelling, the reduced distance of the dipole would cause a reduced pore velocity to keep the same travel time. Concerning the interaction rates between radionuclides, colloids and solid matrix – the main focus of this report – no changes are expected, as they are dependent on the travel time of the mobile constituents.

A second focus of the CFM experiment has been the study of bentonite colloid formation from compacted bentonite. Initially, colloid generation experiments were performed in a range of laboratory setups including artificial fracture cells. However it was always intended to perform at least one in situ colloid formation experiment and a radionuclide-labelled bentonite plug was emplaced in CFM 06.002-i2 in May 2014 to conduct the Long-term In Situ Test (LIT) of bentonite swelling and erosion in the shear zone. The LIT setup is described in detail by Blechschmidt et al. (2017). The migration tests modelled here were in part a preparatory step for the LIT, characterising the likely migration paths using well-controlled initial and boundary conditions prior to the emplacement of the bentonite plug, where the colloid source term would be poorly known due to uncertainties regarding the bentonite colloid formation processes.

The objectives of the CFM migration tests included:

1. Determining an optimal Pinkel surface packer extraction flow rate for the LIT (i.e. low enough to have repository system relevance but not so low that the flow around the plug is not drawn into the Pinkel surface packer)
2. Gaining a better understanding of colloid and radionuclide transport in the flow system that these species will experience after being released due to erosion of the bentonite plug

To accomplish the latter objective, four of the migration tests involved the injection of a tracer "cocktail" that included a conservative dye tracer, well-dispersed FEBEX bentonite colloids (Huertas et al. 2000, Missana & Geckeis 2004) and either radionuclides or homologues. These
experiments have been modelled by researchers (modelling groups) from Gesellschaft für Anlagen- und Reaktorsicherheit gGmbH (GRS), KTH Royal Institute of Technology (KTH), and Los Alamos National Laboratory (LANL) to help identify and characterise the relevant interaction processes between solutes, colloids and fracture filling material in the shear zone during transport. This report focuses on model simulations of Tracer Test Runs 08-01 & 02, 10-01, 10-03 and 12-02; four of the tests in which colloids and homologues/radionuclides were injected into CFM 06.002-i2 and extracted at the Pinkel surface packer. For a fifth homologue test, Tracer Test Run 11-01, no recovery at the Pinkel surface packer was observed due to stagnant flow around CFM 06.002-i2 after the drilling of monitoring boreholes for the LIT.

The field experiments were accompanied by a series of laboratory experiments in order to increase the understanding of relevant processes (e.g. Schäfer & Noseck 2010). These experiments comprised the topics:

1. Colloid formation and erosion behaviour of compacted bentonite including a mock-up experiment for the LIT
2. Stability of colloids in the Grimsel groundwater, bentonite porewater and mixed waters
3. Interaction of colloids with mineral surfaces, e.g. investigating the effects of surface roughness and trivalent cations on the interaction mechanism
4. Interaction of radionuclides with bentonite colloids focusing particularly on the reversibility kinetics of the tri- and tetravalent actinides

The specific objectives of the CFM modelling work can be summarised as follows:

- To formulate a suitable model describing colloid-facilitated transport in the shear zone that has only as much complexity as can be justified by system knowledge but describes all the relevant processes
- To infer transport parameters from the migration tests that might be applied to the LIT
- To link inferred transport parameters to results of laboratory experiments or to independent estimates
- To discuss the implications of the inferred transport parameters and their apparent scale dependence for transport over safety assessment time and distance scales

---

1 The fracture filling material mainly consists of fault gouge.
2 Experimental setup and results

2.1 Background and project organisation

CFM Phase 1 began in 2004 and its main tasks were preparatory studies concerning in situ boundary conditions (including establishing control of shear zone flow with the installation of the megapacker), predictive modelling and a supporting laboratory programme. CFM Phase 2 was performed from 2008 to 2013; it is the phase in which all the colloid and homologue/radio-nuclide migration experiments described and interpreted in this report were conducted. Phase 3 began on 1 January 2014, and it has included the emplacement of the radionuclide-labelled bentonite plug into CFM 06.002-i2 in May 2014.

2.2 Experiment aims and boundary conditions

The aims of the CFM long-term colloid project are listed in Tab. 1.

Tab. 1: CFM project aims and approaches.

<table>
<thead>
<tr>
<th>Aim</th>
<th>How it is addressed in the CFM project</th>
</tr>
</thead>
<tbody>
<tr>
<td>Examine colloid generation rates and mechanisms at the engineered barrier system (EBS) – host rock interface under in situ conditions</td>
<td>Laboratory experiments (e.g. Bentflow (Matsumoto et al. 2009) and other mock-up tests) and in situ test (LIT), including post-test overcoring of bentonite emplacement borehole</td>
</tr>
<tr>
<td>Evaluate the long-distance migration behaviour of EBS-derived colloids in a water-conducting feature in a repository-relevant flow system (i.e. with a low flow rate/water flux)</td>
<td>Colloid tracer tests and monitoring of release from in situ test</td>
</tr>
<tr>
<td>Study the long-term geochemical behaviour (mobility, mineralisation, colloid formation etc.) of radionuclides at the EBS-host rock interface</td>
<td>Laboratory tests (including mock-ups) and monitoring of in situ test near field</td>
</tr>
<tr>
<td>Examine reversibility of radionuclide uptake onto colloids</td>
<td>Laboratory, possibly mock-ups</td>
</tr>
<tr>
<td>Gain experience in long-term monitoring of radionuclide/colloid migration from the repository near field</td>
<td>Design, development and implementation of in situ monitoring systems, and &quot;post-mortem&quot; evaluation of these systems</td>
</tr>
<tr>
<td>Apply the results to improve repository performance assessments and process understanding, optimise EBS design and contribute to &quot;monitoring&quot; and predictive capabilities</td>
<td>Modelling of in situ test and migration tests and post-test overcoring of in situ test will contribute to process understanding and therewith to underpinning performance assessment calculation results.</td>
</tr>
</tbody>
</table>
2.3 History of field activities for site selection, site characterisation and site preparation since 2005

The field activities conducted in Phase 1 of the CFM experiment focused on site selection, site characterisation and site preparation. Colloid transport in a water-conducting feature is expected to take place in an advective flow regime. At the onset of Phase 1 it was clear, therefore, that the key element for the selection of a suitable site at GTS for the CFM experiment was the availability of a water-conducting feature with a well characterised natural flow field. The migration (MI) shear zone at tunnel position AU96 (see GTS overview in Foreword) met this requirement. As the focus of the earlier MI (Frick et al. 1992, Smith et al. 2001), EP (Alexander et al. 2003, 2009), and CRR experiments (Möri et al. 2004), it had been studied already and instrumentation was in place. Numerous hydro- and tracer tests had been conducted, some with active tracers which required the temporary transformation of the AU gallery into a radiation controlled zone. The MI shear zone is an almost two-dimensional feature extending from the KWO main access tunnel towards the VE gallery (location L422 in layout figure in Foreword).

An early task of the CFM Phase 1 site characterisation was the investigation of the approximately 7 m tunnel surface marked by the MI shear zone (tunnel coordinates AU93 to AU100). The focus was on:

1. Detailed mapping of major structural features like ductile shear zones, brittle fractures and fault gouge
2. Hydrological investigations in terms of localised major water inflow points and measuring the groundwater flow rates of these features

Fig. 1 shows the result of the geological mapping of the MI shear zone. The main foliation in the granodiorite is defined by biotite and feldspars which are aligned in parallel to each other. The shear zone was originally formed by ductile deformation. In a later stage of Alpine deformation and following uplift, the shear zone was reactivated. In this brittle deformation phase, cohesionless fault gouge material formed along discrete fracture planes. The main brittle deformation horizon of the MI shear zone is represented by three steep (> 70°) shear planes striking WSW-ENE. They are hydraulically connected and represent a complex water-conducting feature. The transmissivity of the shear zone was found to be, in general, between $10^{-8}$ m$^2$/s and $10^{-6}$ m$^2$/s with very low transmissivity parts where transmissivity is <$10^{-10}$ m$^2$/s.

The main shear plane in the northern part of the mapped zone shows a high degree of brittle deformation overprinting the older ductile features. This main shear plane is also characterised by distinct inflow points (associated with the complex water-conducting feature) where surface packers have been installed (red circles in Fig. 1). These inflow points are openings of up to 10 mm in width and deliver continuous water inflow into the tunnel. The brittle fractures forming the water-conducting feature within the shear zone tend to be associated with fault gouge. More detail on the deformation history and fracture geometry is found in Blechschmidt et al. (2006). The results of the mineralogical analyses and investigations of the chemical composition of discharging groundwater from the MI shear zone are also found in Blechschmidt et al. (2006).

The hydraulic characterisation of the test site is built on tests from the existing boreholes and results from earlier MI, EP and CRR activities. Fig. 2 shows the test site in a 3D block model with the MI shear zone and boreholes at the end of CFM Phase 1. The 86 mm boreholes are equipped with inflatable multipacker systems isolating the MI shear zone interval in each borehole. The isolated intervals are equipped with access lines allowing permanent monitoring of groundwater pressure in the MI shear zone as well as flow lines for hydro- and tracer testing.
Fig. 1: Detailed geological mapping of the MI shear zone between tunnel metres AU93 and AU100, with surface packer locations.
Fig. 2: Schematic of the site of the CFM in situ experiment: a) View along shear zone strike showing borehole array. b) Detail showing the dipole CFM 06.002 – Pinkel surface packer.

Boreholes CFM 06.001 and CFM 06.002 were drilled in 2006. Boreholes CFM 11.001, 2 and 3 were drilled in 2011 for near field monitoring of the LIT. The other boreholes are from previous investigations. Borehole intervals coloured red contain intersections with the main water-conducting feature within the shear zone, blue intervals are rock matrix, and packer intervals are shown in black.

Preliminary hydraulic tests were conducted at the CFM site in March 2005. Hydraulic testing focused on the MI shear zone with the intention to estimate the shear zone transmissivities and to provide data for numerical modelling. Other objectives of the field campaign were to document "static" interval pressures, to measure the natural inflow into the tunnel from the so-called Pinkel and Kalotte surface packer inflow points, and to assess the impact of the sealed overcore boreholes from the EP experiment (BOEX-I and BOEX-II). The 2-day hydraulic testing campaign confirmed the heterogeneous properties of the MI shear zone. For the majority of the investigated shear zone intervals, the estimated transmissivity varied between $6 \times 10^{-8}$ m$^2$/s and $1.4 \times 10^{-6}$ m$^2$/s. The measured hydraulic heads varied within 12.8 m. Interference responses were recorded in all but two monitored boreholes. Further results are provided in Blechschmidt et al. (2006).

Preparation of the test site started with cleaning the rock surface using sandblasting and pressure washing. The cleaning campaign allowed detailed geological mapping and detection of the major inflow points which were then equipped with surface packers (see Fig. 1 for locations). The next step involved sealing the shear planes and, eventually, the entire tunnel surface over a 6 m stretch with special cements and resins. Tunnel inflow continued to be monitored throughout these activities. Pressures have also been recorded continuously since March 2005 in the packed-off borehole intervals in the MI shear zone. The pressure records show responses to tests of the sealing quality, renewed sealing activities, and pressure conditions created for tracer tests etc.
Two tracer tests were performed after the resin sealing (but prior to establishing low-gradient flow fields) within the MI shear zone using uranine (Na-fluorescein) doped water. Tracer Test Run 05-01 was the first tracer test performed after the shear zone was sealed in the second half of 2005. Tracer Test Run 06-01 was performed in January 2006 after a fissure near the Pinkel surface packer was sealed and the shear zone pressures had recovered and stabilised. The objectives of the tracer tests were to obtain advective travel times, assess the recovered tracer and estimate the dispersion parameters in the shear zone flow field from boreholes to the tunnel surface packer intervals when the shear zone was sealed but water was allowed to freely flow from the surface packers.

Two boreholes, CFM 06.001 and CFM 06.002, were drilled and equipped for testing and observation in August 2006 (see Fig. 2). In particular, the hydraulic modelling results showed the boreholes could fill existing data gaps. An inspection with a borehole camera was carried out in each borehole. The camera logs confirmed the position of the shear zone and identified lamprophyre intrusions in the core of CFM 06.001, whereas in CFM 06.002 no clear water-conducting fractures were observed, although a water outflow point was observed at the borehole end (6.85 m). Some weeks later, borehole CFM 06.002 was extended to penetrate the shear zone. Both boreholes were equipped with packer systems and saturated.

By the time of the 3rd CFM Project Meeting in May 2006 it was apparent that the status of the sealing of the MI shear zone did not fulfil the requirements for the in situ experiment. The resin seal developed blisters and cracked at high pressures when flow from the shear zone was restricted. It was decided to install a 5 m long steel mechanical tunnel packer (referred to as megapacker or sub-mountain packer, consisting of a tunnel liner with cement-filled Bullflex packers on each end) to provide mechanical support to allow the resin to resist higher pressures in the MI shear zone. Water in the annular space between the tunnel wall and the megapacker can be pressurised to support the resin sealing. In February 2007 the megapacker and the new boreholes were instrumented and connected to the data acquisition system (DAS).

In the immediate area around the tunnel intersection, the MI shear zone is effectively isolated and does not intersect any other large-scale structure. At a greater distance it is believed that the shear zone intersects the lamprophyre that crosses the tunnel at about tunnel metre AU73 close to the site of the first LTD monopole experiment (overcored in 2010). The local transmissivity of the shear zone around borehole CFM 06.001 (~ $10^{-9}$ m$^2$/s) is slightly lower than the average of the CFM/MI zone (between $10^{-8}$ and $10^{-7}$ m$^2$/s). The hydraulic properties of the lamprophyre and observed pressure interferences with the MI shear zone were analysed in Lanyon & Blechschmidt (2008).

Throughout 2007, a series of five tracer tests (Tracer Test Runs 07-01 to 07-05) was conducted with dyed water to further evaluate the flow field for subsequent colloid migration experiments. The homologue Tracer Test Run 08-01 was carried out in January 2008, followed by the companion Tracer Test Run 08-02 with uranine injection in February into approximately the same flow field. It had been decided that the conservative tracer might cause complexation, so the tests were performed separately. The flow field selected was similar (in terms of outflow from the shear zone) to that used in Tracer Test Run 07-01. The results from Tracer Test Runs 08-01 and 08-02 are discussed in more detail in Section 2.5 and Chapter 5.

One of the three key objectives for the start of Phase 2 was the development and demonstration of an adequate and robust sealing system suitable for the performance of a long-term in situ test. Since the beginning of the project in 2004, numerous considerations eventually resulted in the implementation of three increasingly complex sealing concepts. It was recognised at the beginning of Phase 2 that further improvements would be necessary. Eventually, the 5 m long...
steel liner of the megapacker installed in Phase 1 was left in place while the cement-filled Bullflex packers on each end were replaced with inflatable rubber packers. The new system was put into operation in September 2009 and provided reliable sealing over a range of conditions with no indication of significant leakage over the first few months of observation.

The second key objective concerned the characterisation of borehole CFM 06.002 and the key feature of the shear zone around it as a possible emplacement location for the bentonite source for the in situ test. For this, the lithological and structural features were analysed with an optical borehole scan, core mapping and an impression packer survey. A hydraulic screening test campaign with test intervals in borehole CFM 06.002 and monitoring intervals in this and neighbouring boreholes supported the hydrogeological characterisation of the MI shear zone. The highest transmissivities were associated with the borehole section between 6.40 m and 7.10 m, which contains a single fracture identified in the core, images and the impression packer data (see Fig. 3). The design of the final borehole instrumentation was optimised accordingly. Interval 2 of the triple packer system installed in May 2009 covers this 0.7 m section and was equipped with a PEEK (Polyether ether ketone) dummy to reduce its volume.

![Fig. 3: Photograph of the core section from borehole CFM 06.002 showing the fracture plane at a depth of 6.78 m. To account for localisation difficulties the key feature is generally considered to be in the depth range of 6.70 – 6.85 m.](image)

The results from Tracer Test Run 09-01 demonstrated that the interval around the candidate feature was suitable for the in situ test. The attributes include:

- There was a well-characterised distinct flow feature in interval 2 (6.40 – 7.10 m)
- The feature was well connected to flow paths in the shear zone (cross-hole hydraulic and tracer responses)
- The flow rate through the borehole interval under suitable boundary conditions (outflow from Pinkel surface packer) was consistent with the target range for the in situ test
- The location was suitable for post-test overcoring

While the suitability of the "single fracture" or "distinct flow feature" in borehole CFM 06.002 became apparent, there were discrepancies with respect to its exact location in the borehole from the different investigation methods. All conceivable explanations considered, it appeared most sensible at the time to define the position of the key feature in terms of a depth range which accounts for the recognised uncertainty inherent in the depth information. For further planning purposes the depth of the key feature was considered to be 6.70 – 6.85 m from the borehole mouth.
The third key objective concerned the development of instrumentation for monitoring groundwater chemistry and tracer testing. The surface equipment at the CFM site was augmented in November 2009 with two chemistry cabinets. Although their flexible configurations facilitate tracer testing, they are designed also for the long-term sampling and monitoring required for both migration tests and the long-term in situ test. At the end of 2009, the field setup at the CFM site included 20 monitoring intervals in twelve boreholes, seven surface or short borehole packers at the intersection of the MI shear zone and the AU tunnel, and injection and extraction groundwater monitoring systems.

Tracer Test Runs 10-01 to 10-04 were performed in 2010 with homologues, colloids and conservative tracers (colloids and homologues in 10-01 and 10-03). All were conducted as point dilution tests (cf. Section 2.4) with recirculation of tracer in interval 2 of borehole CFM 06.002 and extraction from the Pinkel surface packer. The suitability of this dipole for the Long-term In situ Test was confirmed. The tracer tests provided field data on colloid and homologue transport at longer timescales than previously achieved under controlled conditions.

Tracer Test Run 10-01 was a homologue/colloid tracer test performed at 48 ml/min extraction from the Pinkel surface packer. The results from Tracer Test Run 10-01 are discussed in more detail in Section 2.5 and Chapter 5.

Tracer Test Run 10-03 was a homologue/colloid tracer test performed at a low extraction from the Pinkel of 10 ml/min. Although homologues and colloids were identified at the Pinkel surface packer, an anomalous loss of uranine was also detected. The results from Run 10-03 are also discussed in more detail in Section 2.5 and Chapter 5.

In 2011, the three monitoring boreholes CFM 11.001, CFM 11.002 and CFM 11.003 were drilled, surveyed, core mapped and equipped with triple packer systems. They are in close proximity (~ 4 cm) and parallel to borehole CFM 06.002 because of the intention to use them for colloid and radionuclide monitoring at small distances from the source, and for resin injection and stabilisation of the key feature in the target shear zone before overcoring takes place at the conclusion of the in situ test.

After drilling these monitoring boreholes, Tracer Test Runs 11-01 and 11-02 demonstrated that a low flow velocity zone was present around CFM 06.002-i2 resulting in very little "dilution flow" through the interval, which necessitated a change to a dipole configuration (i.e. active injection into CFM 06.002-i2) in future tracer tests from this interval. Only a very small injection rate (0.33 ml/min) was necessary and this rate was used for Tracer Test Runs 12-01 and 12-02, the confirmation/preparatory conservative tracer test and the radionuclide/colloid migration test, respectively.

During Tracer Test Runs 11-01 and 11-02 it was also established that at low gradients uranine showed anomalous losses compared with the tracer Amino-G Acid (AGA). The process causing these losses is not understood although it has been suggested that it is associated with low pH conditions in the injection interval. From Tracer Test Run 11-01 onwards AGA has been used as the primary conservative tracer. Tests with eosin (from Tracer Test Run 12-04 on) have shown behaviour similar to that of uranine.

Tracer Test Run 12-01 was a preparatory conservative tracer test to confirm the setup for the subsequent radionuclide/colloid Tracer Test Run 12-02. The results from Tracer Test Run 12-02 are discussed in detail in Section 2.5 and Chapter 5.
Tab. 2 lists the tracer tests performed within the CFM Project from 2005 to 2013. In this report, only the four tests involving colloids and homologues or colloids and radionuclides and one associated conservative tracer test (Tracer Test Runs 08-01 and 02, 10-01 and 03 and 12-02) are discussed further in detail, although other tests are sometimes referred to if they provided information that helped with the interpretations of these five tests. An additional homologue test (Tracer Test Run 11-01) was not considered, since no recovery at the Pinkel surface packer was observed, due to stagnant flow around CFM 06.002-i2 after drilling of monitoring boreholes. Furthermore, for Tracer Test Run 12-02, only the observed transport behaviour of the tri- and tetravalent radionuclides (i.e. $^{243}$Am(III) and $^{242}$Pu(IV)) are discussed in detail in this report. Other radionuclides used in Tracer Test Run 12-02 included $^{22}$Na, $^{137}$Cs, $^{133}$Ba and $^{237}$Np(V), which were not considered in this report.

Tab. 2: Field tracer tests performed within the framework of CFM 2005 – 2013.

Refer to Fig. 4 for locations of boreholes other than CFM 06.002. CFM 11.001, CFM 11.002 and CFM 11.003 are each within 4 cm of borehole CFM 06.002 and were constructed to provide near field monitoring boreholes for the in situ bentonite emplacement test.

CFM 06.002-i1 and CFM 06.002-i2 were located on the same flowing feature in borehole CFM 06.002 (i.e. intersecting the main shear zone fracture). Until 14 May 2009, the main fracture was in CFM 06.002-i1, subsequently following emplacement of a triple packer system the main fracture was in CFM 06.002-i2. RN: Radionuclide.

<table>
<thead>
<tr>
<th>Tracer Test Run</th>
<th>Test type</th>
<th>Injection mode</th>
<th>Injection interval</th>
<th>Shear zone extraction</th>
<th>SZ flow [ml/min]</th>
<th>Additional extraction</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>05-01</td>
<td>Conservative</td>
<td>Injection</td>
<td>BOMI 87.010-i2</td>
<td>Pinkel/ fissure</td>
<td>573</td>
<td></td>
<td>Test prior to sealing</td>
</tr>
<tr>
<td>06-01</td>
<td>Conservative</td>
<td>Injection</td>
<td>CRR 00.003-i2</td>
<td>Pinkel</td>
<td>602</td>
<td></td>
<td>Test prior to sealing</td>
</tr>
<tr>
<td>07-01</td>
<td>Conservative</td>
<td>Injection</td>
<td>CFM 06.002-i1</td>
<td>Pinkel</td>
<td>164.7</td>
<td></td>
<td>Evaluation of CFM 06.002</td>
</tr>
<tr>
<td>07-02</td>
<td>Conservative</td>
<td>Injection</td>
<td>BOMI 87.010-i2</td>
<td>Pinkel</td>
<td>119</td>
<td></td>
<td>Repeat 05-01 low outflow</td>
</tr>
<tr>
<td>07-03</td>
<td>Conservative</td>
<td>Injection</td>
<td>CRR 00.003-i2</td>
<td>BOMI 87.010-i2</td>
<td>75</td>
<td>Slight leakage</td>
<td>Dipole selection tests</td>
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<tr>
<td>07-04</td>
<td>Conservative</td>
<td>Injection</td>
<td>BOMI 87.008-i2</td>
<td>Pinkel</td>
<td>109</td>
<td></td>
<td>Dipole selection tests</td>
</tr>
<tr>
<td>07-05</td>
<td>Conservative</td>
<td>Injection</td>
<td>BOMI 87.008-i2</td>
<td>BOMI 87.010-i2</td>
<td>110</td>
<td></td>
<td>Dipole selection tests</td>
</tr>
<tr>
<td>08-01</td>
<td>Homologue/ colloid</td>
<td>Injection no recirculation</td>
<td>CFM 06.002-i1</td>
<td>Pinkel</td>
<td>160</td>
<td></td>
<td>See Sections 2.4, 2.5, Chapter 5</td>
</tr>
<tr>
<td>08-02</td>
<td>Conservative</td>
<td>Injection with recirculation</td>
<td>CFM 06.002-i1</td>
<td>Pinkel</td>
<td>165</td>
<td></td>
<td>Injection of tracer was followed by water injection. See Sections 2.4, 2.5, Chapter 5</td>
</tr>
<tr>
<td>09-01</td>
<td>Conservative</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>52</td>
<td></td>
<td>Preparation for 10-01</td>
</tr>
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Tab. 2: Cont.

<table>
<thead>
<tr>
<th>Tracer Test Run</th>
<th>Test type</th>
<th>Injection mode</th>
<th>Injection interval</th>
<th>Shear zone extraction</th>
<th>SZ flow [ml/min]</th>
<th>Additional extraction</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-01</td>
<td>Homologue/colloid</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>48</td>
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<td></td>
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<tr>
<td>10-02</td>
<td>Conservative</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>10.4</td>
<td></td>
<td>Preparation for 10-03</td>
</tr>
<tr>
<td>10-03</td>
<td>Homologue/colloid</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>10.1</td>
<td></td>
<td>See Sections 2.4, 2.5, Chapter 5</td>
</tr>
<tr>
<td></td>
<td>Homologue/colloid</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>BOMI 87.010-i2</td>
<td>10.3</td>
<td>Additional extraction late in test</td>
<td></td>
</tr>
<tr>
<td>10-04</td>
<td>Conservative</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td></td>
<td>Higher outflow test</td>
</tr>
<tr>
<td>11-01</td>
<td>Homologue/colloid</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>10.3</td>
<td>Repeat of 10-03 with AGA. No recovery due to stagnant flow around CFM 06.002</td>
<td></td>
</tr>
<tr>
<td>11-02</td>
<td>Conservative</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>Repeat with higher outflow</td>
<td></td>
</tr>
<tr>
<td>11-02</td>
<td>Conservative</td>
<td>Injection</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>Test of injection</td>
<td></td>
</tr>
<tr>
<td>11-03</td>
<td>Conservative</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>CFM 11.001-i2</td>
<td>Near field sampling feasibility test</td>
</tr>
<tr>
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<td>Conservative</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>CFM 11.002-i2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Conservative</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>CFM 11.003-i2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Conservative</td>
<td>Injection</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td></td>
<td>Test of low rate injection</td>
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<tr>
<td>12-01</td>
<td>Conservative</td>
<td>Injection</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12-02</td>
<td>RN/Colloid</td>
<td>Injection</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td></td>
<td>See Sections 2.4, 2.5, Chapter 5</td>
</tr>
<tr>
<td>12-03</td>
<td>Conservative</td>
<td>Injection</td>
<td>CRR 00.003-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td></td>
<td>Dipole feasibility tests</td>
</tr>
<tr>
<td>12-04</td>
<td>Conservative</td>
<td>Injection</td>
<td>CRR 00.003-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>BOMI 87.010-i2</td>
<td></td>
</tr>
<tr>
<td>12-05</td>
<td>Conservative</td>
<td>Injection</td>
<td>CRR 00.003-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>BOMI 87.010-i2</td>
<td></td>
</tr>
<tr>
<td>12-06</td>
<td>Conservative</td>
<td>Injection</td>
<td>BOMI 87.008-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>BOMI 87.010-i2</td>
<td></td>
</tr>
</tbody>
</table>
Tab. 2: Cont.

<table>
<thead>
<tr>
<th>Tracer Test Run</th>
<th>Test type</th>
<th>Injection mode</th>
<th>Injection interval</th>
<th>Shear zone extraction</th>
<th>SZ flow [ml/min]</th>
<th>Additional extraction</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-01</td>
<td>Conservative</td>
<td>Point Dilution</td>
<td>CFM 06.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>CFM 11.002-i2</td>
<td>Sampling feasibility test</td>
</tr>
<tr>
<td>13-02</td>
<td>Conservative</td>
<td>Injection</td>
<td>CRR 99.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>BOMI 87.010-i2</td>
<td>Tests to identify boundary conditions for RN/colloid test in CRR Dipole D-1</td>
</tr>
<tr>
<td>13-03</td>
<td>Conservative</td>
<td>Injection</td>
<td>CRR 99.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>BOMI 87.010-i2</td>
<td></td>
</tr>
<tr>
<td>13-04</td>
<td>Conservative</td>
<td>Injection</td>
<td>CRR 99.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>BOMI 87.010-i2</td>
<td></td>
</tr>
<tr>
<td>13-05</td>
<td>RN/Colloid</td>
<td>Injection</td>
<td>CRR 99.002-i2</td>
<td>Pinkel</td>
<td>25.15</td>
<td>BOMI 87.010-i2</td>
<td>2nd RN-colloid migration test</td>
</tr>
</tbody>
</table>

2.4 Experimental setup and hydraulic conditions during tests

The Tracer Test Runs 08-01 and 02, 10-01 and 03, and 12-02 were performed in a dipole between the injection interval of borehole CFM 06.002 and the extraction point at the Pinkel surface packer at the tunnel wall as illustrated in Fig. 4. The distance between the injection borehole and the extraction point (Pinkel) is ca. 6 m. Details of the experiments are described in Geckeis et al. (2011).

Fig. 4: Transmissivity field and location of boreholes in the shear zone (after Gaus & Smith 2008).

The dipole between borehole CFM 06.002-i2 and the extraction point (Pinkel surface packer) for the CFM experiment is indicated by the red arrow.
While Tracer Test Runs 08-01 and 02, and 12-02 were performed with a defined inflow, Tracer Test Runs 10-01 and 10-03 were performed as point dilution tests. The point dilution tests were conducted by circulating the tracer solution through the injection interval in a closed flow loop and allowing the natural flow in the shear zone to displace the tracer solution from the interval, resulting in an exponential decrease in the tracer concentrations in the loop. In Tracer Test Runs 08-02 and 12-02, the same type of circulation loop was employed, but tracer-free water was continuously injected into the loop at a low rate creating a small gradient away from the interval driving flow into the shear zone. Tracer Test Run 08-01 differed from all the other tests in that the tracer solution was injected directly into the injection interval with no circulation loop, although the injection rate was the same as that in Tracer Test Run 08-02.

The transport velocity of the fluid and thus the residence time of the tracers in the shear zone is mainly determined by the extraction flow rate at the Pinkel surface packer, which can be varied down to a range approaching the natural flow conditions within the shear zone if the tunnel were not present. It is important to recognise that the AU tunnel acts as a large hydraulic sink that draws water from the surrounding shear zone, and the Pinkel surface packer extraction rate serves as a means of manipulating the strength of this local hydraulic sink. Relevant data for modelling, including the injected amounts of the conservative tracer, bentonite colloids and homologue tracers, are provided in Tab. 3.

Tab. 3: Inflow/outflow conditions, injected amount of tracers $M_0$ and recovery of conservative tracers for the considered field tests (Geckel et al. 2011).

<table>
<thead>
<tr>
<th></th>
<th>Tracer Test Runs 08-01 &amp; 02</th>
<th>Tracer Test Run 10-01</th>
<th>Tracer Test Run 10-03</th>
<th>Tracer Test Run 12-02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inflow [ml/min]</td>
<td>10</td>
<td>--</td>
<td>--</td>
<td>0.33</td>
</tr>
<tr>
<td>Outflow [ml/min]</td>
<td>160/165</td>
<td>48</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Injected amount $M_0$ [mg] of tracers considered for modelling</td>
<td>15.4 (08-02 only)</td>
<td>5</td>
<td>9</td>
<td>4.5</td>
</tr>
<tr>
<td>FEBEX bentonite colloids$^1$</td>
<td>15</td>
<td>--</td>
<td>30</td>
<td>210</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>--</td>
<td>11.96 $\times 10^{-3}$</td>
<td>45.48 $\times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$^{159}$Tb</td>
<td>14.3</td>
<td>10.10 $\times 10^{-3}$</td>
<td>45.44 $\times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$^{178}$Hf</td>
<td>23.4</td>
<td>12.78 $\times 10^{-3}$</td>
<td>51.64 $\times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>19.8</td>
<td>14.87 $\times 10^{-3}$</td>
<td>49.78 $\times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$^{22}$Na</td>
<td></td>
<td></td>
<td></td>
<td>2.09 $\times 10^{-3}$</td>
</tr>
<tr>
<td>$^{133}$Ba</td>
<td></td>
<td></td>
<td></td>
<td>8.7 $\times 10^{-6}$</td>
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<tr>
<td>$^{137}$Cs</td>
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<td>2.66 $\times 10^{-4}$</td>
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<td>$^{237}$Np</td>
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<td></td>
<td></td>
<td>2.81 $\times 10^{-4}$</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td></td>
<td></td>
<td></td>
<td>4.99 $\times 10^{-5}$</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td></td>
<td></td>
<td></td>
<td>1.37 $\times 10^{-5}$</td>
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<tr>
<td>Recovery of the conservative tracer [%]</td>
<td>99</td>
<td>84</td>
<td>60$^3$</td>
<td>80</td>
</tr>
</tbody>
</table>

$^1$ Based on Al content measured by ICP-MS

$^2$ Based on Al, Ni. In Tracer Test Run 12-02 of the total 101 mg/l clay colloids, 8.9 mg/l was made up of synthetic montmorillonite traced with Ni (see Reinholdt et al. 2013).

$^3$ Estimated recovery after correcting for uranine degradation (see Appendix A)
2.5 Experimental results

The normalised concentrations of the conservative dye tracers (observed concentrations divided by injected mass) as a function of time in the circulating injection loops of Tracer Test Runs 08-02, 10-01, 10-03, and 12-02 are shown in Fig. 5. Uranine was used as a conservative tracer for Tracer Test Runs 08-02, 10-01, and 10-03, whereas Amino-G Acid (AGA) was used for Tracer Test Run 12-02. The normalised concentrations of the conservative tracers as a function of time in the water extracted from the Pinkel surface packer (i.e. the extraction breakthrough curves) in each of these tests are shown in Fig. 6. The uranine breakthrough curve for Tracer Test Run 10-03 was modified according to the approach given in Appendix A to correct for suggested uranine degradation. Uranine degradation was subsequently confirmed in a test in which both AGA and uranine were used as tracers (Tracer Test Run 11-02), and the results of that test were used to correct for uranine degradation in Tracer Test Run 10-03 (Appendix A). Additional closed-loop recirculation tests also demonstrated uranine degradation.

Fig. 5: Mass normalised concentration injection functions (observed concentration divided by injected mass).

Fig. 7 shows the normalised injection and extraction functions for the conservative dye tracer used in each tracer test involving colloids and homologues/radionuclides plotted together as a function of volume extracted instead of time so that the four tests with significantly different residence times plot similarly on the x-axis scale. A colloid extraction curve is shown for Tracer Test Run 08-01 because a conservative dye tracer was not used in this test. Note that the y-axis scale of the extraction curves in Fig. 7 has been normalised by dividing by the injection concentration ($C_0$) and then multiplying by the ratio of the extraction flow rate to the injection flow rate (i.e. the dilution factor) to adjust them to approximately the same numerical values as the injection curves, which are plotted as $C/C_0$. The injection function for Tracer Test Run 08-01 was calculated based on the injection function for Tracer Test Run 08-02. For Tracer Test Run 10-03, the degradation-corrected uranine injection and extraction functions (from Appendix A) are shown.
Fig. 6: Mass normalised concentration breakthrough curves (observed concentration divided by injected mass).

Fig. 7: Normalised extraction and injection concentration histories plotted as a function of volume extracted.

Uranine in Tracer Test Run 10-03 is corrected for injection loop decay (see Appendix A).

It is apparent from Fig. 7 that the conservative tracer extraction functions mirror the injection functions quite well at late times (after the extraction concentrations have peaked) in each tracer test. Thus, the tails of the observed extraction breakthrough curves are dictated by the slow
decline in concentrations in the injection circuits during the tests, not by dispersion in the shear zone. The implication is that the mean residence times in the shear zone are actually much shorter than the extraction curves might suggest.

Fig. 8 shows the calculated normalised tracer breakthrough curves in only the shear zone as a function of volume eluted in each test, including Tracer Test Run 08-02. These curves were obtained by deconvolving the injection functions from the observed extraction functions of Fig. 7 using the LANL RELAP model (Reimus et al. 2003). The breakthrough curves assume that a 1.5-h tracer pulse was injected directly into the shear zone (to match the 1.5-h injection during the Tracer Test Run 08-01), with the normalised concentrations being divided by the extraction flow rate of each test to make the areas under the curves the same.

It is apparent from Fig. 8 that each test had uniquely different shear zone transport behaviour despite having the same injection and extraction locations. Tracer Test Runs 10-01 and 12-02 had the most similar transport behaviour despite the fact that the extraction rate for Tracer Test Run 10-01 was approximately two times larger than in Tracer Test Run 12-02, and Tracer Test Run 10-01 was a point-dilution test whereas Tracer Test Run 12-02 was a forced injection test. In contrast, the breakthrough curves for Tracer Test Runs 08-01 and 08-02, which were conducted with the same injection and extraction flow rates, are very different in Fig. 8, with Tracer Test Run 08-01 exhibiting almost ideal plug flow behaviour in the shear zone (i.e. very little dispersion). These results indicate that flow pathways in the shear zone are not entirely controlled by injection and extraction flow rates. It is likely that the injection function in Tracer Test Run 08-01 was actually more truncated than the assumed exponential decay associated with an ideally-mixed injection circuit (the injection circuit was not recirculated in this test as it was in Tracer Test Run 08-02 and all the other tests). If the injection function was more truncated than an exponential decay, the shear zone breakthrough curve would be deduced to have more dispersion than ideal plug flow behaviour to match the observed extraction function.

The breakthrough curves of the colloids and homologues or radionuclides in Tracer Test Runs 08-01, 10-01, 10-03, and 12-02 are shown in Figs. 9 to 12.

![Fig. 8: Deduced shear-zone-only conservative tracer breakthrough curves.](image-url)
Fig. 9: Mass normalised concentration breakthrough curves for colloids and homologues of Tracer Test Run 08-01.

Note that the two colloid curves correspond to measurements from two different single particle counter detectors (50 and 100 nm).

Fig. 10: Mass normalised concentration breakthrough curves for colloids and homologues of Tracer Test Run 10-01.
Fig. 11: Mass normalised concentration breakthrough curves for colloids and homologues of Tracer Test Run 10-03.

Fig. 12: Mass normalised concentration breakthrough curves for colloids and radionuclides of Tracer Test Run 12-02.
2.6 Further tracer testing and LIT

Although this report focuses on the migration tests performed in the dipole CFM 06.002-i2 – Pinkel surface packer prior to LIT emplacement it is useful to provide some information on further migration tests and the LIT itself.

2.6.1 Tracer Test Run 13-05

Migration testing immediately prior to the LIT emplacement (Tracer Test Runs 12-05 to 13-04) focused on the feasibility of testing in the dipoles previously used for CRR. As a result a second CFM colloid/radionuclide migration test was performed. Tracer Test Run 13-05 was performed between CRR 99.002-i2 and BOMI 87.010-i2 (known as CRR Dipole D-1). The hydraulic boundary conditions were:

- CRR 99.002-i2 constant rate injection of 0.33 ml/min
- BOMI 87.010-i2 constant rate extraction of 5 ml/min
- Pinkel surface packer constant rate extraction of 25 ml/min

These correspond to flow rates 1/30\(^{th}\) of that used in the CRR colloid/radionuclide tests numbered Run #31 and #32. The results from Tracer Test Run 13-05 are currently being analysed and modelling of the test is ongoing.

2.6.2 Long-term In Situ Test (LIT)

The LIT uses the same dipole as the migration tests discussed in this report (Tracer Test Runs 08-01, 08-02, 10-01, 10-03 and 12-02). The LIT bentonite source is 0.4 m long and comprised of 16 compacted FEBEX bentonite rings. The main water-conducting feature in CFM 06.002 is located between 6.70 and 6.85 mah (metres along hole) and the source was emplaced between 6.55 and 6.95 mah. The four rings between 6.70 and 6.80 mah were fabricated from a mixture of 90 % FEBEX bentonite and 10 % synthetic montmorillonite traced with Zn. 16 open glass vials (four per ring) were inserted into these rings containing AGA tracer and a radionuclide-traced bentonite slurry.

Three monitoring boreholes CFM 11.001, 11.002 and 11.003 were drilled in 2011. These boreholes were completed with packer systems that can be used for monitoring and sampling and subsequent resin injection prior to overcoring the LIT. Interval i2 of each of these boreholes is 0.4 m long, parallel to the bentonite source and contains the intersection with the main water-conducting feature.

After emplacement of the bentonite in May 2014, the outflow from the Pinkel surface packer has been maintained at a constant 25 ml/min (as of March 2016). This is the same hydraulic boundary condition as that used during Tracer Test Run 12-02. The outflow chemistry is continuously monitored (tracer concentration, pH, EH, turbidity and electrical conductivity) and periodically sampled. In addition, water has been extracted for monitoring and sampling at a constant low rate (20 \(\mu\)l/min) from interval CFM 11.002-i2 which was identified as the most suitable interval from analysis of Tracer Test Runs 11-03 and 13-01.
3 Conceptual framework

The conceptual models and governing equations describing flow and transport in the MI shear zone are presented in this section. The shear zone of the CFM experiment consists of a network of open channels embedded in fracture infill material and enclosed by quasi-parallel granite walls. The modelling approach presented here simplifies the complexity of the fracture network by treating the shear zone as a porous medium with effective homogeneous flow properties (not spatially varying).

Due to the large size of the colloids it is assumed that matrix diffusion of colloids does not play a role. Since the breakthrough curves of the homologues and radionuclides considered in this study are dominated by the colloid-bound fractions, matrix diffusion of the solutes is also not regarded. Therefore, the process of matrix diffusion is not included in the description of the conceptual and mathematical models here.

3.1 Flow

Transport calculations are based on the assumption of a steady-state flow field. The generalised Darcy law for two-dimensional groundwater flow (Kinzelbach & Rausch 1995) can account for variable density and viscosity of the groundwater in the case of density-driven flow (Fein & Schneider 1999, Ingebritsen et al. 2007):

\[ q = -\frac{k}{\mu} (\nabla p - \rho g) \]  

with

- \( q \) Darcy velocity \([\text{L T}^{-1}]\)
- \( k \) Intrinsic permeability tensor \([\text{L}^2]\)
- \( \mu \) Dynamic viscosity \([\text{M L}^{-1} \text{T}^{-1}]\)
- \( p \) Pressure \([\text{M L}^{-1} \text{T}^{-2}]\)
- \( \rho \) Bulk density of porous media \([\text{M L}^{-3}]\)
- \( g \) Gravitation vector \([\text{L T}^{-2}]\)

where \( \rho = \rho (c, T) \) and \( \mu = \mu (c, T) \) with the concentration \( c \) of any substance in the groundwater and the temperature \( T \) of the groundwater. At the GTS the mineralisation of the groundwater can be regarded as constant and the temperature in the entire model domain can also be assumed to be constant, such that the density and viscosity are treated as constant. The groundwater flow is therefore described by the mass conservation equation (flow equation) (Fein & Schneider 1999):

\[ \frac{\partial}{\partial t} (\theta \rho) + \nabla \cdot (q \rho) = F^f \]  

(2)
Remark: $d^3f$, one of the codes applied in this study, is a density-driven flow code. Here, the first term of Eq. (2) will become zero, because the density is constant.

The MI shear zone can be approximated as a two-dimensional flow system because it is a roughly planar feature and the surrounding matrix is highly impermeable. The hydraulic conductivity $K \left( K = \frac{k_p g}{\mu} \right)$ is considered to be spatially constant in the two-dimensional system.

A constant model thickness of 0.005 m is assumed, based on the values for the aperture of the water-conducting fractures given in Gaus & Smith (2008); see Section 4.4. Groundwater flow is driven by a hydraulic gradient towards a sink (the Pinkel surface packer), where $p$ is the spatial variable that is solved via Eqs. (1) and (2) given the spatial variability in hydraulic conductivity. The boundary conditions for the pressure are described in Section 4.4. Once the pressure field is solved, vector for the local velocity $q \left( q_x; q_y; q_z \right)$ $[L \ T^{-1}]$ can be calculated at each location $X \left( x; y; z \right)$ using Eq. (1).

Considering a tracer test conducted between injection point B and detection (extraction) point A, the flow takes place from B to A along a mean trajectory defined by $X \left( t; x_B \right)$. Thus, the transport of particles (colloids, tracer ions or molecules) can be considered as movement from B to A along trajectories, the mean of which is $X \left( t; x_B \right)$, or the "flow path" between B and A. Transport can be approximated as a one-dimensional process along $X \left( t; x_B \right)$.

### 3.2 Colloid transport and interactions

The equations for colloid transport and interactions with shear zone surfaces are described in the following subsections. The interactions between the bentonite colloids and solute species are described in Section 3.3. Colloids usually undergo a hydrodynamic chromatography effect, namely staying centre-stream and thus migrating faster than the mean water velocity (Reimus et al. 1995). However, this effect did not play any significant role in the CFM field experiments and therefore it is assumed here that the colloids travel with the water velocity.

#### 3.2.1 Transport

The general form of the Eulerian colloid mass balance equations in non-uniform, steady-state flow is:

\[
\frac{\partial}{\partial t} (\theta C_c) + \text{div}(q_c C_c - \theta D_c \nabla C_c) = -F^t
\]  

(3)

\[
\frac{\partial}{\partial t} (\rho_c C_c^*) = -F^{t*}
\]  

(4)
where

- $q_c$ Darcy velocity of the colloids [L T$^{-1}$]
- $C_c$ Concentration of the colloids in the aqueous phase [M L$^{-3}$]
- $C_c^*$ Concentration of the colloids sorbed to the shear zone material [L$^3$ L$^{-3}$]
- $\rho_c$ Density of the colloids [M L$^{-3}$]

The tensor $D_c$ [L$^2$ T$^{-1}$] describes the diffusion and dispersion effects. $F^t$ and $F^{t*}$ [M L$^{-3}$ T$^{-1}$] are general expressions of the sink-source (exchange) term between the aqueous phase and the shear zone surfaces. Non-Fickian dispersion was not addressed here, since it was not deemed important. Relevant expressions for $F^t$ and $F^{t*}$ are discussed in the next section.

### 3.2.2 Filtration

The interaction of colloids with the aquifer surfaces (in this case fracture filling material in the shear zone) is conventionally described as a first-order kinetic process, i.e. $F^t = k_{cs} \frac{\rho_c}{\theta} C_c$ or $F^{t*} = k_{sc}\rho_c C_c^*$. For idealised conditions the filtration (attachment) rate $k_{cs}$ can be derived from deep bed filtration theory. The common approach of deep bed filtration, neglecting the detachment of filtered colloids, leads to:

$$k_{cs} \rho_b = \lambda_c v_p$$  

(5)

where the bulk density of the porous medium [M L$^{-3}$] is denoted as $\rho_b$, the particle velocity [L T$^{-1}$] as $v_p$ and the efficiency of the filtration is described by the filter coefficient $\lambda_c$ [L$^{-1}$]. Here it is assumed that the mechanism is independent of the amount of already filtrated colloids as it is for clean deep bed filtration. Important parameters are the porosity and the grain size of the sediment particles, the diameter of the colloidal particles, and the viscosity. We refer to the model of Tien & Payatakes (1979), where the filter coefficient is defined as:

$$\lambda_c = \frac{3}{2} \frac{1 - \theta}{d_c} \eta_D \alpha$$  

(6)

In Eq. (6), $\eta_D$ [-] is the collision frequency (i.e. the number of colloid-media collisions per unit length of filter medium and hence the number of opportunities for colloid attachment per unit length) and $\alpha$ [-] is the collision efficiency factor, which is the fraction of collisions that result in colloid attachment. Under the conditions of the field experiment, particularly for an average colloid size in the range of 150 nm (Schäfer & Noseck 2010), the collision frequency $\eta_D$ is dominated by diffusion and can be calculated according to Yao et al. (1971) neglecting interception and sedimentation processes by:

$$\eta_D = 0.9 \left( \frac{k_B T}{\mu d_p d_c v_p} \right)^{2/3}$$  

(7)

where $k_B$ is the Boltzmann constant [L$^2$ M T$^{-2}$ Ω$^{-1}$], $d_p$ [L] is the particle diameter and $d_c$ [L] the collector diameter. Eq. (7) assumes a spherical collector surface, which might require some modification for a fractured medium but was assumed to be a reasonable assumption for the...
fault gouge material in the shear zone. However, the exact modification is not important in this study because $k_{cs}$ is the calibration parameter used in the models described in Chapter 4 to match the field datasets. Thus, the filtration theory parameters $\eta_D$ and $\alpha$, which are incorporated into $k_{cs}$ via Eqs. (5) and (6), were not directly calibrated from the datasets. However, Section 6.5.2 includes a discussion of how these parameters can be related to the observed colloid transport behaviour in the CFM tracer tests.

The colloid detachment rate constant $k_{sc}$ is not addressed in filtration theory (which typically ignores colloid detachment), so $k_{sc}$ is usually experimentally measured or estimated. In this study, it was used as an adjustable fitting parameter to match the field datasets.

3.3 Colloid facilitated solute transport

For interpreting the CFM tests, two mobile and two immobile solute components and one mobile and one immobile colloid component are considered (which can be subject to change for other models depending on the nature and scale of the problem). These components and the interactions between them are depicted in Fig. 13.

![Fig. 13: General concept of considered phases and interactions between them.](image)

The denotation is as follows:

- $C_c$: Mobile colloid concentration [M L$^{-3}$]
- $C_a$: Mobile solute concentration [M L$^{-3}$]
- $C_{amc}$: Solute concentration attached to mobile colloids [M(solute) M(colloids)$^{-1}$]
- $C_{aic}$: Solute concentration attached to immobile colloids [M(solute) M(solid)$^{-1}$]
- $C_c^*$: Immobile colloid concentration [L$^3$(colloids) L$^{-3}$]
- $C_a^*$: Immobile solute concentration [M(solute) M(solid)$^{-1}$]
- $k_{cs}$: First-order transfer rate of colloids from mobile to immobile phase [L$^3$ M(solid)$^{-1}$ T$^{-1}$]
- $k_{sc}$: First-order transfer rate of colloids from immobile to mobile phase [T$^{-1}$]
The solute transport equations in the shear zone have essentially been given by Ibaraki & Sudicki (1995) and Knabner et al. (1996). The continuity equations for the solutes dissolved in the aqueous phase or sorbed to the aquifer material are from Lüthmann et al. (1998):

\[
\frac{\partial}{\partial t}(C_a) + \nabla \cdot (v_a C_a - D_a \nabla C_a) = -F_{as,sa}^a - F_{amc,mca}^a - F_{aic,ica}^a \quad (8)
\]

\[
\frac{\partial}{\partial t} (\rho_b C_a^*) = F_{as,sa}^a . \quad (9)
\]

The mass balance equations for the solutes sorbed to mobile and immobile colloids are given by

\[
\frac{\partial}{\partial t}(C_c C_{amc}) + \nabla \cdot (v_c C_c C_{amc} - D_c \nabla C_c C_{amc}) = -F_{cs,sc}^a + F_{amc,mca}^a \quad (10)
\]

\[
\frac{\partial}{\partial t} (\rho_c C_c^* C_{aic}) = F_{cs,sc}^a + F_{aic,ica}^a \quad (11)
\]

where

\[
F_{as,sa}^a \quad \text{Rate loss of solute from mobile to immobile phase} \quad [\text{M L}^{-3} \text{T}^{-1}]
\]

\[
F_{cs,sc}^a \quad \text{Rate loss of solute sorbed on colloids from mobile to immobile phase} \quad [\text{M L}^{-3} \text{T}^{-1}]
\]

\[
F_{amc,mca}^a \quad \text{Rate loss of solute from mobile aqueous phase to mobile colloids} \quad [\text{M L}^{-3} \text{T}^{-1}]
\]

\[
F_{aic,ica}^a \quad \text{Rate loss of solute from mobile aqueous phase to immobile colloids} \quad [\text{M L}^{-3} \text{T}^{-1}]
\]

\[
D_a \quad \text{Tensor for diffusion and dispersion effects of the solutes} \quad [\text{L}^2 \text{T}^{-1}]
\]

\[
D_c \quad \text{Tensor for diffusion and dispersion effects of the colloids} \quad [\text{L}^2 \text{T}^{-1}]
\]

\[
v_a \quad \text{Flow velocity of the solutes} \quad [\text{L T}^{-1}] = \text{Darcy velocity divided by } \theta
\]

\[
v_c \quad \text{Flow velocity of the colloids} \quad [\text{L T}^{-1}] = \text{Darcy velocity divided by } \theta
\]

In general, all rates may be time dependent.
The mass exchange between the phases shown in Fig. 13 is governed by the following source terms $F$:

$$F_{as,sa} = k_{sa} \frac{\rho b}{a} (f_{as,sa} c_a - c_a^*) = \frac{\rho b}{a} (k_{as} c_a - k_{sa} c_a^*)$$ (12)

$$F_{amc,mca} = k_{mca} c_e (f_{amc,mca} c_a - c_{ame}) = c_e (k_{ame} c_a - k_{mca} c_{ame})$$ (13)

$$F_{aie,ica} = k_{ica} \rho_c c_c^* (f_{aie,ica} c_a - c_{aie}) = \rho_c c_c^* (k_{aie} c_a - k_{ica} c_{aie})$$ (14)

with the sorption isotherms $f_i$ [L$^3$ M$^{-1}$]. Note that the right-hand sides of Eqs. (12), (13) and (14) imply that the sorption isotherms, $f_i$, are assumed to be linear and are approximated by first order sorption and desorption rate expressions. The assumption of sorption linearity is reasonable because the reactive solute concentrations in the CFM field experiments were low enough not to result in saturation of sorption sites. Equilibrium sorption-desorption behaviour can be approximated by using large values for the sorption and desorption rate constants instead of using a $K_d$ approach (the ratio of sorption to desorption rate constant is equivalent to a $K_d$ value if both rates are fast). Note that Eqs. (12), (13) and (14) also imply only a single type of sorption site (i.e., no heterogeneity of sorption sites on the rock matrix or colloid surfaces). Both the sorption linearity assumption and the single-site assumption were relaxed in the LANL modelling approach (Section 4.5).

Consistent with filtration theory, discussed in Section 3.2.2, the interaction of colloids with the fracture filling material can be described as a first order kinetic process according to:

$$F_{cs,sc} = k_{cs} \frac{\rho b}{a} c_c - k_{sc} \rho_c c_c^*$$ (15)

with attachment and detachment rate constants $k_{cs}$ and $k_{sc}$. An irreversible attachment/filtration of colloids can be realised by setting the detachment rate constant to zero. Consistent with this formulation the change of the contaminant concentration caused by colloid fracture filling material interactions is:

$$F_{cs,sc} = k_{cs} \frac{\rho b}{a} c_{c,ame} - k_{sc} \rho_c c_c^* c_{aie}.$$ (16)
4 Governing transport equation transformations for 1D flow

The Eulerian mass balance equations in non-uniform, steady-state flow for colloids (Eqs. (3) and (4)), dissolved solutes (Eqs. (8) and (9)), and colloid-associated solutes (Eqs. (10) and (11)) can be transformed as follows for 1D flow from an injection point to the extraction point.

Assuming that the transport takes place predominantly along the pathway, the mass balance equations (Eqs. (3), (8) or (10)) can be transformed onto the pathway as one-dimensional transport:

\[
\frac{\partial C_i}{\partial t} + U \frac{\partial C_i}{\partial s} - D \frac{\partial^2 C_i}{\partial s^2} = F(C_1, ..., C_N, C_i^*, ..., C_N^*)
\]

(17)

where \(C_i\) is either the colloid, dissolved solute, or colloid-associated solute concentration, \(s\) is the intrinsic length coordinate along the pathway, \(U(s) \equiv |U|\) is the velocity modulus, and \(D = \alpha_s U\), with \(\alpha_s\) being the longitudinal macro-dispersivity [L]. Eqs. (4), (9), and (11) still apply as written, as they do not vary in space (re-written below as Eqs. (22), (23), and (24)). Eq. (17) can either be solved directly with Eqs. (4), (9) and (11) along pathway or a further transformation can be applied to Eq. (17) as follows. Let \(\tau\) denote the mean water residence time at a location along the flow path between B and A. Then, using \(d\tau = ds/\bar{U}\), Eq. (17) can be written (see Cvtekovic & Dagan 1994) as:

\[
\frac{\partial C_i}{\partial t} + \frac{\partial C_i}{\partial \tau} - D_{\tau} \frac{\partial^2 C_i}{\partial \tau^2} = F(C_1, ..., C_N, C_i^*, ..., C_N^*)
\]

(18)

where

\[
D_{\tau} \equiv \frac{\alpha_s}{\bar{U}} = \frac{\tau}{2} = \frac{\tau}{P_{e}}
\]

with \(\zeta \equiv \sigma_s/\tau\) being the coefficient of variation of water residence time between B and A, and \(P_{e} = S/\alpha_s\) and \(\sigma_s^2\) is the water travel time variance.

The transport equations then become:

\[
\frac{\partial C_c}{\partial t} + \frac{\partial C_c}{\partial \tau} - D_{\tau} \frac{\partial^2 C_c}{\partial \tau^2} = -k_{sc} \rho_b \frac{\rho_b}{\rho_c} C_c + k_{sc} \rho_c C_c^*
\]

(19)

\[
\frac{\partial C_a}{\partial t} + \frac{\partial C_a}{\partial \tau} - D_{\tau} \frac{\partial^2 C_a}{\partial \tau^2} = -\frac{\rho_b}{\rho_a} k_{as} C_a + \frac{\rho_b}{\rho_a} k_{sa} C_a - k_{amC} C_a C_c + k_{mcC} C_c C_m - k_{aIC} C_a \rho_c C_c^* + \rho_c k_{ic} C_{aic} C_c^*
\]

(20)

\[
\frac{\partial C_{amC}}{\partial t} + \frac{\partial C_{amC}}{\partial \tau} - D_{\tau} \frac{\partial^2 C_{amC}}{\partial \tau^2} = k_{amC} C_a C_c - k_{mcC} C_c C_{amC} - k_{es} \frac{\rho_b}{\rho_a} C_{amC} C_c + \rho_c k_{sc} C_{aic} C_c^*
\]

(21)

\[
\rho_c \frac{\partial C_c^*}{\partial t} = k_{cs} \frac{\rho_b}{\rho_c} C_c - k_{sc} C_c^*
\]

(22)
\[
\frac{\partial c_a^t}{\partial t} = k_{as} c_a - k_{sa} c_a^t
\]  
(23)

\[
\rho_c \frac{\partial c_{aic}^t}{\partial t} = k_{cs} \frac{\rho_b}{\theta} c_{amc} c_c - \rho_c k_{sc} c_{aic} c_c^t + k_{aic} c_a \rho_c c_c^t - \rho_c k_{ica} c_{aic} c_c^t.
\]  
(24)

Here, Eqs. (19) and (22) are the 1D equivalent to Eqs. (3) and (4) for colloid transport, Eqs. (20) and (23) are the equivalent to Eqs. (8) and (9) for dissolved solute transport, and Eqs. (21) and (24) are the equivalent to Eqs. (10) and (11) for colloid-associated solute transport. Note that we are here not explicitly accounting for radioactive decay of tracers.

### 4.1 Initial and boundary conditions

It is assumed that the initial concentrations of colloids and all solutes in the shear zone are zero. In what follows, the initial and boundary conditions are written in the form of the 1D time-transformed governing Eqs. (19) – (24), although it should be understood that these same conditions apply to the other forms of the governing equations.

At the start of each tracer test, a total mass of solute \( M_a \) [M] is assumed to be dissolved in a volume of water \( V \) [L^3] and mixed with a mass of colloids \( M_c \) [M]. The mixture is equilibrated, and the solute partitions between the aqueous solution and colloids such that the fraction \( f_a [-] \) is in the aqueous solution and \( 1 - f_a \) attached to colloids. The mixture is then injected into the shear zone at point B and carried towards the detection point A by a flow rate \( Q_B \) [L^3 T^{-1}]. The extraction flow rate at point A is \( Q_A \) [L^3 T^{-1}]. The mean water residence time between B and A is \( \bar{\tau} \) [T].

If multiple tracers are injected simultaneously, then the following quantities should be equivalent for all tracers: \( \bar{\tau}, \zeta, Q_A, Q_B, V, D_{tr} \), where these terms are defined in the previous section or directly above (Note: colloids and solute are assumed to be subject to the same macro-dispersion). All rates are assumed to be first order (linear in solute concentration) and the partition coefficients are different for different solutes.

The boundary conditions at \( x_B \) (i.e. \( \tau = 0 \)) and \( x_A \) (i.e. \( \tau = \bar{\tau} \)) are written as follows:

\[
C_c(0, t) - D_{tr} \frac{\partial c_c(0,t)}{\partial \tau} = \frac{M_c}{\varepsilon Q_A} e^{-t/\varepsilon}
\]  
(25)

\[
C_a(0, t) - D_{tr} \frac{\partial c_a(0,t)}{\partial \tau} = f_a \frac{M_a}{\varepsilon Q_A} e^{-t/\varepsilon}
\]  
(26)

\[
C_c(0, t) C_{amc}(0, t) - D_{tr} \frac{\partial C_c(0,t) C_{amc}(0,t)}{\partial \tau} = (1 - f_a) \frac{M_a}{\varepsilon Q_A} e^{-t/\varepsilon}
\]  
(27)

\[
\frac{\partial c_c(t,t)}{\partial \tau} = \frac{\partial c_a(t,t)}{\partial \tau} = \frac{\partial c_{amc}(t,t)}{\partial \tau} = 0
\]  
(28)
where

\[ \epsilon \equiv \frac{\nu}{q_B} \]

is the mean residence time in the injection volume, which is assumed to be ideally mixed [T].

\( x_A \) and \( x_B \) denote the detection and injection locations, respectively, along a one-dimensional pathway.

### 4.2 Evaluation models

Three different models were applied to simulate the field tracer tests. In general, all models considered two mobile and two immobile solute phases and kinetically controlled interaction processes between these, as illustrated in Fig. 13 and reflected in the governing equations of the preceding section. However, each model had a slightly different approach to solving the governing equations or different approaches to representing processes. The differences between the models are discussed in the following sections.

### 4.3 Motivation to use different models

One of the primary motivations for using three different modelling approaches was to evaluate the robustness of the model interpretations and the resulting estimates of colloid and solute transport parameters. If two or three independent modelling approaches produce similar results, then there is greater confidence in not having introduced large modelling errors, and also it can be concluded that the model results are not sensitive to different assumptions in the different models. A second motivation was to evaluate model-based uncertainty in parameter estimates; that is, uncertainty associated with using different assumptions and different approaches to solving the governing equations. Also, since each model included slightly different features, the use of the three models allowed an informal evaluation of the ability to obtain better model fits to the data by accounting for these different features.

The 2D model applied by GRS was the most distinct of the three models in that it was the only model that explicitly solved for a flow field in the shear zone, and it also considered multi-dimensional transport of colloids and solutes. The flow field was determined using the equations of Section 3.1 subject to the boundary conditions imposed by the dipoles in the different tests (see Section 4.1), with the shear zone assumed to have a constant hydraulic conductivity (no spatial variability) because there was insufficient information over the domain of the CFM dipoles to assume otherwise. Both longitudinal and transverse dispersion of colloids and solutes were accounted for in this model.

The two other models are one-dimensional pathway models in which the flow field is not explicitly solved but is indirectly accounted for by matching a mean residence time and a longitudinal dispersion coefficient (i.e. a first and second moment) to the conservative solute breakthrough curves in the tracer tests. Such models are often referred to as black box models because they treat the flow system as a "black box" that imparts a residence time distribution (described by a first and second moment) on tracers without explicitly accounting for the flow pathways that result in the residence time distribution. The justification for using a black box model is that it is generally impossible to know with any certainty where the flow pathways are and how fast each of them is flowing in a channelised flow system such as the MI shear zone. The LANL model solves the 1D model equations in space using Eq. (17) in conjunction with Eqs. (22) – (24), whereas the KTH model solves the time-transformed governing Eqs. (19) – (24).
All the models can account for tracer diffusion into and out of the matrix adjacent to the shear zone, with the water in the matrix porosity being considered stagnant. In effect, this feature imparts a quasi-2D nature to the 1D LANL and KTH models and a quasi-3D nature to the GRS model, with transport in the extra dimension being limited to diffusion. However, this feature is of little importance for the CFM tracer tests because the granodiorite matrix at the GTS has very low porosity, and thus matrix diffusion is not significant over the time scales of the tests.

A specific characteristic of the model applied by LANL is that a two-site approach for sorption processes of the solutes on fracture filling material and colloids can be implemented, allowing different adsorption and desorption rates to be specified for each adsorption site. An "aging" process can be specified in which a first-order rate is used to describe conversion of adsorbed solute from one type of site to the other while adsorbed to the colloid surfaces. The LANL model also can account for a maximum surface site capacity for sorption processes so that adsorption will effectively slow down and sorption isotherms will deviate from linearity as sorption sites are filled up. The model from KTH considers a time-dependent desorption rate from a single sorption site of solutes from the colloids (an exponential decay in the first-order rate constant is allowed). The LANL model can also accommodate time-dependent desorption rate constants from individual sorption sites. One objective of this work was to evaluate whether there is any statistical improvement in the model fits to the tracer breakthrough curves by including the extra model parameters associated with these additional processes (above and beyond a single first-order linear, reversible sorption process).

An overview of the employed models and the calibrated hydraulic parameters is given in Tab. 4.
Tab. 4: Overview of the model assumptions and calibrated hydraulic parameters as applied by the three different modelling groups.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model GRS</th>
<th>Model KTH</th>
<th>Model LANL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionality (flow field)</td>
<td>2D</td>
<td>1D</td>
<td>1D</td>
</tr>
<tr>
<td>Model thickness [m]</td>
<td>$5 \times 10^{-3}$</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>Porosity [-]</td>
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<td>N/A</td>
<td>N/A</td>
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<td>Colloid filtration</td>
<td>Reversible and Irreversible</td>
<td>Reversible and Irreversible</td>
<td>Reversible (up to 2 reactions) and Irreversible</td>
</tr>
<tr>
<td>Number of different adsorption sites on colloids</td>
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<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Solute desorption rates from colloids</td>
<td>Time invariant</td>
<td>Exponential decay allowed</td>
<td>Time invariant, but exponential decay can be specified</td>
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<tr>
<td>Sorption capacity on surfaces</td>
<td>Infinite</td>
<td>Infinite</td>
<td>Finite allowed</td>
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<tr>
<td>Solute-colloid bond aging</td>
<td>Not simulated</td>
<td>Simulated via exponential decay of desorption rate</td>
<td>Accounted for with first-order transformation rate between sites</td>
</tr>
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<td>Dispersion length [m]</td>
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<td></td>
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<td>• Longitudinal</td>
<td>0.3</td>
<td>0.75 m (longitudinal)</td>
<td>Varied with each test to match data</td>
</tr>
<tr>
<td>• Transversal</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient [m$^2$ s$^{-1}$]</td>
<td>$2.0 \times 10^{-11}$</td>
<td>N/A</td>
<td>$1.0 \times 10^{-10}$*</td>
</tr>
<tr>
<td>Permeability [m$^2$]</td>
<td>$5.5 \times 10^{-11}$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* Used for diffusion into the matrix, not longitudinal diffusion within the shear zone
N/A = not applicable

Details of the flow and transport models employed by each modelling group are described in the following sections (Sections 4.4 to 4.6).

### 4.4 2D approach (GRS)

Colloid-bound radionuclide transport is described using the code r$t$ (Fein 2004) based on flow simulations using the code d$3$f (Fein & Schneider 1999). Visualisation was realised on the basis of the software package GRAPE (GRAphics Programming Environment) developed by the Universities of Bonn and Freiburg (GRAPE 1999).

One of the main characteristics of d$3$f is the possibility to calculate the groundwater flow in large model domains over long periods in time. Density-driven flow, resulting from different salt concentrations in the groundwater, is not taken into account in this study, but can be simulated with d$3$f. Two- or three-dimensional models of water saturated, porous, heterogeneous, anisotropic and incompressible media can be set up in form of transient or steady-state flow models. The temperature can be defined as a temporally and spatially variable field, and heat transport can be considered. Transport calculations with r$t$ are based on steady-state or
transient flow fields calculated by \(d^t f\). The most important feature of \(r^t\) is the possibility to simulate contaminant transport in very large model domains for long periods of time. Transport mechanisms, such as advection, dispersion, diffusion and reaction, are simulated according to Kinzelbach (1992) and de Marsily (1986). In addition to radioactive decay, relevant interaction processes, such as sorption, precipitation, and diffusion into immobile pore waters, can be simulated (Fein 2004). All numerical algorithms applied in these codes are based on finite volume methods with robust solvers in the form of multigrid algorithms.

The typical number of fractures in the shear zone and representative aperture widths are given in Gaus & Smith (2008). From these values, an average model shear zone thickness of about 5 mm is derived, which is necessary to reduce the model and boundary conditions to two dimensions.

The flow in the shear zone is determined by the transmissivity field and is mainly dominated by the external boundary conditions (inflow/outflow) of the dipole. The model size is chosen to be large enough to reduce wall effects (Flügge et al. 2010, Appendix B). A schematic of the conceptual model, with boundary conditions for both flow and transport simulations employed for the tracer tests is shown in Fig. 14.

Fig. 14: Geometry and hydrogeological/transport-related boundary conditions of the 2D computer model.

Green: Inflow. Red: Outflow. Blue: Sealed tunnel wall and symmetry axis. Black: Permeable virtual boundaries within the shear zone. Notation: \(c\) = concentration, \(p\) = pressure, \(v\) = fluid velocity, \(f\) = solute mass flux. \(n\) is used either as a subscript to denote the normal component or in fractions in which \(n\) symbolises the normal derivative of the respective variable. The subscript exp describes the velocity derived from the injection and extraction flow in the experiment.

The conceptual and mathematical model for transport of colloids and solutes as well as for the interaction processes is described in detail in the Sections 3.2 and 3.3 and also in Lührmann et al. (1998).

For all interactions of the solutes with fracture filling material and colloids linear isotherms of \(K_d\) type are used. For the interactions of colloids with fracture filling material irreversible filtration processes \((k_{sc} = 0)\) as well as kinetically controlled reversible interactions are applied.
4.5 1D solution in space (LANL)

The LANL model simultaneously solves separate versions of Eq. (17) for the colloids, dissolved solutes, and colloid-associated solutes, along with Eqs. (22) – (24), which account for these species attached to immobile surfaces in the shear zone. An implicit-in-time finite difference algorithm is used to numerically solve the equations in 1D, subject to the boundary conditions given in Eqs. (25) – (28). All of the adsorption processes are modelled as being rate-limited (kinetically-controlled), although the rate constants can be specified as being large enough that the sorption and desorption reactions are effectively always at equilibrium. Unlike the other models, the solute sorption reactions are modelled as having a finite number of sorption sites on the shear zone surfaces or on the colloids. Eqs. (20), (21), (23) and (24) thus become:

\[
\frac{\partial c_a}{\partial t} + \frac{\partial c_a}{\partial x} - D_x \frac{\partial^2 c_a}{\partial x^2} = -\rho \frac{b}{\theta} k_{as} C_a \left(1 - \frac{c_a}{c_{a,max}}\right) + \frac{\rho b}{\theta} k_{sa} C_a^* - k_{amc} C_a C_c \left(1 - \frac{c_{amc} c_c}{c_{ac,max} c_c}\right) + k_{mc} C_c C_{amc} - k_{alic} C_a \rho c C_c^* \left(1 - \frac{c_{alic} c_c^*}{c_{ac,max} c_c^*}\right) + \rho c k_{ica} C_{alic} C_c^* \\
\]

(29)

\[
\frac{\partial c_{amc}}{\partial t} + \frac{\partial c_{amc}}{\partial x} - D_x \frac{\partial^2 c_{amc}}{\partial x^2} = k_{amc} C_a C_c \left(1 - \frac{c_{amc} C_c}{c_{ac,max} C_c}\right) - k_{mc} C_c C_{amc} - k_{cs} \frac{\rho b}{\theta} c_{amc} C_c + \rho c k_{sc} C_{alic} C_c^* \\
\]

(30)

\[
\frac{\partial c_a^*}{\partial t} = k_{as} C_a \left(1 - \frac{c_a^*}{c_{a,max}}\right) - k_{sa} C_a^* \\
\]

(31)

\[
\rho c \frac{\partial c_{alic}^*}{\partial t} = k_{cs} \frac{\rho b}{\theta} C_{amc} C_c - \rho c k_{sc} C_{alic} C_c^* + k_{alic} C_a \rho c C_c^* \left(1 - \frac{c_{alic} C_c^*}{c_{ac,max} C_c^*}\right) - \rho c k_{ica} C_{alic} C_c^* \\
\]

(32)

where \(C_{a,max}^*\) = maximum loading of solute on shear zone surfaces \([M(\text{solute}) M(\text{solid})]^{-1}\), and \(C_{ac,max}^*\) = maximum loading of solute on colloids \([M(\text{solute}) M(\text{colloids})]^{-1}\).

Unlimited sorption capacity (as implicitly assumed in the other models) can be simulated by simply setting these maximum loading parameters to very large values.
Another feature of the LANL model that distinguishes it from the other models is that two solute sorption sites can be specified on both the shear zone and colloid surfaces. The addition of these sites results in duplicative terms in the above equations. For instance, Eqs. (20), (21), (23) and (24) become:

\[
\frac{\partial c_{a1}}{\partial t} + \frac{\partial c_{a2}}{\partial t} - D_{t} \frac{\partial^{2} c_{a1}}{\partial t^{2}} = -\frac{\rho_{b}}{\theta} k_{sa1} c_{a1} \left( 1 - \frac{c_{a1}}{c_{a,\text{max},1}} \right) + \frac{\rho_{b}}{\theta} k_{sa2} c_{a2} \left( 1 - \frac{c_{a2}}{c_{a,\text{max},2}} \right) + \frac{\rho_{b}}{\theta} k_{ca1} c_{a1} c_{c} \left( 1 - \frac{c_{amc1}}{c_{ac,max,1,c}} \right) - k_{mac1} c_{a1} c_{c} \left( 1 - \frac{c_{amc1}}{c_{ac,max,1,c}} \right)
\]

\[
\frac{\partial c_{a2}}{\partial t} = k_{as2} c_{a2} \left( 1 - \frac{c_{a2}}{c_{a,\text{max},2}} \right) - k_{sa2} c_{a2} \left( 1 - \frac{c_{a2}}{c_{a,\text{max},2}} \right)
\]

\[
\rho_{c} \frac{\partial c_{c1}}{\partial t} = k_{cs} \frac{\rho_{b}}{\theta} c_{amc1} c_{c} - k_{ca1} c_{a1} c_{c} \left( 1 - \frac{c_{amc1}}{c_{ac,max,1,c}} \right) - k_{ica1} c_{a1} c_{c} \left( 1 - \frac{c_{amc1}}{c_{ac,max,1,c}} \right) - k_{ica2} c_{a2} c_{c} \left( 1 - \frac{c_{amc2}}{c_{ac,max,2,c}} \right)
\]

\[
\rho_{c} \frac{\partial c_{c2}}{\partial t} = k_{cs} \frac{\rho_{b}}{\theta} c_{amc2} c_{c} - k_{ca2} c_{a2} c_{c} \left( 1 - \frac{c_{amc2}}{c_{ac,max,2,c}} \right) - k_{ica2} c_{a2} c_{c} \left( 1 - \frac{c_{amc2}}{c_{ac,max,2,c}} \right)
\]

where the subscripts 1 and 2 refer to the first and second sorption sites, respectively. The model allows an initial concentration of solute adsorbed to each of the two colloid sites to be specified in the injection cocktail.
One final feature of the LANL model is that an "aging" reaction can be simulated in the injection cocktail. This reaction is a simple first-order conversion of sorbed solutes from site type 1 to site type 2 on colloid surfaces. This aging reaction occurs whether solutes are adsorbed to colloids in the injection cocktail (prior to entering the shear zone) or in the shear zone (either on mobile or immobile colloids). The aging reaction is effectively captured through the addition of two ordinary differential equations that are solved simultaneously with the above equations:

\[
\frac{\partial c_{amc1}}{\partial t} = -\frac{\partial c_{amc2}}{\partial t} = -k_{age}c_{amc,1}
\]  
(37)

\[
\frac{\partial c_{aic1}}{\partial t} = -\frac{\partial c_{aic2}}{\partial t} = -k_{age}c_{aic,1}
\]  
(38)

where \(k_{age}\) is the aging rate constant [T\(^{-1}\)].

4.6 1D time-transformed solution (KTH)

In the KTH model, the model Eqs. (19) – (24) are solved simultaneously using the commercial software Mathematica®. Transport parameters are calibrated so that the model breakthrough curves match the experimental field data.

The most important rate in the transport model is the desorption rate from colloids to aqueous solution, with a first-order rate constant of \(k_{mca}\). For some of the datasets, the best matches between the model and the data were obtained when this rate constant was assumed to be a decreasing function of time, expressed by an exponential term:

\[
k_{mca}(t) = k_{mca0}e^{-t/A}
\]  
(39)

where \(k_{mca}\) [T\(^{-1}\)] and \(A\) [T] are calibrated. The parameter \(A\) dictates the time scale of the decrease in \(k_{mca}\): A larger \(A\) implies a slower decrease, and vice versa.

Eq. (39) is effectively an alternative way of representing the aging reaction described at the end of Section 4.5, wherein instead of representing the aging process as a first-order conversion of sorbed solute from one type of site to another (each site with a different desorption rate constant), the process is described as an exponential decay of a single desorption rate constant for a single site. Eq. (39) has the disadvantage of being less mechanistic than the approach of Section 4.5 in that it implies a continuum of different types of sites with a continuum of rate constants, but it has the advantage of requiring less adjustable parameters. Results from applying the two different approaches are compared and contrasted in Chapter 6.
5 Evaluation of results

Results of simulations conducted by the different modelling groups are described in the following sections. In Section 5.1, the injection functions used by each of the modelling groups are discussed. Section 5.2 presents the general approach to transport modelling taken by the groups. Section 5.3 presents the results of the GRS modelling of 2D flow in the shear zone and conservative tracer transport in Tracer Test Runs 08-02, 10-01, 10-03, and 12-02. The GRS modelling of the colloid and homologue breakthrough curves of Tracer Test Runs 10-01 and 10-03 are also discussed in Section 5.3. Tracer Test Run 08-01 was not modelled by GRS because it lacked a conservative tracer and did not have a definitive injection function, and the colloid and homologue breakthrough curves in Tracer Test Run 12-02 were reserved by GRS for blind predictions that are presented in Section 5.5. In these blind predictions, the results from modelling the colloid transport and colloid-facilitated transport of trivalent and tetravalent homologues in Tracer Test Runs 10-01 and 10-03 were used to predict the breakthrough curves of colloids, Am(III), and Pu(IV) in Tracer Test Run 12-02 to guide the process. In Section 5.4 and 5.6, the LANL and KTH modelling results for Tracer Test Runs 08-01, 10-01, 10-03, and 12-02 are presented. Tracer Test Run 12-02 was not used for blind predictions by these groups, but rather the breakthrough curves were fitted in the same manner as for the other tests to allow a comparison of the transport parameter estimates between tests.

5.1 Injection functions in Tracer Test Runs 08-01/02, 10-01, 10-03 and 12-02

The injection functions used in the LANL modelling for each of the tracer tests considered in this report are shown in Figs. 5 and 7 (Section 2.5). A tracer pulse was injected into the interval in Tracer Test Run 08-01 containing the colloids and homologues, and Tracer Test Run 08-02 the separate dye tracer test performed under equivalent hydraulic boundary conditions. For the point dilution tests (Tracer Test Runs 10-01 and 10-03), in which there was no forced flow into the injection circuit, the flow rate flushing the injection interval was deduced from the slope of a plot of the natural log of normalised tracer concentration ln(C/C_0) in the interval vs. time; i.e. \( Q_{inj} = \frac{d(ln(C/C_0)/dt) V}{dV} \), where \( Q_{inj} \) is the flow rate [L^3 T^{-1}] and \( V \) is the known recirculation volume [L^3] – including borehole interval, lines, tracer tank and surface equipment. The values of \( Q_{inj}/V \) used in the LANL modelling are listed in Table 5. Note that despite the fact that a relatively constant injection rate of 0.33 ml/min was maintained throughout Tracer Test Run 12-02, the slope of ln(C/C_0) vs. time in the injection circuit had two distinct breaks at about 63.6 and 163.6 hours from the start of the test, so the values of \( Q_{inj}/V \) were varied as indicated in Table 5 to accommodate these changes in slope.

<table>
<thead>
<tr>
<th>Tracer Test Run</th>
<th>Time</th>
<th>( Q_{inj}/V )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[h]</td>
<td>[h^{-1}]</td>
</tr>
<tr>
<td>08-01</td>
<td>Entire test</td>
<td>2.186</td>
</tr>
<tr>
<td>10-01</td>
<td>Entire test</td>
<td>0.278</td>
</tr>
<tr>
<td>10-03</td>
<td>Entire test</td>
<td>0.0927</td>
</tr>
<tr>
<td>12-02</td>
<td>0 – 63.6</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>63.6 – 163.6</td>
<td>0.135</td>
</tr>
<tr>
<td></td>
<td>163.6 – end</td>
<td>0.108</td>
</tr>
</tbody>
</table>
The mass normalised concentration injection functions used in the GRS model are shown in Fig. 5 (Section 2.5). For all Tracer Test Runs a constant inflow rate \( Q_{\text{inj}} \) was assumed by GRS. The inflow rate was adapted using the concentration injection functions so that the calculated integrated injected mass exactly matches the given value for the injected mass \( M_0 \) [M] for the conservative tracer in the experiment (values are listed in Section 5.3). The concentration injection function for the colloids and homologues/radionuclides was derived using the respective injected mass \( M_0 \).

### 5.2 General approach

The main purpose of modelling tracer experiments in general and within the CFM project in particular is to improve the understanding and capability of predictive transport modelling. The series of Tracer Test Runs 10-01, 10-03 and 12-02 offer a unique possibility to improve the modelling capability of three-phase transport phenomena under field conditions. All three runs are along the same flow path within the shear zone, although each run contains several tracers and the runs were conducted under different hydrodynamic conditions at varying pumping rates.

In general, all three modeller groups applied a stepwise modelling strategy comprising the following steps:

1. Calibrate the hydraulic parameters using the breakthrough curves of the conservative tracers
2. Characterise the interactions between colloids and fracture filling material by fitting the colloid breakthrough curves
3. Identify and describe the interaction process between homologues/radionuclides and colloids by fitting the homologue/radionuclide curves
4. Use the best-fit parameters to make predictions for the radioactive tracer test in the same dipole under different flow conditions (GRS and KTH)

GRS used the same colloid filtration parameters for Tracer Test Runs 10-01 and 10-03. In contrast, for LANL, the colloid filtration parameters for all tests were allowed to vary to achieve a good fit to each individual colloid breakthrough curve. The only deviation from the procedure described above was for Tracer Test Run 08-01 where the colloid breakthrough curve was fitted first because there was no conservative tracer used in that test.

The KTH approach was to minimise the number of processes and parameters involved, attempting to reproduce the observations in the simplest and most robust way possible. Furthermore, the KTH approach was to gradually build the modelling confidence from the earliest Tracer Test Run (10-01) to the latest run considered here (Tracer Test Run 12-02), by reducing the need for calibration. As many parameters as possible were calibrated in the 10-01 run and then used for "predicting" outcomes of Tracer Test Runs 10-03 and 12-02. In this manner, the KTH approach attempts to explicitly show the accumulation of knowledge about the system. This approach was facilitated by the fact that all three runs are along the same transport pathway.

What makes the "progression of knowledge" from Tracer Test Run 10-01 to 12-02 especially interesting is the fact that in Tracer Test Runs 10-01 and 10-03 homologue tracers were used as proxies for relevant actinides. Tracer Test Run 12-02, however, includes actinides as tracers and therefore provides a unique opportunity to test the possibility of predicting these based on the knowledge gained in using proxies, i.e. the homologues.
5.3 2D approach (GRS)

GRS used the two-dimensional model described in Section 4.4 to simulate flow, transport and interaction processes.

Inflow for Tracer Test Run 08-02 was 10 ml/min and for Tracer Test Run 12-02 it was 0.33 ml/min. The Tracer Test Runs 10-01 and 10-03 were performed as point dilution experiments, but for the model simulations, a certain very small injected inflow of fluid was defined due to numerical reasons. The injection flow rate for Tracer Test Run 10-01 was set to 0.56 ml/min, while it was set to 1.27 ml/min for Tracer Test Run 10-03.

Generally, for all four test runs, the flow was directed from the injection location (CFM 06.002) to the extraction location (Pinkel surface packer at the AU tunnel wall). The lowest flow velocities were observed for the Tracer Test Run 10-03, where the outflow rate was only 10 ml/min, while the highest flow velocities were observed for Tracer Test Run 08-02, where an outflow rate of 165 ml/min was applied (cf. Section 2.4, Tab. 3). The outflow rate tends to control transport times in the shear zone, whereas the inflow rate controls the residence time of the tracers in the injection circuit and thus affects the shape, and especially the apparent dispersion, of the breakthrough curves. The flow fields for the different dipole tests are shown in Fig. 15. They confirm that the flow is dominated by the extraction at the Pinkel surface packer. From all open model boundaries, the flow is directed into the model domain towards the extraction location. From the inflow location at CFM 06.002 the water flows radially and partially reverses the prevailing flow direction in the immediate vicinity of the inflow.
Fig. 15: Velocity vectors of the steady-state flow fields for the considered Tracer Test Runs.

a) Tracer Test Run 08-02. b) Tracer Test Run 10-01. c) Tracer Test Run 10-03. d) Tracer Test Run 12-02. The velocity vectors for all four flow fields have the same scale. If the length of a vector exceeds a threshold value it is cut off for clarity reasons.
In a first step, the non-sorbing solute tracer breakthrough curve of uranine was fitted manually for Tracer Test Runs 08-02 and 10-01 by varying the dispersivity to match the shape of the curve and the porosity to match the peak occurrence time of the curve. The mass normalised breakthrough curves are shown in Fig. 16. Based on these results, the hydraulic parameters of the shear zone were determined (see Section 4.3, Tab. 4).

Then, flow and transport calculations were performed for Tracer Test Runs 10-03 and 12-02 using the same hydraulic parameters but different inflow/outflow boundary conditions and injection functions (cf. Fig. 16). The simulated breakthrough curves show a reasonably good agreement, i.e. all investigated dipole tests covering a transport time between 8 and 200 hours can be described with the same hydraulic parameters. It should be noted that tracer recoveries in the simulations amounted to 100 % and thus were scaled to the recoveries achieved in the field experiments for Tracer Test Runs 10-01 (84 %), 10-03 (60 %), and 12-02 (80 %) (cf. Section 2.4, Tab. 2) to account for the mass losses during the experimental tests. The recovery of Test Run 08-02 was almost 100 %.

Fig. 16: Conservative tracer breakthrough curves for Tracer Test Runs 08-02, 10-01, and 12-02 and colloid breakthrough curve for Run 10-03 in the experiments and the corresponding simulations.

Experiments: continuous line. Simulated breakthrough curves applying the best-fit hydraulic parameters given in Tab. 4: dashed line.

For Tracer Test Run 10-03 a reliable breakthrough curve of the conservative tracer was not available due to problems with the uranine tracer. Although a correction was applied to the 10-03 uranine response for the LANL interpretation (Appendix A), GRS and KTH did not implement any such correction. Only for illustration, the curve for the colloids is shown in Fig. 16, which is also simulated with the same flow parameters, but with additional interaction rates for the colloids. The model parameters for flow and transport of the conservative tracer are listed in Tab. 4. The porosity of 0.115 is in the lower range of porosities observed for the fracture filling material from the shear zone but is still in agreement with values between 10 % and 40 % given in Gaus & Smith (2008). However, considering that flow predominantly occurs...
in the open parts of the brittle fractures the porosity can also be compared with an aperture of an open fracture. Assuming flow through an open fracture in the planar 2D model with a thickness of 5 mm, a porosity of 0.115 correlates to an aperture of 0.58 mm, which is not too far from the cubic law (Witherspoon et al. 1980) aperture of 0.1 mm for a transmissivity of $10^{-6}$ m$^2$/s.

In a second step, the migration of the colloids and their interaction with the fracture filling material are simulated for Tracer Test Run 10-01. The results are shown in Figs. 17 and 18. A slight shift of the experimental colloid breakthrough curve indicates a weak retardation of the colloids. A further characteristic is a weaker increase of the breakthrough curve compared with uranine. Both effects can be described by a kinetically controlled interaction of the colloids with the fracture filling material with a colloid attachment rate $\frac{\partial b}{\partial t} k_{cs} = 0.054$ h$^{-1}$ and a detachment rate $k_{sc} = 0.108$ h$^{-1}$. This ratio corresponds to a retardation factor of about 1.5 for the colloids. However, under the conditions considered here, the mutual reaction of colloids and fracture filling material is not in equilibrium. Further, a filtration rate of 0.01 h$^{-1}$ was applied to account for an additional irreversible filtration.

![Fig. 17:](image-url) Experimental and simulated breakthrough curves for Tracer Test Run 10-01 for the uranine tracer and the colloids, linear scale.

* $k_{cs, irr}$ = irreversible filtration rate constant.
In a third step, homologue transport is simulated. Batch sorption experiments suggest that the tri- and tetravalent cations are strongly sorbed onto the fracture filling material (Huber et al. 2011), i.e. the non-colloid-bound fraction will not migrate through the dipole over the time period the experiment is conducted. Only the colloid-bound fraction is expected to travel at a similar velocity as the fluid.

Therefore, the field experiment results are explained by the following processes. As described above, the homologues are equilibrated with the colloid-bearing solution in advance and are almost completely bound to the colloids, when injected into the dipole. During the transport through the fracture, the homologues desorb from the colloids and subsequently adsorb to the fracture filling material. The rate of these processes is determined by the detachment rate \( k_{mca} \) of the homologues from the colloids, since the adsorption reaction of the homologues to the fracture filling material is assumed to be fast, especially considering the large surface area of fracture filling material available. With an increasing desorption rate \( k_{mca} \), the magnitude of the peak breakthrough and the recovery of the homologue breakthrough curves decrease.

The experimental curves show a difference between the trivalent and the tetravalent homologues. The peak maximum as well as the recovery is higher for tetravalent thorium and hafnium than for trivalent europium and terbium. Consequently, higher desorption rates are expected for the trivalent homologues. In our model the breakthrough curves are quite well described with a desorption rate of \( k_{mca} = k_{ica} = 0.03 \text{ h}^{-1} \) for the tetravalent and \( k_{mca} = k_{ica} = 0.075 \text{ h}^{-1} \) for the trivalent homologues, see Figs. 19 to 22.
Fig. 19: Simulated and experimental breakthrough curves for the tetravalent homologues hafnium and thorium for Tracer Test Run 10-01, linear scale. Best estimate parameters for $k_{mca}$ and $k_{ica}$ are shown.

Fig. 20: Simulated and experimental breakthrough curves for the tetravalent homologues hafnium and thorium for Tracer Test Run 10-01, logarithmic scale. Best estimate parameters for $k_{mca}$ and $k_{ica}$ are shown.
Fig. 21: Simulated and experimental breakthrough curves for the trivalent homologues terbium and europium for Tracer Test Run 10-01, linear scale. Best estimate parameters for $k_{mca}$ and $k_{ica}$ are shown.

Fig. 22: Simulated and experimental breakthrough curves for the trivalent homologues terbium and europium for Tracer Test Run 10-01, linear scale. Best estimate parameters for $k_{mca}$ and $k_{ica}$ are shown.
In addition to comparing the shape of the curves, the mass recoveries of experiment and simulation can be analysed (Section 5.5, Tab. 10). In general, the recoveries of colloids and homologues in Tracer Test Run 10-01 are also quite well reproduced by the model calculations.

The colloid and homologue transport for Tracer Test Run 10-03 was simulated in the same way, see Figs. 23 and 24. Due to a lower extraction rate at the Pinkel surface packer, the travel time was increased compared with Tracer Test Run 10-01. One important question is whether the breakthrough curves and recoveries can be described with the same interaction rates. For the colloids, the interaction parameters as applied for Tracer Test Run 10-01 give a reasonable result with respect to the peak of the breakthrough curve. However, the tailing at travel times of > 400 h is underestimated. Nevertheless, the recovery of 41 % as observed in the experiment is again well reproduced by the calculation with a value of 45.1 % (Section 5.5, Tab. 11). Therefore, it seems reasonable to describe the interaction between colloids and fracture filling material with the same parameters in both dipole tests.

For the homologues it was clear that significantly lower desorption rates have to be assumed in Tracer Test Run 10-03 than those for Tracer Test Run 10-01. The recoveries of the trivalent homologues are similar for both tests. The recoveries of the tetravalent homologues were even slightly higher in Tracer Test Run 10-03 than in Tracer Test Run 10-01. This is unexpected, since a longer travel time should increase the amount of desorbed homologues and therewith lead to a reduced recovery. Therefore, for Tracer Test Run 10-03 lower desorption rates of 0.02 h\(^{-1}\) and 0.0025 h\(^{-1}\) have been applied to describe the breakthrough curves of the tri- and tetravalent homologues, respectively. With these rates, the peaks of the curves are well reproduced but again the tailing and also the recoveries are to some extent underestimated.

![Simulated and experimental breakthrough curves for the colloids as well as for the trivalent and tetravalent homologues europium, terbium, hafnium and thorium for Tracer Test Run 10-03, linear scale.](image)

**Fig. 23:** Simulated and experimental breakthrough curves for the colloids as well as for the trivalent and tetravalent homologues europium, terbium, hafnium and thorium for Tracer Test Run 10-03, linear scale.

Best estimate parameters for \(k_{mca}\) and \(k_{ica}\) are shown.

\* \(k_{cs,irr}\) = irreversible filtration rate constant.
Simulated and experimental breakthrough curves for the colloids as well as for the trivalent and tetravalent homologues europium, terbium, hafnium and thorium for Tracer Test Run 10-03, logarithmic scale.

Best estimate parameters for $k_{ica}$ and $k_{mca}$ are shown.

* $k_{cs, irr} = \text{irreversible filtration rate constant.}$

### 5.4 1D approach (LANL)

The mean residence times and Peclet numbers obtained for each of the four colloid-homologue/radionuclide tracer tests, as well as Tracer Test Run 08-02 (the test intended to be the same as Tracer Test Run 08-01), are listed in Tab. 6. The parameters of Tab. 6 were used to generate the shear-zone-only breakthrough curves shown in Fig. 8.

### Tab. 6: Mean residence times and Peclet numbers for the shear zone as determined using the LANL 1D model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tracer Test Run 08-01</th>
<th>Tracer Test Run 08-02</th>
<th>Tracer Test Run 10-01</th>
<th>Tracer Test Run 10-03</th>
<th>Tracer Test Run 12-02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean residence time [h]</td>
<td>3.6</td>
<td>6.25</td>
<td>22</td>
<td>60</td>
<td>34</td>
</tr>
<tr>
<td>Peclet number</td>
<td>10'000*</td>
<td>13.5</td>
<td>9</td>
<td>17</td>
<td>6.5</td>
</tr>
</tbody>
</table>

* Peclet number is unrealistically large for Tracer Test Run 08-01 (approximating plug flow behavior in the shear zone) because injection function was assumed to be the same as in Tracer Test Run 08-02 despite the fact that there was no recirculation of the injection loop in Tracer Test Run 08-01. See Section 2.5 for additional discussion.
Tab. 7 lists the colloid transport parameters providing the best fits to the colloid breakthrough curves in each test. The best-fitting model curves for both the conservative dye tracer and the colloids in Tracer Test Runs 10-01, 10-03 and 12-02 are shown in Fig. 25 (Tracer Test Run 08-01 is not shown because there was no conservative tracer, but a colloid model curve for Tracer Test Run 08-01 is shown in Fig. 26). In Tracer Test Run 08-01, a single irreversible filtration rate constant provided a good fit to the colloid data, whereas in Tracer Test Runs 10-03 and 12-02, a reversible reaction describing colloid filtration and detachment provided a better match to the colloid data. In Tracer Test Run 10-01, the best fit was obtained by assuming both an irreversible and a reversible colloid filtration reaction were occurring simultaneously. The reversible processes are invoked either to:

1. Account for a delay in the initial arrival of colloids relative to the conservative tracer (Tracer Test Run 10-01) or
2. Provide an improved fit to the tail of the colloid breakthrough curve by allowing for some colloid detachment (Tracer Test Runs 10-03 and 12-02)

The reasons for the differences in the deduced filtration processes in the different tests are unknown. They may reflect the different flow pathways accessed in the different tests, which are evident from Fig. 8, or perhaps they are influenced by the different flow rates and residence times in the different tests. It should be pointed out that there is more uncertainty in the colloid transport parameters estimated for Tracer Test Run 10-03 than for the other tests because they were obtained by comparing the colloid breakthrough curve to a corrected uranine breakthrough curve (shown in Fig. 25), which had greater inherent uncertainty than the conservative dye tracer breakthrough curves in the other tests. Nonetheless, the forward filtration rate constants in all tests are in relatively good agreement (ignoring the rapid forward rate constant for the reversible reaction deduced for Tracer Test Run 10-01), varying between 0.0065 h\(^{-1}\) and 0.016 h\(^{-1}\), which is a range of less than a factor of 2.5. However, to model the colloid-facilitated transport of the homologues in Tracer Test Run 08-01, it was necessary to assume no filtration at all of the colloids because the normalised breakthrough curves of both Th and Hf were higher than that of the colloids in that test, which was considered impossible. The estimate of 0.015 h\(^{-1}\) used above and listed in parentheses in Tab. 7 for Tracer Test Run 08-01 was obtained by matching the colloid recovery, which, based on the raw colloid data, was less than 100 %. It should be noted that the parameters of Tab. 7 were not estimated using an objective least-squares fitting procedure, but rather they were visually fitted.

Tab. 7: Apparent colloid transport parameters in the Tracer Test Runs, as determined using the LANL 1D model.

<table>
<thead>
<tr>
<th>Tracer Test Run</th>
<th>(\frac{p_b}{\theta}k_{cs,irr}) [h(^{-1})]</th>
<th>(\frac{p_b}{\theta}k_{cs}) [h(^{-1})]</th>
<th>(k_{sc}) [h(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-01</td>
<td>0 (0.015)**</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10-01</td>
<td>0.0065</td>
<td>0.2</td>
<td>0.286</td>
</tr>
<tr>
<td>10-03</td>
<td>0</td>
<td>0.01</td>
<td>0.0042</td>
</tr>
<tr>
<td>12-02</td>
<td>0</td>
<td>0.016</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

* \(k_{cs,irr}\) = irreversible filtration rate constant.

** Number in parentheses is best estimate of \(k_{cs,irr}\) in Tracer Test Run 08-01 if the raw colloid data are fitted (i.e. not forcing the colloid concentrations to exceed the homologue concentrations). If it is assumed that the colloid concentrations must exceed the homologue concentrations (which is logical), then the best estimate of \(k_{cs,irr}\) is zero.
Consistent with the modelling procedure described in Section 5.2, only the parameters describing desorption of the solutes from the colloids were used as adjustable parameters to model homologue or radionuclide transport in the tests. None of the other adjustable solute reactive transport parameters had a significant influence on the model fits to the data as long as:

1. The rate constants for adsorption to the shear zone surfaces were large enough that the solutes rapidly adsorbed to these surfaces after they desorbed from the colloids

2. The rate constants for desorption from the shear zone surfaces were small enough that the solutes effectively did not desorb from these surfaces for the remainder of the tests

Under these conditions, the breakthrough curves of the homologues and radionuclides are almost entirely dictated by their desorption rate(s) from the colloids, with the shear zone surfaces acting as a fast and irreversible sink once desorption occurs. The strong dependence on the desorption rates from the colloids is in part due to the nearly complete adsorption of the homologues and tri-/tetravalent radionuclides to the colloids in the injection cocktails.

Several different descriptions of the solute desorption process from colloids were considered. The different model variants are listed in Tab. 8 along with their adjustable parameters (the models are henceforth referred to using the names given in Tab. 8). The motivation for using the different variants was to determine the simplest description of the solute desorption process that best explained the solute breakthrough curves in each test. To do this, the number of adjustable parameters was increased until the fits to the data no longer improved by statistical measures. The number of adjustable parameters in the models ranges from 1 to 4, with the one-site model being the simplest (i.e. a single first-order rate constant) and the two-site hybrid model being the most complex. Note that each of the two-site models can have one adjustable parameter less than indicated in Tab. 8 if the second adsorption site is assumed to be irreversible.
Fig. 25: Simulated and experimental breakthrough curves for the conservative dye tracers and colloids in Tracer Test Runs 10-01, 10-03 and 12-02, using the LANL 1D model for the simulations.

Best estimate parameters are listed in Tabs. 6 and 7.
Tab. 8: Different descriptions of the solute desorption process from colloids considered in the LANL 1D model.

<table>
<thead>
<tr>
<th>Model name</th>
<th>Adjustable parameters</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-site</td>
<td>$k_{mca}$</td>
<td></td>
</tr>
<tr>
<td>1-site exp. decay</td>
<td>$k_{mca}$, $A$</td>
<td>See Eq. (39)</td>
</tr>
<tr>
<td>(similar to KTH model)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aging to 2nd site</td>
<td>$k_{mca,1}$, $k_{mca,2}$, $k_{age}$</td>
<td>Only 2 adjustable parameters if $k_{mca,2} = 0$</td>
</tr>
<tr>
<td>2-site, no aging</td>
<td>$f(1)$, $k_{mca,1}$, $k_{mca,2}$</td>
<td>Only 2 adjustable parameters if $k_{mca,2} = 0$</td>
</tr>
<tr>
<td>2-site hybrid</td>
<td>$f(1)$, $k_{mca,1}$, $k_{mca,2}$, $k_{age}$</td>
<td>Only 3 adjustable parameters if $k_{mca,2} = 0$</td>
</tr>
</tbody>
</table>

Note: $f(1) =$ fraction of adsorbed solute mass initially adsorbed to first site ($f(2) = 1 - f(1)$).

Tab. 9 lists the best-fitting desorption rate parameters associated with several of the model variants for the four tracer tests considered in this report. In some cases, models with more parameters offered no improvement over models with fewer parameters; i.e. the fits converged to a rate or decay constant of zero, or to no initial adsorption to a second site, which effectively reduced them to a simpler model. Models offering no improvement over simpler models are not listed in Tab. 9. Tracer Test Run 08-01 provides a good example of this situation, where the one-site model was not improved on by any of the more complex models for any of the homologues. In fact, if the modelled colloid breakthrough curve was not artificially adjusted to be slightly higher than the Th and Hf breakthrough curves in this test, the best fits to these curves would have had no desorption at all. Figs. 26 to 29 show the best-fitting model curves for each of the homologues or radionuclides in each test, respectively. The dashed lines in these figures are the best-fitting single-site model curves in cases where a single-site model did not provide the best fit to the breakthrough curves.

In reality, any model that can be effectively reduced to a simpler model will always fit the data at least as well as the simpler model and, unless the fit of the simpler model is perfect, the more complex model should be capable of offering a marginal improvement. However, there were many cases where such marginal improvement was not seen in the fitting process, or it occurred only when an adjustable parameter was very close to zero. It should be noted that, although the fitting was conducted quantitatively by minimising the sum of squares differences between the model and data, the best fits were obtained by manual adjustment of the parameters. An automated parameter estimation algorithm was not successfully interfaced with the model during the time available to complete the project. However, it was not apparent that an automated algorithm would have helped significantly in any cases except where there were four adjustable parameters (only the two-site hybrid model) because the parameter space was quite thoroughly interrogated for all cases of up to three adjustable parameters. The response surface for the four-parameter hybrid model was quite complex, so there was less confidence in manually finding a global minimum with this model.
The sums of squares of the residual differences between the models and the breakthrough curves associated with each of the models and corresponding parameter sets listed in Tab. 9 are provided in Tab. 10. Listed next to each residual sum of squares value is the $F$ (Fisher-Snedecor) statistic, which is calculated as:

$$F(1:2) = \frac{(SS_1 - SS_2)/(df_1 - df_2)}{SS_2/df_2}$$  \hspace{1cm} (40)

where

$F(1:2)$  \hspace{1cm} $F$ statistic for evaluating improvement in fit offered by Model 2 over Model 1, where Model 2 has more adjustable parameters than Model 1.

$SS_x$  \hspace{1cm} Sum of squares of residual differences between Model x and data

$df_x$  \hspace{1cm} Degrees of freedom for Model x (number of data points minus number of adjustable parameters used to fit data)

The $F$ statistic is compared with an $F$ value taken from a standard $F$-distribution table to determine whether Model 2 offers an improvement over Model 1 in explaining the data. The $F$ values in the standard $F$-distribution table depend on:

1. The difference in the degrees of freedom between the two models
2. The number of degrees of freedom of the model with more parameters
3. The confidence level of the $F$ test

As an example, if a model with two parameters is compared with a model with three parameters for a dataset that contains 25 data points, and one wants to be confident at the 95 % level that the three-parameter model is better than the two-parameter model, then the appropriate $F$-distribution value is $F(1,22,0.05)$, where $0.05 = 1 - 0.95$. If the value calculated from Eq. (40) is greater than this $F$-distribution value, then the three-parameter model is accepted as being a statistically significant improvement over the two-parameter model at the 95 % confidence level.
Tab. 9: Best-fitting solute desorption parameters determined using the LANL 1D model.

<table>
<thead>
<tr>
<th>Run/solute</th>
<th>Model</th>
<th>$k_{mca,1}$ [h$^{-1}$]</th>
<th>$k_{mca,2}$ [h$^{-1}$]</th>
<th>$f(I)$ [-]</th>
<th>$k_{age}$ [h$^{-1}$]</th>
<th>$k_{mca0}$ [h$^{-1}$]</th>
<th>$A$ [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-01/Th</td>
<td>1-site</td>
<td>0.0136</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>08-01/Hf</td>
<td>1-site</td>
<td>0.081</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>08-01/Tb</td>
<td>1-site Aging to 2$^{nd}$ site</td>
<td>0.192</td>
<td>0.17</td>
<td>0.9</td>
<td>0.016</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-01/Th</td>
<td>1-site Aging to 2$^{nd}$ site</td>
<td>0.0253</td>
<td>0.0176</td>
<td>0.12</td>
<td>0.0058</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>0.015</td>
<td>0.12</td>
<td>0.979</td>
<td>0.0073</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-01/Hf</td>
<td>1-site</td>
<td>0.0368</td>
<td>0.0403</td>
<td>0</td>
<td>0.949</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-01/Tb</td>
<td>1-site Aging to 2$^{nd}$ site</td>
<td>0.074</td>
<td>0.06</td>
<td>0.2</td>
<td>0.0096</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>0.0585</td>
<td>0.2</td>
<td>0.972</td>
<td>0.00955</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-01/Eu</td>
<td>1-site 1-site exp decay</td>
<td>0.086</td>
<td>0.092</td>
<td>0</td>
<td>0.00078</td>
<td>0.0935</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td>0.139</td>
<td>0.107</td>
<td>0.893</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-03/Th</td>
<td>1-site 1-site exp decay</td>
<td>0.003</td>
<td>0.029</td>
<td>0</td>
<td>0.016</td>
<td>0.026</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Aging to 2$^{nd}$ site</td>
<td></td>
<td>0.3</td>
<td>0</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td></td>
<td>0.03</td>
<td>0</td>
<td>0.731</td>
<td>0.0101</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-03/Hf</td>
<td>1-site 1-site exp decay</td>
<td>0.0021</td>
<td>0.0215</td>
<td>0</td>
<td>0.0155</td>
<td>0.0185</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Aging to 2$^{nd}$ site</td>
<td></td>
<td>0.3</td>
<td>0</td>
<td>0.192</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td></td>
<td>0.03</td>
<td>0</td>
<td>0.743</td>
<td>0.0139</td>
<td></td>
</tr>
<tr>
<td>10-03/Tb</td>
<td>1-site 1-site exp decay</td>
<td>0.0415</td>
<td>0.051</td>
<td>0</td>
<td>0.00045</td>
<td>0.052</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>Aging to 2$^{nd}$ site</td>
<td></td>
<td>0.4</td>
<td>0</td>
<td>0.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-03/Eu</td>
<td>1-site 1-site exp decay</td>
<td>0.026</td>
<td>0.0382</td>
<td>0</td>
<td>0.00124</td>
<td>0.0405</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>Aging to 2$^{nd}$ site</td>
<td></td>
<td>0.18</td>
<td>0</td>
<td>0.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td></td>
<td>0.0545</td>
<td>0</td>
<td>0.874</td>
<td>0.00068</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12-02/Am</td>
<td>1-site</td>
<td>0.0163</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12-02/Pu</td>
<td>1-site Aging to 2$^{nd}$ site</td>
<td>0.0077</td>
<td>0.0045</td>
<td>0.052</td>
<td>0.002</td>
<td>0.0045</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>0.0016</td>
<td>0.052</td>
<td>0.898</td>
<td>0.002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Red text indicates best-fitting model (see Tab. 10). The two models yielding equally good fits for "10-03/Hf" have the same number of adjustable parameters ($k_{mca,2}$ is fixed to zero for the second model).
Fig. 26: Simulated and experimental breakthrough curves for the colloids and homologues in Tracer Test Run 08-01, using the LANL 1D model for the simulations. Best estimate parameters are listed in Tab. 9.

Fig. 27: Simulated and experimental breakthrough curves for the colloids and homologues in Tracer Test Run 10-01, using the LANL 1D model for the simulations. Best estimate parameters are listed in Tab. 9.
Fig. 28: Simulated and experimental breakthrough curves for the colloids and homologues in Tracer Test Run 10-03, using the LANL 1D model for the simulations. Best estimate parameters are listed in Tab. 9.

Fig. 29: Simulated and experimental breakthrough curves for the colloids and radionuclides in Tracer Test Run 12-02, using the LANL 1D model for the simulations. Best estimate parameters are listed in Tab. 9.
Tab. 10: Sums of squares of the residual differences between the models and the breakthrough curves associated with each of the models listed in Tab. 9.

<table>
<thead>
<tr>
<th>Run/solute</th>
<th>Model</th>
<th>$SS_{res}$</th>
<th>$F(X:Y)^*$</th>
<th>$F_{sig, 0.05}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-01/Th</td>
<td>1-site</td>
<td>$9.57 \times 10^{-6}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>08-01/Hf</td>
<td>1-site</td>
<td>$5.51 \times 10^{-6}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>08-01/Tb</td>
<td>1-site Aging to 2nd site</td>
<td>$2.74 \times 10^{-6}$</td>
<td>$2.25 \times 10^{-6}$</td>
<td>3.05</td>
</tr>
<tr>
<td>10-01/Th</td>
<td>1-site Aging to 2nd site</td>
<td>$9.46 \times 10^{-7}$</td>
<td>$6.89 \times 10^{-7}$</td>
<td>20.5 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>$6.78 \times 10^{-7}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>10-01/Hf</td>
<td>1-site</td>
<td>$5.46 \times 10^{-7}$</td>
<td>$5.35 \times 10^{-7}$</td>
<td>1.15 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td>$2.87 \times 10^{-7}$</td>
<td>$2.41 \times 10^{-7}$</td>
<td>10.5 (vs. 1-site)</td>
</tr>
<tr>
<td>10-01/Tb</td>
<td>1-site Aging to 2nd site</td>
<td>$1.86 \times 10^{-7}$</td>
<td>$1.54 \times 10^{-7}$</td>
<td>10.6 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>$1.52 \times 10^{-7}$</td>
<td>$1.26 \times 10^{-6}$</td>
<td>11.4 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td>$1.15 \times 10^{-7}$</td>
<td>$1.25 \times 10^{-6}$</td>
<td>34.6 (vs. decay)</td>
</tr>
<tr>
<td>10-01/Eu</td>
<td>1-site Aging to 2nd site</td>
<td>$3.91 \times 10^{-6}$</td>
<td>$2.05 \times 10^{-6}$</td>
<td>46.3 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>1-site exp decay</td>
<td>$2.05 \times 10^{-6}$</td>
<td>$2.05 \times 10^{-6}$</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td>$1.26 \times 10^{-6}$</td>
<td>$1.26 \times 10^{-6}$</td>
<td>107 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>1-site exp decay</td>
<td>$1.25 \times 10^{-6}$</td>
<td>$1.25 \times 10^{-6}$</td>
<td>109 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>$1.13 \times 10^{-6}$</td>
<td>$1.13 \times 10^{-6}$</td>
<td>5.31 (vs. decay)</td>
</tr>
<tr>
<td>10-03/Th</td>
<td>1-site Aging to 2nd site</td>
<td>$3.74 \times 10^{-6}$</td>
<td>$2.24 \times 10^{-6}$</td>
<td>34.2 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td>$1.44 \times 10^{-6}$</td>
<td>$1.44 \times 10^{-6}$</td>
<td>52.7 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>1-site exp decay</td>
<td>$1.44 \times 10^{-6}$</td>
<td>$1.44 \times 10^{-6}$</td>
<td>52.7 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>$1.40 \times 10^{-6}$</td>
<td>$1.40 \times 10^{-6}$</td>
<td>1.43 (vs. aging)</td>
</tr>
<tr>
<td>10-03/Hf</td>
<td>1-site Aging to 2nd site</td>
<td>$2.07 \times 10^{-7}$</td>
<td>$7.18 \times 10^{-8}$</td>
<td>96 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>1-site exp decay</td>
<td>$6.78 \times 10^{-8}$</td>
<td>$6.78 \times 10^{-8}$</td>
<td>105 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td>$3.75 \times 10^{-8}$</td>
<td>$3.75 \times 10^{-8}$</td>
<td>230 (vs. 1-site)</td>
</tr>
<tr>
<td>10-03/Eu</td>
<td>1-site Aging to 2nd site</td>
<td>$7.73 \times 10^{-7}$</td>
<td>$2.08 \times 10^{-7}$</td>
<td>139 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, no aging</td>
<td>$1.80 \times 10^{-7}$</td>
<td>$1.80 \times 10^{-7}$</td>
<td>168 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>1-site exp decay</td>
<td>$1.62 \times 10^{-7}$</td>
<td>$1.62 \times 10^{-7}$</td>
<td>192 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>$1.49 \times 10^{-7}$</td>
<td>$1.49 \times 10^{-7}$</td>
<td>4.36 (vs. aging)</td>
</tr>
<tr>
<td>12-02/Am</td>
<td>1-site</td>
<td>$4.90 \times 10^{-7}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>12-02/Pu</td>
<td>1-site Aging to 2nd site</td>
<td>$1.07 \times 10^{-6}$</td>
<td>$8.31 \times 10^{-7}$</td>
<td>10.4 (vs. 1-site)</td>
</tr>
<tr>
<td></td>
<td>2-site, hybrid</td>
<td>$8.21 \times 10^{-7}$</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Note: Red text indicates best-fitting model.

* $F$ statistic for model with Y parameters vs. model with X parameters, where Y > X (see text).

Model: Sorted by increasing $F$ values for same number of parameters, with best model being the one with the smallest $SS_{res}$ that also has a "passing" $F$ value.
The appropriate $F$-distribution values at the 95% confidence level for each of the calculated $F$ values in Tab. 10 are listed in the right-most column of the table ($F_{sig}$). The red text indicates the best deduced model for each dataset. If two models had the same number of degrees of freedom, then the model with the smallest $F$ value was accepted as being the best model. It follows that when two models with the same number of degrees of freedom also have the same $F$ value, the models are considered equally good (this is the case for the two models listed with the red text for "10-03/Hf" in Tabs. 9 and 10). A discussion of the implications of these model results is provided in Section 6.4.

We note that the fitting procedure did not involve any transformations or weighting of the colloid or homologue breakthrough curve datasets. Somewhat different results than those of Tabs. 9 and 10 would have likely been obtained had the data been transformed or weighted in some way. A logarithmic transformation is often used to avoid biasing fits toward the data points with the largest numerical values (i.e. the peak concentrations), but we chose not to use a log transformation because:

1. The highest concentrations also tend to have the least amount of uncertainty from analytical error, so it is somewhat justified to allow the fits to be biased slightly toward the high-concentration points
2. Concentrations of zero were considered significant, especially in the tails of the breakthrough curves, and zeroes cannot be log-transformed unless they are set to a minimum value like a detection or quantification limit

For Tracer Test Run 08-01, we also excluded the early data points (all points before the peaks) from the fitting procedure because of the very rapid rise in the colloid and homologue concentrations in this test. These rapid rises caused very large sum-of-squares differences between the models and data for a few of the early points, and it was quite apparent that the best fits were being heavily biased by these points at the expense of much poorer fits to the peaks and tails of the breakthrough curves. It was considered more important for explaining homologue desorption behaviour to obtain better fits to the peaks and tails than to fit the sharp early rise of the breakthrough curves.

5.5 GRS blind predictive modelling and evaluation of Tracer Test Run 12-02

Modelling groups were given the opportunity of making "blind" predictions of results from Tracer Test Run 12-02. Strictly, the predictions were Class B (Lambe 1973) in that they were made after the test but during the analysis of laboratory samples. Further, the conservative tracer data was provided to the modellers as input. GRS presented predictions at the CFM Modelling Meeting in June 2012 prior to presentation of the laboratory data (a detailed meeting record was kept).

Blind predictive modelling was conducted for the Am(III) and Pu(IV) transport for Tracer Test Run 12-02. Besides an inert tracer (Amino-G Acid), colloids and radionuclides were injected into the dipole (Blechschmidt et al. 2013). In its model simulations, GRS predicted the breakthrough of tri- and tetravalent radionuclides at the Pinkel surface packer extraction location. Different values for the interaction parameters were employed for these simulations.
The interaction of colloids with the fracture filling material is described with the same parameters as used in Tracer Test Run 10-01 and Tracer Test Run 10-03. Concerning the interaction of the radionuclides with the colloids, three datasets were used for illustration purposes:

**Dataset 1 (DS1), derived from Tracer Test Run 10-01:**
\[ k_{mca}, k_{ica} \text{ (Am (III))} = 0.075 \text{ h}^{-1} \]
\[ k_{mca}, k_{ica} \text{ (Pu (IV))} = 0.03 \text{ h}^{-1} \]

**Dataset 2 (DS2), derived from Tracer Test Run 10-03:**
\[ k_{mca}, k_{ica} \text{ (Am (III))} = 0.02 \text{ h}^{-1} \]
\[ k_{mca}, k_{ica} \text{ (Pu (IV))} = 0.0025 \text{ h}^{-1} \]

**Dataset 3 (DS3), derived as explained in the main text:**
\[ k_{mca}, k_{ica} \text{ (Am (III))} = 0.05 \text{ h}^{-1} \]
\[ k_{mca}, k_{ica} \text{ (Pu (IV))} = 0.014 \text{ h}^{-1} \]

The breakthrough curves for the inert tracer (both for the experiment and the model) and predicted breakthrough curves for colloids and radionuclides using the three different datasets DS1 to DS3 are shown in Fig. 30. As discussed above, we have evidence for a decrease of the desorption rate with increasing travel time. The travel time of Tracer Test Run 12-02 (outflow 25 ml/min) lies between those observed in Tracer Test Run 10-01 (outflow 48 ml/min) and in Tracer Test Run 10-03 (outflow 10 ml/min). Therefore, the most probable prediction was based on desorption rates interpolated between those derived for both runs, namely DS3, which are depicted as bold lines in Fig. 30.

![Fig. 30: Simulated breakthrough curves for the colloids as well as for the trivalent and tetravalent radionuclides for Tracer Test Run 12-02. Assumed values for \( k_{mca}, k_{ica} \) are given. * \( k_{cs,irr} \) = irreversible filtration rate constant.](image-url)
Tab. 11 summarises the experimental and simulated mass recoveries of the tracer, the colloids, and the homologues/radionuclides for each test run considered. As indicated by grey shading, the data for colloids and radionuclides were not available at the blind prediction stage. The experimentally observed decrease in recoveries for the colloids with increasing travel time is well matched by the calculations, indicating that the model representation of filtration is appropriate for the experimental conditions under consideration. As discussed previously only one dataset is used to describe filtration rates and reversible interactions. In general, the recoveries for the homologues are also well reproduced in all runs with exception of the tetravalent homologues (Th, Hf) in Tracer Test Run 10-03. However, the observation of an increased recovery of Th and Hf in the experiment with longer travel time (Tracer Test Run 10-03 compared with Tracer Test Run 10-01) is still surprising and needs to be confirmed in further field tests, which are already planned.

### Tab. 11: Mass recoveries [%] for Tracer Test Runs 10-01, 10-03 and 12-02 and for the model simulations. Grey fields indicate the experiments for which blind predictive modelling was performed. For details about the datasets (DS) used see text.

<table>
<thead>
<tr>
<th></th>
<th>Tracer Test Runs 08-01 &amp; 08-02</th>
<th>Tracer Test Run 10-01</th>
<th>Tracer Test Run 10-03</th>
<th>Tracer Test Run 12-02</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.</td>
<td>DS1</td>
<td>Exp.</td>
<td>DS1</td>
</tr>
<tr>
<td>Tracer*</td>
<td>99</td>
<td>84</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Colloid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>99</td>
<td>84</td>
<td></td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>99</td>
<td>84</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>Th</td>
<td>93</td>
<td>70</td>
<td>32</td>
<td>43</td>
</tr>
<tr>
<td>Hf</td>
<td>78</td>
<td>30</td>
<td>28</td>
<td>46</td>
</tr>
<tr>
<td>Tb</td>
<td>56</td>
<td>54</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Eu</td>
<td>n.a.</td>
<td>14</td>
<td>10</td>
<td>14</td>
</tr>
</tbody>
</table>

* There are some uncertainties in the value of the injected mass $M_0$ for dye tracers which directly impact the calculated recovery. Here, data based on the given weight are used. $M_0$ values derived from fluorometry are slightly different, resulting for example in a recovery of 100 % in Tracer Test Run 12-02.

** Different recoveries related to three different LIBD (Laser Induced Breakdown Detection) analyses performed in the lab and field.

### Further evaluation of Tracer Test Run 12-02

After finalisation of the predictive modelling, the breakthrough curves for colloids and radionuclides were made available to the GRS modelling group. In Fig. 31, the experimental curves for the trivalent radionuclide Am and the tetravalent radionuclide Pu are shown together with the predictive simulation results. The first observation is that the breakthrough curves are higher than the ones predicted with the dataset DS3. It is obvious that the curves calculated with dataset DS2 fit the experimental data much better, indicating a similarly low desorption rate for radionuclides/homologues from the colloids as derived from Tracer Test Run 10-03. Therefore, the curves based on dataset DS2 are shown as bold lines in Fig. 31.
Fig. 31: Simulated and experimental breakthrough curves for the colloids as well as for the trivalent and tetravalent radionuclides for Tracer Test Run 12-02.

Assumed values for parameters in blind predictive modelling for $k_{\text{mca}}$ and $k_{\text{ica}}$ are given.

$^*$ $k_{\text{cs,irr}}$ = irreversible filtration rate constant.

Tab. 12: Mass recoveries [%] for Tracer Test Run 12-02 and for the model simulations. Blue fields indicate the experiments for which blind predictive modelling was performed. For details about the datasets (DS) used, see main text.

<table>
<thead>
<tr>
<th></th>
<th>Tracer Test Run 12-02</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.</td>
</tr>
<tr>
<td>Tracer</td>
<td>80</td>
</tr>
<tr>
<td>Colloid</td>
<td>66*</td>
</tr>
<tr>
<td></td>
<td>34 – 37**</td>
</tr>
<tr>
<td></td>
<td>33 – 38***</td>
</tr>
<tr>
<td>Pu</td>
<td>32****</td>
</tr>
<tr>
<td>Am</td>
<td>~ 16*****</td>
</tr>
</tbody>
</table>

* Recovery measured by LIBD.

** Recovery range derived from Al breakthrough.

*** Recovery range derived from Ni breakthrough (bentonite colloids were spiked with Ni; see Fig. 29 for colloid breakthrough curves based on Ni, Al, and LIBD signals).

**** Recovery after 275 h.

***** Recovery after 200 h.

Similar conclusions can be drawn for the recoveries. The experimental recoveries in Tracer Test Run 12-02 shown in Tab. 12 exhibit a generally good agreement with the modelling results for
dataset DS2. Use of the same interaction data for colloids with fracture filling material as applied for Tracer Test Runs 10-01 and 10-03 (see above) results in a reasonable recovery for the colloids. The recoveries, particularly of Am, are best reproduced with dataset DS2, which confirms the observations from the breakthrough curve shapes. For Pu, a slight increase of the desorption rates $k_{mca}, k_{ica}$ would improve the agreement with the experimental value.

The second observation from the breakthrough curves is of an earlier arrival of the radionuclides compared with the model prediction. This has a number of different possible explanations. One (also indicated by the experimental breakthrough curve of the colloids, not shown) is that the reversible interaction of colloids with the fracture filling material is not so pronounced as in Tracer Test Runs 10-01 and 10-03. A much better fit is derived assuming no reversible interaction of colloids with the fracture filling material. If, in addition, a slight modification to the flow field is introduced by slightly reducing the porosity from 11.5 % to 10.5 %, an acceptable fit as shown in Fig. 32 is achieved. In particular, the shapes of the simulated breakthrough curves for Am and Pu fit the experimental breakthrough curves quite well.

![Simulated and experimental breakthrough curves for the colloids as well as for the trivalent and tetravalent radionuclides for Tracer Test Run 12-02. Experimental colloid curve reduced by $8 \times 10^{-7}$ ml$^{-1}$ corresponding to an offset caused by natural colloids.](image)

Best estimate parameters for $k_{mca}$ and $k_{ica}$ are given.

* $k_{cs, irr}$ = irreversible filtration rate constant

The modelling results are based on several assumptions and the experimental results are affected by uncertainties. For example, the recoveries of the colloids analysed by Laser Induced Breakdown Detection (LIBD) significantly differ from the recoveries detected by Al and Ni signals. The desorption rates for the homologues/radionuclides derived from the breakthrough curves also depend on assumptions regarding the colloid – fracture filling material interactions. The uncertainties and their impact on modelling results will be tackled in the follow-on project.
5.6 Evaluation and prediction results (KTH)

The injection functions (boundary conditions) used in the KTH model are those described in Eq. (25) – (28). The parameters used for each test are as listed in Tab. 13.

Tab. 13: Boundary conditions used in KTH models.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>10-01</td>
<td>0.27</td>
<td>0.55</td>
<td>48</td>
<td>2'000</td>
<td>0.001</td>
</tr>
<tr>
<td>10-03</td>
<td>0.08</td>
<td>0.24</td>
<td>10</td>
<td>3'000</td>
<td>0.001</td>
</tr>
<tr>
<td>12-02</td>
<td>0.24</td>
<td>0.24</td>
<td>25</td>
<td>3'000</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Figs. 33 to 35 compare experimental and modelling concentration vs. time curves for the different tracers, including colloids.

The bases for quantifying transport in the three-phase system of the CFM runs are the breakthrough curves of the non-sorbing tracer and of the colloids. The breakthrough curves of uranine and colloids are comparable as the retention effects of the porous medium (“filter”) on colloids appear to be modest in this system (Figs. 33 to 35). Tab. 14 summarises the calibrated mean water residence time (\(\bar{\tau}\)) for all three runs, as well as the pumping (\(Q_A\)) and injection (\(Q_B\)) flow rates; as can be seen the tests may be classified as very weak dipole tests, effectively being radially converging (Fig. 15). In Tab. 15, four calibrated parameters are summarised: the macro-dispersivity \(\alpha_s = 0.75\) m (corresponding to a coefficient of variation of the water residence time \(\zeta = 0.5\) for the length scale of the flow path of 6 m)\(^2\), the filtration rate of the colloids \(\lambda = \frac{\rho_b k_{cs,irr}}{g} = 0.008\) h\(^{-1}\), the attachment and detachment rates for the colloids \(k_{cs} = 0.07\) h\(^{-1}\) and \(k_{sc} = 0.1\) h\(^{-1}\). Other parameters in Tab. 15 were inferred from independent sources: effective porosity in the shear zone \(\theta = 0.3\), bulk density \(\rho_b = 1.74\) kg/l, and fraction of tracer not attached to colloids in the injection solution \(f_a = 0.001\). An in situ bounding value of the tracer sorption coefficient on fracture filling material of \(K_d > 0.1\) m\(^3\)/kg is an estimate based on batch sorption experiments performed for tri- and tetravalent actinides (Schäfer & Noseck 2010). It is emphasised that all parameters in Tab. 15 are the same for all three tests.

Tab. 14: Calibrated mean water residence time given here together with specified (imposed as boundary conditions) shear zone outflow (\(Q_A\)) and source dilution flow (\(Q_B\)) for Tracer Test Runs 10-01, 10-03 and 12-02.

<table>
<thead>
<tr>
<th></th>
<th>Tracer Test Run 10-01</th>
<th>Tracer Test Run 10-03</th>
<th>Tracer Test Run 12-02</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\bar{\tau}) (calib) [h]</td>
<td>22</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>(Q_A) [ml/min]</td>
<td>48</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>(Q_B) [ml/min]</td>
<td>0.55</td>
<td>0.24</td>
<td>0.24</td>
</tr>
</tbody>
</table>

* Note that the injection rate value \(Q_B\) is generally uncertain for transport calculations. Accounting for the uncertainty yields \(Q_B = 0.24\) ml/min which is somewhat lower than 0.33 ml/min obtained from the dilution measurement. The calculated BTCs with 0.24 or 0.33 are comparable and do not affect the overall conclusions.

\(^2\) Note that \(\zeta\) and \(\alpha_s\) are related using the definition of \(D_f\) (see expression below Eq. (18)).
Table 15: Colloid and tracer transport parameters (as used in KTH models).

<table>
<thead>
<tr>
<th>Porous media</th>
<th>Colloids</th>
<th>Homologue/radionuclide</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_b = 1.74 \text{ kg/l}$</td>
<td>$\rho_b k_{cs} = 0.07 \text{ h}^{-1}$</td>
<td>$f_a = 0.001$</td>
</tr>
<tr>
<td>$\theta = 0.3$</td>
<td>$k_{sc} = 0.1 \text{ h}^{-1}$</td>
<td>$K_d &gt; 0.1 \text{ m}^3/\text{kg}^*$</td>
</tr>
<tr>
<td>$\zeta = 0.5 (\alpha_s = 0.75 \text{ m})$</td>
<td>$\lambda = \frac{\rho_b k_{cs,irr}}{\theta} = 0.008 \text{ h}^{-1}$</td>
<td>Same for tracer and colloid</td>
</tr>
</tbody>
</table>

* Note that the sorption coefficient on fault gouge material $K_d$ parameter was implemented as large sorption and desorption rate constants that had a ratio of $> 0.1 \text{ m}^3/\text{kg}$, which has the effect of causing all solute mass that is desorbed from colloids to become rapidly and effectively irreversibly adsorbed to shear zone surfaces.

The breakthrough curves of tracers Eu, Tb, Hf and Th were modelled using the physical parameters from Tabs. 14 and 15 in Eqs. (17) – (24). The minimum set of calibrated parameters required in the KTH modelling of the CFM tests are summarised in Tab. 16; all other parameters in Eqs. (17) – (24) not appearing in Tabs. 14 to 16 are set to zero, i.e., the corresponding processes are neglected. As can be seen from Tab. 16, the key parameter for reproducing tracer transport is the desorption rate from colloids to the solution. Recall that the tracer injected is effectively entirely sorbed on the colloids. As the transport progresses, the primary process is one of "desorption" of the tracer into the solution, whereby the concentration of tracer on colloids decreases and tracer amount sorbed on fracture filling material increases; although the latter could not be detected.

Table 16: Minimum set of calibrated parameters (KTH models).

<table>
<thead>
<tr>
<th>Run</th>
<th>Desorption parameter</th>
<th>Eu</th>
<th>Tb</th>
<th>Hf</th>
<th>Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-01</td>
<td>$k_{mc0}$ [h$^{-1}$]</td>
<td>0.15</td>
<td>0.1</td>
<td>0.035</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>$A$ [h]</td>
<td>100</td>
<td>400</td>
<td>700</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>$k_{mc0(\text{eff})}$ [h$^{-1}$]</td>
<td>0.1</td>
<td>0.07</td>
<td>0.03</td>
<td>0.012</td>
</tr>
<tr>
<td>10-03</td>
<td>$k_{mc0}$ [h$^{-1}$]</td>
<td>0.3</td>
<td>0.03</td>
<td>0.003</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$A$ [h]</td>
<td>70</td>
<td>400</td>
<td>700</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>$k_{mc0(\text{eff})}$ [h$^{-1}$]</td>
<td>0.2</td>
<td>0.025</td>
<td>0.002</td>
<td>0</td>
</tr>
</tbody>
</table>

Three cases are compared in Fig. 33 for the tracers Eu, Tb, Hf and Th of Tracer Test Run 10-01. The solid curve assumes that the desorption rate is time dependent, decreasing over the course of the tracer test, starting with $k_{mc0}$ and decreasing at a rate $1/A$. $k_{mc0}$ and $A$ values are given in Tab. 16 applied in an exponential model according to Eq. (39); an independent mechanistic base for this relationship has yet to be established. Noting the values of $A$ in Tab. 16, the decrease of the desorption rate is relatively slow given the time-scale of the experiment; roughly 500 h. The
dashed curves in Fig. 33 assume that the desorption rate \( k_{mca} \) is constant, with the "effective" values \( (k_{mca}(\text{eff})) \) given in Tab. 16. As can be seen, these effective values differ slightly from the starting values \( k_{mca0} \) for the time-varying model. Finally, the dotted curves are obtained by neglecting desorption from the colloids, i.e., setting \( k_{mca} = 0 \); in this case the modelled breakthrough curve yields higher values than observed, since all tracer remains on the colloids.

The solid and dashed curves are not very different in Fig. 33, indicating that assuming a time-dependent desorption rate is not critical for the modelling; it improves the comparison between data and model result for Eu, less obviously for Tb and with no difference for Hf and Th. The dotted curve (no desorption) differs significantly for Eu, Tb and Hf, but less so for Th. A summary of the required calibration parameters vs. number of breakthrough curves for Tracer Test Run 10-01 is summarised in Tab. 17.

---

**Fig. 33:** Simulated and experimental breakthrough curves for Tracer Test Run 10-01.

Note that \( k \) in the above figures means \( k_{mca0} \) in the \( k_{mca} \) variable case and \( k_{mca(\text{eff})} \) in the constant case; \( k=0 \) implies no mass transfer, i.e. \( k_{mca}=0 \).
Next, we consider Tracer Test Run 10-03 and summarise the corresponding breakthrough curves in Fig. 34. Tracer Test Run 10-03 is unique in the sense that the pumping rate from the shear zone is very low; 5 times lower than in Tracer Test Run 10-01. All plotting conventions in Fig. 34 correspond exactly to curves in Fig. 33.

**Fig. 34:** Simulated and experimental breakthrough curves for Tracer Test Run 10-03.

Note that the calibration of water travel time for Tracer Test Run 10-03 tests has been done on the colloid breakthrough curve; the model for uranine breakthrough curve shown here uses the mean water travel time calibrated on the colloid breakthrough curve.

Note that for the evaluation of homologue tracers in Tracer Test Run 10-03, the colloid breakthrough curve was directly calibrated as the main carrier of homologues, and not for uranine as in the other runs; the large difference between the uranine and colloid breakthrough curves would require additional interpretation of colloid retardation not observed in other runs. The mean residence time for the colloids is 75 h which is 3.4 times the mean water residence obtained from uranine in Tracer Test Run 10-01 (22 h); pumping flow rate is 4.8 times larger in Tracer Test Run 10-01. The blue and red lines are identical, whereby the difference between the blue dots and the blue line show the level of retardation of the colloids relative to the uranine in Tracer Test Run 10-03.
Under the conditions of Tracer Test Run 10-03, the uranine breakthrough curve displays an anomaly that requires "correction" which is discussed in the previous sections (see also Appendix A). Here, the mean water residence time ($\bar{t}$) was calibrated using the colloid breakthrough curve rather than the uranine breakthrough curve. The desorption rates for tracers Eu, Tb, Hf and Th were then also calibrated. The result of the calibration is summarised in Tab. 16. As can be seen, there is a difference in the calibrated desorption rates $k_{mca}$ between Tracer Test Runs 10-01 and 10-03 (Tab. 16). However, these differences are modest; up to a factor 3 for Tb. The exception is Th, for which the desorption rate is in any case rather low. Note that we use for Tracer Test Run 10-03 the same macro-dispersivity and colloid parameters as were calibrated by manual adjustment in Tracer Test Run 10-01 (see Tab. 15); this is summarised in Tab. 17 where we see that for the six breakthrough curves we have five calibrated parameters, as compared with nine in the case of Tracer Test Run 10-01. Note also that the desorption rates for the tetravalent tracer Hf and Th are consistently lower than for the trivalent tracers Eu and Tb, in both Tracer Test Run 10-01 and 10-03.

Tab. 17: Value of "knowledge ratio" ($\kappa$) during modelling process.

<table>
<thead>
<tr>
<th></th>
<th>10-01</th>
<th>10-03</th>
<th>12-02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibrated parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrodynamic</td>
<td>$\bar{t}$, $\zeta$</td>
<td>$\bar{t}$</td>
<td>$\bar{t}$</td>
</tr>
<tr>
<td>Colloids</td>
<td>$\lambda$, $k_{cs}$, $k_{sc}$</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Tracer</td>
<td>$k_{mca} \times 4$</td>
<td>$k_{mca} \times 4$</td>
<td>--</td>
</tr>
<tr>
<td>Breakthrough curves</td>
<td>Uranine, Coll, Eu, Tb, Hf, Th</td>
<td>Uranine, Coll, Eu, Tb, Hf, Th</td>
<td>AGA, Coll, Pu, Am</td>
</tr>
<tr>
<td>&quot;Knowledge ratio&quot; $\kappa$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#BTC (Breakthrough curves)</td>
<td>6</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>#CP (Calibrated parameters)</td>
<td>9</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>#BTC/#CP</td>
<td>$6/9 = 0.67$</td>
<td>$6/5 = 1.2$</td>
<td>$4/1 = 4$</td>
</tr>
</tbody>
</table>

Given the knowledge and understanding about the system gained through the evaluation of Tracer Test Runs 10-01 and 10-03, "predictions" could be made for the outcome of Tracer Test Run 12-02 for all tracers. One parameter that needed to be calibrated in Tracer Test Run 12-02 was the mean water residence time ($\bar{t}$), using the non-sorbing AGA tracer breakthrough curve. Based on the calibrated mean water residence time of 25 h, and using the parameters calibrated in Tracer Test Runs 10-01 and 10-03, the result of predictive modelling of Tracer Test Run 12-02 is shown in Fig. 35. For the tracer Pu(IV), two curves (dashed and dotted) were modelled using the two values of the desorption rate $k_{mca}$, as maximum and minimum values calibrated for Hf(IV) and Th(IV) in Tracer Test Runs 10-01 and 10-03: 0 and 0.035 h$^{-1}$ (Tab. 16). For the tracer Am(III) we also modelled two curves (dashed and dotted) using the two values of the desorption rate $k_{mca}$, as minimum and maximum calibrated for Eu(III) and Tb(III) in the 10-01 and 10-03 Runs: 0.025 h$^{-1}$ and 0.2 h$^{-1}$ (Tab. 16). As can be seen, there is a consistency in the predicted breakthrough curves with observations. Although there is obvious uncertainty, the data fall within the range of the predicted breakthrough curves for Pu and Am. Note that the concentrations for the actinides are parts-per trillion, or μg/m$^3$ which are very low, yet still detectable, values.
Finally, in Tab. 17, note that for Tracer Test Run 12-02, we had four breakthrough curves and only one calibrated parameter. As can be seen in Tab. 17, the "knowledge ratio" or "information ratio" $\kappa$ defined loosely as $\kappa = \text{number of breakthrough curves} / \text{calibrated parameters}$ increases significantly over the course of the CFM tests, from 0.67 to 4. The overall ratio $\kappa$ for all three runs is $\kappa = 17$ breakthrough curves / 15 calibrated parameters = 1.07. Note that a single tracer test that can be described by the advection-dispersion equation with two parameters would have $\kappa = 1/2$. Our overall value of approximately 1 therefore shows a significant knowledge gain from the CFM tests. The value $\kappa = 1.07$ is based only on evaluating the tracer tests, i.e., not considering flow simulations or using laboratory data. Including results from flow simulations and laboratory data could further improve (i.e., increase) the knowledge ratio for the CFM transport experiments.

Fig. 35: Simulated and experimental breakthrough curves for Tracer Test Run 12-02.
6 Discussion

Transport simulations have been performed using a range of numerical models for selected field dipole experiments performed in a shear zone in granitic rock at the Grimsel Test Site within the international Colloid Formation and Migration (CFM) project. The field experiments involved colloids and tri- and tetravalent homologues or radionuclides, with different travel times achieved by different extraction rates at the outflow location. All models describe colloid-facilitated transport by kinetically controlled interactions between the homologues/radionuclides, the colloids and the surfaces of the fracture filling material in the shear zone. In the following, the results of the different models are compared and discussed. The results are also discussed in the context of independent laboratory experiments and safety assessments over larger temporal and spatial scales.

6.1 Comparative analysis

The different modelling approaches all yielded qualitatively similar results in that colloid transport in the field tracer tests could be described reasonably well as a first-order filtration process, and homologue or radionuclide transport was described as being controlled by the desorption rate of solutes from the colloids. Somewhat better fits to the colloid breakthrough curves were obtained for Tracer Test Runs 10-01, 10-03, and 12-02 by assuming some additional reversible filtration of the colloids, whereas in Tracer Test Run 08-01 a very good fit was obtained using only a single first-order irreversible filtration reaction.

For the homologue desorption process, the GRS model considered only a single first-order desorption reaction, and the deduced rate constants were in good agreement with the other models when only a single desorption reaction was considered. However, the LANL and KTH models achieved better fits to the homologue or radionuclide breakthrough curves in several cases when desorption from the colloids was described using a two-site adsorption model and/or when an aging reaction was allowed that converted some of the adsorbed solute from one type of sorption site on the colloids to the other (see Sections 5.4 and 5.6).

6.2 Comparing parameters

Tab. 18 lists the colloid transport parameters obtained from the different models for Tracer Test Run 10-01, which was the only tracer test for which KTH independently estimated colloid transport parameters. In this case, KTH used a manual calibration between the model and log-transformed data, which was slightly different from the LANL approach using untransformed data. Nevertheless, it is apparent that the colloid transport parameters obtained by the two approaches are in very good agreement. In fact, the GRS model yields the colloid transport parameters that are the most different, although they are still in relatively good agreement with the other models.

Tab. 19 lists the homologue interaction parameters obtained from the different models for Tracer Test Runs 10-01 and 10-03, which are the tests that GRS focused the most effort on. In this table, only the best-fitting model parameters obtained when assuming a single sorption site on colloids are listed for the LANL model because the GRS model is limited to a single adsorption site on colloids. The parameters listed for the KTH model were obtained using the LANL model with the KTH description of the desorption process (i.e. a single site with an exponentially-decaying desorption rate constant, cf. Eq. (39)). These parameters are not necessarily the same as those obtained by KTH modellers listed in Tab. 16 because the LANL model
fits minimised the differences between the model and the untransformed homologue data rather than the log-transformed data.

Tab. 18: Interaction parameters between colloids and fracture filling material used in the three models for Tracer Test Run 10-01.

<table>
<thead>
<tr>
<th></th>
<th>Model GRS</th>
<th>Model KTH</th>
<th>Model LANL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forward rate ( \frac{\partial_\phi k_{cs}}{\phi} ) (attachment) ([h^{-1}])</td>
<td>0.054</td>
<td>0.07</td>
<td>0.2</td>
</tr>
<tr>
<td>Backward rate ( k_{cs} ) (detachment) ([h^{-1}])</td>
<td>0.108</td>
<td>0.1</td>
<td>0.286</td>
</tr>
<tr>
<td>Irreversible rate ( \lambda = \frac{\partial_k k_{cs,irr}}{\phi} ) ([h^{-1}])</td>
<td>0.01</td>
<td>0.008</td>
<td>0.0065</td>
</tr>
<tr>
<td>Resulting retardation factor</td>
<td>1.5</td>
<td>1.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Tab. 19: Interaction parameters between trivalent (III)/tetravalent (IV) homologues, colloids and fracture filling material resulting from the best fit of the field experiments.

<table>
<thead>
<tr>
<th></th>
<th>Model GRS</th>
<th>Model LANL</th>
<th>Model KTH*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Homologue – Colloid</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tracer Test Run 10-01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward rate ( k_{amc} ) ([m^3 kg^{-1} h^{-1}])</td>
<td>Insensitive</td>
<td>Insensitive</td>
<td>Insensitive</td>
</tr>
<tr>
<td>Backward rate ( k_{mca} ) ([h^{-1}])/decay rate A (if used) ([h])</td>
<td>0.03 (IV)</td>
<td>0.0275 (Th)</td>
<td>0.0253 (Th)</td>
</tr>
<tr>
<td></td>
<td>0.075 (III)</td>
<td>0.0368 (Hf)</td>
<td>0.037 (Hf)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.074 (Tb)</td>
<td>0.074 (Tb)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.086 (Eu)</td>
<td>0.0935/350 (Eu)</td>
</tr>
<tr>
<td>Tracer Test Run 10-03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward rate ( k_{amc} ) ([m^3 kg^{-1} h^{-1}])</td>
<td>Insensitive</td>
<td>Insensitive</td>
<td>Insensitive</td>
</tr>
<tr>
<td>Backward rate ( k_{mca} ) ([h^{-1}])/decay rate A (if used) ([h])</td>
<td>0.0025 (IV)</td>
<td>0.003 (Th)</td>
<td>0.026/53 (Th)</td>
</tr>
<tr>
<td></td>
<td>0.02 (III)</td>
<td>0.0021 (Hf)</td>
<td>0.0185/54 (Hf)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0415 (Tb)</td>
<td>0.052/480 (Tb)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.026 (Eu)</td>
<td>0.041/260 (Eu)</td>
</tr>
<tr>
<td><strong>Homologue – Fracture filling material</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward rate ( k_{amc} ) ([m^3 kg^{-1} h^{-1}])</td>
<td>Large</td>
<td>Large</td>
<td>Large</td>
</tr>
<tr>
<td>Backward rate ( k_{mca} ) ([h^{-1}])</td>
<td>Large</td>
<td>Small</td>
<td>Small</td>
</tr>
</tbody>
</table>

* Note that the introduction of a desorption rate decay offered no improvement over a time-invariant desorption rate constant for Th, Hf and Tb in Tracer Test Run 10-01 when untransformed homologue data were used for the model fits. When KTH used log-transformed data for Tracer Test Run 10-01, they obtained parameters of 0.027/4000 for Th, 0.035/700 for Hf, 0.1/400 for Tb and 0.15/70 for Eu.
6.3 Parameter uncertainty and sensitivity

Uncertainty and sensitivity evaluations of the transport parameter estimates were not formally carried out in this study. Instead, emphasis was placed on determining which descriptions of the solute desorption process from the colloids provided the best fits to the solute breakthrough curves (see Section 5.4). It was apparent with all the models and datasets that, once the mean residence time, Peclet number and colloid filtration parameters were estimated from the fits to the conservative tracer and colloid breakthrough curves, the fits to the solute breakthrough curves were by far most sensitive to the parameters describing the solute desorption process from colloids. In fact, all other parameters describing solute transport could take a wide range of values and still offer good fits to the solute datasets provided that they resulted in relatively rapid and strong adsorption to the shear zone surfaces after the solutes desorbed from the colloids. These conditions are generally met if:

\[
\frac{\rho_b}{\theta} k_{as} > 20 k_{amc} C_c \quad \text{or} \quad 1 + \frac{\rho_b}{\theta} K_d > 20
\]  

(41)

Failure to meet these conditions resulted in generally poorer fits to the solute breakthrough curves. On the other hand, as long as at least one of these inequalities was satisfied, the fits were highly insensitive to the exact values of the parameters in the inequalities (for example, $\frac{\rho_b}{\theta} k_{as}$ being a factor of 20 greater than $k_{amc} C_c$ provided essentially the same fit as $\frac{\rho_b}{\theta} k_{as}$ being a factor of 10,000 greater than $k_{amc} C_c$).

There was also very little sensitivity to the maximum adsorption capacity of the solutes on the colloid and shear zone surfaces in the LANL model (the only model that featured this parameter). The fits to the solute breakthrough curves were not significantly improved by adjusting the maximum adsorption capacity to be anything less than effectively infinite (the default values in the other models). Consideration was given to the placement of limits on the number of slow desorption sites on colloids in the two-site models because the high/long homologue tails in Tracer Test Run 10-03 relative to Tracer Test Runs 08-01 and 10-01 might be explained by greater partitioning of the homologues to a limited number of slow desorption sites in Tracer Test Run 10-03 as a result of the much higher colloid concentrations in that test. However, the LANL model does not explicitly account for the initial adsorption processes onto the colloids, which occurs as soon as the homologues are added to the tracer cocktail, long before the field tracer tests start. These early processes are implicitly accounted for by assigning different initial mass fractions of homologues to different sites on the colloids. In fact, it was found that assigning an initially greater fraction of homologue mass to slow desorption sites on colloids tended to significantly improve the fits to the Tracer Test Run 10-03 homologue data, while it did not substantially improve the fits to the data of Tracer Test Runs 08-01 and 10-01 (with the exception of the Eu data in Tracer Test Run 10-01). This result suggests that preferential adsorption to a limited number of slow sites is a possible explanation for the homologue transport behaviour of Tracer Test Run 10-03.

Tracer Test Run 12-02 had a colloid injection concentration that was comparable to Tracer Test Run 10-03, but did not exhibit long tails of the tri- and tetravalent radionuclides as did the tri- and tetravalent homologues in Tracer Test Run 10-03. Thus, for Tracer Test Run 12-02, assigning a greater initial fraction of the radionuclides to slow desorption sites on colloids does not improve the model fits to the experimental data. In fact, for the tetravalent Pu in Tracer Test Run 12-02, the best fit was obtained with an aging reaction that involved conversion of some of the adsorbed Pu from a first site to a second site that had weaker adsorption (faster desorption rate) than the first site. These results suggest that either the radionuclides in Tracer Test Run 12-02 did not preferentially adsorb to a limited number of slow desorption sites on colloids
as the homologues appeared to do in Tracer Test Run 10-03, or the colloids in Tracer Test Run 12-02 simply did not have as many of these slow desorption sites as the colloids in Tracer Test Run 10-03.

It was determined that the homologue/radionuclide desorption parameters were somewhat sensitive to different estimates of the colloid transport parameters because the homologues/radionuclides moved through the shear zone only while adsorbed to the colloids. When colloid recoveries were simulated to be higher (lower filtration rate constants), the homologue or radionuclide desorption rates from the colloids had to be higher to compensate. Likewise, when colloid recoveries were simulated to be lower, homologue/radionuclide desorption rates had to be lower. The ability to fit the homologue/radionuclide breakthrough curves was also affected by the simulated colloid transport behaviour. In the following section, the assessment of different descriptions of the solute desorption process from colloids was conducted while keeping all colloid transport parameters constant (i.e. those of Tab. 7) so as to avoid confusion in the assessment.

6.4 Assessment of alternative descriptions of solute desorption from colloids

The evaluation of alternative descriptions of solute desorption from colloids, for which results are presented in Section 5.4, produced mixed results. For the major part, a two-site model offered a significant improvement over a one-site model, although a one-site model with a single desorption rate constant was considered superior for all of the colloid-facilitated solute datasets in Tracer Test Run 08-01, for Hf in Tracer Test Run 10-01 and for Am in Tracer Test Run 12-02. By far the most significant improvement offered by a two-site model was for the homologue datasets of Tracer Test Run 10-03, which exhibited relatively low peak concentrations followed by long, high tail concentrations, with the ratio of the normalised homologue concentrations to normalised colloid concentrations decreasing throughout the test and approaching one in the tails of the breakthrough curves for Th and Hf. These patterns can only be explained by a decrease in the average desorption rate of the homologues from the colloids over time during the test, and the only way that such a decrease can be accounted for is with at least one second, slower desorption site. This second site must either have sufficient initial homologue mass adsorbed to it to account for the long homologue tail, or there must be an aging reaction converting some of the homologue mass from the faster site to the slower site during the test. In the case of the Th and Hf in Tracer Test Run 10-03, invoking an aging process offers a significant improvement over no aging process. The single-site model with an exponentially decaying first order rate constant fits the Tracer Test Run 10-03 homologue data reasonably well, but, as discussed in the next paragraph, this model can be interpreted as representing two sites rather than the literal interpretation of a single site with a time-dependent rate constant.

Tab. 10 shows that, for each of the homologue datasets in Tracer Test Run 10-03 and for the Eu dataset in Tracer Test Run 10-01, the single-site exponential decay model yielded sum-of-squares differences that were almost identical to those of the two-site model with all of the solute initially adsorbed to the first site and a first-order aging reaction that converted the adsorbed solute from the first type of site to a second site that had a desorption rate constant of zero (i.e. irreversible). Both of these models have two adjustable parameters: the initial desorption rate constant and a time constant for decay of this rate constant in the case of the single-site exponential decay model, and the rate constant for the first adsorption site and an aging rate constant for converting adsorbed solute on this site to a second site (with the second site having a desorption rate constant of zero) in the case of the LANL two-site model. The fact that these
two models yield nearly identical sum-of-squares differences and nearly identical fits in all cases in which the second site was assumed to be irreversible suggests that the two models are essentially equivalent from the standpoint of explaining the solute data. We consider the two-site aging model to be a more plausible description of the desorption process than the single-site model with an exponentially-decaying rate constant because the latter model does not have a sound mechanistic basis (i.e. it implies a continuum of different sites with different desorption rate constants rather than an aging reaction converting solute from one site to another, although the net effect of the decaying rate constant is to effectively mimic the aging process with an irreversible second site).

The improvement of the model fits to the homologue or radionuclide breakthrough curves offered by including a second adsorption site on colloids (over a single site model) was much less significant for tracer tests other than Tracer Test Run 10-03, and, as mentioned above, there was actually no improvement for the three homologue datasets in Tracer Test Run 08-01, for Hf in Tracer Test Run 10-01 and for Am in Tracer Test Run 12-02. While it was concluded that a two-site model was statistically justified over a single-site model in explaining 8 of the 13 colloid-facilitated solute transport datasets, the best-fitting parameters in these cases suggest that there was no consistency in the description of the two-site desorption process. In three cases (i.e. Th and Tb in Tracer Test Run 10-01 and Pu in Tracer Test Run 12-02), the best fits were obtained assuming an aging process and a second site that had a faster desorption rate constant than the first site. The inference in these cases is that the homologues and Pu desorbed from the colloids more rapidly near the end of the respective tests than at the beginning, which is in contrast to the results obtained for all the homologues in Tracer Test Run 10-03 and Eu in Tracer Test Run 10-01.

These inconsistencies from one test to another, particularly with the same homologues in Tracer Test Runs 08-01, 10-01, and 10-03, suggest that either the colloid-facilitated transport processes are truly varying from one test to another or that there are enough random and/or systematic errors in the breakthrough curve data that the similarity in transport behaviour of the colloid-associated homologues between tests is masked by these errors. The first explanation seems more plausible, although the second cannot be entirely ruled out. The variability in colloid-facilitated transport processes from one test to the next could have a number of possible causes. Subtle differences in the preparation procedure for the colloids and the tracer cocktails could potentially result in differences in the association of the homologues with the colloids, leading to stronger or weaker associations or perhaps to differences in aging processes in different tests. Even with complete consistency in cocktail preparations, differences in time elapsed between tracer cocktail preparation and tracer injection in different tests could also influence homologue-colloid associations during the tests if aging processes are significant. The different tests also had different apparent shear zone flow pathways (Fig. 8), so it is quite possible that even if the tracer cocktails were completely identical in all respects, the colloids and homologues may have come into contact with different shear zone surfaces during the different tests, thus resulting in differences in homologue desorption parameters. The different flow rates in otherwise similar flow pathways could have influenced homologue desorption parameters by subtly influencing colloid collision frequencies with shear zone surfaces or collision efficiencies with respect to inducing homologue desorption from colloids. Finally, it is possible that the greater ratio of colloid to homologue concentrations in Tracer Test Run 10-03 relative to the other homologue tests might have resulted in some differences in the colloid-facilitated transport of the homologues in this test. It should be noted that all of these explanations could potentially also explain differences in colloid filtration parameters between the different tests.
It is worth noting that the apparent time-varying changes in desorption rate constants for some of the homologues (and Pu) in some of the tests may have also been caused by differences in transport characteristics of the early and late shear zone flow pathways in the tests. Although the residence times in the shear zone pathways were always quite short compared with the test durations, which suggests that most of the observed tailing can be attributed to the slowly-decaying injection functions rather than dispersion in shear zone pathways (see Fig. 7), it is still possible there were some differences in the shear zone pathways early and late in the tests that may have resulted in apparent changes to desorption rate constants. This could explain why in some cases (Th and Tb in Tracer Test Run 10-01, and Pu in Tracer Test Run 12-02) there was an apparent increase in the desorption rate constant with time when one would normally expect an aging process to result in a decrease in the desorption rate with time.

The possibility that random or systematic errors in the breakthrough curve data could have masked a similarity in the colloid-associated transport behaviour of the homologues between the tests seems less likely than the above potential explanations for the observed differences. In the absence of direct information on these types of errors in the colloid, homologue and radionuclide analytical data, we use a qualitative and empirical measure of how much "noise" there is in each dataset. This measure is the ratio of the sum of squares of differences between the data and best-fitting models to the sum of squares of the model predictions (normalised concentrations) at each observation, which is listed for each dataset in Tab. 20. This ratio effectively provides a measure of the ability of the models to explain the datasets (similar to the ratio of the sum-of-squares regression to total sum of squares, which provides a quantitative measure in the case of a linear regression model). It is apparent that the greatest data scatter relative to the model fits for the homologue breakthrough curves occur in Tracer Test Run 10-01. All other tests had smaller ratios that were comparable with each other, which suggests that greater confidence can be placed in the fits for these tests than for Tracer Test Run 10-01. This result can be qualitatively deduced by looking at the plots of the model curves and data curves in Figs. 26 to 29. Besides the considerable data scatter in Tracer Test Run 10-01, the relatively high early peaks in homologue concentrations followed by steep drops to relatively low tail concentrations made it difficult to fit the Tracer Test Run 10-01 breakthrough curves, resulting in large ratios in Tab. 20. These features also result in the conclusion that two of the four homologue breakthrough curves in Tracer Test Run 10-01 are best explained by an aging process with a second adsorption site on the colloids that has a faster desorption rate constant than the first site (this drives the tails lower more quickly).

It should be noted that some of the scatter in the datasets might be attributable to earth tides that caused periodic fluctuations in the conservative dye tracer breakthrough curves in the longer tests (Figs. 7 and 25). Because the frequency of concentration data was much lower for the offline analyses of colloids and homologues/radionuclides than for the inline fluorescence analyses of the dye tracers, the impact of the earth tides on the colloid and solute concentrations is somewhat uncertain. We speculate that the impact may have been greater for Tracer Test Run 10-01 than for the other tests, although other unknown factors may have played a role in the larger data scatter of this test.
Tab. 20: Ratios of sum of squares of residuals (between model and data) to sum of squares of model predictions for all the best-fitting LANL model simulations.

<table>
<thead>
<tr>
<th>Tracer Test Run/solute</th>
<th>Model</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-01/Th</td>
<td>1-site</td>
<td>0.02</td>
</tr>
<tr>
<td>08-01/Hf</td>
<td>1-site</td>
<td>0.018</td>
</tr>
<tr>
<td>08-01/Tb</td>
<td>1-site</td>
<td>0.02</td>
</tr>
<tr>
<td>10-01/Th</td>
<td>Aging to 2\textsuperscript{nd} site</td>
<td>0.027</td>
</tr>
<tr>
<td>10-01/Hf</td>
<td>1-site</td>
<td>0.037</td>
</tr>
<tr>
<td>10-01/Tb</td>
<td>Aging to 2\textsuperscript{nd} site</td>
<td>0.067</td>
</tr>
<tr>
<td>10-01/Eu</td>
<td>2-site, no aging</td>
<td>0.054</td>
</tr>
<tr>
<td>10-03/Th</td>
<td>2-site, hybrid</td>
<td>0.018</td>
</tr>
<tr>
<td>10-03/Hf</td>
<td>1-site exp decay Aging to 2\textsuperscript{nd} site</td>
<td>0.021</td>
</tr>
<tr>
<td>10-03/Tb</td>
<td>2-site, no aging</td>
<td>0.025</td>
</tr>
<tr>
<td>12-02/Am</td>
<td>1-site</td>
<td>0.018</td>
</tr>
<tr>
<td>12-02/Pu</td>
<td>Aging to 2\textsuperscript{nd} site</td>
<td>0.017</td>
</tr>
</tbody>
</table>

6.5 Link to laboratory investigations

As noted above, desorption is the most relevant aspect of homologue/radionuclide interaction with colloids with regard to the shape of the breakthrough curve and the recovery of the homologues. The desorption rates of homologues obtained from the field experiment can be compared with those from batch experiments performed in ternary systems with homologues, colloids and fracture filling material (Huber et al. 2011).

6.5.1 Interaction of homologues/radionuclides with colloids and fracture filling material

Sorption data for the homologues and particularly the desorption rates from the colloids have been determined by independent batch experiments for the ternary system homologue – colloid – fracture filling material (Huber et al. 2011). In these experiments, the solutes are equilibrated with colloids in solution for a few days before adding the fracture filling material. After addition of the fracture filling material, a fraction of the solutes desorb from the colloids and sorb onto the fracture filling material. Assuming that i) the time dependence of the observed radionuclide distribution between solution and immobile phase (i.e. the fracture filling material) is determined by the desorption rate, ii) that the process is in equilibrium after 7'500 h (the endpoint of the experiment) and iii) neglecting an interaction of colloids with the fracture filling material, Huber et al. (2011) derived detachment rates from the colloids of 0.0037 h\textsuperscript{-1} for the trivalent americium and 0.0014 h\textsuperscript{-1} for the tetravalent elements plutonium and thorium. A batch modelling attempt by GRS using the same sorption coefficients and attachment rates as applied for the field experiment for Am and Pu yielded similar detachment rates (\(k_{\text{mea}}\) and \(k_{\text{ica}}\)) of 0.0035 h\textsuperscript{-1} and 0.0022 h\textsuperscript{-1} for Am and Pu, respectively.
The resulting curves compared with the experimental data are shown in Fig. 36.

Fig. 36: Radionuclide distribution coefficient ($K_d$) between mobile aqueous and immobile phase for experiment (circles, Huber et al. 2011) and simulation (line) as a function of time in the ternary batch system bentonite colloids, fracture infill, and radionuclide.

Top, trivalent Am with: $k_{sa} = 1 \text{ h}^{-1}$, $k_{as} = 2 \text{ m}^3\text{kg}^{-1}\text{h}^{-1}$ and $k_{mca} = 0.0035 \text{ h}^{-1}$, $k_{amc} = 5.6 \text{ m}^3\text{kg}^{-1}\text{h}^{-1}$. Bottom, tetravalent Pu with: $k_{sa} = 1 \text{ h}^{-1}$, $k_{as} = 0.825 \text{ m}^3\text{kg}^{-1}\text{h}^{-1}$ and $k_{mca} = 0.0022 \text{ h}^{-1}$, $k_{amc} = 3.52 \text{ m}^3\text{kg}^{-1}\text{h}^{-1}$.
The results show that the desorption rates, which determine the homologue breakthrough curves and recoveries derived in the model simulations for Tracer Test Run 10-03 are, particularly for the tetravalent elements in a similar range to those derived from independent batch experiments (cf. Tab. 19). For Tracer Test Run 10-01, which was performed at a higher extraction rate and thus had a lower residence time, higher desorption rates are observed. Such a decrease in reaction rates is observed in other natural systems and was also found for the transport of lanthanides bound to humics, e.g. Lührmann et al. (1998). However, Huber et al. (2011) measured desorption rate constants for Am and Pu at two different starting concentrations for each actinide and, if we limit the comparison of laboratory and field results to these radionuclides at their injection concentrations in Tracer Test Run 12-02 \((4.4 \times 10^{-11} \text{ mol/l} \text{ and } 2 \times 10^{-9} \text{ mol/l})\), respectively, then the desorption rate constants predicted by the laboratory experiments would be approximately 0.01 h\(^{-1}\) for Am and 0.002 h\(^{-1}\) for Pu. The desorption rate constants deduced in Tracer Test Run 12-02 were 0.016 h\(^{-1}\) for Am and 0.0077 h\(^{-1}\) for Pu for the LANL one-site model and 0.02 h\(^{-1}\) for Am and 0.0025 h\(^{-1}\) for Pu for the GRS model, which is considered to be a quite good agreement. The higher rates in the field experiments could reflect that the shear zone surface area available for competitive sorption with the colloids was somewhat higher in the field test than in the laboratory experiments.

The reason for the greater homologue desorption rates in Tracer Test Run 10-01 relative to Tracer Test Run 10-03, discussed above, is not yet clear. One explanation might be that the colloid concentration in Tracer Test Run 10-03 was significantly higher, whereas the concentration of homologues was the same. Therefore, a decreased desorption rate of homologues at lower coverage of the bentonite colloids could explain this behaviour. But, so far, there is no experimental evidence for this and, as mentioned previously, there was no improvement in fitting the homologue breakthrough curves with the LANL two-site model when the adsorption capacity of one or both of the adsorption sites on colloids was limited (which is the most plausible mechanistic explanation for stronger adsorption at lower surface coverages). However, better fits were obtained when a greater initial fraction of the homologues was assigned to a slow desorption site for Tracer Test Run 10-03 in the LANL model, which is consistent with a limited number of stronger sites on colloids having a greater influence in this test with the higher ratio of colloid to homologue concentrations.

### 6.5.2 Interaction of colloids with fracture filling material

The results from the field tests indicate a filtration process of the colloids during transport through the shear zone as well as an additional reversible interaction between colloids and the fracture filling material.

#### Filtration theory

One way to describe the interaction process between colloids and the fracture filling material is the filtration theory as described in Section 3.2.2. In the following, the relevant parameters are derived from existing experiments and characteristic data from the investigation of the shear zone (Gaus & Smith 2008).

The attachment process of colloidal bentonite particles on granite infill material under Grimsel groundwater conditions has been investigated in experiments by Degueldre et al. (1996). An attachment factor of \(2 \times 10^{-4}\) was determined from these investigations. All other parameters needed to describe the filtration process (Eqs. (5) – (7)), which are adapted to the conditions of the CFM experiments, are listed in Tab. 21. The viscosity and fluid density are given for the weakly mineralised Grimsel groundwater. For the bentonite colloids, the rock density of bentonite is applied. A collector diameter of \(10^{-4}\) m is selected as an average grain size of the fracture infill material.
Tab. 21: Parameters used for the deep bed filtration approach.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
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<tr>
<td>Dynamic viscosity $\mu$</td>
<td>Ns m$^{-2}$</td>
<td>$1 \times 10^{-3}$</td>
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<tr>
<td>Fluid density $\rho$</td>
<td>kg m$^{-3}$</td>
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<tr>
<td>Colloid density $\rho_c$</td>
<td>kg m$^{-3}$</td>
<td>2'670</td>
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<tr>
<td>Colloid diameter $d_p$</td>
<td>m</td>
<td>$1.5 \times 10^{-7}$</td>
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<tr>
<td>Collector diameter $d_c$</td>
<td>m</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Gravitation constant $g$</td>
<td>m s$^{-2}$</td>
<td>9.81</td>
</tr>
<tr>
<td>Temperature $T$</td>
<td>K</td>
<td>288.15</td>
</tr>
<tr>
<td>Boltzmann constant $k_B$</td>
<td>J/K</td>
<td>$1.38 \times 10^{-23}$</td>
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<tr>
<td>Porosity $\theta$</td>
<td>--</td>
<td>0.15</td>
</tr>
<tr>
<td>Attachment factor $\alpha$</td>
<td>--</td>
<td>$2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

For the particle velocities in the range of $10^{-4}$ to $10^{-5}$ m/s, filtration rates $\frac{\rho_B k_{cs}}{\theta}$ of 0.11 h$^{-1}$ to 0.05 h$^{-1}$ were calculated, which are higher than the irreversible rate of 0.01 h$^{-1}$ derived from the field experiments. However, taking into account that we have assumed an additional reversible attachment process, with rates between 0.054 h$^{-1}$ and 0.2 h$^{-1}$ (cf. Tab. 18), the observed interaction rates fit into the range obtained by deep bed filtration theory. In addition, the values for the collector diameter and the attachment factor are affected by particularly large uncertainties. An increase of the colloid diameter by a factor of 2 would yield a value of $0.015 \text{ h}^{-1}$ for $\frac{\rho_B k_{cs}}{\theta}$ at a flow velocity of $10^{-5}$ m/s, which is already in the range of the observed irreversible filtration rates. Since the flow is expected to be channelised, occurring largely in the open fracture part of the brittle structure, collector diameters in the range of $10^{-4}$ to $10^{-3}$ m are justified. In a similar way, the reduction of the attachment factor reduces the filtration rate $\frac{\rho_B k_{cs}}{\theta}$.

6.6 Implications of the results for nuclear waste repository safety assessments over long time and distance scales

To assess the implications of the CFM Tracer Test Runs results for colloid-facilitated radionuclide transport over longer time and distance scales, it is of interest to examine the scaling behaviour of the desorption parameters for the tri- and tetravalent homologues or radionuclides from the colloids in the Tracer Test Runs 08-01, 10-01, 10-03 and 12-02. Fig. 37 shows desorption rate constants from the colloids for the trivalent homologues and Am as a function of residence time in the shear zone from the four tracer tests. Fig. 38 shows an analogous plot for the tetravalent homologues and Pu. In both cases, the plots reflect the desorption rate constants obtained when only a single adsorption site was assumed on the colloids (estimated using the LANL model). The desorption rate constants for a second site and any aging process on the colloid surfaces are not reflected in these plots so as to keep the evaluation consistent across all tests. A similar plot of the scale dependence of colloid filtration rate constants is not presented here because the filtration rate constants did not exhibit any clear trend with time scale (cf. Tab. 7). There was also an inconsistency between tests of whether the colloid filtration process was reversible or irreversible or both.
In both Figs. 37 and 38, there is a tendency for the desorption rate constants to decrease with residence time. Linear regression fits to the log-log transformed data of Figs. 37 and 38 are shown in Fig. 39. It is apparent that the tetravalent species desorb more slowly than the trivalent species in any given test, although both species have nearly the same slope, implying a similar time-scale dependence. Extrapolation of the desorption rate constant regressions to longer times yields predictions that 99% of the trivalent species will desorb from the colloids after a residence time of about 500 hours and 99% of the tetravalent species will desorb after a residence time of about 1 year. Of course, the uncertainties associated with these extrapolations are quite large, especially for the radionuclides Am and Pu, which, although combined with the tri- and tetravalent homologues for the regressions of Fig. 39, were each only used in one test (Tracer Test Run 12-02). The possibility of more than one adsorption site on colloids and an aging process that converts one type of site to another, as indicated by the best model fits to several of the datasets, casts additional uncertainty on extrapolations of desorption rate constants to longer times. Nonetheless, the tracer test data suggest that the time scales for desorption of the tri- and tetravalent species from the colloids should be relatively short compared with time scales for safety assessment, implying negligible colloid-facilitated transport of the radionuclides over safety assessment time scales of multiple years, even if colloid filtration is minimal. However, an effective irreversible component of association is a possibility that cannot be excluded based on these tests (cf. discussion on page 84).

Fig. 37: Desorption rate constants from colloids vs. time for trivalent homologues and Am(III) in the four Tracer Test Runs.
Fig. 38: Desorption rate constants from colloids vs. time for tetravalent homologues and Pu(IV) in the four Tracer Test Runs.

Fig. 39: Trends of log desorption rate constants from colloids vs. log time (trivalent and tetravalent species) in the Tracer Test Runs.
The apparent time scale dependence of the desorption rate constants in Figs. 37 to 39 are worthy of further discussion. Mechanistically, time-dependent rate constants for specific reactions are not supported by theory or literature data (this point was previously made in Section 6.4 in connection to the exponentially decaying rate constants assumed in the single-site exponential decay model). However, a simple example can illustrate how a small number of reactions or, more accurately, a small number of different types of sorption sites with different corresponding desorption rates, could result in the observed time-dependent behaviour. Fig. 40 shows the desorption rate constants for the tetravalent species as a function of residence time in the Tracer Test Runs (data of Fig. 38) along with a line generated from a simple calculation of the apparent rate constant resulting from a system in which there are 3 types of sorption sites on the colloids, with desorption rate constants of 0.1 h\(^{-1}\), 0.0005 h\(^{-1}\), and 0.00001 h\(^{-1}\). One-third of the mass of the tetravalent solute was assumed to occupy each of the sites at time zero. Even though each of the sorption sites has a time-invariant desorption rate constant, the overall system exhibits time-dependent desorption rate behaviour similar to that observed in the Tracer Test Runs.

![Graph showing apparent desorption rate constants from colloids for the tetravalent species as a function of residence time in the Tracer Test Runs. Red data point is Pu in Tracer Test Run 12-02.](image)

**Fig. 40**: Apparent desorption rate constants from colloids for the tetravalent species as a function of residence time in the Tracer Test Runs. Red data point is Pu in Tracer Test Run 12-02.

The key point in Fig. 40 is that the extrapolation of the Tracer Test Run data to longer time scales will critically depend on the presence or absence of desorption rate constants that are significantly smaller than the rate constants that can be effectively interrogated in the Tracer Test Runs. More specifically, it will depend on the presence or absence of some fraction of sorption sites on colloids that have extremely low desorption rate constants. Even a very small fraction of such sites could result in significant observable colloid-facilitated transport of a radionuclide over long time and distance scales – of course it would also be necessary for a significant fraction of colloids to remain unfiltered over such time scales. The dashed lines in Fig. 40 are intended to qualitatively illustrate the range of potential extrapolations that could
occur over longer time and distance scales depending on the presence or absence of very small rate constants. If there are no rate constants much smaller than those deduced from the Tracer Test Runs, then the extrapolations would flatten out, and colloid-facilitated transport would not be a problem over longer time scales. However, if there are significantly smaller rate constants that were not interrogated by the Tracer Test Runs, then colloid-facilitated transport might still be a problem over longer time scales.

If we consider the ability to observe solute desorption from colloids in the Tracer Test Runs to be equivalent to the ability to observe a 5% difference between the recoveries of the colloids and the colloid-adsorbed solutes (the breakthrough curve data suggest at least a 5% uncertainty), then the minimum colloid filtration rate constant or solute desorption rate constant that can be interrogated in the tracer tests is approximately 0.0002 h\(^{-1}\). This value is calculated from \(\ln(0.95)/(-100 \text{ hr})\), where 0.95 corresponds to a 95% recovery (difference of 5%), and 100 h is approximately the maximum residence time of the CFM tests. This expression comes from a simple manipulation of the expression for the exponential decay of an initial concentration, \(C_0\), associated with a first-order reaction with rate constant \(k\):

\[
\frac{C}{C_0} = e^{-kt}
\]  

(42)

All of the extrapolated mass recoveries vs. time discussed above were based on Eq. (42). Even if the experimental and measurement errors were small enough to observe a 1% difference in recoveries, the minimum observable rate constant would only be \(4.4 \times 10^{-5} \text{ h}^{-1}\), and this rate constant would predict that less than 0.01% colloid-associated radionuclides would still remain adsorbed to colloids after about 25 years. Using a minimum measurable rate constant of 0.0002 h\(^{-1}\), corresponding to a 5% observable difference in recoveries, the prediction would be only about 5 years to reach 0.01% of the solutes remaining adsorbed to colloids. Clearly, with a maximum practical shear zone residence time of around 100 h (beyond which recoveries are not guaranteed because of the ambient flows in the shear zone), the CFM experimental setup has a limited ability to interrogate the very small rate constants that could mean the difference between significant colloid-facilitated transport or no colloid-facilitated transport over safety assessment time scales. The problem is further compounded by the presence of any sorption sites on colloids from which solutes tend to desorb rapidly because this will result in an observed behaviour that completely masks the effects of very slow desorption rates. In effect, if there is any significant observable solute desorption from colloids over the relatively short time scales of the Tracer Test Runs, it will be impossible to see the effects of very slow desorption rates that will matter for safety assessments over long time scales.

The above discussion is not intended to imply that the CFM experimental setup is of no use for obtaining colloid-facilitated transport information relevant to safety assessment time and distance scales. Rather, it is intended to point out the limitations of directly extrapolating the test data to longer time and distance scales. The discussion also helps to provide insights into how future tests might be conducted to better interrogate both colloid filtration rate constants and solute desorption rate constants that might matter in long-term safety assessments. Although a clear scale dependence of colloid filtration rate constants was not apparent from the Tracer Test Runs, such a scale dependence is still very important for safety assessment predictions because, if all colloids are being filtered during transport through the repository system (i.e. no fraction of colloids with extremely slow filtration rate constants exist), colloid-facilitated transport will not be a problem no matter how strongly radionuclides are adsorbed to colloids. The transport time scales achievable in the CFM experimental setup have practical limitations, so suggestions for improvements must necessarily focus on pre-conditioning of the colloids used in the...
injection cocktails and/or on pre-conditioning of the injection cocktails themselves. Two suggestions are put forward here for consideration, although many variations of these, as well as alternative suggestions, are certainly possible:

- Subject the colloids generated by dispersing bentonite in synthetic GTS water to procedures that tend to eliminate or reduce the number of colloids that are more susceptible to filtration prior to injecting them in a CFM field test. For instance, the dispersed colloids could be run through a large laboratory column containing GTS shear zone material, and only the colloids exiting the column could be used in the field injection cocktail. Based on the column residence time and observed column recovery of the colloids, it will be possible to estimate the maximum effective filtration rate constant of the recovered colloids (although this rate constant will not necessarily strictly apply to the shear zone itself).

- Adsorb the target homologues or radionuclides onto the colloids isolated above, and then perform large-scale desorption experiments using shear zone materials in the presence of the colloids to remove homologues or radionuclides that are adsorbed to weaker colloid sorption sites. The maximum effective desorption rate constants associated with homologues or radionuclides that remain adsorbed to the colloids after a certain amount of desorption time could then be estimated, and the remaining colloids and associated homologues could be used as part of an injection cocktail in a GTS field tracer test.

One obvious variation of these suggestions would be to perform a large column transport experiment after absorbing the homologues or radionuclides to the dispersed bentonite colloids and effectively isolating both filtration-resistant colloids and the more strongly-adsorbed solutes in one step. Using an injection cocktail pre-conditioned in these ways in a CFM field test would, in principle, increase the probability of interrogating the small colloid filtration rate constants and small desorption rate constants that will matter over safety assessment time scales.
Selected field tracer experiments were performed in a shear zone in granitic rock at the Grimsel Test Site under quasi-natural flow conditions in a dipole configuration as part of the international Colloid Formation and Migration (CFM) project. The breakthrough curves of conservative tracers, bentonite colloids, homologues and radionuclides in these tests were simulated with different numerical models. The increase of spatial and particularly longer temporal scales compared to the Colloid and Radionuclide Retardation (CRR) project led to significant filtration of colloids and desorption of homologues or radionuclides from the colloids during transport through the shear zone. On that basis, the modelling groups were able to simulate and quantify both processes.

In general, the numerical models each yielded similar transport parameter values for the colloids, homologues and radionuclides. With the 2D GRS approach, the shear zone flow fields were explicitly simulated, and colloid transport was modelled using the same colloid filtration parameters in each simulated test. Also, only a single species-dependent desorption rate constant (single adsorption site) was used to describe homologue or radionuclide desorption from colloids, although this rate constant was allowed to vary for different datasets to obtain the best fits. With the 1D modelling approaches followed by LANL and KTH, the colloid, homologue and radionuclide parameters were all allowed to vary with each test to achieve the best fits to the data, and both one- and two-site adsorption models on colloids with an aging reaction on the colloid surfaces were evaluated for their ability to explain the solute datasets. Despite these differences in modelling approaches, the transport parameter estimates for the colloids and homologues (or radionuclides) were in reasonably good agreement for each of the tests when only a single-site adsorption model was considered (as in the 2D GRS model), suggesting that the parameter estimates were quite robust across the different models.

A major emphasis of the 1D modelling efforts was to evaluate which of several alternative descriptions of homologue or radionuclide desorption processes from colloids best explained the solute breakthrough curves. It was concluded that a two-site adsorption/desorption model for solutes on colloids, typically with an aging process, tended to explain the homologue and radionuclide transport data better than a one-site model (i.e. the inclusion of a second site with one or two additional adjustable parameters was statistically justified for most datasets). Of the 13 homologue and radionuclide datasets considered in this report, a two-site model offered a statistically significant improvement over a one-site model for 8 of the datasets. The five exceptions were Th, Hf, and Tb in Tracer Test Run 08-01, the test with the shortest mean residence time in the shear zone, Hf in Tracer Test Run 10-01, and Am in Tracer Test Run 12-02. Of the 8 datasets best fit with a two-site model, 5 were best explained with a second site that had a much slower desorption rate constant than the first site, and 3 were best explained with a second site that had a faster desorption rate constant than the first site. In 6 of these 8 cases, an aging reaction helped explain the data better than no aging reaction. Intuitively, we would expect that an aging process would result in conversion of adsorbed solute from a faster-desorbing site to a slower-desorbing site, but this was not consistently observed. In the only field-vs.-lab comparison of solute desorption rate constants that was possible for this report, the Am and Pu desorption rate constants estimated for Tracer Test Run 12-02 (when assuming only a single adsorption site on colloids) were in reasonably good agreement with the estimates obtained by Huber et al. (2011) in batch laboratory experiments involving bentonite colloids, radionuclides and fracture filling materials from the GTS shear zone.
The reasons for the inconsistencies between the best-fitting descriptions of the homologue or radionuclide desorption processes from colloids in the different tests are unclear. While there was a general trend of a decreasing desorption rate constant with time scale of the tests if only a one-adsorption-site model was considered, the rate constant for a second site exhibited no clear pattern or trend with test time scale or other test parameters. This result suggests a complexity in the desorption process that probably depends on one or more subtle differences in colloid preparation, tracer cocktail preparation, or perhaps in transport characteristics of shear-zone flow pathways in the different tests.

Extrapolations of the apparent time-scale dependences of the desorption rate constants of the tri- and tetravalent homologues and radionuclides in the CFM tracer tests suggest that all of the homologues or radionuclides should desorb from colloids within a few months or at most a few years, implying that colloid-facilitated transport should not be a problem over safety assessment time and distance scales. However, there is a great deal of uncertainty associated with these extrapolations because the time scales of the tracers tests were too short to effectively interrogate the very slow desorption rate constants that would make a difference in such safety assessments. The scale dependence of colloid filtration rate constants is also very important for safety assessment predictions because even if radionuclides remain strongly adsorbed to colloids, some of the colloids must still be transported over very long distances and times to result in a colloid-facilitated transport problem. While there was no apparent scale dependence of the colloid filtration rate constants in the Tracer Test Runs, we conclude that the time scales of the tracer tests were too short to effectively interrogate the slow filtration rate constants that would make a difference in safety assessments. Some suggestions for how slow filtration rate constants and slow desorption rate constants might be better interrogated in Tracer Test Runs are provided at the end of Section 6.6 of this report.
8 References


9 Glossary

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AGA</td>
<td>Amino-G Acid</td>
</tr>
<tr>
<td>AU</td>
<td>Auflockerungszone (EDZ). The CFM site is located in AU Tunnel, which is named after the EDZ experiment performed there in 1982.</td>
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<tr>
<td>CFM</td>
<td>Colloid Formation and Migration Project</td>
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<td>Colloid and Radionuclide Retardation Experiment</td>
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<td>DAS</td>
<td>Data Acquisition System</td>
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<td>GTS</td>
<td>Grimsel Test Site</td>
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<td>KWO</td>
<td>Kraftwerk Oberhasli AG, operators of the Grimsel hydroelectric plants</td>
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<td>LIBD</td>
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</table>
Appendix A: Corrections for uranine decay in Tracer Test Run 10-03

Purpose of the Corrections

Corrections were made for uranine decay in Tracer Test Run 10-03 to allow estimates of colloid filtration rate constants in this test. If no correction is made for uranine decay, the colloid recovery is calculated to be greater than the uranine recovery (Fig. A-1), which makes it impossible to estimate a meaningful filtration rate constant. Note that it is still possible to estimate desorption rate constants for the homologues from the colloids in Tracer Test Run 10-03 without a uranine decay correction because these estimates are based on comparisons of the colloid and homologue breakthrough curves.

Fig. A-1: Normalised breakthrough curves of tracers in Tracer Test Run 10-03 (concentrations divided by injection mass).

The bentonite colloid concentrations were determined indirectly by measuring Al and subtracting the background Al concentration. Note the low/short tail of the uranine, which causes the colloids, Hf, and Th to have higher recoveries than the uranine, making it impossible to obtain meaningful estimates of colloid filtration rates.
Assumptions/approaches
The assumptions used to make corrections for uranine decay in the injection loop in Tracer Test Run 10-03 are as follows:

1. Uranine decay occurs only in the injection loop/circuit.
   **Rationale:**
   a) There was never any evidence of uranine decay in tracer tests prior to 10-03 (nearly complete recovery in most tests), so it seems unlikely that decay would suddenly start occurring in the shear zone in Tracer Test Run 10-03.
   b) Tracer Test Runs 11-01, 11-02 showed an obvious difference between the injection functions of AGA and uranine, and the only possible explanation for such a difference is some sort of uranine decay process that must have occurred in the injection loop.
   c) Uranine recirculation tests were performed in the recirculation loop excluding the borehole interval and showed significant degradation of fluorescence over time.

2. The difference between the AGA and uranine injection functions in Tracer Test Run 11-02 can be used to estimate a decay constant for uranine that can also be applied to Tracer Test Run 10-03 to make corrections for uranine decay in that tracer test.
   **Rationale:**
   The injection loop in Tracer Test Run 11-02 had the same volume and same basic components as the injection loop in Tracer Test Run 10-03, so the decay rate of the uranine should have been approximately the same in the two tests. A minor difference between the injection loop in the two tests was that the recirculation rate in Tracer Test Run 10-03 was 39.5 ml/min, and the recirculation rate in Tracer Test Run 11-02 was 29 ml/min. It is assumed that this slight difference in recirculation rate did not affect the uranine decay rate. The injection loop pH also differed in the two tests, which is significant because the lower pH of the injection loop in Tracer Test Run 10-03 was considered to be a potential explanation for apparent uranine decay (low pH can suppress uranine fluorescence). However, the pH in the injection loop of Tracer Test Run 11-02 was significantly higher than in Tracer Test Run 10-03 and significant decay was still observed. Also, the pH in the injection loop of Tracer Test Run 10-02 (another test with the same injection loop volume and configuration) was lower than in Tracer Test Run 10-03, but the uranine recovery was still substantially higher in Tracer Test Run 10-02 (~ 90 %) than in Tracer Test Run 10-03 (~ 20 %). It is therefore apparent that pH does not provide an adequate explanation for the observed uranine decay.

3. As an alternative method to correct for uranine decay, the turbidity injection function in Tracer Test Run 10-03 can be used to estimate the uranine injection function based on the observed differences between the uranine and turbidity injection functions in Tracer Test Run 10-01.
   **Rationale:**
   Although the injection loop volumes were different in Tracer Test Runs 10-01 and 10-03 (2'000 vs. 3'000 ml), the recirculation rates were similar (45 – 50 ml/min in Tracer Test Run 10-01 vs. 39.5 ml/min in Tracer Test Run 10-03), so it is reasonable to assume that the ratio of the observed injection decay constants for uranine and turbidity in Tracer Test Run 10-01 would also apply to Tracer Test Run 10-03. Figs. A-2 and A-3 show the measured (non-corrected) uranine and turbidity injection functions in Tracer Test Runs 10-01 and 10-03.
Fig. A-2: Uranine (blue) and turbidity (green) injection functions in Tracer Test 10-01.

Fig. A-3: Uranine (blue) and turbidity (green) injection functions in Tracer Test 10-03.
Correction using differences between AGA and uranine injection functions in Tracer Test Run 11-02

Fig. A-4 shows the injection loop concentrations as a function of time for both AGA and uranine in tracer Tracer Test Run 11-02. The log-linear slope analyses of these data indicated that the slopes through the first 289 hours (when a relatively high net injection rate was imposed) were \(-0.000868\) \(\text{h}^{-1}\) for the AGA and \(-0.009694\) \(\text{h}^{-1}\) for the uranine. If the slope for the AGA is taken as a reflection of the true flow rate through the injection interval, then the difference between the two slopes (0.00883 \(\text{h}^{-1}\)) provides an estimate of the first-order degradation rate constant for the uranine in the injection interval. The fact that the log-linear plot of the uranine concentration is roughly linear implies a first-order uranine decay process (the plot would have curvature if the process were not first order).

Fig. A-4: Log AGA (red) and uranine (blue) concentrations in the injection loop vs. time in Tracer Test Run 11-02.

The uranine injection function in Tracer Test Run 10-03 is shown in Fig. A-5, along with estimates of the flow rate through the injection interval vs. time based on the observed concentration decline of the uranine. Note that the flow rate was estimated separately for three time periods based on changes in slope of the \(\ln(\text{concentration})\) vs. time history, where slope = \(-Q/V\), with \(Q\) = volumetric flow rate \([\text{ml/min}]\) and \(V\) = volume of injection interval \((3'000\ \text{ml})\). This calculation assumes a well-mixed injection interval. The slopes were \(-0.0146\) \(\text{h}^{-1}\) for \(0 – 130\) h, \(-0.0184\) \(\text{h}^{-1}\) for \(130 – 250\) h, and \(-0.0135\) \(\text{h}^{-1}\) for \(> 250\) h. However, the actual flow rates through the injection interval were less than these apparent flow rates because the uranine was decaying in addition to being swept out of the injection interval by flow. The uranine decay constant of 0.00883 \(\text{h}^{-1}\) estimated from Tracer Test Run 11-02 (see above) translates to an effective flow rate of 0.442 ml/min due to decay in Tracer Test Run 10-03. This effective flow rate due to decay must be subtracted from the observed flow rates to obtain the actual flow rates as a function of time in Tracer Test Run 10-03 (alternatively, the decay constant could be added to each of the slopes above and then the flow rates could be calculated from slope = \(-Q/V\) to get the same result). The estimated actual flow rates then become 0.289, 0.479, and 0.234 ml/min for the three different time periods in Tracer Test Run 10-03, respectively.
The next step in the correction was to match the extraction breakthrough curve of Tracer Test Run 10-03 using the observed uranine injection function with the estimates of the actual flow rates through the injection interval, as determined above. This matching process was accomplished as follows. First, the mean residence time and Peclet number (length/dispersivity) in the shear zone were estimated using the RELAP semi-analytical model assuming that the initial apparent injection flow rate in Tracer Test Run 10-03 (0.73 ml/min) was the actual injection flow rate throughout the test (RELAP cannot simulate different apparent and actual injection flow rates). The resulting estimates of mean residence time and Peclet number were 64 h and 15, respectively, with Fig. A-6 showing the fit to the observed uranine extraction curve. The uranine recovery based on these calculations was ~ 19 – 20 % (i.e. the modelled breakthrough curve had to be multiplied by ~ 0.2 to match the observed breakthrough curve), which is in good agreement with the recovery calculated directly from the observed breakthrough curve.

The RELAP estimates of mean residence time and Peclet number were then used as initial estimates in the numerical model described in the main body of this report, with the observed uranine injection function being used as the concentration history in the injection interval and the estimated actual injection flow rate into the shear zone (see above) being used as the simulated injection flow rate. With these assumptions, the best-fitting mean residence time and Peclet number were found to be 60 h and 17, respectively. However, it was found that a better match to the observed breakthrough curve could be obtained by assuming that the injection flow rate was a constant 0.289 ml/min (the initial estimated flow rate) instead of the time-varying flow rates deduced in the analysis described above because the deduced increase in the injection flow rate from 0.289 ml/min to 0.479 ml/min at around 110 hours into the test resulted in a significant inflection in the simulated extraction breakthrough curve at around 150 hours that simply was not observed. This inflection was the result of the significant change in the rate at which tracer was injected into the shear zone at ~ 110 hours plus the significant change in dilution factor at the extraction location once this higher injection rate took effect. Thus, the
mean residence time and Peclet number estimates of 60 hrs and 17 were obtained assuming a constant injection flow rate of 0.289 ml/min throughout the test. The resulting uranine breakthrough curve is shown in Fig. A-6 as the curve labelled "numerical model". The estimated mass participation in the test using these assumptions was about 60 % (i.e. the simulated breakthrough curve had to be multiplied by 0.6 to match the observed extraction breakthrough curve).

![Fig. A-6: RELAP and numerical model fits to uranine breakthrough curve in tracer Tracer Test Run 10-03.](image)

Note that the cyclic fluctuations in the data were not fitted. In the RELAP model it was assumed that the injection flow rate was 0.73 ml/min (first flow rate in Fig. A-5) with the injection concentration history of Fig. A-5, and in the numerical model it was assumed that the injection flow rate was ~ 0.29 ml/min with the same injection concentration history.

The final step in the correction was to use the numerical model to simulate the uranine breakthrough curve that would have been observed if the uranine had not decayed in the injection loop. This was accomplished by assuming the same initial concentration of uranine in the injection loop as in the decaying case but simulating that the injection concentration declined in accordance with the deduced injection flow rate of 0.289 ml/min instead of the more rapid observed concentration decline. The injection concentration function in this case was $C = C_0 \exp(-0.289*60*t/3'000)$, where $t$ is time in hours, 60 is the conversion from minutes to hours, and 3'000 is the volume of the injection loop in ml. The mean residence time and Peclet number in the shear zone were assumed to be 60 hrs and 17, respectively, the same values obtained by matching the observed extraction function when the observed injection function was assumed as the injection concentration history. The resulting breakthrough curve was multiplied by 0.6 to match the mass participation deduced from the numerical model match to the extraction function using the observed injection function. The resulting corrected extraction function is shown in Fig. A-7.
Fig. A-7: Modelled extraction breakthrough curve in Tracer Test Run 10-03 using the numerical model with corrections for uranine decay.

Note that the corrected uranine breakthrough curve is considerably higher than the observed colloid breakthrough curve except at late times, and the dip below the colloid data at late times is relatively minor. Using this corrected uranine extraction breakthrough curve, it is possible to obtain reasonable estimates of colloid transport parameters in Tracer Test Run 10-03.

**Correction using differences between turbidity and uranine injection functions (in Tracer Test Run 10-01)**

As an alternative analysis, it is possible to use the differences in the turbidity and uranine injection functions in tracer Tracer Test Run 10-01 as the basis for estimating what the uranine injection function should have looked like in Tracer Test Run 10-03. Fig. A-8 shows the uranine and turbidity injection functions (natural log of concentrations vs. time) in Tracer Test Run 10-01 over the first 150 hours of the test, which is when the vast majority of the tracer mass was extracted at the Pinkel surface packer. It is interesting that the injection functions suggest that the uranine flowed out of the injection interval faster than the colloids (assuming that colloid concentrations are proportional to turbidity). If we assume that the same ratio of slopes (1.74 times greater slope for the uranine) applies in Tracer Test Run 10-03, then we can multiply the slope of the Tracer Test Run 10-03 turbidity injection function by 1.74 to obtain an estimate of the uranine injection function for Tracer Test Run 10-03. Fig. A-9 shows the turbidity injection function for 10-03 (natural log of concentrations vs. time), with a fitted slope of -0.0032 h⁻¹. If we multiply this slope by 1.74, we get a slope of -0.00556 h⁻¹ for the uranine, which yields an injection flow rate estimate of 0.278 ml/min. This flow rate estimate is in very good agreement with the estimate of 0.289 ml/min at the start of Tracer Test Run 10-03 using the uranine decay correction described above. Furthermore, the near-constant slope of the turbidity function suggests that the injection flow rate may have been more constant than the observed uranine injection function indicated. Perhaps the uranine decay rate in the injection loop fluctuated, which would make it appear that the injection flow rate fluctuated. This may
explain why the observed extraction curve could not be matched very well when the injection flow rate was assumed to fluctuate in accordance with the observed uranine injection function in the preceding analysis.

![Graph](image)

**Fig. A-8:** Uranine and turbidity injection functions in Tracer Test Run 10-01, with linear fits to the data.

![Graph](image)

**Fig. A-9:** Turbidity injection function in Tracer Test Run 10-03, with linear fit to the data.
When an injection flow rate of 0.278 ml/min is used with the observed uranine injection function (decay included), the observed uranine extraction curve can be matched very well assuming a uranine mass participation of ~ 60 % (i.e. essentially identical to the 60 % mass participation in the preceding analysis, which is not surprising given that the deduced injection flow rates are very similar). Furthermore, when a uranine injection function that assumes no decay is used in the numerical model with an injection flow rate of 0.278 ml/min, essentially the same corrected uranine extraction function is obtained as in Fig. A-7. Thus, the turbidity correction and the correction based on the differences in the observed injection functions of uranine and AGA in Tracer Test Run 11-02 lead to essentially the same corrected uranine extraction breakthrough curve (the curve in Fig. A-7). This extraction breakthrough curve and a mass participation of 60 % were used as the basis for estimating colloid transport parameters in Tracer Test Run 10-03.

The turbidity meter appears to respond to both tracer and colloid concentration, probably in a non-linear fashion and the different responses seen in the tests emphasises the importance of obtaining good quality turbidity and fluorescence injection loop measurements in future tests and also in trying to obtain a few samples from the injection loop to verify the injection functions deduced from the online measurements.

The method used within the analyses presented in the main body of the report (based on the difference between the measured AGA and uranine injection functions) is shown as a flowchart in Fig. A-10.
Fig. A-10: Flowchart for correction of the Tracer Test Run 10-03 uranine concentration.
Appendix B: Variations of the GRS 2D model scale

Prior to the model simulations reported in the main text, exploratory simulations of Tracer Test Runs 08-02 and 08-01 using a smaller model geometry were carried out by GRS, the geometry for which is depicted in Fig. B-1. These simulations showed that transport paths are disconnected when the injection and extraction flow velocities become comparable (Fig. B-2), leading to spurious mass losses over virtual boundaries. Therefore, the height and the length of the model were doubled without changing any of the boundary conditions or the distance between the inflow and the outflow location for the simulations discussed here.

Fig. B-1:  Geometry and hydrogeological/transport-related boundary conditions of the 2D computer model. 
For details about the given boundary conditions (colours) see Fig. 14.

Fig. B-2:  Steady-state velocity direction field at outflow rates of 50 ml/min for the small model (ca. 10 m by 3 m). 
For illustration purposes, the length of the arrows is not scaled with the magnitude of the velocity.
For an outflow rate of 50 ml/min and the larger model geometry, none of the transport pathways were disconnected from the outflow area as depicted in Fig. B-3. GRS ran additional comparative model simulations for the outflow rate of 50 ml/min as well as for 165 ml/min and determined the recovered mass fractions at the outflow. For these calculations a non-sorbing tracer (denoted as "Tracer"), a colloid-bound tracer regarding desorption from colloids and adsorption on fracture filling material during transport (denoted as "Tracer + Colloids and Sorption") and a colloid-bound tracer regarding additionally colloid filtration (denoted as "Tracer + Colloids and Sorption + Filtration") were considered. All simulations based on the large model geometry resulted in higher recovered mass fractions than those based on the smaller model geometry, as illustrated in Fig. B-4 and Tab. B-1. Irrespective of geometry, the total injected tracer mass fraction is recovered at the outflow only if the highest outflow rate of 165 ml/min is used. However, for the lower outflow rate of 50 ml/min, the recovered mass fraction was increased from approx. 65 % for the small model geometry to 95.7 % for the large model geometry, i.e. a nearly complete recovery.

Fig. B-3: Steady-state velocity direction field at outflow rates of 50 ml/min for the large model (ca. 20 m by 6 m).

For illustration purposes, the length of the arrows is not scaled with the magnitude of the velocity.
Fig. B-4: Time-dependent recovery of the injected tracer mass for an extraction rate of 50 ml/min.

The solid lines represent the model simulations for the small model geometry, the dashed lines represent the model simulations for the large model geometry. The dashed black line indicates the total injected amount of the tracer. See text for further explanation.

Tab. B-1: Recovered mass fractions for different simulation runs using different outflow rates and considering different processes.

n.e. = not examined.

<table>
<thead>
<tr>
<th></th>
<th>Small model</th>
<th>Large model</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[kg]</td>
<td>[%]</td>
<td>[kg]</td>
<td>[%]</td>
</tr>
<tr>
<td>10 ml Tracer</td>
<td>2.9 × 10^{-6}</td>
<td>21</td>
<td>5.08 × 10^{-6}</td>
<td>36.8</td>
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<tr>
<td>Tracer + Colloids and Sorption</td>
<td>1.9 × 10^{-6}</td>
<td>14</td>
<td>n.e.</td>
<td></td>
</tr>
<tr>
<td>Tracer + Colloids and Sorption + Filtration</td>
<td>7.6 × 10^{-7}</td>
<td>5.4</td>
<td>n.e.</td>
<td></td>
</tr>
<tr>
<td>50 ml Tracer</td>
<td>8.9 × 10^{-6}</td>
<td>65</td>
<td>1.32 × 10^{-5}</td>
<td>95.7</td>
</tr>
<tr>
<td>Tracer + Colloids and Sorption</td>
<td>7.2 × 10^{-6}</td>
<td>52</td>
<td>1.09 × 10^{-5}</td>
<td>79.0</td>
</tr>
<tr>
<td>Tracer + Colloids and Sorption + Filtration</td>
<td>4.7 × 10^{-6}</td>
<td>34</td>
<td>7.56 × 10^{-6}</td>
<td>54.8</td>
</tr>
<tr>
<td>165 ml Tracer</td>
<td>1.4 × 10^{-5}</td>
<td>99</td>
<td>1.38 × 10^{-5}</td>
<td>99.9</td>
</tr>
<tr>
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<td>1.3 × 10^{-5}</td>
<td>91</td>
<td>n.e.</td>
<td></td>
</tr>
<tr>
<td>Tracer + Colloids and Sorption + Filtration</td>
<td>1.0 × 10^{-5}</td>
<td>75</td>
<td>n.e.</td>
<td></td>
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</table>
The impact of enlarging the model is most significant in the case of low extraction rates, but recovery remains $<< 100\%$ even for the large model. We expanded the model area, therefore, to 20.5 m by 20.5 m. Even this large model area does not prevent the transport pathways being disconnected from the outflow location. Now, even at the left boundary the pathways are directed out of the model area (Fig. B-5). This implies that a complete recovery of the injected tracer mass at the outflow would only be achieved by a reduction of the inflow rate, if possible at all.

Fig. B-5: Steady-state velocity direction field at outflow rates of 10 ml/min for the large model (20.5 m by 20.5 m).

For illustration purposes, the length of the arrows is not scaled with the magnitude of the velocity.

With these variations of the model scale, it was demonstrated that the model size has a strong impact on the flow and transport simulations as can be seen in the recovered mass fractions for the small and the large model.