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Geochemical Evolution of the L/ILW Near-field

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Summary

The deep geological repository for low- and intermediate-level radioactive waste (L/ILW) and the emplacement rooms for long-lived intermediate-level radioactive waste (ILW) contain large amounts of cement based materials (concrete, mortar) used for waste conditioning, tunnel support (shotcrete) and the backfill of cavities. The waste inventory is composed of a wide range of organic and inorganic materials. This study describes the spatial and temporal geo-chemical evolution of the cementitious near-field, and the interactions with the technical barriers and the surrounding host rock.

The spatial and temporal evolution of the cementitious near-field is governed by several coupled externally and internally induced processes. The development of saturation by groundwater ingress from the host rock is of vital importance for many processes. Full or partial desaturation of the emplacement caverns, of the adjacent host rock or of the technical barriers in the access tunnels will reduce or even prevent the transport of dissolved species and therefore significantly impede chemical reactions. Saturation of the near-field is controlled by the inflow of water from the host rock, by the transport of partly dissolved gases from the near-field into the host rock and in the engineered gas transport system, and by the transport of humidity in the gas phase. The production of gas by anoxic corrosion of metals and by microbial degradation of organic wastes also consumes water. In addition, the mineral reactions which give rise to concrete degradation, such as carbonation or alkali-silica-aggregate reactions may also consume or produce water, respectively. However, these reactions (as well as the microbially driven gas production) require only a minimum humidity in the gas phase in the near-field so that a liquid film forms along mineral surfaces in which dissolved substances may react with each other.

In this study the description of cement degradation is consistent with that in previous studies. It is expected that the degradation of the cementitious near-field will occur in several phases. The first phase of cement degradation is related to the hydration of cement minerals.

In this phase the pore water has a pH of 13 or even higher as a consequence of the high content of dissolved alkali hydroxides. This phase will persist only for a short period of time, especially in situations where advective transport dominates.

A constant pH of 12.5, buffered by the equilibrium with portlandite, determines the second phase of the cement degradation. The alkali concentration is reduced by mineral reactions and/or solute transport. This phase will persist for a long time, especially when clogging of the cement-clay interface occurs and/or the transport is governed by diffusion.

In the third phase of the cement degradation the portlandite is completely dissolved due to the reaction with silicates/aluminates present in the near-field and carbonate in the groundwater of the host rock or associated with reactive waste materials. The pore water is in equilibrium with calcium-silicate-hydrates (C-S-H) which gives rise to a pH value near 11 or even lower. The Ca/Si ratio of C-S-H will change towards lower values (Ca/Si < 0.84).

In a very late phase of the cement degradation the formation of carbonates, clays or zeolites will cause the pH to drop to near neutral values. The geochemical evolution of the cementitious near-field is influenced by various processes. The most important ones are considered to be the interactions with the host rock, the interactions with waste, the degradation of cement minerals by alkali-silica-aggregate reactions and by cement carbonation.

The diffusive and advective exchange of pore water between the cementitious near-field and the host rocks gives rise to mineral reactions and changes of the pore water pH. Mineral reactions at the interface were investigated with the help of numerical models. The clay minerals of the host rock are dissolved and transformed into secondary minerals (e.g. zeolites) up to a distance of a few dm in 100'000 years (period considered in safety analysis for the L/ILW repository). For the case of higher water fluxes in the host rock this zone extends possibly up to 1 m over the same time scale. The sorption capacity of host rocks with low water fluxes and where transport is diffusion-dominated is not affected by these mineral changes. For host rocks where transport occurs mainly through fissures (Marl), the effect of the mineral formation on the sorption capacity of the host rock is taken into account in the provisional safety analyses for Stage 2 of the Sectoral Plan.

Beyond this transition zone and further into the host rock, a zone will develop with an elevated pH of 8 – 9, but without significant mineralogical changes. This zone extends a few meters into the host rock in the case of a diffusive transport regime, whereas in the downstream direction it may reach more than thousand meters in the case of higher water fluxes and very low host rock porosities. For a diffusion dominated regime the portlandite in the cementitious near-field will be dissolved up to a distance of 2 m from the near-field – host rock interface. In the region where portlandite dissolution occurred, the concrete pore water pH will drop to values corresponding to the third phase of the cement degradation. In the case of higher water fluxes from single facial units of the host rock into the caverns the portlandite dissolution front may extend a further few meters downstream in 100'000 years, while in the portlandite-depleted region all the cement minerals will completely degrade with time.

If the concrete aggregate contains SiO_2, the cement minerals may degrade due to an alkali-silica-aggregate reaction. Silicon dioxide from concrete aggregates will react with portlandite and form C-S-H phases. This causes a decrease of the pore water pH and results in a complete dissolution of the cement minerals in the long term. The temporal progression of this reaction is poorly known. From available kinetic constants of mineral dissolution reactions it is inferred that the alkali-silica-aggregate reaction could be relatively fast, i.e. concrete degradation might occur within some hundreds to a thousand years.

The degradation of organic waste in a cementitious repository will presumably happen predominantly by methanogenesis which will produce CH_4 and CO_2. Due to the unfavorable conditions (high pH), the microbial activity driven degradation process will be low. The released CO_2 will degrade the concrete surrounding the organic waste by carbonation. A prediction of the degradation rates of the organic waste is difficult since the rates depend not only on pH but also on the availability of water and the presence of certain nutrients such as phosphor and nitrogen. All of these factors limit the microbially mediated degradation of organic compounds. Based on our current knowledge it can be assumed that low-molecular weight organic materials will degrade within about 1'500 years. The degradation rates of the high-molecular-weight organic substances (polymeric materials) are highly uncertain. It is expected that the degradation may take at least some thousands of years, but probably up to several tens or hundreds of thousands of years, if they degrade at all. The effects of radionuclide complexation in a cementitious environment are taken into account in preparing the corresponding sorption database used in the provisional safety analyses for Stage 2 of the Sectoral Plan.

Some organic waste materials will react with the surrounding materials, assuming that water availability is not a limiting factor. Particularly important is the anoxic corrosion of metals (incl. steel) which can produce large amounts of H_2. Corrosion products (e.g. rust) could contribute to the degradation of the surrounding cement minerals. Note that this again requires a connected water phase in the pores which allows dissolved substances to be transported. The general

description of concrete degradation has not changed in this work compared to previous studies. A consequence is that the current concepts for radionuclide transport (retention) and radionuclide solubilities are not changed. It is therefore recommended to retain previously used descriptions for radionuclide solubility and radionuclide sorption (K_d-concept). In particular, the occurrence of colloid facilitated radionuclide transport is considered to be very unlikely since the host rock and near-field pore water chemistries give rise to very low colloid stabilities which will significantly reduce colloid concentrations.

Zusammenfassung

In einem Tiefenlager für schwach- und mittelaktive Abfälle (SMA) und in den Lagerkavernen für langlebige mittelaktive Abfälle (LMA) werden grosse Mengen an zementhaltigen Materialien (Mörtel, Beton) für die Konditionierung der Abfälle, für den Ausbau der Einlagerungskavernen (Spritzbetonschale) und für die Verfüllung von Hohlräumen verwendet. Das Abfallinventar in einem solchen "Zementlager" ist durch eine grosse Vielfalt an organischen und anorganischen Materialien charakterisiert. Die vorliegende Studie beschreibt die räumliche und zeitliche geochemische Entwicklung des Zement-Nahfelds und seine Wechselwirkungen mit technischen Barrieren und dem angrenzenden Wirtgestein.

Das räumliche und zeitliche Auftreten der Evolutionsstadien im Zement-Nahfeld wird durch zahlreiche miteinander gekoppelte innere und äussere Einflüsse gesteuert. Von zentraler Bedeutung für viele Prozesse ist die Entwicklung der Wassersättigung. Eine teilweise oder vollständige Entsättigung der Lagerkavernen, der angrenzenden Wirtgesteinsbereiche oder der Barrierensysteme in den Zugangsstollen verlangsamt oder verhindert den Transport gelöster Stoffe in der Wasserphase und limitiert so chemische Reaktionen. Die Wassersättigung wird vom Zustrom von Porenwasser aus dem Wirtgestein, dem Transport von z.T. in Wasser gelösten Gasen aus dem Nahfeld ins Wirtgestein und innerhalb des Engineered Gas Transport System, sowie dem Feuchtigkeitstransport in der Gasphase reguliert. Die Produktion von Gas durch bakteriellen Abbau von organischen Abfällen und der anoxischen Korrosion von Metallen setzt nicht nur Gas frei, sondern verbraucht auch Wasser. Weiterhin können die zur Degradierung zementhaltiger Materialien führenden Mineralreaktionen Wasser verbrauchen oder auch freisetzen. Solche Reaktionen benötigen aber (wie auch die bio-chemische Gasproduktion) in jedem Fall ein Mindestmass an Gasfeuchte um einen Wasserfilm an Mineraloberflächen ausbilden zu können, in welchem gelöste Stoffe miteinander reagieren können.

Im Vergleich zu früheren Betrachtungen ändert sich die generelle Beschreibung der Zementdegradation in dieser Studie nicht. Es wird erwartet, dass das Zement-Nahfeld verschiedene geochemische Stadien durchläuft.

Das erste Stadium ist mit der Hydratisierung der Zementmaterialien verbunden. Das Porenwasser ist durch hohe pH-Werte (13 oder höher) und erhöhte Werte von gelösten Alkalihydroxiden charakterisiert. Dieses Stadium wird insbesondere in Situationen mit advektivem Transport nicht sehr lange andauern.

Im zweiten Stadium wird der pH-Wert des Porenwassers durch das Gleichgewicht mit Calciumhydroxid (Portlandit) auf einem Wert von etwa 12.5 gepuffert. Die Konzentrationen der gelösten Alkalihydroxide sind durch Transportprozesse und/oder Mineralreaktionen abgesenkt. Dieses Stadium wird insbesondere in Situationen mit einer verringerten Porosität an der Zement-Tongrenzfläche und/oder in Situationen mit diffusivem Transport sehr lange dauern.

Im dritten Stadium ist der Portlandit durch Reaktionen mit Silikaten/Aluminaten und Karbonaten des Wirtgesteins oder reaktiver Abfälle verbraucht. Der pH-Wert des Porenwassers wird durch das Gleichgewicht mit Calcium-Silikat-Hydraten (C-S-H) auf Werte nahe 11 oder sogar darunter gehalten, wobei sich die Zusammensetzung der C-S-H-Phasen in Richtung eines geringeren Ca/Si Verhältnisses verschiebt (Abreicherung von $Ca(OH)_2$ aus den C-S-H-Phasen bis Ca/Si < 0.84).

In einem sehr späten Stadium werden durch die Bildung von Karbonaten, Tonmineralen oder Zeolithen langfristig nahezu neutrale pH-Werte erreicht.

Die geochemische Entwicklung des Zementnahfelds wird durch verschiedene Prozesse beeinflusst. Als wichtig erachtet werden die Wechselwirkungen mit dem Wirtgestein, die Wechselwirkungen mit den eingelagerten Abfällen, die Degradierung von Zementmaterialien durch Alkali-Kieselsäure-Reaktionen und die Karbonatisierung.

Der diffusive und advektive Austausch von Porenwässern zwischen Zementmaterialien und dem Wirtgestein führt zu Mineralreaktionen und Änderungen des pH-Werts im Porenwasser. Diese Reaktionen wurden mit Hilfe von numerischen Modellen untersucht. Ausgehend von den Materialgrenzflächen werden in den Wirtgesteinen Tonminerale bis zu einigen dm in 100'000 Jahren (Betrachtungszeitraum der Sicherheitsanalyse für ein SMA-Lagers), bei grossen Wasserflüssen im Wirtgestein vielleicht auch bis zu 1 m aufgelöst und in andere Minerale (z. B. Zeolithe) umgewandelt. Die Sorptionskapazität des Wirtgesteins in dem der Wasserfluss langsam ist und die Diffusion den Transport dominiert, wird durch die Mineralumwandlungen nicht beeinflusst. Der Einfluss auf die Sorptionskapazität der geklüfteten Wirtgesteine, wird in den provisorischen Sicherheitsanalysen für SGT E2 berücksichtigt.

Daran anschliessend wird sich eine Zone mit einem leicht erhöhten pH-Wert im Porenwasser von 8 – 9 entwickeln, welche noch nicht mit signifikanten mineralogischen Änderungen verbunden ist. Diese Zone erstreckt sich in einem diffusiven Transportregime über einige Meter um das Lager, während sie sich bei advektivem Transportregime mit höheren Wasserflüssen und einer sehr niedrigen Porosität des Wirtgesteins auch über mehr als tausend Meter in Abstromrichtung ausbreiten kann. Im Zementlager selbst könnte der Portlandit in einem diffusiv dominierten Transportregime bis zu einer Entfernung von etwa 2 m von der Grenzfläche zum Wirtgestein aufgelöst werden. Hinter der Auflösungsfront sinkt der pH des Porenwassers ab und das dritte Stadium der Betondegradierung wird erreicht. Im Falle von grösseren Wasserflüssen von einzelnen lithofaziellen Einheiten des Wirtgesteins in die Kavernen könnte sich die Portlanditauflösungsfront in 100'000 Jahren einige Meter in Fliessrichtung verschieben, wobei hinter der Front die Zementmaterialien mit der Zeit vollständig degradiert werden.

Falls Beton kieselsäurehaltige Zuschlagstoffe enthält können Zementmaterialien durch die Alkali-Kieselsäure-Reaktionen degradiert werden. Hierbei reagieren kieselsäurehaltige Zuschläge mit Portlandit und bilden C-S-H Phasen. Dieser Prozess führt zum Absinken des pH-Werts im Porenwasser und wird langfristig zu einer vollständigen Auflösung der Zementmaterialien führen. Über den längerfristigen zeitlichen Verlauf dieser Reaktion ist wenig bekannt. Die Bewertung bekannter Reaktionsgeschwindigkeiten lässt allerdings den Schluss zu, dass die Zementdegradation durch diesen Prozess relativ schnell, d.h. in einigen hundert bis tausend Jahren erfolgen könnte.

Die Degradierung organischer Abfälle in einem Zementlager wird vermutlich überwiegend mittels Methanogenese erfolgen, wobei CO_2 und CH_4 freigesetzt werden. Infolge der ungünstigen Lebensbedingungen (hohe pH-Werte) wird die für die Degradierung notwendige mikrobielle Aktivität sehr gering sein. Das freigesetzte CO_2 wird das die Abfälle umgebende Zementmaterial mittels Karbonatisierung degradieren. Die Degradierungsraten der organischen Abfälle sind schwer vorherzusagen, da sie neben dem pH-Wert von weiteren schlecht quantifizierbaren Faktoren wie der Verfügbarkeit von Wasser und bestimmten Nährstoffen wie Phosphor und Stickstoff abhängen. Diese Faktoren wirken auf die mikrobiologisch gesteuerte Degradierung limitierend. Basierend auf dem heutigen Kenntnisstand lässt sich vermuten, dass niedermolekulare organische Materialien innerhalb von etwa 1'500 Jahren abgebaut werden. Die Abbauraten hochmolekularer organischer Substanzen sind mit grossen Unsicherheiten belastet. Es wird erwartet dass der Abbau mindestens einige tausend Jahre benötigt, aber eher bis zu einigen zehn- oder gar hunderttausend Jahren dauern könnte. Der Einfluss der Radionuklidkomplexierung in einer zementhaltigen Umgebung, wird bei der Erstellung der entsprechenden Sorptionsdatenbasis, welche für die provisorische Sicherheitsanalyse angewandt wird, berücksichtigt.

Einige anorganische Abfälle werden, genügend Wasser vorausgesetzt, mit den umgebenden Materialien reagieren. Herauszuheben ist hier die anoxische Korrosion von Metallen (inkl. Stahl), welche eine erhebliche Menge an H_2 produzieren kann. Die Korrosionsprodukte (z. B. Fe_3O_4, FeOOH) wiederum können zur Degradierung der umgebenden Zementmaterialien beitragen. Voraussetzung ist wiederum eine Wasserphase, in der gelöste Stoffe transportiert werden können.

Im Vergleich mit früheren Arbeiten hat sich die generelle Beschreibung der Zementdegradation nicht geändert. Damit sind auch die sich ergebenden Konsequenzen für den Radionuklidtransport (Retention) und die Radionuklidlöslichkeiten gleich geblieben. Es wird deshalb empfohlen, die bisher verwendeten Ansätze bezüglich der Beschreibung der Radionuklidlöslichkeit und der Radionuklid-Sorption (K_d-Konzept) beizubehalten. Ebenso wird der kolloidgetragene Radionuklidtransport als sehr unwahrscheinlich erachtet, da die Wirtgestein- und die Nahfeldporenwasserchemie weiterhin zu sehr geringer Kolloidstabilität führen und Kolloidkonzentrationen dementsprechend sehr niedrig sind.

Résumé

D'importantes quantités de matériaux cimentaires (mortier, béton) sont utilisées dans les dépôts en profondeur destinés aux déchets de faible et de moyenne activité (DFMA) et dans les cavernes de stockage pour les déchets de moyenne activité à vie longue (DMAVL). Ces matériaux sont employés dans le cadre du conditionnement des déchets, de l'aménagement des cavernes de stockage (revêtement en béton projeté) et du remblayage des structures sou-terraines. L'inventaire des déchets dans un tel dépôt est caractérisé par une grande variété de matériaux organiques et anorganiques. La présente étude décrit l'évolution géochimique, dans l'espace et dans le temps, du champ proche composé de matériaux cimentaires (ci-dessous «champ proche»), ainsi que ses interactions avec les barrières techniques et la roche d'accueil avoisinante.

Les différents stades de l'évolution, spatiale et temporelle, du champ proche sont fonction de nombreux facteurs interconnectés, aussi bien internes qu'externes. L'évolution de la saturation joue en l'occurrence un rôle central pour de nombreux processus. Une désaturation partielle ou totale des cavernes de stockage, de certaines zones de la roche d'accueil et des systèmes de barrières dans les galeries d'accès ralentit, voire empêche le transport des substances dissoutes dans la phase aqueuse et limite ainsi les réactions chimiques. La saturation en eau dépend de différents facteurs: afflux d'eau interstitielle provenant de la roche d'accueil, transport de gaz partiellement dissous dans l'eau entre le champ proche et la roche d'accueil voisine ainsi qu'à l'intérieur du système aménagé de transport des gaz («Engineered Gas Transport System») et enfin transport de l'humidité durant la phase gazeuse. La dégradation bactérienne de déchets organiques et la corrosion anoxique des métaux génèrent non seulement des gaz, mais nécessitent également de l'eau. En outre, les réactions minérales aboutissant à la dégradation de matériaux cimentaires peuvent tantôt consommer, tantôt dégager de l'eau. A noter que de telles réactions nécessitent dans tous les cas un minimum d'humidité dans la phase gazeuse (à l'instar de la production de gaz biochimique) afin qu'une pellicule d'eau puisse se former sur la surface minérale, permettant aux substances dissoutes de réagir entre elles.

La description générale de la dégradation du ciment faite dans la présente étude ne s'écarte guère des observations antérieures. On escompte que la géochimie du champ proche passera par différents stades.

Le premier stade correspond à l'hydratation des minéraux du ciment. L'eau interstitielle se caractérise par un pH élevé (13 ou supérieur) et des teneurs élevées en hydroxydes alcalins dissous. Cette phase ne devrait pas durer très longtemps, surtout en cas de transport advectif.

Au deuxième stade, le pH de l'eau interstitielle est ramené à une valeur de 12.5 environ, par équilibrage avec le portlandite ($Ca(OH)_2$). Les concentrations d'hydroxydes alcalins dissous sont réduites par des processus de transport et/ou des réactions minérales. Cette phase durera très longtemps, surtout dans des situations où la porosité est réduite à l'interface ciment-argile et/ou en présence d'un régime de transport diffusif.

Au troisième stade, la portlandite aura été épuisée par les réactions avec des silicates/aluminates de la roche d'accueil ou des déchets réactifs. Le pH de l'eau interstitielle baissera à environ 11, voire en dessous, par équilibrage avec les calcium-silicate-hydrates (C-S-H). A noter que la composition des phases C-S-H se déplacera en direction d'un rapport inférieur Ca/Si (appauvrissement de $Ca(OH)_2$ dans les phases C-S-H, jusqu'à atteindre Ca/Si < 0.84).

A un stade très avancé, on parviendra à un pH presque neutre, par la formation de carbonates, de minéraux argileux ou de zéolithes.

L'évolution géochimique du champ proche subit l'influence de différents processus. Sont considérés comme importants les interactions avec la roche d'accueil et avec les déchets stockés, la dégradation des matériaux cimentaires par le biais de réactions alcali-silice et la carbonation.

Les échanges diffusifs et advectifs entre les eaux interstitielles des matériaux cimentaires et de la roche d'accueil entraînent des réactions minérales et des modifications du pH de ces eaux. Ces réactions ont été étudiées à l'aide de modèles numériques. En partant des interfaces entre les matériaux, on escompte que les minéraux argileux de la roche d'accueil seront dissous sur quelques dm dans 100 000 ans (période considérée pour l'analyse de sûreté d'un dépôt pour DFMA). En cas de flux d'eau importants les minéraux seront éventuellement dissous jusqu'à 1 m et ils peuvent être transformés en d'autres minéraux (zéolithes). La transformation minérale n'influe pas sur la capacité de sorption de la roche d'accueil caractérisée par des écoulements lents et un régime de transport dominé par la diffusion. L'influence sur la capacité de sorption de roches d'accueil fissurées est prise en compte dans les analyses de sûreté provisoires pour SGT E2.

Par la suite, une zone se formera où l'eau interstitielle présentera un pH légèrement supérieur à la normale (8 – 9), mais où ne surviendra encore aucune modification minéralogique significative. Dans le cas d'un régime de transport diffusif, cette zone s'étendra sur quelques mètres autour du dépôt. Si le régime de transport est advectif, que les flux d'eau sont plus importants et la porosité de la roche d'accueil est très basse, elle peut atteindre plus de mille mètres en direction des flux. A l'intérieur du dépôt lui-même, la portlandite pourrait, dans le cas d'un régime essentiellement diffusif, être dissoute jusqu'à une distance de 2 m de l'interface avec la roche d'accueil. Derrière le front de dissolution, le pH de l'eau interstitielle baisse. Le troisième stade de dégradation du béton est alors atteint. Si des flux d'eau plus importants devaient atteindre les cavernes par certains lithofaciès de la roche d'accueil, il est possible que le front de dissolution de la portlandite progresse de quelques mètres en aval d'ici à 100'000 ans. Derrière le front, les matériaux cimentaires seront entièrement dégradés avec le temps.

Si le béton contient des adjuvants à l'acide silicique, les matériaux cimentaires peuvent être dégradés par la réaction alcali-silice. Dans ce cas, ces adjuvants interagissent avec la portlandite pour former des phases C-S-H. Ce processus se traduit par une baisse du pH de l'eau interstitielle et aboutira à long terme à une dissolution totale des matériaux cimentaires. On connaît encore mal le déroulement à long terme de cette réaction. Sur la base de vitesses de réactions connues, on peut toutefois avancer que la dégradation du ciment par ce processus pourrait avoir lieu assez rapidement, c'est-à-dire en l'espace de quelques centaines, voire un millier d'années.

La dégradation des déchets organiques dans un dépôt comprenant des matériaux cimentaires se fera probablement par méthanogenèse, processus libérant du CO_2 et du CH_4. Au vu des conditions de vie défavorables (pH élevé), l'activité microbienne, nécessaire à la dégradation, sera très faible. Le CO_2 dégagé dégradera par carbonation le matériau cimentaire entourant les déchets. Il n'est pas vraiment possible de prédire quel sera le taux de dégradation des déchets organiques. Ce processus dépend en effet du pH, mais aussi de facteurs difficilement quantifiables, par exemple de la présence d'eau et de différents nutriments tels que le phosphore et l'azote. Ces facteurs ont un effet limitatif sur la dégradation microbiologique. Sur la base des connaissances actuelles, on escompte que les matériaux organiques de faible poids moléculaire seront dégradés en l'espace de 1'500 ans environ. Il y a par contre une grande incertitude concernant les taux de dégradation des substances organiques de poids moléculaire élevé. On estime que leur dégradation prendra au moins quelques milliers d'années, mais plutôt jusqu'à quelques

dizaines voire des centaines de milliers d'années. L'influence de la complexation des radio-nucléides dans un milieu contenant du ciment est prise en compte dans l'établissement de la base de données de sorption, sur laquelle se fonde l'analyse de sûreté provisoire.

Certains déchets anorganiques réagiront avec les matériaux environnants, à condition qu'il y ait de l'eau en quantités suffisantes. Dans ce contexte, il convient de relever la corrosion anoxique des métaux (acier compris), laquelle peut dégager de grandes quantités de H_2. Les produits de corrosion (p. ex. la rouille) peuvent à leur tour favoriser la dégradation des matériaux cimentaires environnants. La condition préalable est encore une fois une phase aqueuse permettant le transport des substances dissoutes.

La description générale de la dégradation du ciment diffère peu des travaux antérieurs. Les déductions concernant le transport des radionucléides (rétention) et leur solubilité restent par conséquent inchangées. Il est dès lors recommandé de conserver les principes appliqués jusqu'ici pour décrire la solubilité et la sorption des radionucléides (concept de coefficient de distribution). De même, on considère le transport colloïdal des radionucléides comme très peu vraisemblable, du fait que la chimie de l'eau interstitielle dans la roche d'accueil et le champ proche induit une très faible stabilité colloïdale, signifiant de très basses concentrations en colloïdes.

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1.1   The Swiss programme to build a deep geological repository in a clay host rock

In Switzerland, the Nuclear Energy Law requires that all types of radioactive waste be disposed of in deep geological repositories (KEG 2003). The Swiss Radioactive Waste Management Programme (Nagra 2008a) foresees two types of deep geological repositories: a high-level waste repository (HLW repository[1]) for spent fuel (SF[2]), vitrified high-level waste (HLW) and long-lived intermediate-level waste (ILW), and a repository for low- and intermediate-level waste (L/ILW repository[3]).

In response to Stage 1 of the Swiss sectoral plan for Deep Geological Repositories ("SGT", BFE 2008), Nagra proposed six siting regions for the L/ILW repository, three of which are also suitable for the HLW repository.

In Stage 2 of the Sectoral Plan at least two sites for each repository type will be selected for further investigations in Stage 3, the aim of which is to identify a single site for each repository type.

Thus, the Radioactive Waste Management Programme in Switzerland is moving towards the realisation phase for deep geological repositories. Previously, the rather generic studies and approaches were sufficient for the needs and aims of the programme. However, now, potential siting regions and host rocks have been identified and the need is to carry out studies orientated towards site-specific conditions taking into account potential changes occurring in time and space. The emphasis is on providing information and data which are relevant to the "real systems", whether this be the far-field host rock or the near-field components. This also means that a new level of quality in the treatment of the wide variety of processes involved needs to be introduced. The components may interact with one another over time, changing mineralogies, porosities and physico-chemical characteristics.

Description of the L/ILW repository

This report summarizes our understanding of the geochemical evolution of the L/ILW repository for up to 100'000 years, the time period considered in safety analysis for the L/ILW repository. All potential siting regions for the L/ILW repository have clay-rich sediments as a host rock. These are the Opalinus Clay (Südranden, Zürich Nordost, North of Lägern, Jura Ost, Jura-Südfuss), the 'Brown Dogger' (Zürich Nordost, North of Lägern), the Effingen Member (Jura-Südfuss) and t h e Helvetic Marls (Wellenberg). The L/ILW repository concept is characterized by the use of large amounts of cementitious materials for waste conditioning, tunnel support and tunnel backfill.

The safety of the SF/HLW and the L/ILW repositories is ensured by a multi-barrier concept (Section 3.1). Barriers include the waste matrix, steel drums, emplacement containers, the tunnel backfill and the host rock.

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[1]   German: HAA-Lager.

[2]   According to current legislation, spent fuel is classified as radioactive waste.

[3]   German: SMA-Lager.

The multi-barrier system is key for providing the safety functions of the L/ILW repository (Nagra 2008b). Important isolation and confinement mechanisms are:

- the fixation of radionuclides in the cement/bitumen matrix of waste drums

- the containment inside waste container

- the isolation with backfill mortar in emplacement tunnels

- limited hydraulic permeability of the host rock

The release of radionuclides is attenuated by

- low leaching rates of cement matrices in waste drums

- low corrosion rates of metallic waste components

- sorption of radionuclides on the cementitious (grout, cement) and clay materials (host rock, sand/bentonite backfill)

- low radionuclide solubilities in (concrete and host rock) pore waters

- low groundwater fluxes in the emplacement tunnels and host rocks

The role of chemistry

All of the confinement and attenuation mechanisms mentioned above depend on chemical processes or are influenced by them to various degrees. For example:

- The chemical interactions of waste with the concrete/bitumen matrix may influence the fixation capacity in the waste drums.

- Metal corrosion may breach the steel drums.

- Cement and grout degradation may weaken the waste isolation with time.

- Cement/clay interactions may reduce the mechanical stability of host rocks and tunnel support. This may favour the creation of features that allow channelling for transport.

- Waste-clay-cement interactions may increase or decrease the leaching rates of radio-nuclides.

- Waste-clay-cement interactions may lower (locally or globally) the pH in the concrete compartments and increase metal corrosion.

- Alteration of mineral assemblages (dissolution of clay minerals in host rocks, transformation of cement minerals) may alter radionuclide sorption.

- Dissolution of minerals may increase porosities and foster groundwater flow into the repository.

- Precipitation of minerals near material interfaces may lower porosities and decrease groundwater flow and diffusive transport.

- Changes in the chemical environment (e.g. pH, ionic strength) may cause the production of colloids or influence their stability.

Aim of this report

The aim of this report is to describe the expected temporal and spatial evolution of the chemistry of cementitious materials and their interactions with adjacent engineered and natural barriers and to assess the impact of possible changes to the transport and retardation of radio-nuclides.

Methodologies used to assess the geochemical evolution

We used a combination of literature reviews, mass balance and reactive transport calculations to develop a view on the expected geochemical repository evolution and to assess the importance of processes and process couplings.

Information from literature reviews and mass balance calculations give indications on the maximum possible changes of barrier materials, but they provide limited insight into the spatial and temporal evolution of the overall system, the specific influence of single processes (e.g. pore space changes), and on the feedback between different processes.

To overcome such shortcomings we performed reactive transport calculations which specifically reflect the host rocks and concrete materials foreseen in the Swiss disposal design (Berner et al. 2013, Kosakowski & Berner 2013). Such reactive transport calculations not only allowed refined mass balance calculations to be made, but also introduced a new qualitative view into the system evolution since several processes, and their mutual impacts, could be considered simultaneously (Section 3.1.2). These models are believed to provide an important step towards a more realistic evaluation of real systems. Currently, they still have a limited predictive capability because not all conceivable processes can be considered.

Setting up these coupled models required the refinement of geochemical models for cementitious (concrete) and clay-based materials, and, in particular, the development of a consistent set of thermodynamic data valid for both types of materials. For concrete materials a recent thermodynamic database CEMDATA07 (based on Lothenbach & Wieland 2006, Matschei et al. 2007, Lothenbach & Winnefeld 2009) was included to describe cement minerals in terms of solid solutions. For clay-based materials, the reference Nagra/PSI database was supplemented with newly evaluated solid solution thermodynamic data for montmorillonite. Note that the inclusion of smectites as a reactive component has been discussed in a recent paper on Opalinus Clay pore water modelling (Pearson et al. 2011), but is not, as yet, considered in most clay pore water models.

1.2   Organization of the report

The report is split into two main parts. Section 2 provides an integral description of our current view on the geochemical evolution of the repository.

Section 3 then gives more information on the disposal system and provides descriptions of processes that influence either the geochemical evolution of the cementitious near-field or the radionuclide transport properties of the far-field.

The appendices summarize the setup of the reactive transport models. In addition, summaries of the pore waters defined for the various concrete degradation stages are presented.

A list of features, events and processes related to the geochemical evolution of the cementitious near-field is also covered in this report and is given in Tab. 1.1. An overview of potential impacts on radionuclide transport is presented in Tab. 1.2.

Tab. 1.1:   Features, events and processes that influence the geochemical evolution of the cementitious near- and far-field covered in this report.

	Cementitious near-field	**Host rocks**	**Access tunnel – backfill**
Diffusive solute transport	Section 3.3.2	Section 3.3.2	Section 3.3.2
Advective solute transport/water flow	Section 3.3.3	Section 3.3.3	Section 3.3.3
Saturation/gas production	Sections 3.3.1 & 3.4.1 – 3.4.2	--	--
Clogging at interfaces	Section 3.3.4	Section 3.3.4	Section 3.3.4
(Internal) Concrete degradation	Section 3.4.5	--	--
Organic wastes	Section 3.4.1	--	--
Inorganic wastes	Section 3.4.4	--	--
Metallic wastes and iron/steel	Section 3.4.4	--	--
Heterogeneity of near-field	Section 3.5		
Colloids	Section 3.6.1	Section 3.6.2	--

Tab. 1.2:   List of the sections covering features, events and processes related to geochemical changes that influence radionuclide transport.

	Cementitious near-field	**Host rocks**	**Access tunnel – backfill**
Change of transport parameters	Section 3.3.4	Section 3.3.4	Section 3.3.4
Change of far-field sorption parameters (pH plume)	--	Sections 3.3.2 & 3.3.3	Sections 3.3.2 & 3.3.3
Change of near-field sorption parameters (concrete evolution)	Sections 3.3 & 3.4	--	--
Colloids	Section 3.6	Section 3.6	--

2   Expected evolution of the L/ILW disposal system

2.1   General description of the disposal system and its evolution

Disposal system

A L/ILW repository is characterized by high waste volumes on the one hand, and by low radiotoxicities on the other. The wastes are typified by large variability and heterogeneity in physicochemical properties. Thus, the design of the engineered barrier system for a L/ILW repository differs from that of an SF/HLW waste repository where the waste volume is smaller and better characterized. Apart from the radioactive waste, the principal materials in a L/ILW repository are hydrated cements, aggregate materials and steel. Usually the wastes are solidified/ embedded in a cement/mortar matrix, which itself is contained in steel drums. These drums are mainly needed for interim storage, handling and transport prior to emplacement. Some wastes are also embedded in bitumen. For the construction of the tunnels, a reinforced concrete or shotcrete liner support is used. Specifically designed mortars (e.g. "monocorn" mortar) will be used for the backfilling of the remaining cavities. The concrete and mortar aggregates are considered to consist of siliceous materials (primarily quartz), but calcareous materials (limestone) are an option. In summary, the backfilled tunnels contain, in addition to the radioactive waste, chemically reactive hydrated cements, significant amounts of steel (drums, tunnel support and construction materials) and concrete aggregates.

The surrounding host rocks are clay-rich sediments (Opalinus Clay, 'Brown Dogger', Effingen Member, Helvetic Marls). These rocks are characterized by similar solid phase assemblages, similar pore solution compositions and by the presence of significant fractions of strongly sorbing clay minerals. Detailed descriptions of the host rocks are published in Nagra (2008b, 2010).

Chemical reactions in the disposal system

Chemical conditions in the repository, as well as their temporal changes, are driven by the interactions between hydrated cement, steel, aggregates and clays. Considering the chemical nature of the major materials involved, two processes dominate: reactions of cement minerals with aggregate/clays and the corrosion of iron. The chemical reactions only proceed if a sufficient amount of water is present, either as a (stagnant or mobile) aqueous phase or a humid atmosphere. Chemical gradients, in particular those associated with the strongly alkaline nature of the cementitious materials, dictate the reaction directions, and the principles of chemical thermodynamics play a large part in the fundamental reaction products of the interactions. However, it should be noted that kinetics can also play a significant role in determining the types of products of the interactions of the barrier materials (Savage et al. 2007). Diffusion is the dominant transport process in stagnant systems. Advective transport is exclusively relevant in mobile fluid phases. According to Nagra (2010), diffusion-controlled processes dominate in the near-field of a L/ILW repository.

However, this already complicated system description becomes extremely complex if interactions between the different processes are taken into account. Although individual processes might operate on different temporal and spatial scales, they are strongly coupled via key parameters such as porosity and water content. An example of such a coupling is porosity clogging on the mm to cm scale at clay-cement interfaces, which might hinder the large-scale mass transport across the interface. Spatially heterogeneous material distributions, and the complex scale-dependent structure of pore space, increase the degree of complexity.

Hence, in order to assess the importance of individual processes on the total system, it is necessary to evaluate many parameters and model many processes simultaneously. For example, it is our current understanding that all processes that are influenced by pore space changes or change the pore space itself are important. This includes fluid movement, solute diffusion, saturation state, chemical swelling, and precipitation/dissolution controlled by reaction kinetics.

Understanding the release of radionuclides from the repository, the actual goal of any safety assessment, can only be achieved with sufficient reliability when the detailed system behaviour is known at an adequate level.

Evolution of the near-field during the operational phase and after closure

The schematic sketch in Fig. 2.1 (Nagra 2008a), shows the evolution of the tunnel near-field during the operation phase and after closure. During repository operation, and for some time after closure, the geochemical processes in the repository will be dominated by the desaturation in the vicinity of the tunnels. Shortly after repository closure, the re-saturation is hindered by gas production due to the degradation of organic materials and the anaerobic corrosion of steel. The period of gas generation might be very long, and a complete re-saturation of the near-field might require more than 100'000 years (Nagra 2008a). It is believed (Nagra 2008a), that *hydrogeochemical sealing processes will be restricted principally to the water-saturated pore space within the micro- and meso-pores*. During the time before full saturation is achieved, transport processes in the fluid phase will be hindered or slowed down considerably. The oxidizing conditions during the operation phase will change to reducing conditions once the oxygen in the entrapped atmosphere is consumed.
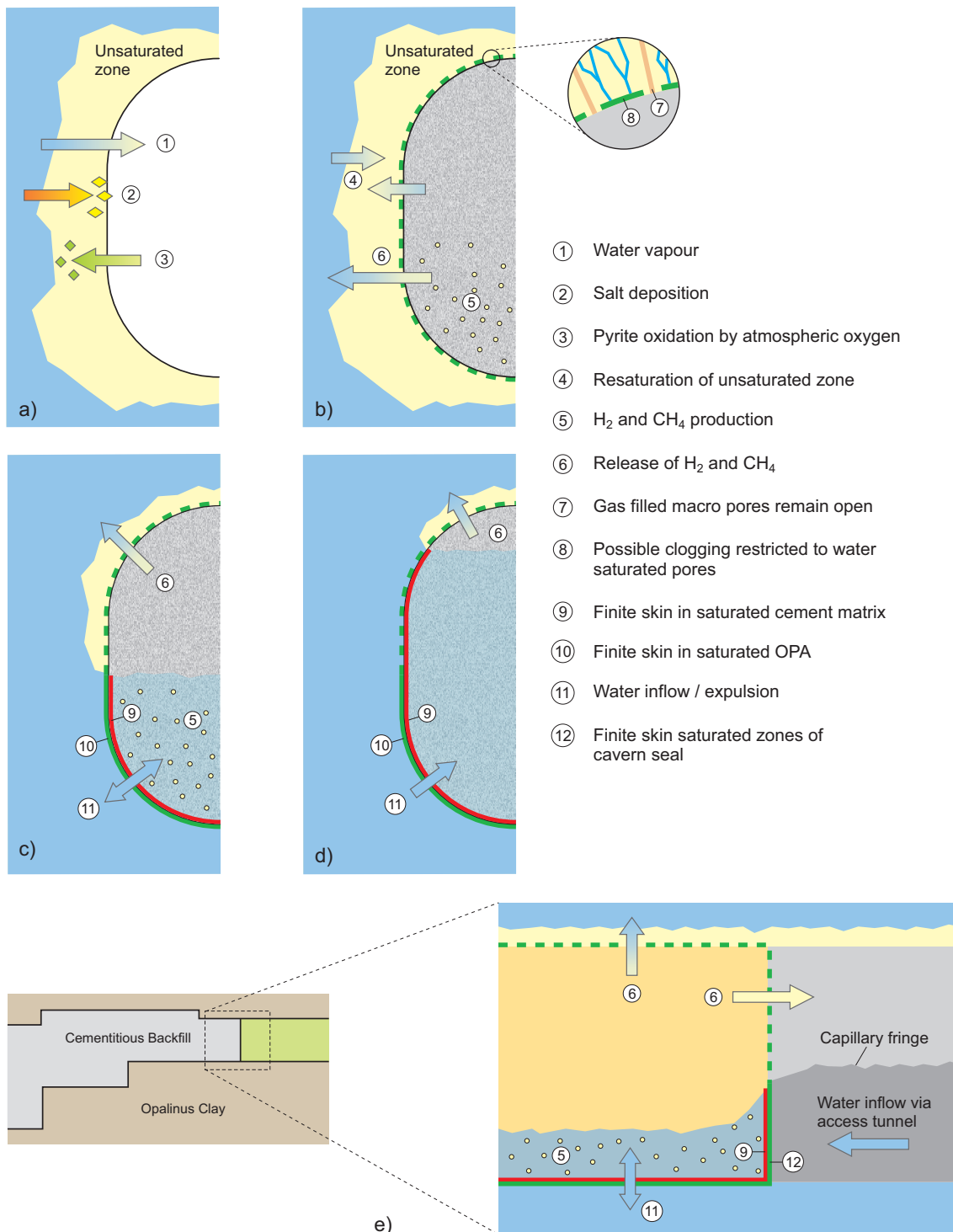
Fig. 2.1:   Schematic sketch showing the evolution of tunnel near-field during the operation
             phase and after closure (from Nagra 2008a).

         a)   Development of a de-saturated zone and observed geochemical processes during
                     operation phase
         b) – d)   Mass transfer processes and geochemical processes in early, mid and late stages
                     after closure
         e)   Mass transfer processes and geochemical processes near the tunnel plug after
                     closure

Evolution of the tunnel near-field after complete re-saturation

For a fully water saturated repository, three major processes were identified that will contribute to the degradation of concrete materials, and may alter host rock properties: diffusive exchange of solutes between the concrete compartment and the host rock, and internal degradation of concrete due to the reaction of cement phases with the aggregates and waste materials. A schematic sketch of an unaltered emplacement tunnel is shown in the upper left corner of Fig. 2.2. The other sketches illustrate the effects of diffusive transport (upper right), advective transport (lower left) and internal degradation of concretes by alkali/silica aggregate reactions and waste-concrete reactions (lower right). The impact of these processes will be summarized in the following sections and more detailed descriptions are given in Section 3.
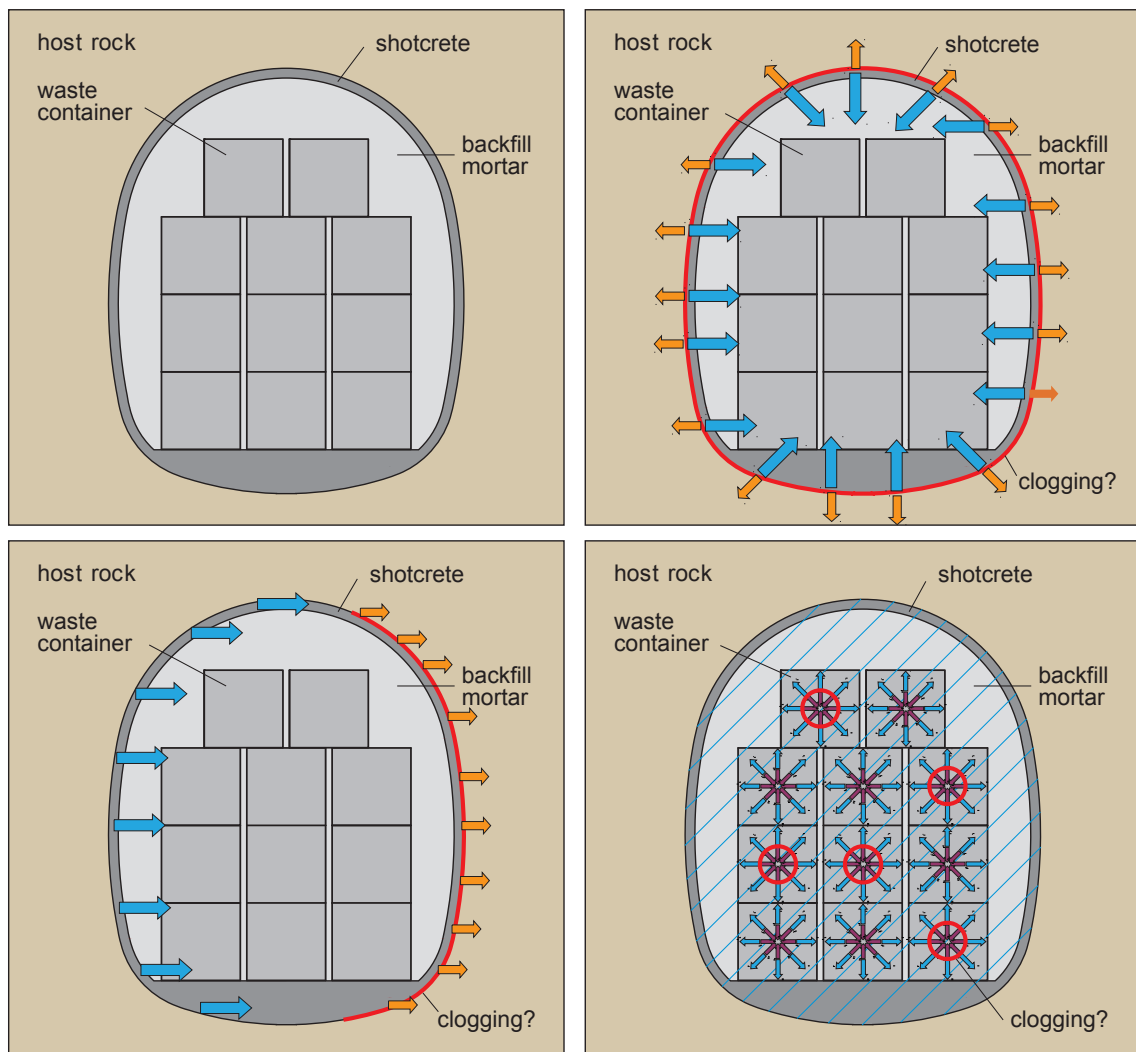
Fig. 2.2:   Schematic sketch of an unaltered emplacement tunnel (upper left).

Effects of diffusive transport across clay – concrete interfaces (upper right), advective transport of host rock waters into the tunnel and cement pore waters into host rocks (lower left) and internal degradation of concretes by alkali/silica aggregate reactions (lower right, blue hachure) and wastes-concrete reactions (lower right). The arrows indicate the directions in which alteration and reaction fronts progress. Red colours indicate possible zones of porosity clogging.

2.2   Expected extent of the pH plume

In the porous host rocks considered, the diffusive transport of solutes dominates, and therefore governs, the spatial extent of the pH plume (see Section 3.3.2 for details). Observations from natural analogues, as well as reactive transport calculations, indicate porosity clogging on a cm scale for clay-cement interfaces in diffusion controlled transport regimes. The host rock pore water pH may increase to values between 8 and 9 over several meters (for diffusive transport only), and up to more than thousand meters in the downstream direction in case of additional advective transport, within 100'000 years.

We expect that the porosity close to clay/concrete interfaces will decrease significantly with time (Section 3.3.4). This will decrease the water flow and diffusive mass fluxes across the interface (including radionuclide fluxes).

Spatial heterogeneity such as mineralogy, porosity and fracturing may prevent the complete sealing of clay-cement interfaces, but since the considered host rocks are very homogeneous, we do not believe that such features will cause significant deviations from the expected geochemical evolution of the system.

Further, we have not considered the effect of mechanical processes within the near-field (e.g. fracturing), which may also change porosity or open transport pathways. However, it should be noted that open- and water-filled pathways may clog with time in a comparable manner to the clogging scenario for fractured rocks (Section 3.3.3).

If the water movement in a host rock is along fractures – potentially relevant for Effingen Member and Helvetic Marls – transport will be dominated by advection as outlined in Section 3.3.3. We consider two rather extreme scenarios for addressing changes in the host rock properties due to a high pH plume:

- The fractures clog at the discharge area, due to the precipitation of calcite or C-S-H for example, which strongly reduces the advective water flow through the system and consequently slows down the degradation of concrete. This scenario limits the further propagation of the pH plume. However, it does not stop the internal degradation of concrete by alkali/silica aggregate reactions.

- The fractures remain open (at least partially) and the high pH solution from the cementitious repository reacts with the fracture walls of the host rock. This seals the host rock matrix (fracture surfaces) and consequently the high pH plume propagates quickly along the fractures. It has to be noted that this second ("channeling") scenario might lead to high water fluxes through the repository, which in turn would cause substantial and accelerated cement degradation.

2.3   Concrete degradation

Diffusion

Diffusive solute exchange across the host rock/concrete interface may cause the dissolution of significant amounts of portlandite in 100'000 years, if transport across the interface is assumed to be not affected by porosity clogging. The results of reactive transport calculations (described in detail in Section 3.3.2) show that the portlandite might be dissolved up to a distance of two meters from the tunnel walls. Portlandite dissolution is accompanied by a change in the Ca/Si ratio of C-S-H phases, characterized by lower values towards the interface. The degradation of concrete is not expected to generate a single degradation front where all cement minerals are

transformed at the same time and location. Instead, we expect several sequential mineral transformations spatially distributed in the system. The progress of the reaction fronts slows down with time, and for each reaction front a unique apparent diffusion coefficient can be defined. An exact quantification of the progress of portlandite dissolution and other mineral reactions with time is currently not possible since these depend on many model parameters which are not well known at present. Examples of such parameters are the exact composition of the concretes, thermodynamic and kinetic data such as reaction rates and "reactive" surface areas, effective diffusion coefficients in different materials, and porosity-diffusivity relationships (Sections 3.3 and 5.1). In addition, if feedback between solute transport and porosity clogging is considered, the extent of the concrete alterations is reduced considerably.

Groundwater flow

The flow of host rock pore water through the emplacement tunnels will degrade the concrete (Section 3.3.3). The degree of degradation and the propagation of the degradation front will depend directly on the water flux and the pore water composition. Higher salinity pore water will accelerate concrete degradation. For advective transport the reaction fronts all proceed with individual velocities. Front velocities remain constant in space and time as long as the material composition (host rock or concrete) does not change or heterogeneities do not influence the flow field. Due to low water fluxes in the low permeability host rocks, concrete degradation due to advective transport is generally minimal (see Section 3.3.3 for details). However, for host rocks that contain transmissive features (i.e. Helvetic Marls or Effingen Member with horizontally aligned transmissive features) higher water fluxes are possible and concrete degradation extending up to a few meters (in downstream direction) in 100'000 years seems possible (see Section 3.3.3 for details). After degradation, the concrete will be composed of non-reacted aggregates, carbonates and hydroxides (hydrotalcite and brucite for the Effingen Member pore water). Due to the heterogeneous nature of the permeability in the emplacement tunnels, we do not expect a homogeneous progress of the alteration fronts. The areas with high permeability (tunnel backfill) will be subjected to the highest water fluxes and will therefore be degraded first. Cracking of the concrete, and heterogeneities due to the emplacement of waste, may cause a strong channelling of the flow. This could result in a spatially and temporally heterogeneous concrete degradation. Concrete dissolution is not expected to cause porosity reductions, in contrast to concrete transformation in the presence of carbonate. Instead, porosity enhancement is expected due to the dissolution of the cement minerals without formation of secondary phases. The dissolved substances are expected to cause mineral precipitation in contact with the host rock material or clay backfill materials (Fig. 2.2). Such precipitation may clog the "outflow boundary" which will decrease the water flow through the emplacement tunnels or channel the flow towards permeable regions.

Alkali-silicate-aggregate (ASR) reaction

The thermodynamic instability of silicate aggregates (e.g. quartz, feldspars) embedded in a cementitious matrix is a fact, and, irrespective of kinetic constraints, has to be assessed in connection with the long-term evolution of the cementitious near-field. In contrast, thermodynamic stability is ensured in the case of calcite aggregates.

The sequence of phases appearing and disappearing during the (cement) neutralization processes can be predicted based on the available thermodynamic data (Section 3.4.5). This sequence corresponds to the phase sequence as described in the state-of-the-art literature on alkali silicate reactions (Hou et al. 2004, Naus 2007). Note that a general agreement on the phase sequences, although thermodynamic properties of individual phases are less well known.

When coupling chemical reactions with transport issues we are generally dealing with dynamic systems. In such cases the kinetic characteristics of the reactions become important. If transport times are much slower than the progress of a particular chemical reaction, the principles of instantaneous chemical equilibrium are applicable. Note that alkali-silicate-reactions are not driven by macroscopic solute transport. These reactions are a result of a thermodynamic disequilibrium between cement phases and aggregate. ARS is controlled by the kinetics of the dissolution of (silicate) aggregates. Information on the dissolution rates of silicate reactants is sparse, and essentially absent for the precipitation rates of secondary products. In addition, the development of reaction rims may change the microscopic transport characteristics and (usually) slows down the overall reaction progress. Furthermore, the ongoing ASR reactions consume water which needs to be transported to the reaction front either in a liquid or a gaseous form (water vapour). The water transport in turn depends on the global water transport characteristics of the particular system in question. Understanding such processes again calls for a sophisticated coupling of chemical and transport processes on microscopic and macroscopic levels. Hence, it is not surprising that present day literature does not provide any information on the temporal aspects of the propagation of ASR beyond the lifetime of existing concrete structures (Section 3.4.5).

The temporal evolution of the internal degradation currently remains an open issue because too many relevant parameters are poorly defined. However, preliminary estimates reveal that the internal degradation due to ASR could be fast (Section 3.4.5). This means that the cement degradation stage determined by portlandite saturation could potentially last for a much shorter period of time than anticipated from degradation scenarios based on diffusive or advective transport of host rock pore waters.

Organic wastes

Decomposition of low molecular weight (LMW) and high molecular weight (HMW) organic materials can take place via biotic, abiotic or radiolytic processes (Section 3.4). Abiotic decomposition under alkaline conditions was observed in the case of cellulose, while the radiolytic decomposition of bitumen could generate LMW organic compounds. In general the hydrolysis of HMW organic compounds is considered to be the first step for the subsequent microbial degradation. Biotic degradation is expected to be slow under the hyperalkaline conditions of the cementitious near-field. Nevertheless, the near-field will not be sterile. Mass balance calculations suggest that the Mn-reducing and Fe-reducing microbial degradation routes for organics are negligible due to the low inventories for Mn(IV) and Fe(III) in hardened cement paste. Note that large quantities of Fe(0) exist in the near-field (waste materials, waste packages, steel reinforcements, etc.), but it is presently unclear how much Fe(0) will be converted to Fe(III) bearing phases (magnetite) and to which degree Fe(III) can be utilized by microbial activity. To some degree microbial decomposition of organics by sulphate-reducing microorganisms might occur, although the SO_4^{2-} inventory in the near-field is limited by the sulphate content of the cement paste. Note that sulphate ingress from the host rock will be limited by the long time scale of the near-field re-saturation process. Thus, the decomposition of organic matter is expected to predominately occur via methanogenesis, which produces CO_2 and CH_4. The exceptional environmental conditions, high pH, and the limited availability of water and growth-controlling nutrients, such as phosphorous, could be factors which strongly limit the microbially mediated degradation of organic matter in the repository.

The decomposition of LMW organic materials is expected to take place mainly during the early oxic and anoxic stages of the repository, and will be completed within a time span of less than 1'500 years according to the best available knowledge (Section 3.4.1). The time scale for the decomposition of the slowly degrading HMW organic materials under anoxic conditions was

estimated to range from several thousand years to some tens to hundreds of thousands of years. The degradation concept currently applied by Nagra predicts the degradation of LMW and HMW organic materials within a period of a few thousand years. This approach seems to be conservative in view of the slow hydrolysis reactions of HMW organics.

The generation of CO_2 could have an impact on the mineral composition of the cement matrix and consequently on the retention properties of the cementitious near-field (Section 3.4.2). No interaction with cementitious materials is expected in the case of CH_4 (Section 3.4.1). CO_2 production in the waste packages is expected to locally transform mainly portlandite into calcium carbonate and AFm phases into monocarboaluminate. Carbonation of the cement matrix due to the decomposition of organic matter is expected to be a local process, and the temporal evolution is determined by microbial activity. The porosity decrease due to the formation of carbonate-containing minerals affects the local transport properties, and the retention of dose-determining anions, such as iodide, chloride and selenite, could be strongly reduced due to the carbonation of AFm phases. The effect of carbonation on the retention of metal cations is expected to be negligibly small since the main sorbing cement phase, C-S-H, will not be affected as long as portlandite is present in the cement matrix. Nagra's safety criteria is defined such that at most 2/3 of the total inventory in the cement matrix is allowed to degrade by carbonation, thus ensuring the presence of portlandite in all parts of a repository containing type-1[4] low- and intermediate level wastes (Section 3.4.3).

Inorganic wastes

Inorganic waste materials will be subject to transformation processes in the repository depending on their chemical stability under the hyperalkaline, reducing conditions (Section 3.4.4). Some materials are expected to persist over geological time scales (e.g. graphite). Other materials may slowly decompose over time, or consist of elements that make up the cement. Decomposition of the latter materials is expected to change the amount of existing cement phases, but will not completely alter the mineral composition of hardened cement paste (HCP), and therefore will have no influence on retention properties.

Metallic materials (except Ag) and steel will be subject to anoxic corrosion, which produces H_2. The production of H_2, and to a lesser degree the production of CH_4 and CO_2 due to the degradation of organic material, is the major driving force for the partial de-saturation of the repository near-field over a long period of time (Sections 3.3.1 and 3.4.4, Nagra 2008a).

The release of products during the course of the corrosion of magnesium, aluminium and iron (steel) could alter the mineral composition of cementitious materials. High inventories of Mg in the waste matrix are considered to promote the formation of cement minerals that stabilize the cement. Thus, any adverse effects of Mg corrosion on the cementitious materials due to changes in the porosity and sorption properties are expected to be limited. By contrast, the corrosion of Al and Fe could cause changes in the mineral phase composition of cement having possible effects on anion retention. First mass balance calculations illustrating the possible consequences are outlined in Section 3.4.4.

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[4]   Group 1 waste does not contain materials in amounts which could reduce radionuclide retention. In contrast, Group 2 waste has larger inventories of such materials, which may result in an increase of radionuclide mobility.

2.4   Expected concrete degradation stages and the impact on radionuclide transport

Concrete degradation stages

Principally, we retain the "classical" cement/concrete degradation stages that have been formulated in earlier studies (Nagra 1994, e.g. 2002a). These stages are:

1. The first stage is related to freshly hydrated cement/concrete. The pore water is characterized by high pH values (13 and above) due to the significant amounts of dissolved alkali hydroxides. No exchange with the surrounding host rock has occurred.

2. The second stage is designated as the portlandite stability stage. This stage is characterized by the presence of portlandite. The pore water has a pH ~ 12.5 and a lower ionic strength. The mobile alkali hydroxides have exchanged to a large degree with the solutes of the surrounding host rock pore solutions (see below).

3. The third stage is called the low-pH stage. It is characterized by the absence of portlandite due to its complete dissolution or its reaction with silicates/ aluminates or even with carbonate. This stage is further characterized by modified C-S-H-phases depleted in $Ca(OH)2$ and by pH values of ~ 11 or below.

However, what might change in comparison to earlier studies is the time scale over which a certain stage is valid. Earlier studies assumed external water fluxes only and the principle of fluid exchange cycles (compare Section 3.2.1). In the fluid exchange cycles approach the concrete pore water is exchanged by the same volume of host rock pore water and the resulting system is re-equilibrated (mixing tank model). In this procedure all soluble alkali hydroxides are removed in the first step so the approach is only applicable for very permeable, advection-dominated systems. When following this fluid exchange cycle approach, host rock pore waters can be grouped into two different types of pore waters for Stage B, mainly differing in ionic strength, i.e., the Opalinus Clay/'Brown Dogger' and the Helvetic Marls case with an ionic strength ~ 0.2 mol/L, and the Effingen Member case with I ~ 0.6 mol/L.

The current sites under investigation are dominated either by diffusive transport or subject to a considerable influence of diffusive transport (compare alteration distances in Tabs. 3.3, 3.4 and 3.5). Therefore, a much more realistic approach is to consider a diffusion-dominated exchange of pore waters between the concrete and the surrounding host rock. Such calculations have been performed for all host rocks, using the Stage A pore water and the corresponding host rock pore waters as starting points (Section 3.3.2). Since the host rock pore waters differ in ionic strength and also in porosity (and consequently in the transport parameters), a whole series of potential type B pore waters depending on time- and spatial coordinates results from these evaluations (Kosakowski & Berner 2011c). The concrete systems and reference pore waters for the Opalinus Clay case deduced from the above considerations are listed in the Appendix, Section A4.

The following general conclusions may be drawn:

- Assuming equivalent diffusion parameters for solutes, diffusive transport in the Helvetic Marls is slower because the porosity is lower. Consequently, the time to reach complete exchange is longer than in for example the case of Opalinus Clay.

- The pore water of the Effingen Member has a higher chloride content than the pore waters of Opalinus Clay or Helvetic Marls. Although steeper concentration gradients induce higher driving forces, complete exchange needs more time due to its smaller transport porosity.

- The effects of diffusive and advective transport are decreased by an eventual partial water de-saturation of the near-field. Water de-saturation of the pore space will strongly decrease the effective transport porosity and corresponding water and solute fluxes between host rock and concrete compartments.

- Decreasing porosities, which slows down transport, might decrease concrete degradation caused by advective and diffusive transport at host rock – concrete and waste – concrete interfaces. In contrast, considering internal degradation by aggregate – cement reactions as outlined above, might lead to much shorter time scales for stages A and B (see Fig. 2.2).

- Thermodynamic model calculations provide indications that the neutralization process may even lead to a fourth degradation stage where the backfill material resembles a clay rock phase assembly more than hydrated cement. However, up to now the understanding of the complete degradation of concretes (with the formation of zeolites and clay minerals) is not well developed and includes speculative elements. For this fourth stage the sorption properties of the phase assemblage might be similar to that of a clay system.

Radionuclide solubilities

The speciation and solubilities of safety relevant radionuclides depend on the local chemical regime and the timeline of the system evolution. If timescales for the high-pH stages A and B are short, a short timescale of potentially enhanced solubilities due to the formation of anionic hydroxo species of metal cations can be expected.

A key impact on solubilities is expected to arise from the nature of the transport scenario, i.e., whether advection or diffusion dominated transport predominates.

In a diffusion-dominated system consisting of a concrete compartment in contact with a clay host rock, the chemical regime changes the most near the interface adjacent to the host rock. In the host rock the influence of high pH from the concretes becomes much less relevant because the pH is strongly buffered.

The situation is different in the advection-dominated system, usually attributed to water flow in fractured rock. In these cases, solubilities and speciation in the cement/concrete compartment become important. The established high pH solution, including the dissolved radionuclides, is transported fast and complete re-equilibration in the fractures does not occur.

In the case of solubility controlled concentrations, a pH decrease due to enhanced internal or external degradation could lead to lower radionuclide solubilities (no anionic hydroxo species), which may decrease radionuclide fluxes. In the case of sorption controlled concentrations, however, radionuclide sorption decreases with decreasing pH, which would increase radionuclide fluxes.

In addition, the quality of speciation and solubility calculations of safety relevant nuclides strongly depends on the completeness and quality of the database.

Radionuclide retention

Since the principal characteristics of the degradation stages do not change, it is recommended that the same K_d-approach as used in the earlier safety assessments should be applied. For specific cases, such as the large inventories of organic materials, aluminium and iron in the Group 2 waste compartments, or high Cl concentrations in the near-field pore water of a

repository situated in the Effingen Member host rock, a potential impact on the retention of dose-determining anions should be considered. The impact of large inventories of iron in some waste sorts on radionuclide retention is uncertain. It is currently unknown how much of the sorption controlling cement minerals will react with iron corrosion products to produce different phase assemblages.

EDTA, cyanide, gluconic acid, isosaccharinic acid and ammonia are considered to be the most important complexing ligands which could have an influence on radionuclide uptake by cementitious materials. Sorption reduction factors can account for the possible impacts on radionuclide speciation. The latter is determined by the actual concentrations of the complexing ligands in the waste compartments. The relevant sorption reduction factors and ligand concentrations need to be estimated individually for the two waste categories (Group 1, Group 2).

Colloids, if they exist in significant concentrations, and if they are mobile, might act as carriers for radionuclides and accelerate radionuclide transport. As outlined in Section 3.6, both cement (near-field) and clay (far-field) colloids are expected to be physico-chemically unstable in the engineered barrier system and in the host rocks (e.g. coagulation, attachment to surfaces, dissolution, and filtration). The colloid concentrations are expected to be very low. The mobility of colloids is very low in the porous host rocks. Only fast advective transport in fractures might be a conceivable transport scenario which could have an impact on radionuclide mobility.

2.5   Uncertainties

This section does not deal with individual parameter uncertainties such as thermodynamic constants, diffusion coefficients or K_d values. These uncertainties are dealt with in specific sections of this report.

The present description of the different processes relies on the classical conceptual approach where individual processes are analysed separately under the assumption that the time scales are different and feedback (coupling) among processes is ignored. We believe that the main conceptual uncertainties are associated with the fact that in reality the systems are complex and several processes proceeding on similar time scales may interact with one another.

The de-coupled treatment relies on the assumption that it is possible to identify a process that governs the system evolution. Based on the summaries for the different processes in Section 2.1 it is not possible to unambiguously identify any single process that dominates the spatial or temporal geochemical near-field evolution. The following process and time couplings were identified:

- Diffusive exchange between the cementitious near-field and the host rock is expected to cause minor concrete degradation within the first 100'000 years.

- Diffusive exchange across concrete/clay interfaces might seal off the emplacement tunnels and inhibit solute and mass transport across the interface within relatively short times (hundred(s) to thousands of years).

- The effect of advective transport of host rock water into the cementitious near-field strongly depends on the water flux. The water flux in most host rocks is very low and concrete degradation is rather low. In addition, water fluxes may be changed by precipitation/dissolution of minerals.

- Internal degradation of concrete (ASR) and waste – cement reactions may cause a fast degradation of the concrete. There is a high degree of uncertainty associated with the time scales of these reactions (kinetic parameters, reactive surface areas). These reactions consume water and are therefore limited by the availability of water.

- The waste – cement reactions and the corrosion of metals will cause a (partial) de-saturation of the repository and delay the re-saturation. Depending on the host rock properties, and on the design of the engineered barrier system, the de-saturation regime may last between a few thousand years and more than 100'000 years.

- This de-saturation will slow down advective and diffusive transport (of solutes and water) in the repository and delay the associated concrete degradation. The change of effective transport parameters in the system strongly depends on poorly known transport parameters under partially saturated conditions

  - Clogging at concrete/clay interfaces may be possible under water-saturated conditions.

  - As long as water is present in sufficient quantities, internal concrete degradation and waste-cement reactions will continue. It may well be that under partially saturated conditions the internal concrete degradation is the dominating degradation process.

Based on this analysis we identify two major aspects of conceptual uncertainties affecting most transport, mechanical and chemical processes:

- the evolution of microscopic pore space
- the availability of water

Evolution of pore space

Precipitation and dissolution processes are always associated with volume changes. The extent of these volume changes is well known, but the impact on the geometry of the pore space is not well known. The geometry of the pore space is a key factor for various relevant material properties such as pore size distribution, connectivity, reactive surfaces, and affects not only transport and mechanical properties but also subsequently chemical parameters such as kinetic rates. There is also a strong dependency on capillary pressure – saturation properties and on the pore size distribution in partially saturated media.

Most currently available chemical, mechanical and transport models describe macroscopic changes of porosity, but do not account for microscopic changes, or for the competition between different processes. It is conceivable that lack of microscopic knowledge may give rise to a significant uncertainty on the macroscopic scale. For example, the time dependence of mineral precipitation/dissolution can be described by macroscopic rate laws, which require a microscopic knowledge of rate constants and reactive surface areas and their change with pore space alterations. These microscopic parameters are largely unknown for most minerals, especially for the case of mineral precipitation.

Repository saturation of and the availability of water

The availability of water plays a key role in the system evolution. Usually, the classical view begins with a fully saturated system.

Internal degradation by alkali silicate reactions, as well as metal oxidation reactions and the microbial degradation of organics are only possible in the presence of sufficient amounts of water since these reactions consume substantial amounts of water. The water has to be

transported to the reaction front or has to be available from a "reservoir" i.e. water filling the pore space (porosity). The actual availability of water, as a solvent and reactant, is the key limiting process.

Despite all the shortcomings outlined for the pore space changes, well-developed concepts for transport by diffusion, or by advection, or both, in fully saturated media are currently available. It is possible to estimate total porosities and their changes through dissolving/precipitating phases. Furthermore, concepts on how the changing porosities might affect transport are available.

If water is partly replaced by a gas phase, however, we are faced with a more complex system because we have to deal with two phases (fluid and gas) which occupy variable portions of the pore space. The actual gas/fluid ratio is itself a complex function of, for example, pore size distribution, pressure, temperature, external and internal sinks/sources for gas and water.

It is well known (Section 3.3.1 and Nagra 2008b) that the diffusive and advective transport of solutes is significantly slowed down, or even ceases, in partially saturated media. All processes that rely on water and solute fluxes will therefore be limited by the partial saturation of the system, especially the evolution (degradation) of external (host rock/concrete) and internal (waste/concrete) interfaces. The diffusion of water vapour in the gas phase might be the dominating water transport process under partially saturated conditions. Vapour diffusion is relatively fast, but the total flux may be limited by the relative humidity at the given pressures and temperatures.

If water is removed from the available porosity by reactions, this internal consumption of water produces a humid system in which narrow pores contain the remaining water and the wider pores are filled with gas and water vapour. In such systems the water transport (to reaction fronts) is enhanced due to the fast diffusion of water vapour via the gas phase, but the solute transport (towards the far-field) in a connected fluid phase will be slowed down. This interplay between water consumption, gas/vapour production and nuclide transport in partly saturated systems could be an important aspect which is at present only poorly understood.

3   Evolution of transport properties of the disposal system: relevant processes

This section begins with a summary of the disposal system (Section 3.1), followed by a review on the Swiss and international literature on the evolution of a cementitious repository and on clay/cement interactions (Section 3.2). We continue with a review and description of how transport processes influence the repository evolution (Section 3.3). The interactions of cement phases with several waste sorts and with aggregates are presented in Section 3.4. Section 3.5 assesses the role of spatial heterogeneity on near-field evolution. Finally, the possibility of colloid formation in the near-field and in the adjacent host rock is reviewed (Section 3.6).

3.1   Overview of the disposal system

This section consists of a summary of the disposal system and makes use of information and repository lay-outs given in Nagra (2008a, 2010).

3.1.1   Description of the disposal system

General concept

The conceptual outline of a deep geological repository for L/ILW is shown in Fig. 3.1. The repositories will be placed at a suitable depth (between 200 and 800 m below the surface) in one of the host rocks selected during SGT Etappe 1 (Nagra 2008c). According to Table 3.1-1 in Nagra (2010) two repositories, one for SF/HLW/ILW and one for L/ILW will be constructed at different sites, or possibly a combined disposal facility at one site.

The safety concept for the planned repositories is described in Nagra (2008a) and is based on a multi-barrier system as shown in Fig. 3.2. The barrier elements are, in the case of L/ILW, the waste matrix, the disposal container, the mortar backfilling in the emplacement tunnels, the backfilling and sealing of the underground structures, the host rock and any confining rock units.
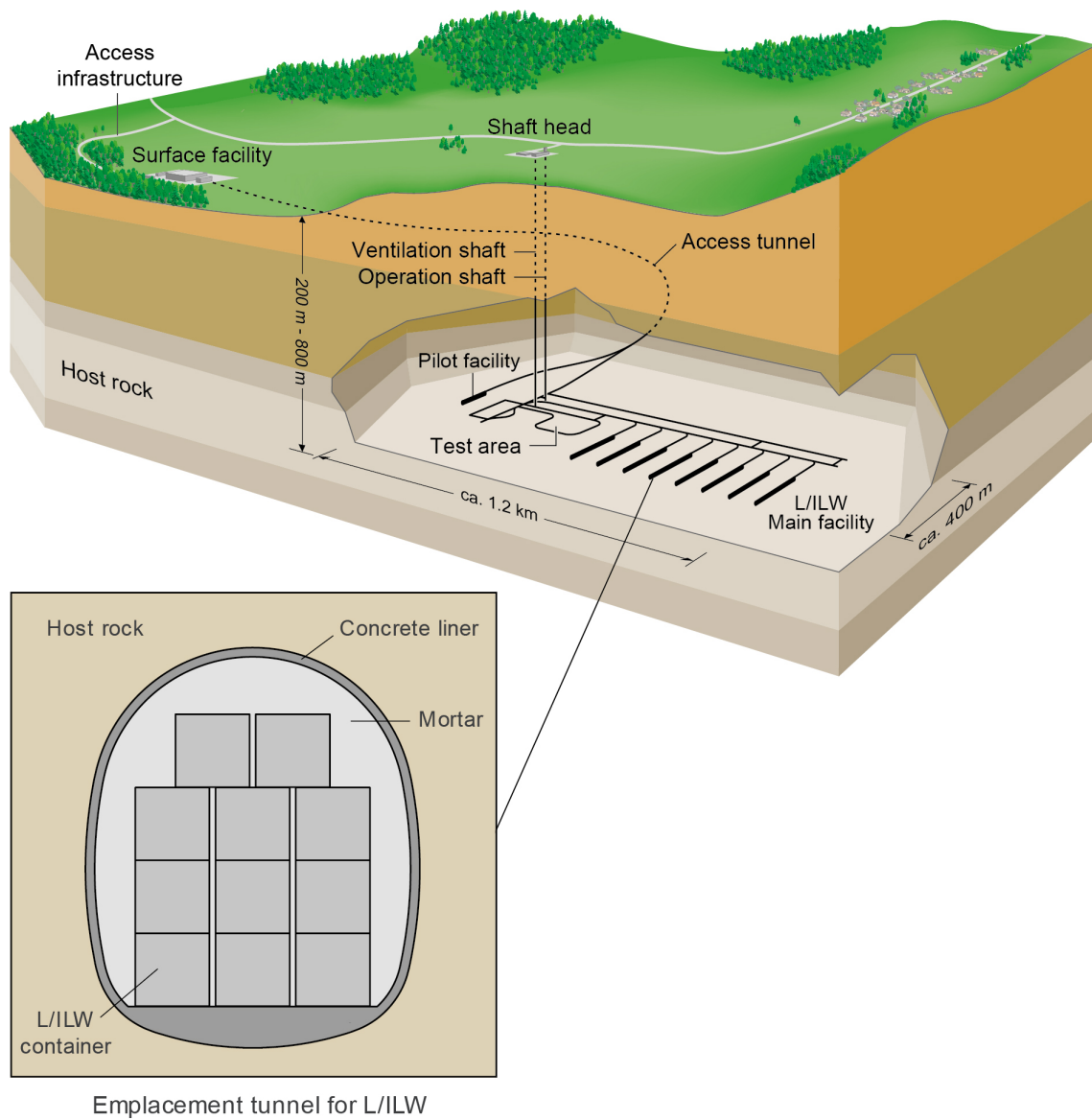
Fig. 3.1:   Conceptual outline of a deep geological repository for L/ILW (Nagra 2008a).

Safety barrier system for L/ILW

Waste matrix (various materials)

- Fixation of radionuclides in the waste matrix
- Slow degradation rate of the waste matrix

Disposal container

- Containment of the waste for a restricted time period
- Thereafter: Restricted water inflow and retention of radionuclides (sorption on container materials and corrosion products)

Backfill (cement mortar)

- Suitable interface between disposal containers and the host rock
- Favourable radionuclide retention properties
- Favourable conditions for long-term stability of the disposal containers

Host rock

- Low groundwater flux
- Favourable structure of the pore space
- Favourable geochemical conditions for radionuclide retention
- Favourable conditions for long-term stability of the engineered barriers

Geological situation

- Favourable host rock configuration for arrangement of the disposal caverns
- Favourable conditions for long-term stability of the barrier system
- Absence of raw materials deposits that would be workable in the foreseeable future

Placement of disposal caverns deep underground

- Isolation of the waste
- Prevention of unwanted access
- Protection from unintentional intrusion
- Protection from erosion

Fig. 3.2:   Reference safety barrier concept for L/ILW (Nagra 2008a).

Emplacement tunnels

Section 5.2.1 in Nagra (2010) gives an overview on the possible types of L/ILW emplacement tunnels (Fig. 3.3). The use of a specific tunnel type depends on the mechanical properties of the host rock and the overburden at a specific site. Most of the investigations in this report are based on tunnels of type K09 as shown in Fig. 3.3.
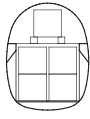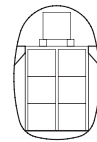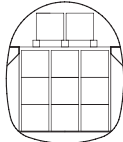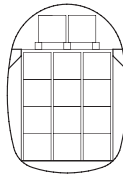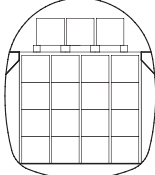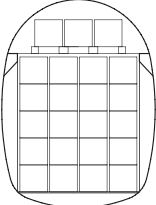
K04	K06	K09	K12	K16	K20
LRF: 58 m^2 LH: 9.5 m LB: 7.3 m	LRF: 77 m^2 LH: 11.9 m LB: 7.6 m	LRF: 110 m^2 LH: 12.6 m LB: 10.4 m	LRF: 136 m^2 LH: 15.0 m LB: 10.6 m	LRF: 182 m^2 LH: 16.1 m LB: 13.4 m	LRF: 215 m^2 LH: 18.5 m LB: 13.6 m

Fig. 3.3:   Planned tunnels types (Nagra 2010).

LRF: clear crossectional area; LH: clear height; LR: clear width

Access tunnel and shaft

The access tunnel provides the connection between surface installations and the emplacement tunnels. According to Nagra (2008a) Section 2.3.4, it will have a clearance cross section of approx. 31.8 m^2 corresponding to an excavated cross-sectional area of approx. 42.2 m^2. The overall length is assumed to be 2.4 km.

Backfilling and sealing

The voids between the drums in each disposal container will be backfilled with a porous free-flowing mortar (Mayer & Wittmann 1996). After emplacement of the containers in the disposal tunnel is finished, the void space between waste containers and tunnel lining, as well as transfer- and unloading area will be backfilled with a stiff porous mortar composed of mono-grained aggregate material and hardened cement paste (type M1 mortar, Jacobs et al. 1994). It is the most permeable component of the engineered barrier system providing a large pore space (porosity ~ 0.24). This backfill mortar is designed to contain an accessible volume to the gas formed in the emplacement tunnel and to ensure mechanical stability by filling the voids between the waste containers. Each tunnel is sealed with a concrete plug. A schematic view of the backfilled system is shown in Fig. 3.4.

Heterogeneity of the waste matrix

More than 200 materials (substances, chemical compounds, etc.) present in the different waste sorts have been listed in the framework of the Swiss disposal programme MIRAM 12 (Nagra 2013). A few of the materials are present in almost all waste sorts (e.g. cement for solidification, steel) while others are found only in a few waste sorts (e.g. magnesium, graphite). Many of the

materials are expected to take part in chemical reactions (e.g. corrosion of metals, degradation of organic matter etc.), which convert them into degradation products. Others will remain virtually unchanged over geological timescales (e.g. graphite). Furthermore, some of the materials or their degradation products may react with the cement paste of the near-field and thus influence its barrier function, while others are expected to have no significant impact on the near-field. The influence of individual classes of materials, such as metals or organic matter, on the long-term performance of the near-field can be assessed based on expected chemical transformation processes and on the evaluation of possible interactions between the materials or their degradation products and cement paste.
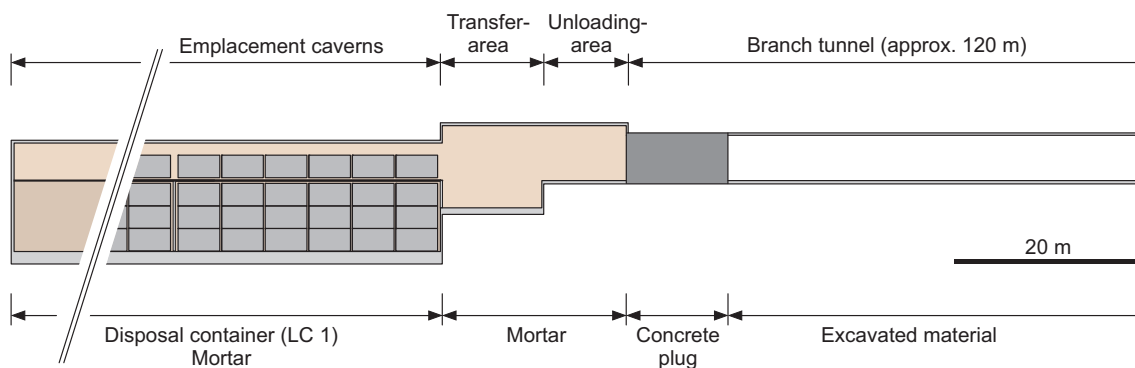
Fig. 3.4:   Longitudinal section of L/ILW emplacement tunnel after closure (Nagra 2008a).

Repository operation and closure

An overview of the concepts for repository operation and closure is given in Nagra (2008a) Section 2.4. It can be summarized as follows: After filling an individual tunnel with waste packages, it is backfilled with cementitious grout and mortar. The direct access to the tunnel is plugged with concrete at the tunnel entrance. Once the waste emplacements in all tunnels have been completed, the operation and access tunnels are backfilled with a sand/bentonite mixture. A concrete plug separates the backfilled underground facilities from the shaft, the pilot facility and the test areas. This part of the repository stays open during an observation phase. After the end of the observation period, all underground facilities will be backfilled and sealed.

3.1.2   Repository evolution as complex interactions between processes with feedback loops

In the last ten years the availability of more sophisticated software tools has allowed the assessment of complex systems taking into account several processes and their interactions. Although it is not yet possible to model a repository with all the relevant process couplings in a predictive way, the available models are well suited to investigate selected process couplings and their possible effects on the geochemical evolution. Also, from the experimental point of view, information from more specifically designed experiments is available, for example in the European Union FP7 "FORGE" project.
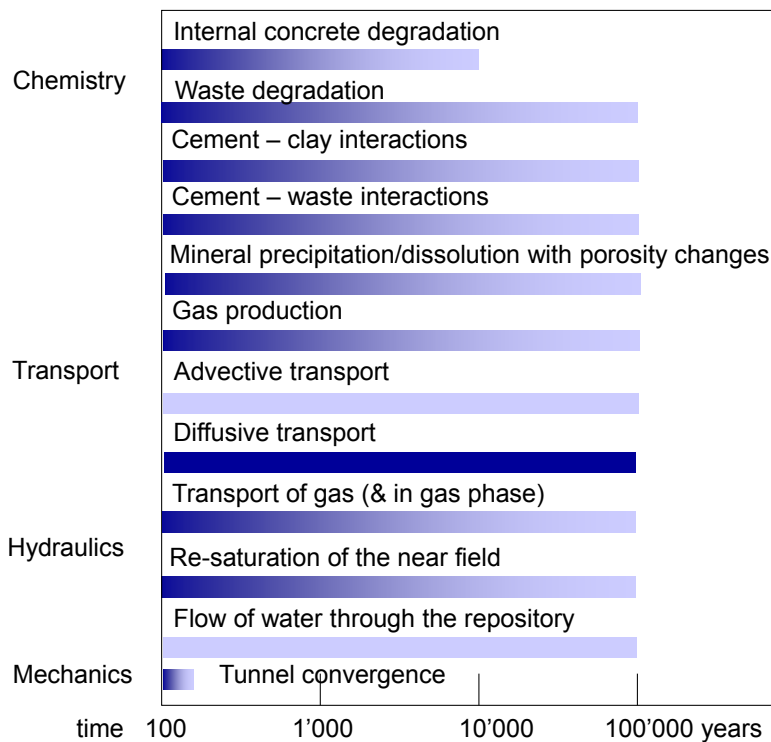
Fig. 3.5: Chemical and physical processes influencing the evolution of a cementitious repository.

Coupling between processes are not considered. The color intensity and the length of the bars indicate, in a qualitative way, the impact of the individual process.

Fig. 3.5 shows the main relevant processes that are currently believed to influence the geo-chemical evolution in all types of host rocks. For individual host rocks the time scales may vary. The colour intensity indicates in a non-quantitative way their expected importance over time. Most of these processes are described in more detail in this report. Some process couplings are now included in the analysis; for example, the influence of advective and diffusive transport on cement-clay interactions. Other important couplings need to be investigated in the future. As outlined in Section 2, this especially concerns the interaction between the availability of water in terms of repository re-saturation, gas-production, internal concrete degradation and precipitation/dissolution reactions under partially saturated conditions. In addition, the influence of spatial material heterogeneities has not been thoroughly investigated.

Chemistry

Concretes, clays and wastes are chemically very different materials. Their interactions are likely to be influenced by various chemical and transport processes and their coupling. At clay-cement material interfaces, mineral precipitation /dissolution and kinetics, and (to a minor degree) ion exchange reactions, might alter the pore space with accompanying changes in material properties (transport and mechanical characteristics). Similar effects can be expected locally for the interactions of waste and cement materials inside the waste drums and emplacement containers.

The evolution of the safety barrier system depends on chemical processes or is influenced by chemical processes to various degrees. For example:

- The chemical interactions of waste with the concrete/bitumen matrix may influence the fixation capacity in the waste drums.

- Metal corrosion will eventually breach the containment of the steel drums.

- Cement and grout degradation may weaken the waste isolation with time.

- Cement/clay interactions may weaken the mechanical stability of host rocks and tunnel support. This may result in producing features of higher hydraulic conductivity and effecttive diffusivity.

- Waste – clay – cement interactions may increase or decrease the leaching rates of radionuclides.

- Waste – clay – cement interactions may lower (locally or globally) the pH in the concrete compartment and influence metal corrosion rates.

- Alteration of mineral assemblages (dissolution of clay minerals in the host rocks, transformation of cement minerals) may alter radionuclide sorption.

- Dissolution of minerals may increase porosity and increase the water flow into the repository.

- Precipitation of minerals near material interfaces may lower porosity and decrease the water flow and diffusive transport.

- Changes in the chemical environment (e.g. pH, ionic strength) may cause the production of colloids or increase their stability.

Gas production

Gases (H_2, CO_2, CH_4) will be produced by the anaerobic corrosion of metals and by microbial degradation of organic matter (Nagra 2002a). CO_2 will react with the cement material causing carbonation and porosity changes near the source. In contrast, H_2 and CH_4 are not expected to interact with cementitious materials but the formation of these gases will determine the pressures in the near-field, and, depending on the over-pressure, delay the re-saturation of the emplacement tunnels. The amount of gas (H_2, CH_4) generated as a function of time depends on the inventories (steel, organic matter) and rates, i.e. the corrosion rate in the case of H_2 and the degradation rate of organic matter in the case of CH_4 (Wiborgh et al. 1986, King 2008, Nagra 2008a, Newmann & Wang 2010). It is expected that the total duration of the gas generation phase will not exceed 200'000 years (Nagra 2008a).

Redox conditions

Several waste sorts will consist of, or contain, metallic materials, in particular steel materials. The latter materials include waste packages (e.g. steel drums, etc.), the reinforced waste containers (e.g. reinforcement with bars, fibres etc.) and the construction materials (e.g. anchors, bolts, etc.), which are susceptible to corrosion (oxic, anoxic) over time (Wersin et al. 2003). Consumption of the residual oxygen in the near-field is expected to occur after repository closure due to the aerobic corrosion of metals, which generates no H_2 gas, and the degradation of easily degradable organic matter (Nagra 2002a). Thus, redox conditions are expected to be oxidizing in the early stage of a L/ILW repository, similarly to those reported for an ILW repository (Wersin et al. 2003). In the latter study, it was estimated that the oxic stage will last over a period < 1'000 years, depending on the state of saturation of the near-field.

After O_2 depletion, the near-field will remain anoxic. Redox conditions will be determined by various reactions between dissolved and solid redox-active species in the alkaline environment of the near-field. It has been stated that the redox potential will largely be determined by the anaerobic corrosion of steel (Wersin et al. 2003). The latter process produces a thin magnetite-film on the steel surface and the redox-active species were considered to be magnetite and dissolved Fe(II). Note, however, that other waste materials could have an effect on redox conditions. For example, the degradation of large amounts of organic matter could reduce the redox potential.

Temperature

A relatively short-term temperature increase might occur in a cementitious repository due to the heat of hydration from mortar used for backfilling. It is expected that the temperature increase will be less than 5 °C in the case of the LLW repository due to the absence of large amounts of heat emitting waste. According to Tab. 4.2-2 in Nagra (2010) the measured geothermal gradients from surface to the bottom of potential host rocks are between 33 °C/km (Wellenberg) and 56 °C/km (SB Schafisheim). The measured ambient temperatures in the potential host rocks range from 26 – 53 °C, depending on the location of exploration boreholes. A temperature rise in the range of 5 to 10 °C is not expected to have a significant impact on the complex interplay between chemical and physical processes.

According to Nagra (2002a), Section 5.4.2, the ILW repository will contain small quantities of heat emitting wastes. Together with the hydration heat from the mortar, these wastes will cause a temperature increase of a maximum of 12 °C over a period of several decades. It is not expected that the temperature in the near-field of ILW emplacement tunnels exceeds 60° C (Nagra 2004).

Radiolysis

Possible effects of radiation related processes are summarized in Nagra (2002a), Section 5.4.1. The effects of radiation related processes are assumed to be negligible. Locally oxidizing conditions might occur for waste sorts with a very high α-activity (compacted fuel hulls and ends) since H_2O_2 will be produced by α-radiolysis.

Rock mechanics

Mechanical processes such as tunnel convergence might also change the pore space and the associated transport parameters (Section 5.4.3 in Nagra 2002a). Tunnel convergence is expected to induce (micro-) cracks at surfaces and interfaces, which would enhance the transport of solutes and would override any effects of pore clogging due to mineral precipitation. The enhanced transport will accelerate mineral transformations at the interfaces and mineral precipitation might re-close the (micro-) cracks (pathways).

Transport and hydraulics

In terms of transport, the water saturation state, the water flow and the diffusion of solutes across material interfaces will strongly influence the extent and time-scale on which chemical processes occur. At the beginning, the emplacement tunnels and the host rock pore waters will not be in equilibrium. In terms of solute concentrations, the compartments will proceed towards equilibrium predominantly by diffusive transport across the concrete – host rock interfaces. The water saturation state of the repository, and possible porosity reduction at material interfaces, will slow down the equilibration process and may even prevent the complete equilibration between the emplacement tunnel and host rock pore waters within 100'000 years.

Due to the very low permeability of the argillaceous host rocks, fluid and solute transport are dominated by diffusion. The long time scale of the diffusive processes, which limit the rate of chemical changes, implies that such systems cannot be readily studied in laboratory experiments. Consequently, the information from relevant analogues (natural and industrial), and the results from reactive transport calculations, in combination with simple mass balance calculations, are normally used to assess possible changes of the engineered and natural barriers on performance assessment relevant time scales.

For some processes, and process couplings, there is little or no information in the literature. This includes the interactions of chemical and mechanical processes and in particular the long-term chemical evolution under partially saturated conditions.

3.2   Literature overview

This section contains a summary of relevant literature for the evolution of a cementitious repository. It does not aim to present an exhaustive list of all work carried out but instead focuses on the most important Swiss milestone publications and some more recent publications that are important for the conceptual considerations in this report.

3.2.1   Earlier Swiss work on the expected evolution of the near-field system

Work related to the Wellenberg site

The first fully developed Swiss concept for a low- and intermediate-level cementitious radio-active waste repository was developed for the Wellenberg site in the 1990s. The expected "normal" geochemical evolution of a LLW repository in Helvetic Marls is summarized in Nagra (1994), Section 2.3.2.

The assumed inventory was 94 wt.-% concrete or mortar, 4 wt.-% steel and 1 wt.-% high molecular weight organic waste, as well as other wastes in smaller quantities. Cement phases, steel and organics, in combination with flowing groundwater determine the chemical characteristics of the near-field relevant for radionuclide transport. Cement paste will be degraded slowly by groundwater flow through the repository. Anaerobic steel corrosion will determine the redox conditions (see below). The degradation of organic material will generate gases, and dissolved low molecular weight organic products which could accelerate concrete degradation and influence the sorption of radionuclides on the concrete phases.

The concrete pore waters will evolve in three steps in an advective transport regime:

a) The pH is high, 13.5 > pH > 12.5, due to dissolved alkali metal hydroxides. It takes the equivalent of about 10 pore water exchanges to reduce the pH to 12.5.

b) The pH is buffered by portlandite and remains stable at about 12.5; this condition remains until portlandite is completely dissolved.

c) The pH decreases continuously during dissolution of the remaining cement minerals. The final pH of 10.5 is reached after ~ 1'000 pore water exchanges.

The corrosion of metals will govern the redox conditions in the emplacement tunnels. Soon after closure the remaining oxygen will be consumed by corrosion processes and strongly reducing conditions will develop. Over several thousands of years the steel, and other metals, will undergo anaerobic corrosion. After the complete oxidation of the metals, the redox conditions will be conditioned to that of the intruding formation water.

Colloids may be generated, which can act as carriers for radionuclides provided they are stable.

Gases will be produced by the degradation of organic materials and by the anaerobic corrosion of metals. Gas production will be strongest directly after the closure of the repository. Gas production rates for both metal corrosion and organic matter degradation will fall quickly and will decrease to zero within one thousand to ten thousand years (Section 2.3.2.3 and Figure 2.3-4 in Nagra 1994). The span of time for gas production is much shorter than in later studies (Nagra 2008a).

Entsorgungsnachweis (Opalinus Clay)

The expected "normal" geochemical evolution of an ILW near-field in Opalinus Clay is summarized in Nagra (2002a) in Section 5.4.4. This description is complemented by a report edited by Mäder (2003).

It is assumed that the pore water chemistry in the near-field will be determined by the concrete and steel materials in the emplacement tunnels. In addition, smaller quantities of other metals and organic waste and the "inflowing" host rock pore water influence the pore water chemistry.

The concrete pore waters are assumed to evolve in the same three steps as described above for the Wellenberg site.

Due to the very low permeability of Opalinus Clay, transport will be dominated by diffusion. The characteristic diffusion time of OH^- in Opalinus Clay is in the order of one thousand years for one meter. This will cause the Phase A ("young" water, pH 13.5) of cement degradation to exist for thousands of years and phase B (portlandite buffered water, pH 12.5) is expected to be maintained for hundreds of thousands of years.

The high-pH concrete pore waters will interact with the surrounding host rock. Zones with porosity reduction are expected to occur near the concrete/Opalinus Clay interface due to precipitation of calcite, Mg-silicate/aluminate-hydroxide and illite for Phase A concrete waters. Phase B concrete pore waters are expected to form C-S-H phases and zeolites. Mass balance calculations by Mäder & Adler (2004) indicate, that a high pH plume would extend about 4 meters into the host rock, consuming about 10 % of the total buffering capacity of the Opalinus Clay components. Such conditions can probably only be reached after an extremely long time (millions of years).

The latter study also indicates that a zone with increased pH (from 10.1 to 11), but without major mineral changes, may extend no further than 10 meters into the rock within one million years.

The corrosion of metals will govern the redox conditions in the emplacement tunnels (Wersin et al. 2003). Soon after closure the remaining oxygen will be consumed by corrosion processes and strongly reducing conditions will develop. Due to contact with water vapour, the anaerobic corrosion of steel will occur. Steel corrosion, and the corrosion of waste packages, will be the main contributor to H_2 (gas) production. After all iron is consumed, the redox potential will increase again to reach the redox conditions as prevailing in the host rock pore water (reducing conditions buffered by pyrite and siderite occurring in the Opalinus Clay).

3.2.2 Other reviews/international state of the art

Cement/clay interaction

Gaucher & Blanc (2006) give an overview of publications on experiments, natural analogues and modelling related to cement/clay interactions. Based on their literature review, they state that it is premature to make any definite conclusions on the consequences of an alkaline disturbance in a clay medium. They say further that although the mineralogical consequences of an alkaline disturbance are fairly well-known, nevertheless knowledge of the thermodynamics of the clays, zeolites and cement phases needs to be improved (see also Savage et al. 2007 on this topic). Large uncertainties remain in the field of dissolution kinetics and mineral precipitation, and especially for the dissolution kinetics of montmorillonite. Finally, they state that numerical *simulations will become increasingly representative inasmuch as we are able to take into account a specific geometry, the complexity of the concrete and bentonite mineralogical systems; to incorporate the surface chemistry of the clays, zeolites and C-S-H; and to consider a mineralogical control of the pCO$_2$ and* <u>*the evolution of the porosity*</u>.

A general overview on the status of cement/clay interactions in repository environments is given in Metcalfe and Walker (2004). Some of the main points drawn from this workshop are: *Over PA-relevant timescales, a high pH plume could conceivably propagate significantly through a bentonite buffer, but the potential overall consequences for safety depend on the disposal concept. Varied mineral dissolution, precipitation and alteration reactions will cause inter-related temporal changes in porosity, permeability and mechanical properties. A holistic understanding of these changes is needed to evaluate the overall safety implications. ….Additional work should focus on developing integrated interpretations using presently available data and improved coupled models of bentonite alteration should be developed. Future experiments should concentrate on determining mineral dissolution rates under alkaline conditions. The need for communication, between management, researchers investigating cement-bentonite interactions, and workers in the construction industry who will design and implement the barrier systems, was also emphasized.*

Wang et al. (2010) presented the results of a feasibility study on the disposal of radioactive waste in a cementitious repository in Boom Clay. They give an extensive overview of the work carried out in Belgium, Switzerland and France on cement – clay host rock interactions, a summary of studies on bentonite-cement interactions, and present some results of the ECOCLAY II project. They conclude that the nature of the alkaline plume disturbance in clay materials is relatively well understood. Clay and accessory minerals tend to be dissolved and C-S-H-phases, zeolites and calcite will precipitate. This is accompanied by porosity clogging in a diffusion dominated transport regime. The temporal mineralogical and porosity evolution

remains uncertain, especially while kinetic reaction parameters are uncertain and difficult to quantify accurately. They carried out geochemical coupled transport simulations using an approach similar to the work presented here in Sections 3.3.2 and 3.3.3. Their simulations took into account mineral dissolution/precipitation, ion exchange, surface complexation and considered diffusive and advective transport. Their results, in terms of the spatial extent of pH increases, mineralogical changes and porosity changes, are very similar to our results summarized in Sections 3.3.2 and 3.3.3.

Baker et al. (2002) summarize the work carried out by NIREX on a concept for radioactive waste disposal in a cementitious repository. They present arguments based on their own laboratory experimental programme, the work on the Maqarin natural analogue and some thermodynamic and reactive transport modelling. Their overall conclusions are that there is a good understanding of the mineral assemblages that are produced when high pH water interacts with silicate rocks, that pore sealing (clogging) in an alkaline disturbed zone is probable, that pore sealing results in an overall reduction of flow through the repository, that the host rock heterogeneity in terms of spatial mineral variation and fracturing results in a complex and heterogeneous evolution of the geochemical and transport parameters, and that it is presently still difficult to provide a quantitative estimate of the extent of the alkaline disturbed zone.

Recent work in UK has concentrated mainly on the development of modelling methodologies capable of examining the spatial and temporal evolution of pH and mineral reactions in the near-field of a cementitious disposal site (Hoch et al. 2009, Small & Thompson 2010). Hoch et al. (2009) used a two-dimensional reactive transport model to investigate groundwater flowing around a cementitious repository. For most of the investigated scenarios they found that the groundwater flow in the repository is reduced significantly due to a porosity decrease at the upstream edge of the vault. They listed several simplifications and uncertainties that limit the applicability of their own and similar models. This includes the unknown porosity-permeability relationship, the role of cracks for flow and transport, which is typically not considered in continuum models, some severe uncertainties in the occurrence of thermodynamically predicted mineral reactions and the inability of continuum models to model sub-grid processes such as the formation of low-permeability skins.

Small & Thompson (2010) used one- and two-dimensional models to investigate the mineralogical and porosity changes in a 300 m long vault and the chemical evolution waste packages that are backfilled with cementitious material. All simulations were based on advective transport scenarios. In their conclusions they highlight the strong buffering capacity of cementitious materials, but also mention that flow field heterogeneities might have a strong influence on the geochemical evolution.

Grandia et al. (2010a, 2010b) investigated clay-cement interactions for the Swedish design concept in which concrete plugs and concrete bottom plates are in contact with the clay backfill in the emplacement tunnels. Their reactive transport calculations are based on a complex geochemical setup for cement phases which utilize discretized solid-solution models for the C-S-H-phase. Porosity changes due to dissolution/precipitation are back-coupled to transport only in some of their models, mainly related to diffusive transport across clay-cement interfaces. They found that these interfaces tend to clog quickly due to the precipitation of ettringite. The ettringite precipitation is mainly driven by the high concentration of sulphate in the (clay) backfill pore water which is diffusing into the concrete. Recently a comparative modelling study of clay-cement interactions observed at the Tournemire Underground Rock Laboratory was published in Soler et al. (2014). The modelling work reproduces observations from a 15 year old contact between concrete and claystone (compare Section 3.3.4). The analysis of the material interface shows dissolution front for portlandite in the concrete, and a reduction of porosity at

the interface due to precipitation of C-S-H, ettringite and calcium carbonate. Three modelling teams, each one using a different code, modelled the system and conducted a sensitivity study with respect to rock and concrete composition, thermodynamic and kinetic parameters, and the influence of inclusion of cation exchange or existence of small fractures (Soler 2013, Watson et al. 2013, Yamaguchi et al. 2013). All modelling teams could reproduce the main experimental findings, *with details in mineralogy, porosity and alteration distances changing between different sets of assumptions and calculation teams and codes.*

3.3 Influences of mass and solute transport processes on system evolution

This section details the influence of transport processes on the geochemical evolution of the repository. We start with the influence of water and humidity transport on the availability of water in Section 3.3.1 since the diffusion of solutes (Section 3.3.2) and advective transport (Section 3.3.3) depend on the existence of a connected water phase. Finally, we summarize the available information on porosity clogging and the influence on transport in Section 3.3.4.

3.3.1 Water transport and saturation

Overview/general description

During the operation and observation phase, all open sections of the repository cause a spreading zone of partial de-saturation in the host rock. Once the open parts of the repository are backfilled, the adjacent host rock and the backfilled sections will start to re-saturate. Due to the very low permeability of the host rocks, it will take up to 30'000 years to reach full hydrostatic equilibrium in the repository (Nagra 2008a, Section 4.2.3). Faster saturation can be expected if water flow into the repository is enhanced by, for example, additional inflow through a fracture zone or by increasing the permeability of the plugs and seals.

Directly after repository closure, another process will influence the re-saturation of the repository. Gas is generated in the repository due to the anaerobic corrosion of metals (Nagra (2008a), Section 3.3.1, and Section 3.4.4 of this report) and the degradation of organic matter (Nagra (2008a), Section 3.3.2, and Section 3.4.1 of this report).

The competition between repository re-saturation and gas production in the repository is described in Section 4.4 of Nagra (2008a) and in Lemy et al. They conclude that the time scale for repository re-saturation is of the order of tens of thousands to over a hundred thousand years.

Information from model/experimental studies/natural analogues/observations in nature

To the best of our knowledge specific experimental investigations into the effect of partial-saturation on the geochemical evolution of the near-field of a cementitious repository have not been conducted to date. So far experiments have concentrated on gas productions rates and the gas transport properties of the repository (Nagra 2008a, Lemy et al. 2010).

Savage (2009) conducted a review of the experimental data associated with the development and properties of cement-bentonite interfaces with implications for gas transport. He concluded that:

The evolution of the near-field of a Swiss repository for L/ILW is complex, with the potential for the development of chemical and mineralogical perturbations at a number of interfaces between barriers (cement-rock; cement-sand/bentonite etc.). The review conducted here shows that:

- *There is no experimental evidence for the development of chemical and mineralogical perturbations at cement/concrete-bentonite interfaces in partially-saturated systems.*

- *There are no measurements of gas permeability of cement-bentonite interfaces, even for fully-saturated systems*

- *Modelling techniques are now able to simulate geochemical processes in partially-saturated systems.*

Any physicochemical perturbations at cement-bentonite interfaces will be strongly linked to the saturation state of the materials concerned:

- *Unsaturated samples of cement-bentonite show no evidence of reaction, even over very long timescales (125 years at Tournemire). This indicates that gas transport will not be affected under unsaturated conditions.*

- *Saturated samples of cement-bentonite show variable behaviour, depending upon fluid transport mechanisms and cement pore fluid compositions:*

  - *Advective systems with very high pH pore fluids (pH ≥ 13.5) show porosity increases, dramatic (permanent) decrease of swelling pressure, and increases in diffusivity/ hydraulic conductivity. These features suggest that gas permeability will be increased under these conditions.*

  - *Diffusive systems with pore fluids with pH < 13 show mainly porosity decreases, slight decreases in swelling pressure, and decreases in diffusivity/permeability. Carbonation may exacerbate the decrease of permeability. These features suggest that gas perme-ability will be decreased under these conditions.*

It is anticipated that partially-saturated systems will lie somewhere between these two extremes, depending upon fluid transport conditions and the stage of cement pore fluid evolution. Further research is needed to clarify the effects under unsaturated conditions.

Availability of water in the repository

The availability of water is a key factor in the geochemical evolution of clay and cement materials. Without sufficient water, many transport and chemical processes will be slowed down considerably or even stop completely.

Based on the pore size distributions, the relations between capillary pressure and water saturation, and other information given in Nagra (2008a), we made some estimates on the availability of water in a "de-saturated" repository.

The maximum possible gas pressure (lower bound of fracture pressure) in a reference L/ILW repository in northern Switzerland is 8.125 MPa (Table 3-3 in Nagra 2008a: lithostatic pressure at repository level with 325 m overburden and a rock density of 2.5 Mg/m^3).

The (capillary) pressure – saturation curves can be connected to pore size distributions as described in Nagra (2008a), Appendix A. Their calculations showed that about 70 % of the pore space in a repository is filled with gas for a pressure of about 10 MPa (which corresponds to a minimum pore radius of 10^{-8} m for gas accessible pores). Fig A-4 in Nagra (2008a) states that

the gas available volume is dominated by mortars used for backfill as their pore size distribution is dominated by larger pores. Pore size distributions of construction and waste fixation concrete show a higher fraction of small pores; consequently gas saturation is significantly lower in these materials.

The interpretation in terms of residual water content of this estimation is that the minimum average water content in the concretes is about 30 % of the overall porosity. Mortars used for backfill will have lower, and construction and waste fixation concretes will have higher residual water contents. It can be assumed that the gas phase will be in a connected pore network. The same is not necessarily true for the water phase, where, especially in the highly porous backfill mortars, residual water trapping may dominate.

Hydrogen gas dissolution in the water phase can be estimated as described in Section 3.2.1 of Nagra (2008a). In addition, the equilibrium moisture content of hydrogen can be calculated according to Dalton's law assuming that water vapour and hydrogen behave as ideal gases. We have made such a calculation using GEMS-PSI and the results are shown in Tab. 3.1.

Tab. 3.1:   The system water – water vapour – hydrogen at P/T as calculated with GEMS-PSI based on ideal mixture of gaseous components and SUBGRD data (Johnson et al. 1992).

Pressure/ temperature	Solubility of $H_{2(g)}$ in $H_2O_{(l)}$ [g/kg H_2O]	Solubility of $H_{2(g)}$ in $H_2O_{(l)}$ [g/dm^3 H_2O]	Distribution of $H_2O_{(g)}$ in $H_{2(g)}$ [g/kg $H_{2(g)}$]	Distribution of $H_2O_{(g)}$ in $H_{2(g)}$ [g/dm^3 $H_{2(g)}$]
1 bar/25 °C	0.00153	0.00153[5]	287.7	0.0234
1 bar/38.5 °C	0.00139	0.00138	642.5	0.0500
10 bar/38.5 °C	0.0147	0.0146	60.7	0.0472
81.25 bar/38.5 °C	0.112	0.111	7.80	0.0493
100 bar /38.5 °C	0.135	0.135	6.42	0.0500

From the above values in Tab. 3.1, it is clear that the volumetric equilibrium moisture content of H_2 gas (Column 5) increases with temperature.

As it is very difficult to completely de-saturate the Opalinus Clay, we can assume that the equilibrium moisture content in the gas phase is reached everywhere. In addition, the moisture diffusion in the gas phase is relatively fast since diffusion coefficients in gases are 4 orders of magnitude higher than in water. Although we have an advective transport of gas out of the repository, we can assume that we will have an equilibrium moisture content in both the solid and gas phase everywhere in the repository[6].

---

[5]   0.00158 g/dm^3 from Table 3-1 of Nagra (2008a)

[6]   If advective transport of gas (and moisture) out of repository is more effective than the diffusion of water vapour (moisture) into the repository, the situation might arise where water in the gas phase is consumed by anaerobic corrosion of metals. If the moisture content of the gas phase drops below a certain threshold the anaerobic corrosion of metals will stop due to lack of water. Hydrogen gas production will stop and advective gas fluxes decrease due to loss of pressure. Moisture diffusion and re-saturation processes will take over and transport water into the repository, which increases moisture content of gas phase and re-starts anaerobic corrosion.

Time perspective

Even without considering gas production, the re-saturation of the repository is likely to occur within a period of several thousands to a few tens of thousands of years. Taking into account gas production, the complete re-saturation may occur over an even longer time frame i.e. tens of thousands to over a hundred thousand years (Nagra 2008a).

Uncertainties

This high variability in the temporal evolution of saturation has a direct impact on the uncertainty in the geochemical evolution. Saturation directly affects the availability of water and solutes for chemical reactions. Diffusive and advective mass fluxes decrease strongly with decreasing saturation, therefore the geochemical processes driven by transport are delayed or even stopped as long as full repository saturation is not reached.

At material interfaces, where water saturations remain high (e.g. host rock – high performance structural concrete) the geochemical evolution of the interfaces may be slowed significantly (compare Section 3.3.4 and Nagra 2008a), but will not stop completely.

3.3.2 Diffusion

Overview/general description

The reactive diffusive transport of solutes is described in its simplest form by

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_e(\theta, x)\frac{\partial C}{\partial x_j}\right) + R \tag{3.1}$$

where C [mol/m^3] is the concentration of a particular species, R [mol/m^3/s]a chemical source/sink term representing the change in solute mass of the species due to chemical reactions, and D_e [m^2/s] are the components of the effective diffusion tensor, which depends on the porosity θ [-].

An effective diffusion coefficient D_e is often calculated using Archie's law from the so-called formation factor F, the porosity θ and a diffusion coefficient in water D_w [m^2/s]

$$D_e = FD_w = \theta^m D_w. \tag{3.2}$$

Here m is an exponent, which can vary for different kinds of porous media (rock types) from 1.3 (unconsolidated sediments, e.g. sand) up to 2 in well cemented (clay-free) sediments. The diffusion coefficient in free water for electrolyte solutions varies between 1.1×10^{-9} m^2/s and 2.1×10^{-9} m^2/s at 25 °C (see Table 6.2-2 from Flury & Gimmi 2002).

In cement pastes and mortars the exponent of Archie's relation was estimated to be between 1.5 and 2.5 (Tumidajski et al. 1996). In addition, more complex models were developed which use pore size distributions and cement compositions to predict diffusivities and other transport properties (Garboczi 1990, Bentz 2000, Oh 2004, Tumidajski 2005, Bejaoui & Bary 2007,

Courcelles et al. 2011). Jougnot et al. (2009) presented data on the dependence of the diffusion coefficient of ions in the Callovo-Oxfordian argillite on saturation.

For clay rocks, van Loon (personal communication) estimated a mean value of $m = 2.5$ and the following modified relation:

$$D_e = 2 \cdot 10^{-9} \theta^m + 1 \cdot 10^{-11} \theta^{0.85}$$

(3.3)

The transport of radionuclides in the host rocks (Opalinus Clay, Effingen Member, 'Brown Dogger', rock matrix of Helvetic Marls) is predominantly diffusive with effective diffusion coefficients given in (Nagra 2010).

It is most likely that diffusive processes over clay/cement interfaces induce porosity reductions by dissolution/precipitation reactions and reduce diffusive and advective transport across corresponding interfaces (clogging). Compared to the repository lifetime, this clogging takes place on a short time scale. For a clogged interface the extent of pH changes in the various host rocks (pH-plume) is considered to be small.

The evolution of the concrete is coupled to the transport regime and the host rock evolution. In the case of clogging, the concrete compartment is sealed from the host rock and its evolution is driven only by internal degradation reactions (including reactive silica from aggregates and/or waste degradation products such as CO_2).

Information from natural analogues/observations in nature

A natural analogue for the alteration of clays by high-pH solutions was found at the Maqarin site (northern Jordan). A very detailed description of the site can be found in Smellie (1998). In samples from Maqarin it was found that the pores in the rock matrix adjacent to fractures were blocked by precipitates. The precipitates were produced by a diffusive exchange of solutes across the fracture surface between the high pH fluid in the fractures and the rock pore water. The zones with mineral alterations and pore blocking extended only a few centimetres from the fracture surfaces into the porous rock.

Supporting model studies/experimental studies

In Tab. 3.2 the extent of host rock alterations due to diffusive transport over concrete – host rock interfaces was obtained from the results of diffusive transport calculations without back-coupling of porosity changes to transport (Kosakowski & Berner 2011c). These simulations did not take into account the additional internal degradation of the concrete. According to the $\sqrt{Dt}$ dependence for diffusive transport distances, the alteration depths for 10'000 years were scaled with a factor of 3 to approximate the situation after 100'000 years. It should be noted that the simulations are based on a chemical equilibrium approach. Even for the case of no coupling between porosity changes and solute diffusion (i.e. constant effective diffusion coefficient), the simulation results have a dependence on the grid size. Therefore, the progress of dissolution fronts with time can be compared between simulations with the same grid, but the absolute positions of dissolution/precipitation fronts in time have to be interpreted with care and need to be confirmed by experiments.

Tab. 3.2: Estimated effects of host rock alterations after 100'000 years caused by a constant diffusive exchange across a concrete – host rock interface.

The values are extrapolations from simulations carried out up to 10'000 years (Tab. A3.2). According to the $\sqrt{Dt}$ dependence of diffusive transport distances, the alteration extensions for mineralogical changes and pH at 10'000 years were scaled with a factor of 3 to approximate the situation after 100'000 years.

Location/host rock	Mineralogical changes	pH plume
Opalinus Clay	Major mineralogical changes < 0.4 m	< 0.3 m pH > 10 < 0.5 m pH > 8.0
Effingen Member	Major Mineralogical changes < 0.4 m	< 0.5 m pH > 10 < 0.7 m pH > 8
Helvetic Marls, clayish rock matrix	Major Mineralogical changes < 0.1 m	< 0.7 m pH > 10 < 4 m pH > 8

Major mineralogical changes: The meaning here is that the smectite fraction (represented by montmorillonite) is completely converted to phases such as phillipsite (representative of zeolites), illite, C-S-H-phases and additional minor phases. It is important to note that the cation exchange properties of the smectite phase have completely disappeared in this area of major mineralogical changes.

Minor mineralogical changes are possible within the extent of the pH plume. The meaning here is that the pH is buffered to around 8.4 by the presence of smectite clays (montmorillonite). The cation exchange properties are still available, although changes in the cation distribution (i.e. Ca/Na ratio) may occur. Only a few percent of the clay host rock minerals are affected by the changes.

The above alteration distances compare well with the results of Traber & Mäder (2006) who predicted a maximum depth of 30 cm of significant mineral alteration and a 23 cm wide zone with pH > 9 after 50'000 years for Opalinus Clay.

Based on simple mass balances Mäder & Adler (2004) investigated the limiting case where all of the hydroxide released diffuses into the Opalinus Clay and then reacts with clay minerals (represented by kaolinite) and quartz to form laumontite and C-S-H phases. He concluded that with such a reaction 1 m^3 of Opalinus Clay would be able to buffer 4 m^3 of the concrete typical for an ILW waste repository. The kaolinite dissolution front would extend 0.5 m into the host rock when the reactive Ca(OH)$_2$ inventory of the concrete was consumed.

Diffusive changes in the concrete compartment

The progress of portlandite dissolution fronts, as summarized in Tab. 3.3 were estimated by Kosakowski & Berner (2011c) for Opalinus Clay, Effingen Member and Helvetic Marls. As an example, we show the progress of the dissolution front for Opalinus Clay in Fig. 3.6. The points denote the values extracted from the numerical model. It is possible to fit the position x of the dissolution front with time t by a typical diffusion law $x \sim \sqrt{D_a t}$, where $D_a = 1.114 \times 10^{-12} \pm 0.026 \times 10^{-12}$ m^2/s is an apparent diffusion coefficient[7]. The fit and its confidence and prediction bands are also included in Fig. 3.6. Extrapolation of the dissolution distance to 100'000 years gives roughly 1.9 m $\pm$ 0.25 m.

For the results on host rock alteration, we note that the simulation results have a dependence on the grid size. Therefore, the progress of dissolution fronts with time can be compared between simulations with the same grid size, but absolute positions of dissolution/precipitation fronts in time have to be interpreted with care.

In contrast to the case of advective transport (cf Section 3.3.3), a C-S-H dissolution front could not be observed although the C-S-H phase is changing its composition towards lower C/S ratios near the interface.
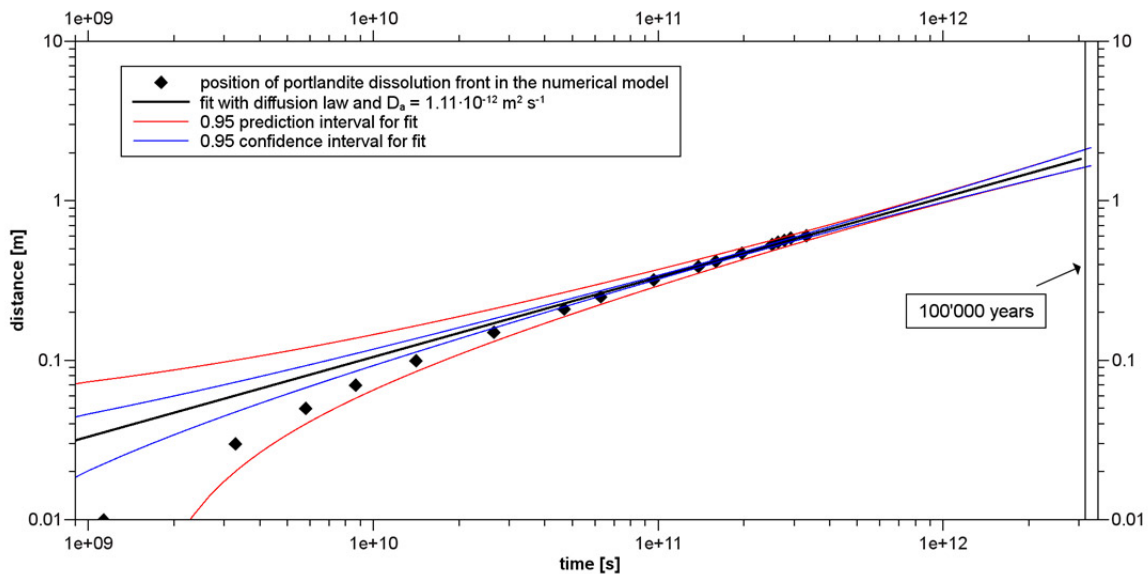
Fig. 3.6:   The points denote the progress of the Portlandite dissolution front with time near the Opalinus Clay – concrete interface if effective diffusion coefficients over the interface are held constant (no pore blocking).

The progress can be approximated by a diffusion law.

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[7]   Please note that this apparent diffusion coefficient includes the retardation of a reaction front due to chemical reactions driven by the diffusion of all participating dissolved species (Eq. 3.3), which results in a coupled system of diffusion equations. The position of the reaction front approaches asymptotically, in space and time, to the position given by D_a due to the finite numerical discretization.

Tab. 3.3:   Estimated extent of concrete alterations after 100'000 years caused by diffusive transport only.

The values are extrapolations from simulations carried out up to 10'000 years (Tab. A3.2).

Host rock	Extension of portlandite dissolution in 100'000 years due to diffusion [m]
Opalinus Clay/'Brown Dogger'	~ 1.9
Effingen Member	~ 1.6
Helvetic Marls (Wellenberg, valley level)	~ 0.9

The above calculated distances of portlandite dissolution are based on two main assumptions i.e. the diffusive flux across the interface is constant (no clogging), and the geometry of the system is 1D linear. In reality, we expect clogging at interfaces, which should, in principle, decrease the mass flux across the interface. In addition, a tunnel cross-section is approximately circular which requires an axisymmetric 1D model setup[8]. A comparison of axisymmetric and linear 1D models shows that both model types give similar results for the dissolution front progress as long as the fronts are close to the interface. When the dissolution progress reaches the interior of the emplacement tunnels, the dissolution in the case of axisymmetric conditions is faster than for a linear geometry. Consequently, the diffusion fronts moving in opposite direction, i.e. into the host rock, are slowed down.

Although Traber & Mäder (2006) also used 1D diffusive models, their simulation results of the evolution of the concrete compartment are not completely identical with the results of Kosakowski & Berner (2011c). Traber & Mäder (2006) used kinetic constraints on the precipitation/dissolution of minerals, whereas Kosakowski & Berner (2011c) used a thermodynamic equilibrium approach. Both models will only calculate the same results if the mineral reaction rates are transport controlled and not kinetically controlled. In Traber & Mäder (2006) the internal degradation of the concrete dominates the evolution in the concrete compartment after several thousands of years (compare Section 3.4.5), whereas Kosakowski & Berner (2011c) the aggregate is assumed to be non-reactive (inert). Traber & Mäder (2006) observe a portlandite dissolution front with an extent similar to that given in Kosakowski & Berner (2011c) in only few thousand years. After all portlandite is dissolved the C-S-H phases with higher Ca/Si ratios are altered gradually to C-S-H with lower Ca/Si ratios. Hydrotalcite is typically the last mineral to be consumed. After 50'000 years the pH values are generally still higher than 10.5.

Boundary conditions/additional information

In order that diffusive transport can take place, a connected water phase in the rock is necessary. Since parts of the repository system are only partially saturated for potentially long times, water connectivity is not ensured (Section 3.3.1).

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[8]   In such a model setup the cross section of a finite element at a distance r from the tunnel midpoint is set according to the equivalent cross section of a circular segment at the same distance.

Time perspective/uncertainties

The present reactive transport simulations give a good insight into the behaviour of alteration zones and the progress of reaction fronts. The results are particularly helpful when comparing the impact of various specific conditions (e.g. constant advective or diffusive transport parameters). The predicted maximum spatial extent of mineral alteration and pH increases in the host rocks are remarkably close between different studies (Traber & Mäder 2006, Kosakowski & Berner 2011c) even if they are based on different discretisations, chemical setups and in the way kinetics are handled.

However, we recognize that there is a strong sensitivity of the time behaviour of clogging processes on the numerical mesh size and kinetic parameters (Traber & Mäder 2006, Trotignon et al. 2006, Marty et al. 2009, Kosakowski & Berner 2011c).

We also note that there is limited knowledge on the relationship between porosity and transport parameters in many media. Together with the inherent uncertainties in thermodynamic and kinetic data, and given the limits of existing conceptual models, we therefore recognize that there are large sources of potential uncertainties. Hence, the estimated time scales have to be interpreted with care. This uncertainty can only be reduced by additional experimental data and by investigation of natural/industrial analogues, which provide information on (short) alteration distances after long times.

3.3.3   Water transport (advection)

Overview/general description

The reactive transport of solutes is normally described be the Advection-Dispersion-Reaction-Equation (ADE)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(v_i C\right) + \frac{q_s}{\theta}C_s + R \quad . \tag{3.4}$$

Where C [mol/m^3] is the concentration of a particular species, R [mol/m^3/s] a chemical source/sink term representing the change in solute mass of the species due to chemical reactions, D_{ij} [m^2/s]are the components of the dispersion tensor, θ [-] denotes the porosity and q_s [1/s] an internal water source/sink term (volumetric flow rate per unit volume of porous medium) with a specific solute concentration C_s [mol/m^3].

The components of the fluid (solvent) velocity v_i [m/s] have to be known in order to calculate the advective transport. For the fluid velocities, the conceptual model of fluid flow in rocks is important. For the same water flux, the fluid velocities in rocks conceptualized as a porous medium can be orders of magnitude lower than in rocks treated as a fractured medium. The same effect applies to porosities; in fractured media the effective (averaged) porosities are normally much lower than in porous media.

The review paper by MacQuarrie & Mayer (2005) gives a general overview on reactive transport modelling in fractured rocks. They discuss several processes that might influence the extent of pH-induced changes in fractured rocks near a cementitious repository:

- Several observations (see references in MacQuarrie & Mayer 2005) reveal that clay mineralogy in fractures often strongly differs from the mineralogical composition of a granitic matrix. This reflects that generally water-rock interactions are much more pronounced within the fractures than in the matrix adjacent to the fracture.

- Alteration of the matrix adjacent to the fracture is very limited in space.

- Dissolution and precipitation reactions change transport properties of fractures and rock matrix due to porosity changes. Detailed consequences of such changes are currently not clear, except that lower porosities usually slow down transport. Extremes include complete system self-sealing, but also the formation of highly permeable preferential flow channels.
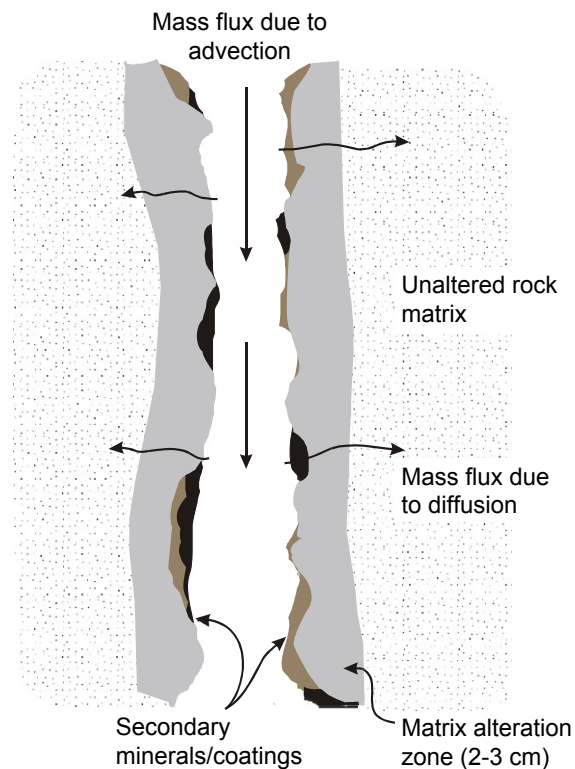
Fig. 3.7: Schematic representation of conditions near the fracture-matrix interface (from MacQuarrie & Mayer 2005).

Effects of advective transport on near-field evolution and on host rocks

Generally most host rocks that are investigated in the framework of stage II of the Sectorial Plan (Opalinus Clay, Effingen Member, 'Brown Dogger', the rock matrix of the Helvetic Marls) are characterized by the absence of water conducting features, or features with strong permeability or diffusivity contrast (Section 4.3 in Nagra 2010). They can therefore be conceptualized as homogeneous porous media in terms of advective and diffusive transport. In some host rocks

lithological units exist which contain water conducting features typical for fractured rocks ('Brown Dogger' – 'Kalk/Sandkalk-Abfolgen' (SKA), Effingen Member – "Kalkbankabfolgen" (KBA), Helvetic Marls – cataclastic shear zones) (Nagra 2008d, 2010).

Because of conceptual differences, the effects of advective transport have to be evaluated differently in host rocks conceptualized as **porous media** and **fractured rocks**. We treat the backfilled emplacement tunnels as a porous medium with average properties and concrete composition.

Fractured host rocks

In the framework of the Sectorial Plan (Section 1), for the fractured host rocks ('Brown Dogger' – SKA, Effingen Member – KBA, Marl – cataclastic shear zones) or for single transmissive features, no unique scenario for advective transport can be defined. Possible scenarios are bounded by two limiting cases, i.e. system **self-sealing** and the formation of **high-permeability preferential flow channels**. The first case would lead to a scenario close to the homogeneous porous medium case. The second case would be equivalent to a rapid transport of radionuclides in a highly alkaline environment.

Section 2.4.6 of Nagra NTB 94-06 (Nagra 1994) contains a process description for the extent of the pH plume in fractured rock. Two extreme cases are described: (1) clogging of the water-conducting features causing an isolation of the repository and (2) the clogging of the fracture wall matrix leaving open fractures which results in highly channelled water flow and the fast transport of radionuclides.

In Section A5.6 of Nagra (2010) the radionuclide transport pathways and the host rock for the proposed site "Wellenberg" are conceptualized as fractured rock. The hydraulic parameters correspond to those given in Tab. 2.4-1 in Nagra (1994) with flow velocities in the cataclastic shear zones given as 0.63 m/a (range: 0.06, 6.3 m/a). The mineralogy of the cataclastic shear zones is very similar to the average composition of Helvetic Marls which was chosen for the reactive transport calculations in Kosakowski & Berner (2011c).

We consider two rather extreme scenarios for addressing changes in host rock properties of fractured rocks due to a high pH plume:

1. The fractures clog at the discharge area where high pH water enters the fracture e.g. due to the precipitation of calcite. This stops the (advective) water flow through the whole system and consequently the concrete degradation by ground water flow. This scenario would also stop any further advective propagation of the pH plume. Such a scenario is supported by model calculations (Pfingsten 2002, Soler 2003), field experiments (Mäder et al. 2006) as well as by information gathered from natural analogues (Smellie 1998, Steefel & Lichtner 1998, Mäder et al. 2006). However, clogging of fractures will not stop the diffusive transport of solutes and water in the porous rock matrix. The repository will be sealed completely from the host rock only if the fractures and porous host rock are both clogged.

2. The fractures stay open (at least partially), and the high pH solution from the cementitious repository reacts with the host rock fracture walls. This seals the host rock matrix (fracture surfaces) and the high pH fluids travel very fast along the fractures. The process of sealing the matrix porosity was, for example, discussed by Lichtner & Eikenberg (1995). It has to be noted that this second scenario might lead to high water fluxes through the repository, which in turn would cause substantially accelerated cement degradation.

A critical factor is the water flow velocity in the fractures. The effect of fluid velocities in fractures on porosity changes in fractures and fracture walls was shown by a comparative modelling study related to the Maqarin natural analogue (Watson et al. 2011, Shao et al. 2013). High flow velocities prevent the equilibration of high pH water with the host rock mineralogy as mixing with host rock pore water is incomplete due to short residence time of the high pH water in the fractures. This results in nearly constant water composition in the fracture and induces the diffusion of high pH solution into the fracture wall rock. The solution will react with the wall rock mineralogy and may induce sealing of the wall rock for long distances (Shao et al. 2013). Low flow velocities in the fracture facilitate the sealing of fractures, as high pH water will mix with host rock pore water in the fractures which causes the precipitation of minerals.

<u>Porous host rocks</u>

The advective transport of solutes for the host rocks (Opalinus Clay, Effingen Member, 'Brown Dogger' rock matrix of Helvetic Marls) which can be conceptualized as homogeneous porous media is normally very low. In these rocks diffusive transport of solutes is dominating (Tab. 3.4). When considering the effects of fractures (Tab. 3.5) for Effingen Member and Helvetic Marls somewhat higher water fluxes are possible (Nagra 2010).

An estimate of the effects of advective transport (via the Darcy fluxes given in Nagra 2010) on the mineralogical changes is given in the following Tabs. 3.4 and 3.5. The extent of the pH plume and the depth of the mineralogical changes are estimated based on the calculations of Kosakowski & Berner (2011c).

Tab. 3.4:   Estimated extent of host rock alteration in the direction of water flow caused by advective transport of a high pH solution through the host rock.

Effects of higher Darcy fluxes due to the existence of fractures or transmissive features are not considered in this table.

Location/host rock	Darcy flux [m^3/m^2s]	Mineralogical changes	pH plume (down gradient)
Opalinus Clay/'Brown Dogger'	1×10^{-13}	Major mineralogical changes < 0.05 m	< 3 m: pH > ~ 8.4 < 6 m: pH 7.4 – 8.4 > 6 m: no pH change
Effingen Member	1×10^{-12}	Major mineralogical changes < 0.25 m	< 0.2 m: pH > 9 0.2 – 40 m: pH 6.5 – 8.6 >40 m: pH > 8 – 9 >80 m: no pH change
Helvetic Marls, clayish rock matrix	4×10^{-12}	Major mineralogical changes < 0.1 m	< 15 m: pH > 9 – 10 15 – 25 m: pH 7.5 – 8.5 > 25 m: pH 8 – 9 > 1'400 m: no pH change[9]

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[9]   The simple 1D model of Kosakowski & Berner (2011c) for assessing extent of pH plume includes only a 40 m thick host rock. The effects of pH plume exceeding the model extension of 40 m were extrapolated by calculating the progress of water ingression from total water flow in 100'000 years divided by host rock porosity. The large spatial extension of pH increase in Helvetic Marls is related to the extremely low porosity, the dismissal of dimensional effects (transversal dispersion/diffusion) and neglecting retardation of pH front due to pH buffering by amphoteric sites at clay mineral surfaces.

Major mineralogical changes: The meaning here is that the smectite fraction (represented by montmorillonite) is completely converted to phases such as phillipsite (representative of zeolites), illite, C-S-H-phases and additional minor phases. It is important to note that the cation exchange properties of the smectite phase have completely disappeared in this region of major mineralogical changes.

Minor mineralogical changes are possible within the extension of the pH plume. The meaning here is that pH is buffered to around 8.4 by the presence of smectite clays (montmorillonite). The cation exchange properties are still available, although changes in the cation distribution (i.e. Ca/Na ratio) may occur. Only a few percent of the clayish host rock phases are affected by changes.

Evolution of the concrete compartment (near-field)

We treat the backfilled emplacement tunnels as a porous medium. The advective transport in the tunnels is governed by the local hydraulic field in the host rocks. Water, with a composition specific to a particular host rock, enters the emplacement tunnel and interacts with the concrete, thus altering the water composition and inducing mineralogical changes. After passing through the tunnel the altered water enters the host rock formation again and is re-equilibrated with the host rock, which may induce further mineralogical changes near the outflow interface.

A special case is the inflow of high pH water from the emplacement tunnels into the backfilled (sand bentonite) access tunnel system. This case is described elsewhere (Kosakowski & Berner 2011d). The case of flow in the opposite direction i.e. from the access tunnel system into the emplacement tunnels is covered in Kosakowski & Smith (2014).

The evolution of the concrete compartment is coupled to the host rock evolution. In the case of clogging, the concrete compartment is sealed from the host rock and its evolution is driven only by internal degradation reactions (including reactive silica from aggregates and/or waste degradation products such as CO_2).

When advective transport dominates over diffusive transport, the magnitude of the water flow through the emplacement tunnels as well as solute concentrations (i.e. carbonate, sulphate) governs the concrete degradation/conversion.

For highly transmissive features in the host rock, the water flow, as well as the volume affected in the concrete compartment, have to be known. For high flow rates, concrete degradation may be very fast.

Groundwater "leaving" the host rock formation and passing through the cementitious structure affects and alters the concrete. The consequences of this formation water flow are summarized in Tabs. 3.4 and 3.5. Figs. 3.8 – 3.10 show the relation between the position of the portlandite dissolution front and the water flow into a concrete column of 10 m length for Opalinus Clay/ 'Brown Dogger', Helvetic Marls and Effingen Member. The red points mark the position of the reaction fronts where the C/S ratio in the C-S-H solid solution model reaches 0.83 (the composition of tobermorite). The water flow is expressed as pore water exchange cycles based on an initial concrete porosity of 0.2. A cumulative flow of 1 m^3/m^2 therefore corresponds to 5 pore water exchange cycles. The vertical lines mark the number of pore water cycles that are exchanged at the given Darcy flux (from Tab. 3.4) during 100'000 years.

The values for the Darcy fluxes are taken from Kosakowski & Berner (2011a) and give an indication of the magnitude of possible Darcy fluxes under realistic hydraulic conditions.

There is additional concrete alteration induced by internal reactions and cement-waste inter-actions (reactive silica from aggregates, CO_2 from organic wastes, etc.). Such additional alterations are not included in Tab. 3.5.

Tab. 3.5:   The estimated extent of concrete alteration after 100'000 years caused by advective transport of host rock pore water through the emplacement tunnel.

Column 4 lists the number of concrete pore volumes based on the Darcy flux in the host rock and calculated for the particular concrete porosity of 0.2. The derivation of water fluxes is given in Kosakowski & Berner (2011a).

Host rock	Darcy flux $[m^3/m^2s]$ in concrete	Water flow in 100'000 years $[m^2]$	Exchanged pore volumes in concrete for a porosity of 0.2 after 100'000 years	Extension of portlandite dissolution due to advection [m]	Extension of portlandite dissolution due to diffusion and advection [m]
Porous host rocks					
Opalinus Clay/'Brown Dogger'	1×10^{-13}	0.32	~ 1.6	< 0.01	~ 1.9
Effingen Member	1×10^{-12}	3.16	~ 16	~ 0.08	~ 1.7
Helvetic Marls, clayish rock matrix	4×10^{-12}	12.6	~ 64	~ 0.2	~ 1.2
Host rocks with fractures/transmissive features					
Helvetic Marls (Wellenberg, valley level), similar Darcy fluxes for cataclastic shear zones and for disturbed zones	4×10^{-12} (large scale conductivity) + 4×10^{-12} (small scale transmissive elements)	25.3	~ 128	~ 0.4	~ 1.4
'Brown Dogger', horizontal limestone layers	~ 2×10^{-12} (adjusted to tunnel height of 10 m)	6.32	~ 32	~ 0.12	~ 2.0
Effingen Member horizontally aligned transmissive elements	~ 5×10^{-11} (adjusted to tunnel height of 10 m)	158	~ 800	~ 3.5	~ 5.1

Opalinus Clay / 'Brown Dogger'

Opalinus Clay / 'Brown Dogger'
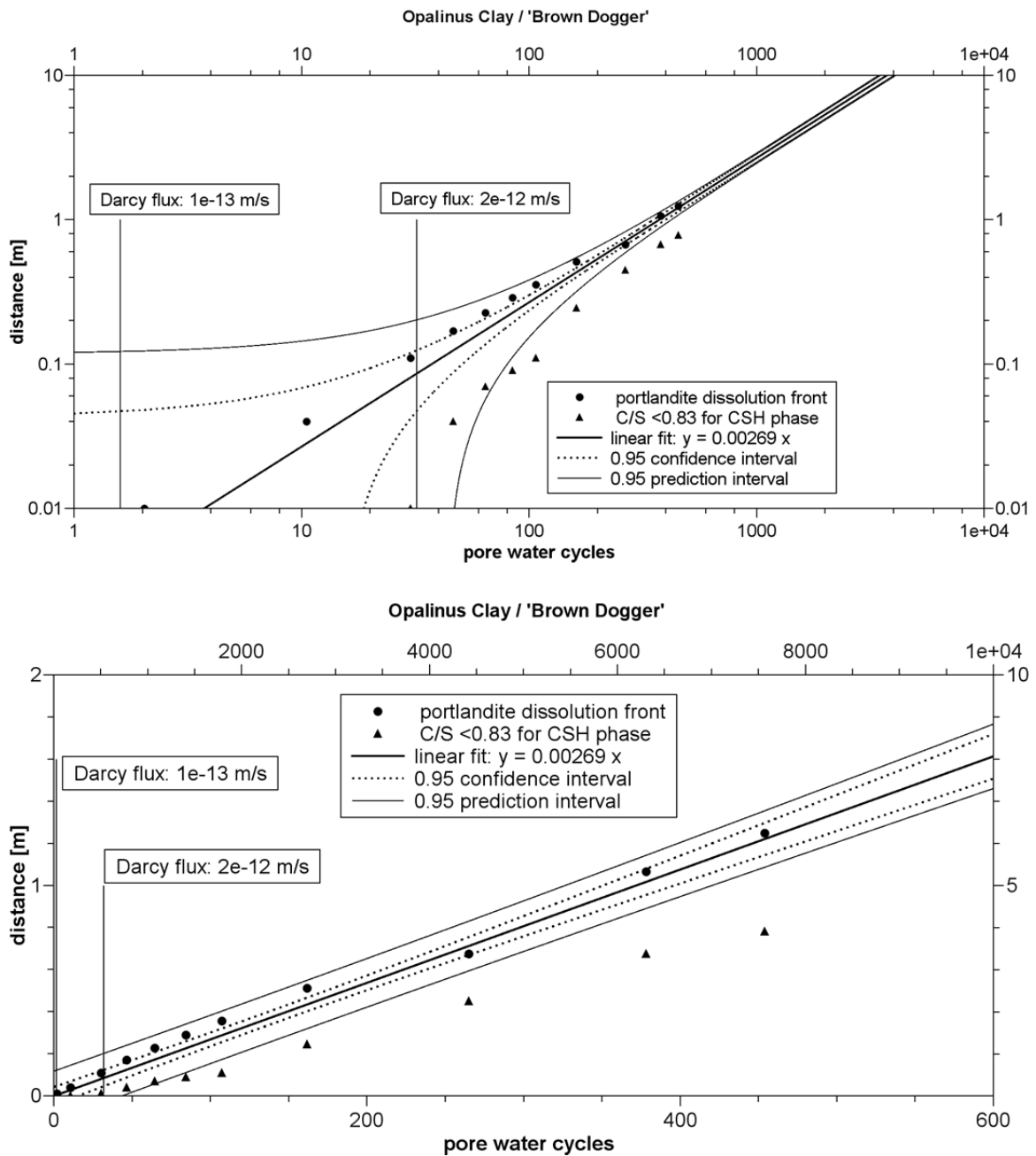
Fig. 3.8:   The progress of the portlandite dissolution front and the front with C/S ratio < 0.83 in C-S-H for the case of advective flow into the emplacement tunnels.

Note that the upper figure uses a logarithmic scaling for both axes, whereas the lower figure shows the same curves with linear axis. The x-axis denotes pore water cycles. About 3'700 pore water cycles are needed to reach a portlandite dissolution distance of 10 m. The vertical lines mark the number of pore water cycles that are exchanged at the given Darcy flux within 100'000 years.
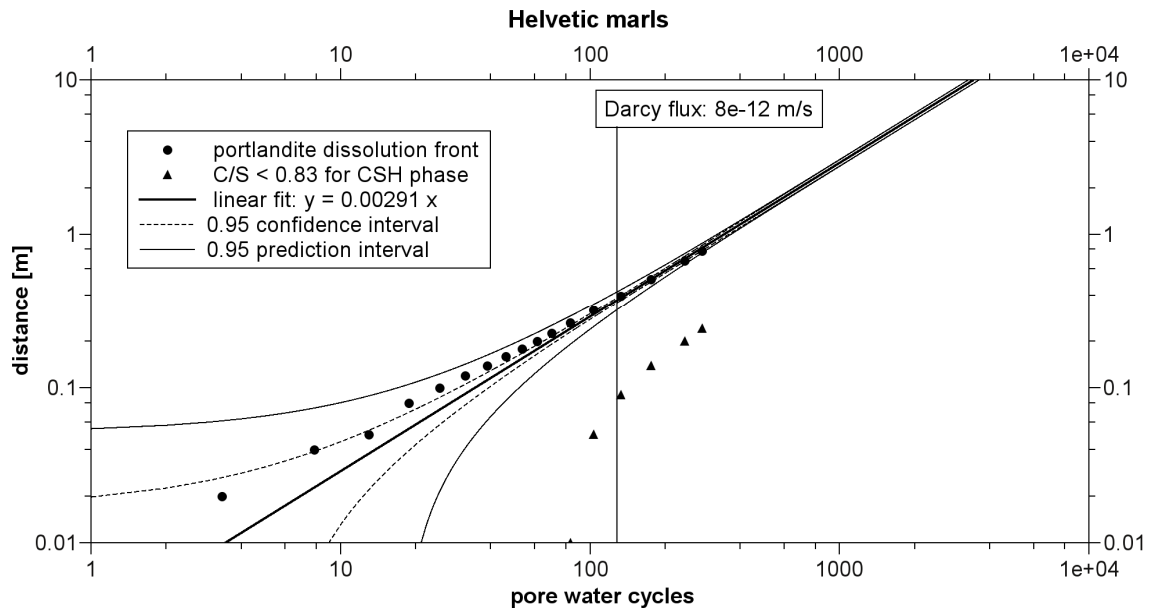
Fig. 3.9:   The progress of the portlandite dissolution front and the front with C/S ratio < 0.83 in C-S-H for the case of advective flow into the emplacement tunnels for the case of Helvetic Marls.

The logarithmic x-axis denotes pore water cycles. The vertical line marks the number of pore water cycles that are exchanged at the given Darcy flux during 100'000 years. About 3'400 pore water cycles are needed to reach a portlandite dissolution distance of 10 m.

Fig. 3.10:   The progress of the portlandite dissolution front and the front with C/S ratio < 0.83 in C-S-H for the case of advective flow into the emplacement tunnels for the case of Effingen Member.

The logarithmic x-axis denotes pore water cycles. The vertical lines mark the number of pore water cycles that are exchanged at the given Darcy flux during 100'000 years. About 2'400 pore water cycles are needed to reach a portlandite dissolution distance of 10 m.
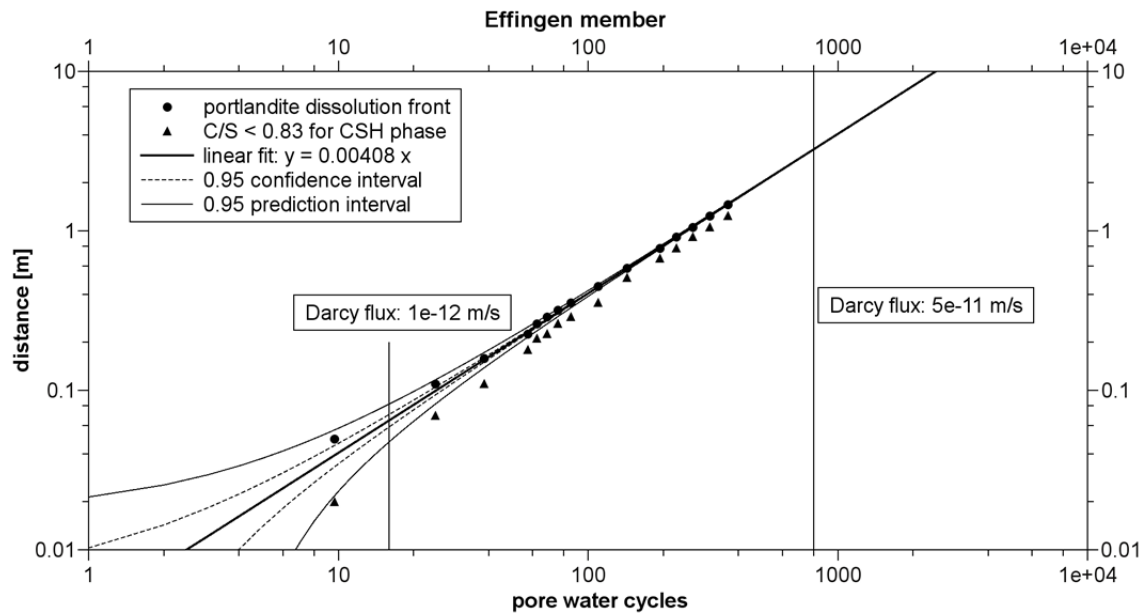
Information from natural analogues/observations in nature

A natural analogue for the alteration of clays by high-pH solutions was discovered at Maqarain (northern Jordan). A very detailed description of the site can be found in Smellie (1998). At the site, hyperalkaline waters, similar to cement waters with a high pH, circulated through fractures in a clayey biomicrite (limestone). The fracture surfaces show dissolution of different minerals, whereas within the fractures different opening/closing episodes may have taken place with complex mineralogical sequences. In the extended summary of Smellie (1998) it is stated that the evidence from Maqarin shows that:

- The sequences of minerals predicted by thermodynamic and coupled modelling are similar to those observed in hyperalkaline alteration zones.

- The rock matrix may be accessible to diffusion of aqueous species even during the phase of on-going wall-rock alteration.

- The narrow aperture fractures will probably be self-healing.

In the framework of the hyperalkaline plume in fractured rock (HPF) experiment (Mäder et al. 2006, Soler et al. 2006) it was found among other things that:

- The injection of high pH-solution into fractured rock decreased the overall hydraulic conductivity of the fractures, changed the geometry of the flow field and resulted in channelled flow.

- A kinetic formulation for mineral dissolution was necessary for modelling the experimental results.

- The fracture zone appeared to be very heterogeneous, which limited the applicability of deterministic model approaches.

Boundary conditions/additional information

Advective transport is limited to the occurrence of a connected water phase. Such a connected water phase may not exist in parts of the repository where strong de-saturation has occurred.

Time perspective/uncertainties

Alteration distances for advective scenarios are linearly related to the water flux. Each uncertainty in the hydraulic field introduces a similar uncertainty in space and time for alterations related to advective transport. Advective water fluxes depend on the hydraulic conductivities of the rock and on the local pressure gradient. Most potential host rocks, not only those that contain connected fracture systems, are characterized by anisotropy in the hydraulic conductivity. On the one hand, with low pressure gradients the water flow is low even in relatively permeable media. On the other hand, local pressure gradients and the corresponding water fluxes can be increased due to the local geometry and material configuration. For example, a tunnel backfilled with materials that have a higher permeability than the surrounding host rock may cause a channeling of groundwater flow through the tunnel. This might cause a significant increase in water flux compared to the flux in undisturbed host rock.

Current reactive transport simulations give a good insight into the behaviour of alteration zones and the progress of reaction fronts. The results are particularly helpful when comparing the impact of various specific conditions (e.g. constant advective or diffusive transport parameters). However, we recognize that there is a strong sensitivity of the time behaviour of clogging processes on the numerical mesh size and kinetic parameters (Traber & Mäder 2006, Trotignon et al. 2006, Marty et al. 2009, Kosakowski & Berner 2011c).

We also note that there is only limited knowledge on the relation between porosity and transport parameters, as well as thermodynamic and kinetic data. Given the limits of existing conceptual models, we therefore recognize that there are large sources of potential uncertainties. Thus, the evaluated absolute times scales have to be interpreted with care.

3.3.4   Potential porosity change by dissolution/precipitation

Overview/general description

Reactive transport calculations of cement/clay interactions show large porosity changes due to precipitation/dissolution of minerals near the interface. Most of the modelling studies investigate the geochemical evolution of interfaces in low permeability media where diffusive transport dominates. They calculate a strong porosity reduction in narrow zones. The clogging of the pore space leads to a strong reduction of advective and diffusive mass fluxes across the interface which essentially stops the geochemical alteration processes and significantly slows down radionuclide migration across the interface.

Experimental validation of these findings under realistic transport conditions and with real materials is difficult. Advective and diffusive fluxes in clay media are very low and significant alterations of pore space due to cement/clay interactions are expected to occur only after relatively long times, possibly tens or hundreds of years. Some evidence for pore blocking (Savage 2009, see e.g. Savage et al. 2010) from long term observations on concrete/clay interfaces at the Tournemire industrial analogue (Soler et al. 2014) and from the Maqarin natural analogue (Pitty & Alexander 2014) and from reactive transport calculations (compare next section) exists.

Information from modelling studies/experimental studies

We have collected information on modelling/experimental studies from recent review papers on cement/clay interactions or similar topics (Saripalli et al. 2001, Gaucher 2004, Metcalfe & Walker 2004, MacQuarrie & Mayer 2005), and recent scientific publications.

Gaucher & Blanc (2006) give an overview of publications on experiments, natural analogues and modelling related to cement/clay interactions (see Section 3.3.2 for more details).

Savage et al. (2002) modelled the alteration of bentonite by hyperalkaline fluids at a cement-bentonite interface in a diffusive transport environment. They found a maximum porosity increase of up to 80 – 90 % over a narrow zone of 1 – 2 cm wide close to the cement pore fluid-bentonite contact. All their simulations (except the one with alternative aqueous speciation data for Si) showed a complete clogging of the porosity within a few centimetres beyond the interface after a maximum time of 3'200 years. Trotignon et al. (2006, 2007) did numerical modelling on the durability of concrete engineered barriers in contact with mudrock (clay host rock). They believe that one key process is the progressive localized cementation of the altered mudrock. Their results suggest that a sharpening of the cementation front will occur and lead to low cementation depths into the mudrock (~ 0.2 m).

Watson et al. (2007) modelled the interaction of low pH cements and bentonite. They found that the extent of bentonite degradation is likely to be much less for low pH cement pore waters than for OPC pore waters. In some of the cases investigated they observed complete porosity blocking within 1'000 years due to the precipitation of laumontite (a Ca-zeolite), for other cases porosity blocking was not observed. They concluded that their model results depend very much on the geochemical model setup i.e. on the use of solid-solution models for the C-S-H gels, on uncertainties concerning the precise mechanism of the rate of montmorillonite dissolution at elevated pH, on the role of dissolved Si and on the consideration of secondary minerals.

The group of Laurent De Windt and Jan van der Lee at the Ecoles des Mines de Paris used the HYTEC code to model the evolution of clay-cement interfaces (De Windt et al. 2001, 2004, 2007, 2008, De Windt & Badreddine 2007). De Windt et al. (2004) found that the precipitation of calcite, or minerals with a high molar volume such as C-S-H and zeolites, may lead to a significant decrease of the pore volume at the cement/claystone interface. As an example the authors present a case where the porosity on the clay side of the interface is clogged within 2,500 years. They conclude that *this result should be considered with care. The clogged area is relatively thin and may thus be mechanically fragile. The model assumes a homogeneous precipitation within a representative elementary volume and a complete sealing of the pore space. Clogging is more heterogeneously distributed and imperfect in reality.*

De Windt et al. (2008) carried out numerical modelling in order to match the mineralogical and petrographic observations from a borehole sealed by concrete and over-cored at the Tournemire site after 15 years of concrete/argillite interactions. They found that kinetic considerations of precipitation and dissolution reactions were necessary to reproduce the mineralogical changes observed on the argillite site of the interface. They could match qualitatively the major mineralogical alterations, although still some differences between experiment and modelling in terms of the formation of single mineral phases existed. Unfortunately, no quantitative data on the porosity reduction are available from the experiments or the models.

Based on short term experimental data on mineralogical transformations Fernández et al. (2009) modelled the interaction of concrete with a bentonite barrier and also carried out long-term predictions on the behaviour of the interface. They found that total clogging occurred after 5'000 years. They found several sources of uncertainties in the system; kinetics of mineral dissolution/precipitation reactions for many minerals are not known, coupling between geo-chemical processes and thermo-hydro-mechanical properties is normally not considered, clay specific processes such as anion exclusion are also not included in the modelling studies. They found a fundamental lack of detailed knowledge on how the processes operate at the pore scale, and how such detail could be up-scaled.

Read et al. (2001) present results of experiments on the interaction of ordinary Portland cement with Boom Clay over a period of 18 month at 20 °C. The experimental results were analysed with help of reactive transport modelling. On both sides of the clay-cement interface they found 100 – 250 μm wide reaction zones. They observed a portlandite dissolution front that increases the porosity of the cement. They additionally conducted experiments at elevated temperatures (85 °C). On the clay side of the interface they found a very narrow (10 μm) zone where gels were formed with compositions close to hydrotalcite and sepiolite. They do not report a porosity change for this zone.

Marty et al. (2009) investigated intensively the influence of reaction kinetics and mesh refine-ment on the numerical modelling of concrete/clay interactions. They investigated an interface between concrete and the Callovo-Oxfordian argillite in a fully saturated diffusive transport regime. A major result of their study is that clogging times strongly depend on the spatial

discretization of the model/interface domain. The inclusion of kinetic limitations on geo-chemical reaction rates also influences the clogging times. If kinetics strongly controls the mineral precipitation/dissolution, the dependency of clogging times on spatial discretization is weakened. They conclude: *A simulation as representative as possible of temporal and spatial scales of cementation processes must then be supported by more comparative data such as long term experimental investigations of natural analogues.*

Boundary conditions/influence of saturation

Studies on the influence of water saturation on cement/clay interface processes are sparse. A review on the changes of hydrological properties of aquifer media due to chemical reactions was carried out by Saripalli et al. (2001). Based on their review, they gave recommendations for future research. Some topics relevant to the evolution of cement/clay interfaces are: changes in the specific solid (mineral)-water contact area as a function of the degree of water saturation, effect of the water saturation itself on the diagenetic processes (including precipitation and dissolution), pore and particle size distribution models and the coupling of geochemical models to flow and transport.

Tinseau et al. (2006) performed a mineralogical characterization and mass-balance calculations of the Tournemire argillite after in situ interaction with concretes. They differentiate between dry and wet contacts and conclude that no significant modifications of the argillite were observed after 125 years in the absence of water, except for pyrite dissolution and gypsum precipitation. In the presence of water, precipitation of gypsum, recrystallization of mixed-layer clays, neoformation of zeolites and K-feldspars overgrowth were observed. At the concrete/ argillite interface dolomite neoformation and leaching of chloride and kaolinite occurred. The mineral alterations increased with contact time, low flow rate and the nature of the concrete. Gaboreau et al. (2011) quantitatively characterized the porosity at a cement – clay – rock interface after 15 years of interaction and could for the first time verify porosity clogging. They could show that the perturbations (in terms of mineralogical and porosity changes) were limited to 3.5 cm and 1.5 – 2 cm from the interface in cement and clay rock respectively. The concrete and clay rock were not homogeneous and contained a fissure network. Alterations were observable near the material interface and near the fissures. The porosity in the concrete increased due to portlandite dissolution, whereas the porosity in the clay rock was strongly reduced, which the authors attributed mainly to precipitation of C-(A)-S-H phases. The corresponding mineralogical data were published in Techer et al. (2012).

Burnol et al. (2006a, 2006b) simulated the degradation of a concrete/clay interface and investigated the influence of temperature, de-saturated conditions and porosity variations. They state that they observed an "occlusion" of the porosity close to the interface, but did not report any details on this finding.

Gherardi et al. (2007) published a numerical study on "self-limiting" and "self-enhancing" cap rock alteration induced by CO_2 storage in a depleted gas reservoir. Although this system is not identical to a clay-cement interface, the behaviour in terms of porosity changes has some similarities. They found that *when a free CO_2-dominated phase migrates into the cap rock through pre-existing fractures, or through zones with high initial porosity acting as preferential flow paths for reservoir fluids, low pH values are predicted, accompanied by significant calcite dissolution and porosity enhancement. In contrast,* when *fluid-rock interactions occur under fully liquid-saturated conditions and a diffusion-controlled regime, pH will be buffered at higher values, and some calcite precipitation is predicted, which leads to further sealing of the storage reservoir.*

Information from natural analogues/observations in nature

An exhaustive overview on the available experimental and natural analogue data on cement/clay interactions is given by Gaucher & Blanc (2006). Other extensive overviews of experimental data are given in Metcalfe & Walker (2004) and Savage (2011). There are many data on the mineralogical evolution of such interfaces and also newer studies (Cuevas et al. 2006, Yamaguchi et al. 2007). What is missing are quantitative experiments that can be used to "calibrate" numerical models in terms of the evolution of porosity and which provide data on porosity-permeability and porosity – diffusivity relationships at different water saturations.

A natural analogue for clogging in rock walls due to contact with high-pH solutions flowing in fractures was found at Maqarin (northern Jordan) (Smellie 1998). This system was modelled by Steefel & Lichtner (1998). They predicted that the porosity of the rock matrix was clogged after as short a time as 10 – 50 years to a distance of 2 – 3 mm into rock, depending on the reactive surface areas used to control mineral precipitation/dissolution in the simulation. The main contributing minerals were identified to be ettringite and to a small extent tobermorite, hille-brandite and foshagite. New simulations by Shao et al. (2013) using the most recent thermo-dynamic setup for cement and clay minerals, confirmed the porosity clogging.

Although the observations at the Tournemire industrial analogue and at the Maqarin natural analogue are related to very different time scales (15 years vs. 100 k years of interactions), they both indicate that clogging is possible.

Time perspective/uncertainties

From an experimental perspective, clogging processes at interfaces have not yet been well investigated. There are some indications that clogging at clay-cement interfaces does indeed occur. The time behaviour is uncertain. Observations from the Tournemire industrial analogue (Gaboreau et al. 2011) show significant porosity clogging after 15 years.

In addition, the following effects may influence pore space clogging:

- mechanical stability of the interfaces (tunnel convergence, cracking due to precipitation pressure)

- material inhomogeneities (Gaboreau et al. 2011) and the transport regime

- the saturation state of the interface (cf Section 3.3.1)

The influence of heterogeneous rock compositions and spatial variability of porosity on the clogging process, as well as the mechanical stability of such zones, has not yet been investigated.

3.4   Interactions between cement and waste

This section describes the effect of interactions between the different barrier materials with the wastes. We start with the degradation of organic materials in Section 3.4.1; we then describe in more detail the effects of gas production in Section 3.4.2, and finally summarize the effects of organic ligands on sorption and speciation in Section 3.4.3. Other waste – cement interactions and their effects on concrete degradation are listed in Section 3.4.4. Finally, we summarize our understanding of the alkali silica reaction in Section 3.4.5 which could accelerate concrete degradation.

The interactions between cement and waste may influence the mobility of the radionuclides in the near-field. In order to optimize the efficiency of the chemical radionuclide retention properties of the near-field, it is planned to split the waste into two groups. Waste sorts containing materials with potentially adverse effects on radionuclide retention (Group 2 waste sorts) are emplaced in a separate section of the repository to avoid a detrimental effect on the other waste sorts (Group 1 waste sorts). A detailed description on the grouping of the waste sorts is given in (Schwyn 2008). The description in this section will provide arguments to define criteria for splitting the waste into Groups 1 and 2.

3.4.1 Degradation of organic materials

Overview/general description

The waste sorts to be disposed of in the ILW and L/ILW repositories contain high-molecular-weight (HMW) polymers such as bitumen, cellulose, concrete admixtures, detergents, graphite[10], ion exchange resins (polystyrene backbone), plastics, PVC, and rubber, as well as low-molecular-weight (LMW), monomeric organic materials, such as citric acid, ethylene-diaminetetraacetic acid (EDTA), gluconic acid, oxalic acid, hexamethylenetetramine, and tartaric acid. Biotic, abiotic or radiolytic processes are responsible for the degradation of the organic materials after disposal. Microbially mediated decomposition of organic matter cannot be excluded even under the hyperalkaline conditions of the cementitious near-field as substrates (carbon source) and oxidants (electron acceptors) will be present. The rates and the degree of decomposition seem to be influenced by the chemical environment (pH, redox conditions and temperature), the microbial activity under repository conditions, and the chemical nature of the organic matter.

The rates and degrees of decomposition are compound specific. HMW organic waste such as bitumen, polystyrene, PVC and rubber are considered to decompose much slower (if at all) than LMW organic waste and cellulose, concrete admixture or detergents. In safety assessments, Nagra simplifies the quantification of the decomposition by dividing the organic compounds into two categories with different gas production rates, i.e. fast (category 1; rate = 0.07 mol gas/kg a) and slowly degrading waste sorts (category 2; rate = 0.005 mol gas/kg a) (Wiborgh et al. 1986, Nagra 2008a). The assumed rate for slowly degrading organic compounds is not very well supported and might be much too high (Warthmann et al. 2013).

The decomposition of LMW organics, cellulose, concrete admixtures and detergents is expected to be rapid and be complete within the oxic and early anoxic states of a repository, i.e. before and shortly after repository closure (estimated duration < 1'500 years, based on category 1 kinetic rates for LMW organic wastes). The decomposition of some HMW polymeric organic matter is expected to be very slow and, at least for some materials, will not be completed over the entire lifetime of the repository. In particular, bitumen, graphite, plastics, polystyrene, polyvinylchloride, rubber, and ion exchange resins may not entirely degrade in the cementitious near-field of a repository in the long term (Hallbeck 2010). Cleavage or hydrolysis is the first and often limiting step, to transform long chain polymeric matter into soluble and smaller molecules accessible to biodegradation.

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[10] Graphite is an inorganic material, but as a potential carbon source it is treated together with HMW polymers in the following sections.

Biotic degradation of organic matter occurs in the presence of nitrate-, manganese-, iron- and sulphate-reducing micro-organisms, which can mediate the degradation process under anoxic conditions tentatively described for high pH conditions as follows:

$$C_6H_{12}O_6 + 4.8\ NO_3^- \rightarrow 6\ CO_2 + 2.4\ N_2 + 3.6\ H_2O + 4.8\ OH^- \tag{3.5}$$

$$C_6H_{12}O_6 + 24\ FeO(OH) + 24\ HCO_3^- \rightarrow 6\ CO_2 + 24\ FeCO_3 + 18\ H_2O + 24\ OH^- \tag{3.6}$$

$$C_6H_{12}O_6 + 3\ SO_4^{2-} \rightarrow 6\ CO_2 + 3\ H_2S + 6\ OH^- \tag{3.7}$$

$$C_6H_{12}O_6 + 12\ MnO_2 + 12\ HCO_3^- \rightarrow 6\ CO_2 + 12\ MnCO_3 + 6\ H_2O + 12\ OH^- \tag{3.8}$$
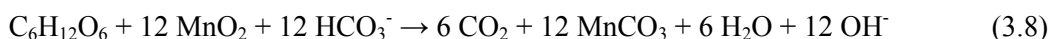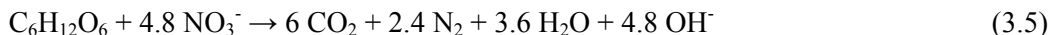
Hence, the classic redox progression of terminal electron-accepting processes might occur in the order NO_3^-, and $Mn(IV)$, $Fe(III)$ and SO_4^{2-}.

The decomposition reactions imply the formation of CO_2 by microbial degradation of organic matter whereas the formation of CH_4 does not occur. The NO_3^- inventory in the waste is small, while hardened cement paste (HCP) contains large inventories of $Fe(III)$ and SO_4^{2-}. In contrast, manganese is a trace element in cement (<200 ppm MnO_2). Estimates of the material inventories show that the total amounts of NO_3^-, $Fe(III)$, SO_4^{2-} and $Mn(IV)$ required for the microbially mediated oxidation of the organic materials is in all cases larger than the known inventories of the above electron acceptors accessible in waste materials and HCP (Wieland & Berner 2012). Hence, only a small portion of the organic matter is expected to decompose by microbial degradation using NO_3^-, $Fe(III)$, SO_4^{2-} and $Mn(IV)$ as terminal electron acceptors. Consequently, the decomposition of organic matter is expected to occur predominately via methanogenesis, which produces CO_2 and CH_4:

$$[C_6H_{10}O_5]_x + x\ H_2O \rightarrow x\ C_6H_{12}O_6 \tag{3.9}$$

$$C_6H_{12}O_6 \rightarrow 3\ CO_2 + 3\ CH_4 \tag{3.10}$$

Reactions 3.9 and 3.10 account for the degradation of cellulose where the polymeric molecule $[C_6H_{10}O_5]_x$ is hydrolyzed to form the monomeric glucose unit (Wiborgh et al. 1986). Decomposition of the $C_6H_{12}O_6$-unit produces equal amounts of CO_2 and CH_4. Note that the ratio of CO_2 to CH_4 produced depends on the mean oxidation state of carbon in polymeric compounds (C(0) in the case of $C_6H_{12}O_6$). Mineralization of organic matter to CO_2 by a fermentative process producing CH_4 has previously been considered in performance assessment in line with the above considerations (Nagra 2008a). This approach is further in line with the assumption of complete thermodynamic redox equilibrium in the C-H-O system.

Hydrolysis (biotic, abiotic) controls the degradation of cellulose under alkaline conditions, while ion exchange resins may be converted by radiolytic degradation to amines, other nitrogen containing ligands and LMW carboxylic acids such as oxalate. In the case of cellulose, α-isosaccharinic acid (α-ISA) and β-isosaccharinic acid (β-ISA) are considered to be the most important degradation products with respect to the amount of products formed and complex formation with radionuclides (Van Loon & Glaus 1998). While there is agreement on the type of degradation products formed, further information on the time period over which complete degradation of cellulose might occur is controversial. Based on the present, partially controversial information, it is expected that abiotic cellulose degradation is a slow process, yet fast enough to allow complete degradation of cellulose in the long term (Glaus 2010).

The consumption of Fe(III) and SO_4^{2-} by microbial decomposition of organics, which includes the production of CO_2, could alter the mineralogical composition of the cement matrix. Cement alteration may have an impact on radionuclide retention in the cementitious near-field (see Section 3.4.2 for CO_2 induced degradation of HCP). Furthermore, the abiotic degradation of cellulose and ion exchange resins could generate organic ligands that influence the speciation of radionuclides and enhance radionuclide mobility in the near-field (Section 3.4.3).

In HCP the large Fe(III) content is likely to be bound in ferrite (C_4AF) and Fe siliceous hydrogarnet. Dissolution of the Fe(III) bearing cement faces caused by Fe(III) consumption during microbial degradation of organics results in the release of mainly Ca and Al to the cementitious system, while simultaneously CO_2 is being formed by the decomposition of organic material. Supersaturation with respect to calcium monocarboaluminate (AFm-CO_3: $Ca_4Al_2(CO_3)(OH)_{12} \cdot 6H_2O$) is expected, which causes the precipitation of this solid. In addition, calcium silicate hydrates (C-S-H) might form due to Si release during the course of the dissolution of Fe siliceous hydrogarnet. Transformation of the Fe(III)-bearing phases to AFm-CO_3 causes only minor changes in the total volume of HCP (< 5 %), thus the influence on the porosity of the near-field is slight. Most likely it has no adverse effect on radionuclide retention. The transformation reaction depletes Fe-bearing mineral phases (C_4AF, Fe siliceous hydrogarnet), which only have a low capacity for cation and anion immobilization.

Ettringite (AFt: $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) is the main SO_4^{2-}-bearing mineral in $CaCO_3$-containing cement pastes. Recent sorption studies, however, suggest that small traces of calcium-monosulfoaluminate (AFm-SO_4: $Ca_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O$) might co-exist in the presence of ettringite. The former mineral is responsible for anion binding by HCP. Consumption of SO_4^{2-} during the course of the microbial decomposition of organic materials is expected to give rise to the dissolution of AFt and AFm-SO_4 (if no other SO_4^{2-} source is available in the waste matrix), which releases Ca and Al to the cementitious system. In combination with the CO_2 production (excess CO_2 due to degradation of organic material, compare Section 3.4.2), AFm-CO_3 and in addition calcite is formed. The formation of the new minerals causes changes in the total volume of HCP (< 10 %). A detrimental effect on the retention of some anions by the cement matrix is expected due to the dissolution of AFm-SO_4. Note that anion binding to AFm-SO_4 is significant while binding to AFm-CO_3 is much weaker. Therefore, decomposition of organic matter by sulphate-reducing organisms could reduce anion retention in the near-field, but no major impact on cation retention is anticipated.

When other electron acceptors, in particular SO_4^{2-} are depleted, a fermentative process (methanogenesis) which produces CH_4, is expected to be the main route for the degradation of organic materials. The rate of CH_4 generation depends on the degradation kinetics of the respective materials. If the production of methane is faster than the loss from the near-field by diffusion it accumulates in the gas phase due to its low reactivity and solubility. The concentration of dissolved CH_4 will be low and the interaction of CH_4 with the hydrophilic surfaces of cement minerals is expected to be insignificant. Therefore, the effect of CH_4 on the performance and retention properties of cementitious materials is expected to be negligibly small.

Boundary conditions/additional information

The extent of microbial activity determines the rate and degree of the biotic decomposition of organic matter under the hyperalkaline conditions of a cementitious near-field. The near-field will not be sterile, but the hyperalkaline conditions of the cementitious near-field certainly pose extreme conditions for life. Therefore, microbial activity will be low. Further, it will be strongly influenced by the amount and accessibility of internal and external sources of growth-limiting

nutrients (i.e. phosphorous) and oxidants (e.g. NO_3^-, Fe(III), SO_4^{2-}), and the availability of water and organic matter. In particular, the availability of water, phosphorous and nitrogen are expected to limit the degradation of the organics.

Cleavage or hydrolysis is the first and often limiting step to transform long chain polymeric materials into soluble and smaller molecules which can be degraded by microorganisms. Hydrolysis is either purely abiotic (hydrolysis, radiolysis), or mediated by extra-cellular enzymes excreted by microorganisms. While abiotic hydrolysis of cellulose and the radiolytic decomposition of ion exchange resins under hyperalkaline conditions have been investigated in detail, this process is only poorly understood for other polymeric organic waste materials.

Information from experimental studies

The degradation or transformation processes of organic materials are either biotic or abiotic or radiolytic in nature. Biotic processes may play a subordinate role under the hyperalkaline conditions of the cementitious near-field because microbial processes are expected to be slowed down (Pedersen et al. 2004). However, if the chemical conditions change in a way favouring microbial growth, microbial processes may become dominant.

Several experimental studies have shown that microbial communities can develop under the hyperalkaline conditions in cementitious systems (Wieland (2010b) and references therein). To the best of our knowledge, however, investigations on the influence of microbial activity on the mineralogical composition of HCP and its impact on the performance of the cementitious barriers have not been carried out.

Hallbeck (2010) suggests that the decomposition of easily degradable LMW organic compounds such as citric acid, EDTA, gluconic acid, hexamethylenetetramine, oxalic acid, and tartaric acid, and a few HMW organics (biodegradable detergents, concrete admixtures) is likely to be fast, and is hence expected to occur at an early stage in the development of the repository, i.e. "from the time of construction to 100 years after repository closure". Furthermore, the complete degradation of cellulose is likely to occur within less than 1'500 years (see above).

The degradation process of some HMW materials (bitumen, graphite, rubber, plastics, PVC) under alkaline conditions is less certain (Hallbeck 2010). Radiolytic decomposition of bitumen could generate LMW organic compounds for microbial degradation (Wiborgh et al. (1986) and references therein). Small organic molecules were suggested to be present in bitumen leachates at high pH. Furthermore, it was shown that short-chain n-alkenes originating from bitumized materials could be biodegraded into methane under anaerobic conditions (Wieland 2010b and references therein). Hallbeck (2010) assumed that the leaching of small organic molecules occurs in the early phase of repository life, and that these molecules are subject to oxidative biodegradation. The degree of oxidation depends on how easily polar groups are accessible to oxygen, which can be different for different types of bitumen (Valcke et al. 2009).

Graphite is a stable material under anaerobic conditions over geological time periods. Under oxidizing conditions, however, slow degradation is considered possible (Hallbeck 2010, Wieland 2010b). Rubber shreds were found to be subject to minimal degradation, if at all, under alkaline conditions, and no chemical reactions or microbial attack gave rise to noticeable decomposition in short-term experiments (Wieland (2010b) and references therein).

Although detailed long-term studies are lacking, the results from the short-term studies indicate that rubber will be chemically stable over a very long period of time under anaerobic hyper-alkaline conditions. Hallbeck (2010) assumed that rubber is less degradable than plastics. The

susceptibility of plastic materials to biodegradation depends on various factors such as the polymer characteristics (e.g., crystallinity, type of functional groups, plasticizers, additives added to the polymer etc.), the type of organisms involved, and the nature of pretreatments (Wieland 2010b and references therein). Polyethylene and polyester are known to be only slightly biodegradable, while aliphatic polyesters, polyethers, polyurethanes, and polyaimides are easily biodegraded (Hallbeck 2010 and references therein). Up to now there is no evidence that polystyrene and PVC, the dominating polymers in the waste, are degradable under anaerobic conditions (Warthmann et al. 2013). Abiotic hydrolysis and oxidation are the first steps during environmental degradation of polymers (Shah et al. (2008) and references therein). Hence, both oxo- and hydro-biodegradable plastics undergo breakdown processes in a first step which produce smaller fragments accessible to biodegradation.

Abiotic degradation of cellulose was observed under alkaline conditions (Glaus & Van Loon, 2009, Van Loon & Glaus, 1998, and references therein). Fungi under aerobic conditions, and bacteria under anaerobic conditions, produce enzymes needed to metabolize cellulose (Wieland 2010a and references therein). Whether these living organisms will be capable of metabolizing cellulose under alkaline conditions is poorly known. Radiolytic degradation of cellulose is less important, but radiolytic degradation is important in the case of spent ion exchange resins (Glaus 2010). The functional groups used to bind the various radioisotopes in ion exchange resins may not be stable under long term irradiation, and ion exchange resins convert to LMW organic or inorganic compounds such as amines, oxalate or other nitrogen containing ligands and low-molecular weight carboxylic acids (Hummel & Van Loon 1999, Van Loon & Hummel 1999).

Chemical degradation of concrete admixtures is poorly understood. Mobilization of the LMW fraction consisting mainly of monomers is expected, based on their chemical structures (Wieland 2010a, and references therein).

Time scales

The decomposition of LMW organic materials and cellulose is expected to take place during the oxic and early anoxic stages of the L/ILW and ILW repositories (< 1'500 years). The decomposition of the slowly degrading HMW organic materials is expected to occur in the long term, i.e. under the anoxic repository conditions. Note that evidence has been provided that polystyrene and PVC may not degrade at all (Warthmann et al. 2013). The different time scales for the degradation of LMW and cellulose on the one hand, and the polymeric HMW organic matter on the other, have been taken into consideration in performance assessments (e.g. Nagra 2004, 2008a).

The availability of water is crucial for the microbially-mediated decomposition of organic matter, which is controlled by the hydraulic properties of the host rock. The availability of growth-limiting nutrients, in particular phosphorous, could be an additional factor limiting microbial activity and the degradation of organic matter over time.

Uncertainties

Uncertainties exist regarding the degree to which HMW organic material will be degraded over time. These uncertainties involve the kinetics of abiotic cleavage or hydrolysis, which transform long chain polymeric matter into soluble and smaller molecules accessible to biodegradation and therefore control the dynamics of microbial activity under hyperalkaline conditions. The degradation rates of HMW organic materials, and the gas generation rates, are based on limited

information, available mainly from earlier studies on the degradation of cellulose and bitumen (Wiborgh et al. 1986). In safety assessments (Nagra (2004, 2008a) it is assumed that the decomposition of LMW organic material is completed within some ten thousand years or complete degradation may not occur at all.

Further uncertainties exist regarding the influence of the microbial activity of iron- and sulphate-reducing microorganisms on the composition of HCP in the near-field. It is poorly known whether $Fe(III)$ and SO_4^{2-} will be important electron acceptors that can be mobilized from the cement matrix by microbial activity. In particular, the microbially-induced dissolution of SO_4^{2-}-bearing cement minerals, which are mainly responsible for the retention of anions by the cement matrix, could have an adverse effect on the long-term release rate of some dose-determining anions.

Cleavage of cellulose fibres (or cellulose hydrolysis, respectively) is considered to be the first and rate determining step of the degradation (biotic or abiotic) of cellulose. Under the strongly alkaline conditions of a cementitious near-field (typically pH > 12) it is expected that biotic (microbial) degradation will be limited due to low microbial activity under the given conditions (Rizoulis et al. 2012). This implies that abiotic cleavage of cellulose could prevail, provided that degradation of cellulose can take place at all.

3.4.2   Impact of CO_2 on the degradation of cement

Overview/general description

Carbonation of hydrated cements involves the transformation of portlandite ($Ca(OH)_2$), calcium silicate hydrates (C-S-H) ($xCaO \cdot SiO_2 \cdot nH_2O$), ettringite and AFm to calcium carbonate, gypsum and other secondary aluminium and silica oxyhydroxides (Venhuis & Reardon 2001). Portlandite and C-S-H are the most abundant cement phases in HCP and therefore they are considered to preferentially undergo transformation. For example, in cement paste produced from Portland cement CEM I 52.5 N HTS (Lafarge, France), which is currently in use for the solidification of L/ILW in Switzerland, the proportions of $Ca(OH)_2$ and C-S-H are ~ 20 wt.-% and ~ 50 wt.-% (Lothenbach & Wieland 2006), indicating that the CO_2 neutralization capacity of hydrated cement is substantial.

Carbon dioxide generated by aerobic or anaerobic microbial degradation of organics will react in hyperalkaline water and to form predominately carbonate:

$$CO_2(g) + 2\ OH^- \rightarrow CO_3^{2-} + H_2O \qquad\qquad (3.11)$$

In the cementitious near-field, dissolved carbonate will react primarily with portlandite:

$$Ca(OH)_2 + CO_3^{2-} \rightarrow CaCO_3 + 2\ OH^- \qquad\qquad (3.12)$$

The overall reaction is:

$$Ca(OH)_2 + CO_2(g) \rightarrow CaCO_3 + H_2O \qquad\qquad (3.13)$$

The corresponding reactions for complete or partial carbonation of a C-S-H phase can be expressed as follows:

$$xCaO \cdot SiO_2 \cdot nH_2O + CO_2(g) \rightarrow xCaCO_3 + SiO_2 + nH_2O \qquad (3.14)$$

$$1.6CaO \cdot SiO_2 \cdot xH_2O + 0.8CO_2(g) \rightarrow 0.8CaCO_3 + 0.8CaO \cdot SiO_2 \cdot yH_2O + (x-y)H_2O \qquad (3.15)$$
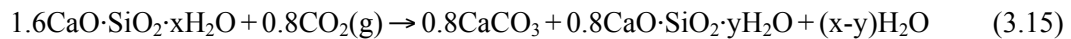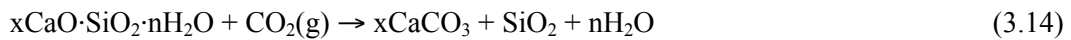
In Nagra's performance assessment studies the maximum amount of portlandite allowed to be converted into calcite by the degradation of organic matter was set at 2/3 of the total portlandite inventory in HCP in the case of the group 1 waste compartments (Nagra 2014, Schwyn 2008). This threshold value ensures that the retention controlling cement minerals are still present despite the (partial) transformation of portlandite into calcite. Therefore, with respect to radionuclide retention, the barrier function of HCP is expected to be maintained during the course of the evolution of the near-field. Further, this value allows the maximum loadings of the various organic materials per volume of HCP in the tunnel to be achieved (Wieland & Berner 2012). Changes in the Ca/Si ratio of C-S-H phases due to carbonation are expected to be small, thus allowing C-S-H as CO_2 capturing phases to be ignored.

It should be noted that, contrary to the case of Group 1 waste, an adverse effect on radionuclide retention in Group 2 waste could occur. The degradation of the large inventories of organic materials associated with Group 2 waste would produce such large amounts of CO_2 that the HCP could be completely carbonated and thereby influence the radionuclide retention.

The carbonation process could have an influence on the immobilization of metal cations and anions. Cationic waste constituents have a lower leachability from carbonated HCP than from non-carbonated HCP probably due to the reduced permeability of the cementitious materials (Wieland & Berner (2012) and references therein). Note that the reduction of the Ca/Si ratio of C-S-H due to carbonation is not expected to have a significant impact on cation retention. In contrast, anionic waste constituents could show greater leachability upon carbonation due to the transformation of AFm-SO_4 to AFm-CO_3.

Boundary conditions/additional information

CO_2 is produced by the decomposition of organic compounds with electron acceptors (e.g. SO_4^{2-}) or by methanogenesis and is controlled by the microbial activity in the course of the repository evolution. Allowing for the Group 1 waste compartment of the repository only 2/3 of the total inventory of portlandite to be dissolved by the degradation of organic materials over time ensures that the phase assemblage in the cement matrix will be stable. This limit implies that no additional processes should be operative which could further diminish the amount of portlandite in the cement matrix, such as cement degradation by interaction with host rock pore water. Cumulative effects, however, could reduce the portlandite inventory to a level where a detrimental effect on the mineral composition takes place.

Information from experimental studies

Carbonation of cement paste due to CO_2 ingress is a well-known phenomenon (Reardon et al. 1989, Wieland & Berner 2012 and references therein). The OH⁻ and Ca^{2+} ions consumed during the course of cement carbonation arise mainly from the dissolution of $Ca(OH)_2$ (Eqs. 3.3 – 3.13). During carbonation mainly portlandite is converted into calcite. This is supported by the finding that in cement paste higher concentrations of calcite were observed around portlandite crystals (Reardon et al. 1989).

The leachability of cations and anions was studied in standardized static and dynamic tests using carbonated samples (Venhuis & Reardon 2001). Carbonation resulted in lowering the leachability of cations (strontium, caesium), which was explained by a significant reduction in porosity and permeability of the carbonated cementitious materials. The leachability of anions (chloride, nitrate, arsenate) was found to increase with increasing degree of carbonation (Venhuis & Reardon 2001). This is explained by the release of anions from ettringite and calcium monosulfoaluminate which converted into CO_3^{2-} bearing cement minerals during the course of carbonation.

Experimental studies on the degradation of organic materials in cement paste and the impact on mineral composition of the paste could not be found in the open literature.

Time scales

The time span over which the degradation of cement paste occurs is controlled by the temporal evolution of CO_2 generation. This process is determined by the decomposition rates of LMW and HMW organic materials in the near-field (Section 3.4.1).

Uncertainties

Uncertainties exist regarding the time span over which LMW and HMW organic materials degrade in a repository environment (Section 3.4.1).

3.4.3   Organic ligands: impact on sorption and aqueous speciation

Overview/general description

Radioactive waste may contain compounds that could influence radionuclide mobility in the cementitious near-field. Within the Swiss disposal concept it is foreseen to dispose of waste sorts with high inventories of "disturbing compounds" in separate compartments in order to minimize any adverse effects on radionuclide mobilization in waste sorts with lower inventories of "disturbing compounds".

EDTA, cyanide (CN^-), gluconic acid (GLU), isosaccharinic acid (ISA) and ammonia (NH_3) are considered to be the most important complexing ligands for radionuclides (Schwyn et al. 2003, Nagra 2008b). The maximum concentrations in the near-field listed in Tab. 3.6 were estimated on the basis of the MIRAM 12 inventories (Nagra 2013). The concentration limits given in Tab. 3.6 are applied to classify waste sorts as Group 1 and Group 2. Group 1 waste sorts do not contain the above complexing ligands at concentration levels which could reduce radionuclide sorption on cementitious materials or enhance their solubility. In contrast, Group 2 waste sorts have larger inventories of the above complexing ligands which result in aqueous concentrations that could influence radionuclide mobility.

Tab. 3.6: Complexing ligands in the L/ILW repository.

Material	Waste sort with maximum pore water concentration	Maximum concentration [mol/L]	Concentration limit* [mol/L]
EDTA	BA-G-KB-F2-SMA	0.027	10^{-3}
Gluconic acid**	BA-Z-X-C1-SMA-a	4.9×10^{-6}	10^{-5}
Cyanide	BA-B-S-F2-SMA	0.13	10^{-5}
Isosaccharinic acid	BA-PH-PF-Z3-ATA	1.2×10^{-3}	10^{-4}
Ammonia***	BA-G-HB-F2-SMA	0.67	0.1

* Limits for Group 1 and 2 waste sorts
** Recommended limit based on in-house studies (Wieland 2014)
*** Recommended limit based on the study of Van Loon & Hummel (1999), applicable only in Stage C of the cement degradation (Thoenen 2013)

EDTA

Instantaneous release of this organic ligand from the BA-G-KB-F2-SMA waste sort into the pore water yields a maximum concentration of ~ 0.03 mol/L in the near-field (Tab. 3.6). Speciation calculations predicted that EDTA influences the speciation of only a very few cations under alkaline conditions, i.e. Ni and Pb (Hummel 1993).

Gluconic acid

The majority of cemented waste sorts will contain gluconic acid (GLU) which is used as concrete admixture during waste solidification. Maximum GLU aqueous concentrations are given in Tab. 3.6. They are controlled by sorption on HCP, which can be modelled by a Langmuir isotherm (Glaus et al. 2004). The complexation of safety-relevant radionuclides or representative chemical analogues at high GLU concentrations in some waste sorts will be accounted for in terms of sorption reduction factors (Wieland 2014).

Cyanide

Prussian Blue ($Fe^{III}_4[Fe^{II}(CN)_6]_3$) is only present in one waste sort (BA-B-S-F2-SMA). Prussian Blue readily dissolves under alkaline conditions (Hummel 2004). Free cyanide would be released if hexacyanoferrate ($Fe(CN)_6^{4-}$) is further decomposed in the cementitious near-field. However, the latter compound is expected to be stable in the dark even under alkaline conditions (pH >8), while complete photodecomposition occurs in the light within days. Hence, assuming complete decomposition of $Fe(CN)_6^{4-}$ to free cyanide is a very conservative approach to assess the maximum impact on radionuclide sorption. Biodegradation of free cyanide under anaerobic conditions was observed to occur in laboratory systems, while biodegradation under field conditions, particularly under the hyperalkaline conditions of a cementitious near-field, has not yet been studied. On the assumption that biotic or abiotic decomposition of free cyanide can be excluded, high CN^- concentrations may result in the waste sort BA-B-S-F2-SMA (Tab. 3.6). Hummel (2004) showed that cyanide influences the speciation of only a very limited number of metals, in particular Ni and Co.

Cellulose degradation products

A few waste sorts contain cellulose which degrades under alkaline conditions. The maximum loading in some waste sorts is about 14 % of the HCP mass. The main degradation products of cellulose are α- and β-ISA which are powerful complexing agents, in particular for 3- and 4-valent actinides. The kinetics of cellulose degradation is still disputed due to significant differences between the rate constants determined in short-term and long-term experiments and those deduced from degradation studies at enhanced temperatures (Glaus 2010). Furthermore, it was observed that α-ISA can be converted to short chain aliphatic carboxylic acids with only moderate complexing properties in the presence of stoichiometric amounts of oxygen. The concentration of ISA in the near-field pore water was estimated by considering ISA sorption on HCP, which was modelled using a simplified one-site Langmuir isotherm. Sorption reduction of radionuclides caused by high ISA concentrations (ISA $>10^{-4}$ mol/L) in the pore water for some waste sorts (Tab. 3.6) has to be taken into account in performance assessment.

Ammonia

Spent ion exchange resins are considered to be the main source of NH_3 and amines (methylamine, dimethylamine and trimethylamine). Radiolytic degradation is an important process which generates ammonia, amines, other nitrogen-containing ligands and low molecular weight carboxylic acids. The concentration of ammonia was estimated based on the inventory of spent ion exchange resins with quaternary ammonium groups (Wieland & Berner 2012). The maximum concentration of ammonia in the near-field pore water was estimated to be 0.67 mol/L for the BA-G-HB-F2-SMA waste sort. A concentration limit of 0.1 mol/L is recommended as the limit to be used to classify Group 1 and Group 2 waste sorts under pore water conditions in Stage C of cement degradation (Tab. 3.6). The latter value was estimated on the basis of the thermodynamic calculations reported earlier by Van Loon & Hummel (1999), indicating no effect on radionuclide solubility and sorption at 0.1 mol/L ammonia.

Polymeric organic materials and detergents

The effect of polymeric organic materials and their degradation products on radionuclide solubility and sorption was found to be negligibly small compared to that of cellulose degradation products (Wieland & Berner (2012) and references therein). Therefore, it is expected that polymeric organic materials, and detergents, have only a negligibly small influence on radionuclide solubility and sorption.

Concrete admixtures

Concrete admixtures are unavoidable components of cements used for the conditioning of radioactive waste and of concretes used for the construction of the cement-based deep geological repository. In most cases concrete admixtures are polymeric organic compounds which are often poorly defined and, owing to proprietary reasons, have only partly known compositions. The most important components are polynaphthalene-sulfonic acids, polymelamine-sulfonates, lignosulfonates, gluconic acid and polycarboxylate-ether based molecules. It was observed that all concrete admixtures, with the exception of the formerly used gluconic acid and lignosulfonates, form only weak complexes with radionuclides. For example, the use of modern polycarboxylate-ether based concrete admixtures at typical levels leads to concentrations in the pore water of the cementitious near-field (solid-to-liquid ratio of ~2 kg/L), which are expected to have no adverse effect on radionuclide uptake by HCP. Currently there are no indications that possible degradation products of concrete admixtures have stronger complexing properties than

their parent compounds. Hence, sorption reduction effects caused by concrete admixtures will not be taken into account. Gluconic Acid is a special case which is treated separately (see above).

Boundary conditions/additional information

The degradation of cellulose, polymeric materials, and spent ion exchange resins, the sorption properties and chemical stability of the degradation products under hyperalkaline conditions, and the inventory of concrete admixtures (e.g. gluconic acid) determine the pore water concentrations of radionuclide complexing ligands. Biodegradation of these materials may play a subordinate role under the hyperalkaline conditions of the cementitious near-field because microbial activities will be at a low level. Radiolytic degradation of cellulose is of less importance and the kinetics of chemical degradation is associated with large uncertainties. Biotic and chemical degradation of concrete admixtures is likely to occur. Radiolytic processes are important in connection with the stability of ion exchange resins in a cementitious near-field.

Information from modelling/experimental studies

Experimental studies on the complexation of radionuclides by EDTA under hyperalkaline conditions are lacking. Possible effects on radionuclide mobilization were assessed on the basis of thermodynamic calculations (Hummel 1993).

Metal cyanide complexes, such as $Fe(CN)_6^{4-}$, decompose to free cyanide in UV-vis light, while the complexes are stable in the dark even under alkaline conditions (Hummel 2004) and references therein). It is expected that the effect of gamma-irradiation on the decomposition of metal cyanide will depend on the dose rate in the near-field (Hummel 2004). Biodegradation of free cyanide under anaerobic conditions was reported in laboratory systems, but the extrapolation of these findings to field conditions, particularly the hyperalkaline conditions of a cementitious near-field, is uncertain (Wieland & Berner (2012) and references therein). The thermodynamic calculations by Hummel (2004) showed that free cyanide has only an effect on the speciation of Ni and Co under alkaline conditions.

The sorption of GLU onto HCP can be modelled in terms of a two-site Langmuir-type isotherm (Glaus et al. 2004), while the approximation by a one-site Langmuir isotherm is possible at lower concentrations (GLU $\leq 10^{-4}$ mol/L) (Bradbury & Van Loon 1996). Several authors have investigated the influence of GLU on the uptake of safety-relevant radionuclides by HCP (Glaus 2010 and references therein). These studies show that GLU only forms strong complexes with tetravalent actinides (An(IV)). Gaona et al. (2008) recently reviewed the speciation scheme and the stability constants of, An(IV)-GLU complexation. The complexation constants reported by these authors indicate the formation of strong An(IV)-GLU complexes in solution which explains sorption reduction at GLU concentrations $\geq 10^{-5}$ mol/L.

Glaus (2010) published a detailed review of recent experimental status concerning the degradation of cellulose under the conditions of a cementitious near-field, the chemical stability of the main degradation products α- and β-isosaccharinic acids and their complexation behaviour with radionuclides. The experimental studies on the complexation behaviour of α-ISA with safety-relevant radionuclides unequivocally showed a significant effect on the speciation of metal cations (Glaus 2010 and references therein). The results show significant sorption reductions caused by α-ISA at ligand concentrations $> 10^{-4}$ mol/L.

The review by Glaus (2010) further summarizes our current understanding on the degradation of ion exchange resins, which produces ammonia and amines, and on the effect of these ligands on radionuclide complexation. The main conclusions presented earlier by Van Loon & Hummel (1995) are still valid. First, the radiolytic and chemical (alkaline) degradation of products of organic ion exchange resins have no or only negligible influence on the speciation of radionuclides in a cementitious near-field and therefore their specific consideration in safety analysis is not required. Secondly, the nature of the ligands formed allows significant complexation with "soft" metals such as Ag and Pd, which are not dose-determining elements in performance assessment.

Greenfield et al. (1992, 1994) studied the influence of polymeric materials and their degradation products on radionuclide solubility. Note that the above studies are currently the only source of information on the complexation of radionuclides by the degradation products of these materials. The authors investigated radionuclide solubilities in solutions prepared from aged crushed cements and up to 20 wt.-% of polymeric materials. They observed no detrimental effects on radionuclide solubilities. Therefore, sorption reduction effects caused by polymeric materials and their degradation products are not taken into consideration when assessing the radionuclide uptake by HCP.

The complexation of radionuclides by concrete admixtures has been investigated with the aim of developing a generic approach for assessing their impact on radionuclide mobility (Glaus et al. 2004 and references therein). The degradation products of concrete admixtures, which mainly consist of organic monomers, are expected to be very weak complex formers (Wieland & Berner 2012 and references therein).

Time scales

The time span over which radionuclide complexing ligands persist depends on the scenarios invoked for the possible degradation or transformation of organic matter. Chemical and radiolytic processes facilitate the generation of the ligands while biodegradation will significantly reduce their impact over time.

Uncertainties

The main uncertainties are associated with the kinetics involved in the different possibilities for biotic, abiotic and radiolytic degradation or transformation reactions. These reactions control the pore water concentrations of most of the radionuclide complexing ligands. In particular, the kinetics of abiotic cleavage (or hydrolysis), which transforms long chain polymers into smaller more soluble molecules, is not well known.

3.4.4   Other wastes – cement interactions

Overview/general description

Inorganic waste materials are expected to be subject to transformation processes in the repository. The degree of transformation depends on the chemical stability of the waste materials under the hyperalkaline, reducing conditions of the cementitious near-field. Potential processes are listed in Tab. 3.7 for the inorganic waste materials. Based on this appraisal, the waste materials have been classified as "reactive" or "inert" with respect to possible impacts on HCP.

"Reactive" materials are expected to convert into products over the time scale of a repository which may have an adverse effect on the mineral composition of HCP.

Inert materials, such as Be, B_4C, Cu, and Zircaloy, are expected to persist over geological time scales, or they decompose with time and generate reaction products that have no significant influence on the mineral composition of HCP.

Other materials mainly consist of components in the cement matrix. For example, asbestos, ash, ceramics and glass are such types of materials which decompose over time and generate products with compositions similar to that of cement-type minerals. Hence, decomposition of these waste materials is expected to have only a minor effect on the mineral composition of HCP.

Most metallic materials, incl. steel will be subject to anoxic corrosion which produces H_2 (Section 3.2.1). The corrosion rates of the different metals, i.e., Al, Fe, Mg, Pb and Zn, may differ. The reaction products expected to be formed due to the corrosion of Pb and Zn (mainly sulphides, carbonates and hydroxides) have no adverse effect on HCP because no change in the mineral composition of HCP is expected. The interaction of Pb^{2+} with the cement matrix is dominated by surface sorption onto cement minerals, while Zn^{2+} can be taken up into the C-S-H structure. Both processes cause only minor changes in the mineral composition of HCP.

Some metals, e.g. Mg, Al and Fe (in steel), will corrode over time and the corrosion products potentially alter the mineral composition of HCP. Magnesium is expected to show little reaction with HCP and forms mainly brucite ($Mg(OH)_2$) according to:

$$Mg_{(s)} + 2\ H_2O \rightarrow Mg(OH)_{2(s)} + H_{2(g)} \tag{3.16}$$

Thermodynamic calculations show that small amounts of Mg may react with the cement matrix to form hydrotalcite-type phases. The latter phase forms at the expense of $AFm\text{-}CO_3$ and small amounts of calcite and portlandite form at the same time. Calcite is formed until the carbonate is exhausted; excess calcium promotes formation of portlandite. Ettringite is not affected. Thus, enhanced inventories of Mg promote the formation of portlandite and calcite which promotes the chemical stability of the cement matrix. Corrosion of Mg gives rise to changes in the total volume (< 10 %). Overall, the influence of Mg on porosity changes, and on the sorption properties of HCP caused by changes in the mineral composition, is expected to be small.

Metallic Al may readily corrode under anoxic conditions to generate $Al(OH)_3$ and hydrogen gas as follows:

$$Al(0) + 1.5\ H_2O \rightarrow Al(OH)_3 + 3/2\ H_2 \tag{3.17}$$
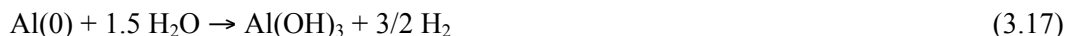
The precipitation of α- and γ-$Al(OH)_3$ (gibbsite and bayerite), and the formation of strätlingite , could occur which would cause changes in the mineral phase composition. Thermodynamic calculations revealed that high inventories of Al lead to the dissolution of portlandite and ettringite, while hydrogarnet, calcium hemicarboaluminate and calcium hemisulfoaluminate form. The addition of 40 g $Al(OH)_3$ to 406 g HCP reduced the inventory of portlandite by 2/3 of its initial value. Volume changes were found to be insignificant.

The behaviour of Fe species in cementitious environments is poorly understood. Zero-valent iron is expected to corrode under anoxic conditions to form Fe^{2+} according to:

$$Fe_{(s)} + 2\ H_2O \rightarrow Fe^{2+} + 2\ OH^- + H_{2(g)} \tag{3.18}$$

Ferrous iron compounds may form under near-field conditions, e.g. $Fe(OH)_2$, FeS, $FeCO_3$. Under anoxic conditions and at temperatures above 80 °C, $Fe(OH)_2$ is unstable and converts to magnetite via the Schikorr reaction:

$$3\ Fe(OH)_{2(s)} \Leftrightarrow Fe_3O_{4(s)} + H_{2(g)} + 2\ H_2O \tag{3.19}$$

The transformation of $Fe(OH)_2$ at ambient temperature is very slow or does not occur at all. The interaction of Fe^{2+} with the cement matrix is uncertain. Replacement of Ca^{2+} by Fe^{2+} in Ca bearing cement minerals, such as portlandite, ettringite, AFM- and C-S-H-phases, is unlikely due to the very different ionic radii of the cations in six-fold coordination (Fe^{2+}: 0.78 Å; Ca^{2+}: 1.00 Å). Substitution of Mg^{2+} (0.72 Å) by Fe^{2+} could occur in hydrotalcite-type phases, due to similar ion size. Note, however, that Mg^{2+} predominantly forms $Mg(OH)_2$ in cementitious environments and therefore Mg^{2+} – Fe^{2+} exchange is unlikely.

In some waste sorts the inventories of Mg, Al and Fe per mass of HCP in the tunnel are large. Thermodynamic scoping calculations based on the HTS model reported by Berner (2009) indicate potential impacts of Al and Fe on the cement composition, while no effect was predicted in the case of Mg. However, without including the release rates of Al(III) and Fe(II)/ Fe(III) from corrosion products (e.g. magnetite) and the re-precipitation rates of secondary products, it is currently not credible to assess detailed overall long-term impacts on HCP.

Boundary conditions/additional information

The availability of water controls metal corrosion. The corrosion process may be inhibited by the formation of a corrosion layer on the metallic waste over time.

Information from experimental studies

Experimental studies showed that Pb^{2+} interaction with cementitious materials predominantly occurs via the formation of surface complexes on C-S-H phases at low Pb inventories while Zn^{2+} can be taken up into the structure of C-S-H phases (Wieland & Berner 2012 and references therein).

Several studies have investigated the interaction of Mg^{2+} with concrete and HCP (Wieland & Berner 2012 and references therein). In all of these studies the predominant formation of brucite was reported, while hydrotalcite-type phases containing Mg were found to form only in small amounts.

The corrosion of aluminium produced a porous zone at the interface between the metal and the cement matrix filled with corrosion products (Wieland & Berner 2012 and references therein). The main corrosion products observed in ordinary Portland cement (OPC) were aluminium hydroxides (gibbsite, bayerite) and strätlingite. The amount of gibbsite was found to increase with time.

The corrosion of iron has been thoroughly investigated under alkaline and anaerobic conditions (Chitty et al. 2006, Féron et al. 2008, King 2008, Duffó et al. 2010, Neff et al. 2010, Newmann & Wang 2010, Kursten et al. 2011, McGlinn et al. 2008). Iron hydroxide ($Fe(OH)_2$) and magnetite were reported to be the main corrosion products. The ferrous hydroxide was reported to convert slowly to magnetite via the Schikorr reaction at enhanced temperatures and under anoxic conditions, while the compound was stable at temperatures below 100º under anoxic conditions.

Time scales

The corrosion of magnesium and aluminium is expected to be fast. The exact corrosion rate depends on the impurity elements present in the metals. The formation of protective layers, e.g. the formation of brucite or bayerite, may inhibit the dissolution in the long term. In contrast, the corrosion of iron in alkaline media was found to be very slow under anoxic hyperalkaline conditions (corrosion rate ≤ 50 nm/a).

Uncertainties

The corrosion kinetics and the degree of interaction of Mg^{2+}, Al^{3+} and Fe^{2+} with components of the cement matrix are only partly understood. For example, while the experimental investigations suggest that $Al(OH)_3$ is the dominant corrosion product, the extent of strätlingite formation in the course of the corrosion of Al metals is difficult to quantify. Similarly, Fe^{2+} could react with HCP, e.g. by substituting Mg^{2+} in hydrotalcite-type phases. Nevertheless, the degree to which this substitution occurs is uncertain since Mg^{2+} forms predominantly $Mg(OH)_2$ in cementitious environments.

Tab. 3.7: Overview on the chemical reactions of inorganic waste interacting with HCP.

Inorganic waste	Comment	Reactivity/impact
Aluminium (Al)	Oxidation to Al(III) by Al(0) + 1.5 H_2O $\rightarrow Al(OH)_3 + 3/2\ H_2$; gas problem; question of grain sizes (kinetics); new cement minerals may be formed from ($Al_2O_3 + 3H_2O$); aluminate cements?	Reactive – formation of new cement-like minerals – impact possible
Asbestos	$Mg_3Si_2O_5(OH)_4$; a composition similar to those of the aggregates; long term thermodynamic stability not clear in cementitious environment; known to be used as aggregate in concretes	Probably hardly reactive – chemical impact not relevant
Ash	Generally oxidized materials; show usually alkaline reaction; common to cementitious materials; may show pozzolanic reaction; formation of new, cement-like minerals if portlandite is available	Reactive – formation of new cement-like minerals – impact not relevant

Tab. 3.7:   (continued)

Inorganic waste	Comment	Reactivity/impact
Beryllium (Be)	No further information available; relevant compounds probably just $BeO/(OH)_2$ and $BeSO_4$; $BeSO_4$ soluble in water; sulphate forms double salts; Be could be taken up by AFm/AFt phases replacing $CaSO_4$; highly toxic from a chemical point of view; release to environment has to be controlled	Inert – important in conjunction with toxicologic issues
Lead (Pb)	Pb(0), Pb(II); reactions with S^{2-}, CO_3^{2-}, SO_4^{2-}, Cl^-	Reactive – impact not relevant
Boron carbide (B_4C)	Chemically nearly inert and very hard material; no chemical reaction below 1'000 ºC; resistant against nitric acid and HF	Inert
Metals	Production of H_2 gas through anoxic corrosion; may produce oxides with different sorption properties; corrosion probably kinetically controlled (or by surface); formation of new minerals may induce volume/porosity changes.	See Fe, Mg, Al
Magnesium (Mg)	Formation of cement-like minerals possible; volume changes	Reactive – formation of new cement-like minerals – impact possible
Iron (Fe)	Pyritic & magnetitic phases; formation of cement-like minerals possible, volume changes	Reactive – formation of new cement-like minerals – impact possible
Copper (Cu), silver (Ag)	Formation of sulfides and precipitation	Inert
Steel	Release of carbon species; Fe source; release of alloyed metals like Ni, Cr, Mn	Reactive (see Fe)
Inorganic residuals	No specific information available	Unknown
Metallic residuals	No specific information available	See Metals
Zink (Zn)	Production of H_2 gas, forms soluble products; interaction with C-S-H	Reactive – impact not relevant
Zircaloy (Zr)	Resulting in ZrO_2, which is inert; release of alloyed metals	Inert
Ceramics, glass	Acid/base reactions similar to those considered in pH-plume issues may occur; question of kinetics and reactivity; chemical composition resembles that of cementitious materials	Reactive – impact not relevant

3.4.5 Interactions between cement and aggregate (internal degradation)

Overview/general description

The reaction of alkaline materials such as alkali hydroxides or portlandite with siliceous aggregates is well known under the name of ASR (alkali silica reaction). In standard concrete structures, ASR may, within a few years, lead to internal pressure and structural damage induced by the general reaction scheme:

$$SiO_{2(quartz, aggregate)} + portlandite(Ca(OH)_2), alkali\ hydroxides + water$$

$$\rightarrow calcium\text{-}silicate\text{-}hydrates(C\text{-}S\text{-}H) + alkali\text{-}silicate\text{-}hydrates \tag{3.20}$$
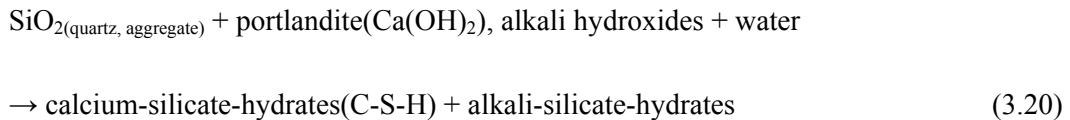
Structural damages may occur because neo-formed C-S-H-phases have larger volumes than the starting solids. The concrete and construction industry usually inhibits such types of reactions by using non-reactive siliceous aggregates or by adding pozzolanic reactants to the fresh concrete mixture to pre-neutralize alkali hydroxides at the early stages of the hardening process. This pozzolanic reaction is in fact also one way to produce a so-called low-pH concrete (using highly reactive silica as reactant).

It is common in waste management to consider three stages of degradation in the lifetime of cementitious structures and their pore waters (Sections 2.3, 2.4 and 3.2.1). A typically short-time early high-pH stage (Stage A, pH above 13) determined by high concentrations of alkali hydroxides, is followed by a stage where portlandite dominates. The duration of this second portlandite-stage (Stage B, pH ~12.5) may last for quite long times, depending on the water flux through the cement structure. A third stage, Stage C, is characterized by the absence of portlandite and, consequently, by the degradation of C-S-H-phases, degrading from high C/S (Ca/Si)-ratios to low C/S-ratios. This is also strongly dependent on the formation water flux through the system. All of these considerations have been made under the assumption that the concrete aggregates are inert. However, from a thermodynamic point of view this assumption is valid for calcite aggregates, but for quartz it may be too simplistic (Kosakowski & Smith 2014).

Boundary conditions/additional information

The question arises what happens when mass transport between the concrete and the surrounding materials slows down as a consequence of pore space blocking (Kosakowski 2010, e.g. Kosakowski & Berner 2011c). In such a case, neutralization reactions may progress internally until one of the reactants is exhausted and/or to a point where some kind of equilibrium is reached. Finally, the system may reach a state somewhere between clay rock and concrete in the pH range between 9 and 10. The detailed final stage of this "clayish equilibrium system" is difficult to predict because it depends on a large variety of not yet well-known thermodynamic and mass balance constraints.

Our understanding of these "internal neutralization" process steps, based on the presently available thermodynamic data, is as follows.

Firstly, dissolved SiO_2 reacts with portlandite and high C/S-ratio C-S-H-gels to form C-S-H phases exhibiting lower C/S-ratios. In a next step, dissolved SiO_2 attacks the aluminate monocarbonate phase, which is converted to the C-A-S-H (calcium-aluminium-silicate-hydrate) phase strätlingite. Then, the ettringite is attacked, and, in parallel, C-S-H-phases with lower C/S-ratios increase and the pH falls to about 12. Under theses pH conditions the stability fields

of phillipsite (a zeolite phase) and gibbsite are entered. The pH drops further, and at a pH-value around 11 illite becomes stable. The C-S-H phases degrade to a tobermorite/amorphous SiO_2 solid solution with a formal C/S-ratio significantly below 1. The pH drops to around 10.3, ettringite disappears and smectite phases (e.g. montmorillonite) become stable. Released sulphate (from ettringite) is re-precipitated as gypsum and the remaining solid assembly resembles more and more a clayish system at elevated pH.

Information from model studies/experimental studies/natural analogues/ observations in nature

ASR causes severe problems for functionality and durability of concrete structures and is therefore a very active field of research (fore recent lierature reviews see e.g. Lindgård et al. 2012, Pan et al. 2012). Unfortunately not much information is available beyond the typical lifetime of concrete structures. A comprehensive overview on the ASR is given in a recent Oak Ridge National Laboratory report prepared for the US Nuclear Regulatory Research (Naus 2007). The report describes in detail how the ASR leads to expansion, cracking and loss of strength, stiffness and durability. Unfortunately, the word "kinetics" is not mentioned in the report. One learns that the alkali silicate reactions typically occur within 5 to 10 years after construction and how one can circumvent concrete deterioration by using non-reactive aggregates. Charlwood (2009) reviews the long-term evolution of concrete dams and how they are influenced by several ageing and deterioration phenomena. He reports, that ASR slows down in some dams after several years, but other dams show ongoing expansion and resulting distress (from ASR) even 50 years after construction. He remarks that for the latter cases ASR and associated expansion *may possibly continue essentially indefinitely*.

Hou et al. (2004) give a comprehensive description of the ASR. They describe a series of experiments at 80 ºC in the presence and absence of portlandite. Low C/S-ratio C-S-H gel is formed in the presence of portlandite, and high C/S-ratio C-S-H gel, alkali-silicate-hydrate gel (ASH), is formed in the absence of portlandite. Reaction kinetics are not specifically mentioned but the results suggest a dissolution rate of about 8.4×10^{-5} mol/m^2·s for opal at (80 ºC, pH 14). With about 70 references, the authors cover the state-of-the-art literature.

Dove & Nix (1997) evaluated the effect of IA and IIA cations on the dissolution rate of quartz at 200 ºC. In pure water (pH 7) they found a dissolution rate of 3.4×10^{-8} mol/m^2·s. This rate increases in metal chloride solutions in the order $Mg^{2+} < Ca^{2+} \approx Li^+ \approx Na^+ \approx K^+ < Ba^{2+}$. The authors found a linear relationship between the log of the reaction rate and the log of the water exchange constant for the corresponding cation (Dove & Nix 1997, Dove 1999).

Traber & Mäder (2006) modelled concrete/Opalinus Clay interactions using a reactive transport model. They kinetically constrained the different mineral reactions. For the reaction of the quartz aggregate at high pH they used a pH dependent kinetic law far from quartz equilibrium, identical to the kinetic law given below. Based on the available thermodynamic and kinetic data they calculate mineral sequences very similar to those given in the previous paragraph. In particular, Traber & Mäder (2006) also predict a reduction in the porosity in the clay caused by low-density, neo-formed phases (e.g. zeolites). They calculated more than 10 times lower concrete alteration rates by ASR than in this report (next section), which can be attributed to differences in the parameterization of the rate law.

Timescale

A key question is the time scale on which the above described internal neutralization process occurs. Also of importance is the comparison with "neutralization" reactions caused by formation waters in the case of non-blocked systems.

Palandri & Kharaka (2004) have compiled a rate parameter database for applications in geochemical modelling. For the dissolution of quartz at ambient temperature, they give the (simplified) pH-dependent rate equation:

$$dm/dt \text{ [mol/s]} = (\text{surface area [m}^2]) \times k \text{ [mol/s·m}^2] \times a_{H+}^{-0.5}, \tag{3.21}$$

where k has a value of $10^{-16.29}$ and a_{H+} is the activity of the proton.

We applied this rate equation to our reference concrete (monokorn concrete with a grain size of 2.8 mm, surface area 1330 m^2 per m^3 of concrete) and calculated a quartz dissolution rate of 2.4×10^{-7} [mol/s] per m^3 of concrete (Kosakowski et al. 2011).

For simplicity, if this rate is assumed to be constant, it then takes only about 107 years to react 3 % of the total SiO$_2$ which is sufficient to fully neutralize the free portlandite. After about 205 years the monocarbonate phase is converted to strätlingite (5.7 % of SiO$_2$ reacted), after 363 years the strätlingite disappears and after 466 years (12.9 % of SiO$_2$ reacted) the pH drops to about 10 when zeolites and smectites start forming.

The assumption of a constant reaction rate is not completely unrealistic since only a relatively small part of the SiO$_2$ reacts. In addition, the ASR proceeds at constantly high pH when no specific mechanism is "foreseen" to remove alkali metals from the pore solution. On the basis of current understanding this removal of alkali metals occurs only at a late stage, when zeolites and smectites are formed by taking up dissolved alkali metals. During this zeolite and smectite forming process the pH drops steeply to about 10.

Uncertainties

The above given reaction time is surprisingly short, and leads to the question as to whether the applied rate equation and its parameters really make sense. A consistency check can be made by applying the rate equation to low-pH ESDRED concrete where SiO$_2$ reaction rates have been measured (Lothenbach & Winnefeld 2009). ESDRED concrete includes reactive silica fume with a grain size of only 11 μm, leading to a very high reactive surface. For such a high reactive surface area Eq. 3.20 predicts that only 14 years are required to neutralize the concrete system down to pH of about 10. This is in accord with the preliminary results of Lothenbach & Winnefeld, who report that about 3 years is required for the depletion of most of the reactive silica.

Interestingly, the neutralization reaction proceeds at a constantly high pH when no specific mechanism is "foreseen" to remove alkali metals from the pore solution, i.e. when no alkali silicate hydrates (ASH) are formed. Using our present thermodynamic database without including ASH-phases, the removal of alkali metals occurs only at a late stage in the reaction scheme, i.e. when zeolites and smectites are formed by taking up dissolved alkali metals. Simultaneous to the formation of zeolites and smectites, the pH drops steeply to about 10.

Hence, the predictions from the rate Eq. 3.20 seem to be not too far from reality, and we conclude that the internal neutralization of concrete by reacting SiO_2 may be a reasonably fast process at high pH. However, our estimate does not consider the slowdown of the reaction rate caused by the pH drop induced by alkali removal, nor does it consider the changing surface area as a function of the ongoing quartz dissolution processes. Some authors propose the passivation of quartz surfaces with time, as quartz grains might be covered with reaction products (Soler et al. 2011). However, other authors assume that crystallisation pressure and/or precipitation of e.g. crystalline C-S-H in aggregates cause cracking of aggregates resulting in the creation of new (reactive) quartz surface areas (Bazant 2000, Lindgård et al. 2012). In summary, it is proposed that considering an uncertainty of at least one order of magnitude (towards slower reactions or longer reaction times) would be appropriate.

The long duration of a Stage B situation anticipated in former studies could, in fact, be much shorter, independent of the diffusive equilibration with host rock pore waters or the externally driven water flow through the system, if ASR reactions are considered as outlined above. Hydrated cement phases have distinct sorption properties which disappear when the phases react. However, the product phases of the neutralization processes also have sorption properties, and it is a matter of conjecture and the subject of further investigations to determine the net impact of "neutralization".

3.5   Evolution of the near-field considering heterogeneity on different spatial scales

Overview/general description

To date the system of engineered barriers in the L/ILW emplacement tunnel (Section 3.1.1) has not yet been considered explicitly in PA. The materials inside the tunnel are assumed to be homogenized ("mixing-tank" approach) and the impact of chemical (and biological) reactions on the near-field chemistry, saturation state and radionuclide transport has been evaluated based on mass balance calculations (Section 3.4). Therefore, it has been assumed in PA that the containment such as drums and waste packages do not have any barrier function and that radionuclides can diffuse freely in the near-field. This results in a conservative estimate that all radionuclides are distributed homogeneously in the near-field after closure of the tunnel. This determines the source term of radionuclide release into the host rock.

In this section we describe qualitatively the possible consequences if the barrier functions of containments, along with the heterogeneous material (waste) distributions in the near-field, were to be considered in future assessments.

Following the description of the Engineered Barrier System (Section 3.1), and according to Fig. 3.11, we can identify at least three different spatial scales at which heterogeneities and containments are relevant: waste packages (drums), containers and tunnels (near-field).
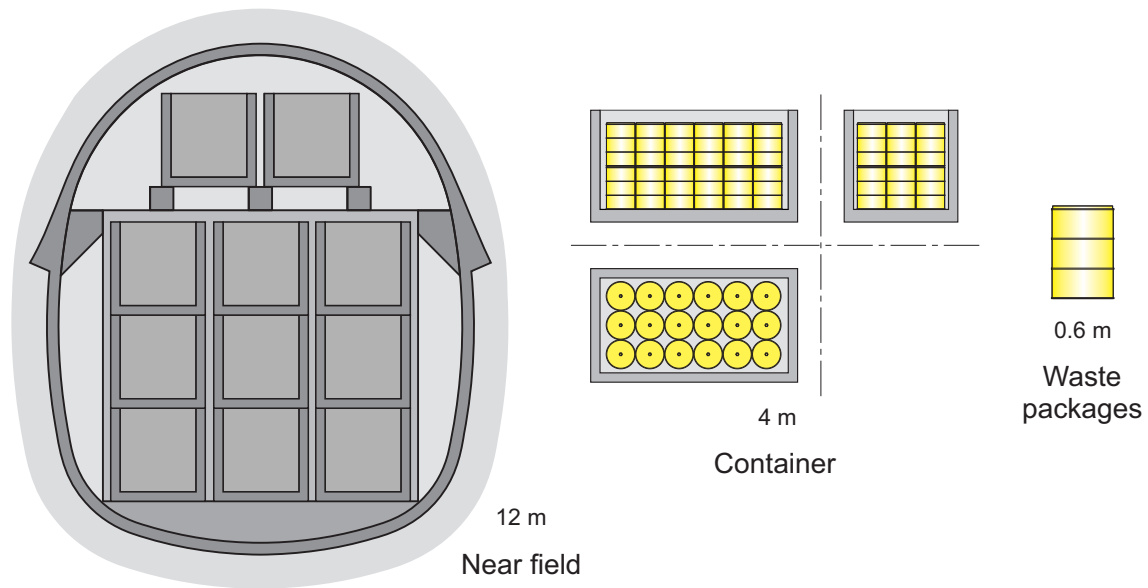
Fig. 3.11:   Elements of different scales which are present in a L/ILW near-field.

Single drum

The volume of a typical package (drum) is about 0.2 m^3. The steel walls are at least 1 mm thick and isolate the content of a drum from the environment. As long as the steel containment is intact, it effectively separates the interior from the environment and the evolution of the interior can be assessed independently. For a homogeneous wall corrosion rate of 1.0×10^{-6} m/a in an alkaline environment (Duffó et al. 2010) it would take at least between 500 years (two sided corrosion) and 1'000 years (corrosion only from one side) to corrode the steel. Note, however, that pitting corrosion might decrease the time of leak tightness considerably.

In terms of (water/gas/solute) transport between these different scales, the walls of the steel drums play a key role. In the case of an "intact" drum, water cannot enter the interior. Directly after loading the drums, the porosity of the concrete stabilizing/solidifying the waste materials is filled with water. This provides a connected water phase allowing the diffusion of water and solutes. In the course of time water is consumed by various (bio)chemical reactions and gas will be produced (Section 3.4). After some time water flow/diffusion is inhibited in the liquid phase since the gas filled pores block pathways and water transport will only be possible via the gas phase (differences in vapour pressure). It can be assumed that gas can escape (and enter) through one or more small openings in the drum walls (mm dimensions or smaller) or by vents. Numerical calculations (Kosakowski & Jakob 2014) show that equilibration of humidity differences between surrounding and interior of drums by diffusion in the gas phase may last between several months (openings of 1 cm diameter and/or high effective diffusion coefficients for humidity) and up to several years (openings of 1 mm and/or low effective diffusion coefficients for humidity). Throughout the following description/considerations we assume that such small openings do not exist and that there is no other significant pathway for water into the drum.

In a drum several interacting and competing (bio)chemical processes will determine the geochemical evolution as long as the interior of the drum is isolated from the environment (Tab. 3.8). We believe that the following processes are relevant: degradation of organic material (Section 3.4.1), corrosion of metals (Sections 3.4.4), concrete degradation (Section 3.4.5) and carbonation of cement (Section 3.4.2).

The above-mentioned processes will result in a very different behaviour of the different waste sorts depending on the contents of the drums of each waste sort, i.e. the amounts of organics, concrete and steel. Typical examples of waste sorts are:

BA-G-HB-F2-SMA – resin bituminised in 200-l-drum (Nagra 2013)

This is a very stable waste sort due to its very low water content and small amounts of readily degradable organics. The steel drum will probably not corrode from inside (due to the lack of water) and waste packages are expected to remain intact over very long periods of time (> 1'000 years for homogeneous corrosion).

BA-B-HP-F2-SMA – resin in polystyrol in 200-l-drum (Nagra 2013)

This will be a stable waste sort with high water content, large amounts of silicates (sand) and small amounts of readily degradable organics. There is sufficient internal water available for complete corrosion of the steel walls. Depending on the speed of the ASR (alkali silica reaction), which consumes part of the available water, the possibility of carbonating the cement paste by the degradation of organics might be limited. The pH in the drums will remain high for relatively long times (until failure of the steel containment, which is > 500 years for homogeneous corrosion).

BA-PH-PF-F2-SMA – Pu-/β/γ-containing wastes cemented in 200-l-drum (Nagra 2013)

This is a rather reactive waste sort with moderate water content due to the large amounts of readily degradable organics (cellulose) and slowly degradable organics (rubber, plastic, PVC). The ASR may consume substantial amounts of water. However, sufficient internal water will be available for iron corrosion and complete carbonation of the cement paste by the degradation of organics. The pH in the drum is expected to decrease quickly and thus strongly enhance the corrosion of drum walls. Hence, the steel containment is expected to remain intact only up to 500 years for homogeneous corrosion.

Tab. 3.8:   Processes controlling the evolution of a drum.

Process	Water balance	Time behaviour	Gas	Result	Limiting factors
Microbial degradation of organic material	Consumes water	Exponential decay function, two groups: slow and fast decay, conservative estimates of degradation rates	Produces CO_2 and CH_4	Carbonation of cement	Availability of water
Corrosion of metals	Consumes water	Slow at constant rate, depends on pH (pH decrease will accelerate corrosion)	Produces H_2	Enhanced corrosion rate will decrease lifetime of steel containment	Availability of water
Concrete degradation (ASR)	Consumes water	Slow at near constant rate (pH dependence), uncertain time behaviour, depends on reactivity of aggregates	--	pH decrease	Availability of water
Carbonation of cement	Frees water	Exponential time behaviour (coupled to availability of CO_2)	Consumes CO_2	pH decrease	Availability of CO_2

Waste packages and emplacement tunnel

A waste package (container) contains up to 36 drums (see Figure 2.5 in Nagra 2008a). The walls of the waste packages are made from high quality concrete with a low permeability and porosity. This provides a barrier that limits water flow and diffusion of dissolved species. The void space between drums will be filled with a highly porous mortar, allowing gas storage, providing an alkaline chemical environment and limiting the corrosion of the steel walls of the drums.

Shotcrete walls stabilize the emplacement tunnels. The emplacement tunnels contain many waste packages (containers). The remaining void space between the waste packages and the host rock is also backfilled with a highly porous mortar. It is assumed that the large amount of cement-based materials will create an alkaline environment.

After backfilling with mortar, some amounts of either free water or water entrapped in cement pastes in packages and in the tunnel can be consumed by the various reactions outlined above. Due to the limited amount of water available in the near-field, the long term availability of water and water transport is governed to a very large degree by water ingress from the host rock, which competes with gas pressure build-up (gas escaping from the drums) in the near-field. Possible scenarios for the latter process were calculated in Nagra (2008a) and in Senger & Ewing (2009). These calculations show that gas pressures will reach maximum values between 1'000 and 10'000 years after closure of the repository. It is expected that high gas pressures result in low water saturation in the whole repository. Water may enter through the seals and

will (partially) saturate the lower parts of the emplacement tunnels within less than 1'000 years (see repository seal model in Senger & Ewing 2009). If a connected water phase is not present (anymore), water can only be transported via the gas phase (differences in vapour pressure). The water content of cement materials in equilibrium with the humidity of the gas phase depends on the pore size distribution. The pore size distribution of the backfill mortar is very different from that of concrete used for making the container walls and the supporting structures. The average pore size is in the millimetre range for the backfill, while micro-pores dominate in the concretes. Therefore, the residual water saturation in the backfill mortar is much smaller than in the concretes for the same vapour pressure. Water transport (in fluid and gas phase) is limited by the permeability of container walls. However, according to Nagra (2008a) some container designs do not have a low-permeability lid. Note that water or water vapour may easily enter through the backfill mortar, if lids are made of cementitious mortar or if low permeable lids or walls have cracks.

From the point of view of chemical reactions the processes listed in Tab. 3.9 are considered to control the evolution of the waste packages and emplacement tunnels.

Tab. 3.9:   Processes controlling the geochemical evolution of waste packages and emplacement tunnels.

Process	Water balance	Time behaviour	Gas	Result	Limiting factors
Corrosion of metals	Consumes water	Slow at constant rate, exact rates depend on pH, partial pressure $H_2(g)$, etc.[11]	Produces H_2	Causes drums to fail after 500 to 1'000 years	Availability of water (gas humidity)
Concrete degradation (ASR)	Consumes water	Slow at near constant rate (pH dependence), exact time behaviour uncertain	-	pH will decrease and accelerate metal corrosion	Availability of water (gas humidity), reactive aggregate
Carbonation	Frees water	Coupled to availability of CO_2 from drums)	Consumes CO_2	pH will decrease and accelerate metal corrosion	Only possible after concrete inside the drums is degraded
Interaction with host rock		Driven by diffusion (square root with time, see Section 3.3.2) or advection (linear with time, see Section 3.3.3)	-	Degradation of concrete, pH will decrease	Connected water phase (diffusion) or water flow (advection), no pore blocking at interface

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[11]   High H_2 partial pressure will destabilize iron bearing cement phases with accompanying changes of cement pore water chemistry. According to Section 2.8.2 of Nagra (2008a) increase of hydrogen partial pressure will slightly decrease iron corrosion rates. Other studies (Kursten et al. 2011 and references therein) report no substantial influence of hydrogen partial pressure on iron corrosion under alkaline conditions.

Time scales/uncertainties

As indicated in Tab. 3.8, concrete degradation, the degradation of organic material and the corrosion of metals occur simultaneously on similar time scales and, in particular, all of these reactions consume water. In addition, the various processes are interrelated. For example, carbonation of concrete is directly linked to the availability of CO_2, which is produced by the degradation of organic matter. Metal corrosion rates depend on pH and therefore fast concrete degradation gives rise to an early pH drop, which accelerates metal corrosion. If the availability of water is limited, the fastest processes dominate and consume the largest portion of the water. Most reaction/degradation rates are only poorly known and therefore "conservative" estimates (fast rates) are commonly used (compare e.g. Sections 3.4.1 and 3.4.5). This might not necessarily lead to "conservative" scenarios for the evolution of the waste sort in a drum. For example, fast internal degradation of concrete via ASR might consume the largest portion of water which in turn stops metal corrosion (from the inside) and therefore prolongs the lifetime of the steel walls of a drum and reduces H_2 production.

An additional aspect that has not yet been discussed so far is the effect of small and micro-scale material heterogeneities near the steel containment of a drum (Féron et al. 2008, Neff et al. 2010). It is conceivable that such heterogeneities change the geochemical environment locally and may cause galvanic or crevice corrosion of the drum walls (Smart et al. 2004, Kursten et al. 2011). Such pitting corrosion may happen very fast and would negate the barrier function of the steel containment. After containment failure, a free exchange of fluids, solutes and gases with the environment can be assumed.

After the failure of a drum due to the corrosion of the wall, two possibilities for radionuclide transport, depending on the availability of water, seem possible:

1. In a de- or partially water-saturated environment there will probably be no connected water phase present, which then prohibits large-scale transport of solutes and radionuclides. Nevertheless, it can be assumed that the diffusion of water vapour in the gas phase will be effective and will provide humidity, which allows chemical reactions in tunnels, packages and drums to proceed after the steel drums have corroded.

2. In a fully water saturated environment there will be sufficient water present, thus allowing chemical reactions to proceed. A connected water phase allows the diffusion of solutes and radionuclides.

A key factor for the release of radionuclides is the time scale needed to produce a connected water phase in the vicinity of a drum. Model calculations indicate that full saturation of the entire tunnel only occurs after a very long period of time (> 10'000 years, Nagra 2008a). This would be enough time, even with conservative estimates, to degrade the concrete by carbonation and ASR reaction (Section 3.4.5) due to water supplied via the gas phase and would result in a low-pH stage of the concrete environment (Stage C in Section 2.4) even before re-saturation of the near-field is completed.

3.6   Cement and clay colloids

This section summarizes the status of knowledge regarding the creation, stability and fate of cement and clay colloids in Section 3.6.1 and 3.6.2, respectively.

3.6.1   Cement colloids

Overview/general description

Cementitious materials are expected to be the main source of colloids in the repository near-field due to the large amount of cement emplaced in the tunnels. The gel-type semi-crystalline hydrates of the mineral assemblage of HCP, in particular C-S-H and calcium aluminates (AFm-type phases), could disperse if the concentration of alkaline and alkaline-earth metal cations at the HCP/water interface is below the critical coagulation concentration (CCC) threshold, or in the case of high water flow. For oxide-type colloids, the CCC is typically around ~ 1 mmol/L in Ca^{2+} solutions and about a factor of 100 larger in Na^+ and K^+ containing solutions. The alkali and Ca concentrations in the near-field are determined by the interaction of infiltrating groundwater with the cementitious materials. Rapid release of alkalis in the early stage of the cement degradation, and portlandite and C-S-H solubilities in the later stages of cement degradation control the pore water conditions. The high ionic strength (range $\sim 0.01 - \sim 0.3$ mol/L) determined by the presence of NaOH and KOH along with the high Ca concentrations (range $\sim 2 \times 10^{-3} - \sim 20 \times 10^{-3}$ mol/L) of cement-type pore water in all of the stages of cement degradation, are favourable for keeping a low colloid inventory in solution since colloid-colloid interaction and colloid attachment to surfaces is favoured. Hence, favourable conditions for those processes limiting colloid dispersion in the cementitious near-field are expected to prevail throughout the various stages of the cement degradation. In general, colloid mass concentrations were determined to be typically below 100 µg/L in leachates from cementitious materials under conditions of quasi-stagnant water flow. Furthermore, these colloids were found to be C-S-H-type solid materials.

Cement-type colloids are subjected to chemical alteration in the pH range $10.5 - 12.5$, which transforms C-S-H phases with high C/S ratios into C-S-H phases with lower C/S ratios. Chemical instability of C-S-H phases is anticipated to occur below pH ~ 10. Therefore, it is conceivable that complete dissolution of C-S-H-type near-field colloids occurs at the interface between the cementitious near-field and the host rock, where hyperalkaline cement-type pore water and pore water with pH < 10 intermix. Consequently, it is anticipated that the transport of cement-type colloids in the fractures of the host rock can only occur if cement-type pore water conditions are retained i.e. pH above ~ 10.

Cement-type colloidal matter is expected to play a minor role in radionuclide migration from the near-field into the far-field, because

1. the concentration of dispersed colloids is very low in the near-field, which limits colloid-facilitated radionuclide transport

2. cement-type colloidal matter is expected to be unstable i.e. to dissolve, at the interface between the near and far-fields, thus releasing radionuclides associated with the colloidal material

Information from experimental/modelling studies

Laboratory-scale experiments indicate that colloids will be present in the saturated cementitious near-field of a L/ILW repository. The colloids have a composition similar to that of C-S-H phases, which are the main component of HCP (Ramsay et al. 1988, Fujita et al. 2003). Calcium silicate hydrate phases are poorly crystalline, gel-like materials with a high surface area and colloidal properties (Wieland 2010a and references therein).

The concentration of cement-type colloids in the pore water of a porous backfill mortar has been reported to be very low, i.e. far below 1 mg/L, with measured values of 0.01 – 0.2 mg/L (Wieland & Spieler 2001). Fujita et al. (2003) determined the colloid concentration in leachates collected from different cement formulations and found that their concentrations ranged between 10^{11} and 10^{12} particles/L. This corresponds to a colloid mass concentration ranging between ~ 0.1 and ~ 1.1 mg/L on the assumption that a large portion of the colloidal matter was C-S-H phases with a mean particle diameter 100 nm. The influence of high ionic strength and high Ca concentrations on colloidal stability has been demonstrated in numerous studies (Wieland 2001 and references therein, Filella 2007). The surface charge of cement particles is low (either slightly negative or positive) or zero over the entire pH range of cementitious systems (10.5 < pH < 13.5) (Wieland 2010a and references therein). This promotes aggregation and surface sorption of cement-type colloidal matter.

C-S-H-type materials undergo incongruent dissolution in the pH range 10.5 – 12.5 due to the transformation of C-S-H phases with high C/S ratios into C-S-H phases with lower C/S ratios (Berner 1988, Harris et al. 2002). Furthermore, C-S-H phases were found to dissolve rapidly below pH < 10 (Schweizer 1999).

The impact of C-S-H-type colloids on radionuclide mobilization in the cementitious near-field of a L/ILW repository was predicted to be negligibly small due to the low concentration of colloids in the cementitious near-field (Wieland et al. 2004). Uptake of radionuclides by C-S-H-type materials is a reversible or partly reversible process, depending on the radionuclide involved (Wieland 2010a and references therein).

Natural analogues

Colloid concentrations ranging between 0.03 mg/L and 0.19 mg/L were determined in the hyperalkaline groundwater at the Maqarin natural analogue site (Wetton et al. 1998). The concentrations varied depending on the sampling site and the method used for estimating the colloidal mass. The pH of the groundwater at the Maqarin site was found to be 12.74 with high concentrations of calcium (16.8×10^{-3} mol/L). The colloid concentrations from field measurements agree very well with values determined in laboratory studies (Wieland 2001), supporting the idea that the low concentration of dispersed colloids in cement-type pore waters is determined by the specific chemical conditions.

Boundary conditions/uncertainties

High ionic strength and Ca concentrations in the millimolar range limit colloidal dispersion. Furthermore, a low inventory of dispersed colloids requires a low flow or stagnant water in the near-field in order to minimize colloid generation. Under (quasi-) stagnant flow conditions the shear forces generated are expected to be too small to allow colloid generation by colloidal disaggregation or the detachment of surface-bound colloids.

While cement-type colloidal material is chemically unstable in contact with groundwater from the host rock, calcium-carbonate-type colloidal matter may be chemically stable in both the near and far-fields. However, their impact on radionuclide migration is expected to be very limited due to the significantly lower sorption capacity of calcium carbonate compared with cement-type colloidal matter.

Time scales

The hydraulic properties of the host rock control the time-dependent evolution of the cementitious near-field. The temporal composition of the cement-type pore water in the near-field, in particular with respect to pH, ionic strength and Ca concentration, is controlled by mineral reactions occurring in the course of the different stages of cement degradation. The latter parameters eventually control the inventory of dispersed colloids in a cementitious near-field with a quasi-stagnant flow regime.

3.6.2   Other (clay) colloids

Colloid properties around the cement – host rock formation

Colloids are present in all kind of water, even in quasi-stagnant water where they are found at rather low concentrations (Degueldre et al. 2009). Their concentrations however may be enhanced by chemical and/or physical gradients (Degueldre 1997, McCarthy & Degueldre 1993, Ryan & Elimelech 1996). This section summarizes the information in the literature and applies the concept of colloid generation to a pH plume and the associated chemical plume around the cement – host rock formation interface.

Literature review

Experiments in model systems have been performed to test the theories of colloid mobilization. First, for colloid mobilization by chemical perturbations the effects of changing pH, ionic strength, and water component concentration are summarized. For colloid mobilization by physical perturbations, the effect of increasing water velocity and flow has been investigated earlier (McCarthy & Degueldre 1993, Degueldre 1997).

• Colloid mobilization by chemical perturbations

  Colloid mobilization is usually described by two competing processes: (1) attachment of colloids to "collector" grains under mutual attraction conditions; and (2) release of colloids from the grains through changes in pH, ionic strength, or the concentration of some aqueous species that alters the surface charge of the colloids or grains of the host rock. In the first case, experiments were performed in model systems of well-characterized colloids and grains. In the second, a series of tests attempted to release colloids from natural sediments by flushing with solutions with varying the chemistries.

• Colloid mobilization by increasing pH in model systems

  Kallay et al. (1987) summarized the experiments of Matijević and colleagues which explored the effects of solution chemistry changes on colloid release from surfaces. Using packed column techniques, Clayfield & Lumb (1966) attempted to relate the rate of colloid release from porous media surfaces to the potential energy change between the colloids and grains. Studying the particle adhesion and removal in a model system, Kolakowski & Matijević (1979) measured the release rate of chromium hydroxide ($Cr(OH)_3$) colloids from glass beads. The chromium hydroxide colloids were attached to the glass beads at low pH values for which oppositely charged colloid and bead surfaces were produced. The rate of colloid release increased as the pH of the solution was increased from 9.6 to 11.5. However, at pH 12.6, the release rate declined to an intermediate value. This decrease in colloid release rate observed at very high pH (> 12) was also observed, and is likely to be caused by an increase in ionic strength from the addition of NaOH. The solutions used in these experiments were not buffered against changes in ionic strength. In all of these experiments,

increases in pH cause increases in the release rate and in the total amount of particles released. The increase in the extent of particle release was attributed to a decrease in the retention of particles by surface heterogeneities on the collectors.

Recognition of these surface heterogeneities led Matijević and colleagues to adopt two-population and continuous distribution models of attached colloids (Kallay & Matijevic 1981, Thompson et al. 1984). In the two-population model, one population of colloids was released from the surface quickly after the high pH solution was added, and the other population was considered to be permanently bound following lateral translation to sites of lower energy.

- Colloid mobilization by increasing pH in natural sediments

Studies of the effect of pH on colloid mobilization from natural sediments in laboratory columns have produced consistent results in that an increase in pH causes an increase in colloid mobilization (Vaidya & Fogler 1990). A dramatic increase in the clay colloid release rate was observed when the pH of a solution passing through an iron oxide-coated sand exceeded a pH of about 8 (Ryan & Gschwend 1994). At normal pH the surface charge of goethite is positive which cements the kaolinite colloids to the quartz grains. At higher pH-values, the surface charge of the goethite was reversed, resulting in repulsive conditions and rapid colloid release.

The mobilization of natural colloids from an iron oxide-coated sand aquifer was studied by (Bunn et al. 2002), focusing on the effect of pH and ionic strength. The field experiments were conducted by injecting sodium hydroxide into the natural gradient of the ground water. The laboratory experiments were conducted in columns of undisturbed, oriented sediments and in columns of disturbed, randomly orientated sediments. In the field, the breakthrough of the released colloids coincided with the pH pulse and lagged the bromide tracer breakthroughs. Here again, the breakthrough behaviour suggested that the progress of the elevated pH front controlled the transport of the mobilized colloids. The experiments showed that the total mass of colloid release increased with increasing pH until the associated increase in ionic strength limited the release. A decrease in ionic strength did not mobilize significant amounts of colloids in the field.

- Colloid mobilization by decreasing ionic strength in model systems (chemical variations)

As reviewed and investigated by Kallay et al. (1987), changes of ionic strength may induce colloid mobilization. According to colloid release theory, a decrease in ionic strength causes an increase in the repulsive interactions between colloids and grains and thus promotes colloid detachment. Most experimental results obtained by Matijević and colleagues demonstrate that this is qualitatively correct (Kallay & Matijevic 1981).

However, Kallay et al. (Kallay et al. 1986), observed that more hematite colloids were released from glass beads at 10^{-2} mol/L sodium nitrate than at 10^{-3} mol/L. Ryan & Gschwend (1994) investigated the effect of ionic strength in a similar system containing hematite colloids and quartz sand grains. In this system, decreases in ionic strength pro-moted increases in the extent and release rate of colloids. The conditions promoting release, pH 11 and 0.1 to 0.001 mol/L sodium nitrate are reasonable, because both the hematite and quartz surfaces carry highly negative charges.

A similar examination of the $Cr(OH)_3$ – glass system by Kolakowski & Matijević (1979) showed a similar trend, with slight differences attributed to the greater size and slower diffusion of the $Cr(OH)_3$ colloids. The increase in the extent of colloid release with decreasing ionic strength may have been caused by double layer repulsion between adjacent colloids, as Johnson & Elimelech (1995) and Liu et al. (1995) found in studies on the effect of ionic strength on blocking and colloid deposition dynamics. As the ionic strength

decreases, colloids, which were attached to small, favorable regions of the surface grains under high ionic strength conditions, begin to push each other off the surface because of the lateral repulsion due to the expansion of double layers.

- Colloid mobilization by decreasing ionic strength in natural sediments

Studies of colloid mobilization in the clay-containing Berea Sandstone were quite sensitive to changes in ionic strength (Vaidya & Fogler 1990). In contrast, changes in ionic strength of over four orders of magnitude (from 0.5 to 5×10^{-4} mol/L) produced only a slight increase in the colloid release rate from an iron oxide-coated sand (Benedetti & Boulëgue 1991). This result suggests that the change in ionic strength did not affect the ability of the positively charged goethite to bind the negatively charged clay colloids. Changes in solution chemistry which reversed the surface charge of the goethite were required to initiate colloid release.

- Colloids near the concrete – host rock interface

The colloid occurrence, stability and mobility in the water of the considered potential host rocks have been evaluated, and colloids were found to be of minor relevance. The potential host rocks (Opalinus Clay, Effingen Member, 'Brown Dogger' and Helvetic Marls) have been identified for a L/ILW repository. In contrast to the homogeneous Opalinus Clay litho-facial units where hydraulic flow may govern fluid transport cannot be totally excluded in the other potential host. However, due to the high salinity in all of these potential host rock waters, the colloid concentration is expected to be very low ($< 10^5$ /mL for 100 nm sized particles or [col] < 1 µg/L) because of the very large attachment factor of the colloids in these saline ground waters. These properties restrict the potential transport of radionuclides by colloids in quasi-stagnant conditions (see Tab. 3.10).

The study of the pore water in the Opalinus Clay formation was performed in a comprehensive way using a paleo-hydrochemical approach to identify the relevant parameters determining the water and the colloids (Degueldre et al. 2003).

Tab. 3.10:   Colloid main parameters and concentrations in host rock waters of Opalinus Clay, Effingen Member (ranges associated with salinity variations), 'Brown Dogger' Helvetic Marls.

Conditions: aquifer in quasi stagnant conditions, *I* ionic strength, *a* attachment factor, *N* colloid number concentration, [col] colloid concentration, * for colloid size of 10 – 100 nm; Data from (Degueldre 2010).

Water	Effingen Member	'Brown Dogger'	Helvetic Marls	Opalinus Clay
Type	Na-Cl	Na-Cl	Na-Cl	Na-Cl
Na [mol/L]	$3.7 – 7.3 \times 10^{-1}$	1.6×10^{-1}	2.0×10^{-1}	1.6×10^{-1}
Cl [mol/L]	$5.7 – 11 \times 10^{-1}$	1.6×10^{-1}	2.0×10^{-1}	1.6×10^{-1}
pH [-]	$7.3 – 6.8$	7.2	7.5	7.2
α [–]	$10^{-1} – 10^{0}$	10^{-1}	10^{-1}	10^{-1}
$N_{(100nm)}$ [1/ml nm]	$10^{4} – 10^{3}$	$10^{5} – 10^{4}$	$10^{4} – 10^{5}$	$10^{4} – 10^{5}$
$N_{(>100nm)}$ [1/ml]	10^{5}	5×10^{5}	5×10^{5}	5×10^{5}
[col]* [ppb]	0.1	0.5	0.5	0.5

The precipitation of calcite at the interface is obvious in the case of pure diffusion (Opalinus Clay).

In the case of a fractured host rock (Effingen Member, 'Brown Dogger' and Helvetic Marls), the advection and mixing of Ca^{2+} or CO_3^{2-}/HCO_3^- rich waters through the interface boundary might allow the formation of extended plumes of these ions and resulting in only a partial clogging of the water bearing features. Calcite (limestone) is known to attach very strongly to the surfaces of sedimentary rocks, and the generation of colloidal calcite is likely to be an artefact. However, colloid mobilization may occur with increasing pH (as reported above for the cases in the literature survey). In addition to the pH increase, changes in the composition and ionic strength may have a colloid generating effect. However, little effect should be expected due to changes in the ion composition because the ionic strength of the groundwater remains similar along the pH plume.

It should, however, be noted that if any clay colloid material is released by a pH change, the effect is restricted due to a calcite coating. Finally, the movement of water into narrower water bearing features may induce a physical transient (water velocity), which would promote colloid erosion. However, the flow rate variation, which is the determining factor, is not expected to be large enough to contribute significantly to colloid generation.

Even if colloids (clays, silicates, hydroxide polymers) are generated in a pH plume, it is expected that once they reach the groundwater system of the sedimentary formation, where their attachment factor ranges from 10^{-1} to 1 (for clay), they would coagulate or attach themselves to the host rock, thus limiting their migration.

Uncertainties

The time evolution of the system presents major uncertainties in the process of colloid formation and transport, and requires additional work. For a complete assessment of the system a study on the formation of fission product and actinide compounds that can be generated in colloidal or polymeric form or associated with organic colloids (Santschi et al. 2002), in the vicinity of the cement sedimentary rock interface is required.

Other parameters need to be investigated. For example, Shang et al. (2008) calculated forces exerted on colloids and found that electrostatic and van der Waals interactions and hydrodynamic forces were all less important than capillary forces in controlling colloid release. In one experiment, the ionic strength of the infiltration solution was increased so that colloid attachment was favourable but nevertheless colloids were mobilized and eluated with the infiltration front, implying that non-DLVO[12] forces, such as capillary forces, played a prominent role in colloid mobilization.

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[12]   DLVO forces: named after Derjaguin, Landau, Verwey and Overbeek. A theory that describes the force between charged surfaces interacting through a liquid medium considering van der Waals forces and electrostatic repulsion due to double layer formed by counter ions.

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Appendix A

A1 Host rock and engineered barrier system materials

Our state-of-the-art geochemical model uses a single, unified thermodynamic setup for the consistent reactive modelling of mineral transformations and porosity evolution. A key feature of this geochemical setup is the fact that it simultaneously includes concretes, host rocks and tunnel backfill materials (Berner 2009, Kosakowski & Berner 2011a, 2013, Berner et al. 2013). We summarize the important features of the model for the different materials in this section.

The model includes the pore water compositions (if available, e.g. for host rocks (Mäder 2009a, 2009b, 2009c), the porosity and the mineralogical composition of bentonite, bentonite/sand, concrete, Opalinus Clay/'Brown Dogger', Effingen Member and Helvetic Marls. All materials are modelled with one consistent thermodynamic setup where the pore waters are determined by mineral equilibria.

Sand/bentonite

A sand/bentonite mixture may be used as backfill material in the access tunnels. The setup essentially utilizes the bentonite model. The mineralogical setup is based on a 20/80 wt.-% mixture of dry bentonite/sand. More detailed results for the interaction between sand/bentonite and other tunnel backfill materials are given in Kosakowski & Smith (2014).

For the setup, we take 1'173.18 g of pre-saturated bentonite from Table 5.5 of Berner (2011), which corresponds to 1'000.6 g of dry bentonite. We mix the bentonite with 4'000 g of quartz. After adding 610 g of Opalinus Clay pore water we get a (total) volumetric water content of 0.3 for the mixture. The actual available porosity for transport (volumetric amount of free water) is then ~ 0.23 since some of the water is bound as interlayer and surface water to the montmorillonite phase (Berner 2011).

The definition of montmorillonite, the main constituent of bentonite, includes cation exchange processes and amphoteric $\equiv SOH$ sites as described in Bradbury & Baeyens (2002). In common reactive transport codes based on the Law of Mass Action (LMA) approach for solving geochemical equilibria, cation exchange processes are usually accounted for assuming that the clay mineral is represented by a X-"ligand" initially occupied with Na^+. We implemented a more chemically plausible solid solution model of ion exchange in clay.

A detailed description of the montmorillonite, its setup and calibration is given in Berner (2011). The structural formula is taken from Tournassat (2004):

$$(Si_{3.98}Al_{0.02})(Al_{1.55}Fe^{3+}_{0.09}Fe^{2+}_{0.08}Mg_{0.28})O_{10}(OH)_2 \cdot 4.84\ H_2O$$
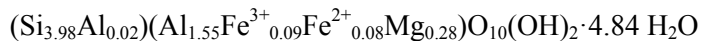
where the remaining charge of 0.38 per (above) formula unit is compensated by the sum of potentially exchanging cations

$$\Sigma(cations) = X_1 \cdot Na + X_2 \cdot 2 \cdot Ba + X_3 \cdot 2 \cdot Ca + X_4 \cdot 2 \cdot Fe + X_5 \cdot K + X_6 \cdot 2 \cdot Mg + X_7 \cdot 2 \cdot Sr \quad (A1.1)$$

and $X_{1,2...7}$ denote the cation occupancy (equivalent fractions) of the clay (Berner 2011). The amount of 4.84 chemically bound H_2O corresponds to a water content of 18.95 wt.-%. This water is equivalent to two layers of water in the clay interlayer; therefore the structural formula represents bi-hydrated clay.

The cation exchange capacity (CEC) of this montmorillonite is 1'018.7 meq/kg for "dry" montmorillonite and 825.7 meq/kg for the bi-hydrated montmorillonite.

Opalinus Clay/'Brown Dogger'

The aim of the host rock models was to simultaneously reproduce pore water compositions, mineralogical compositions, total water content, anion accessible porosity and CEC. Our main assumption is that we can describe all cation exchange phases by the montmorillonite solid solution model we developed for the MX-80 bentonite. In the present version of the model the montmorillonite phase is the only cation exchanging phase (it replaces the X-"ligand" mentioned above).

In addition we inserted an illite phase $(K_{0.6}Mg_{0.25}Al_{2.3}S_{i3.5}O_{10}(OH)_2$. Its composition and the thermodynamic data were taken from Wolery & Jove-Colon (2004). Mäder (2009c) discusses a discrepancy between calculated and measured K^+ concentrations in the Opalinus Clay pore water. We also found this discrepancy and decided to adjust the stability of the illite phase (by adding +3'500 J/mol) instead of changing the exchange constants of the montmorillonite phase.

The setup includes a Ca, Na, K - phillipsite solid solution as an indicator for the occurrence of zeolite minerals. Relative stabilities for the individual phillipsite end-members were taken from the THERMODDEM DB (Blanc et al. 2012). Absolute stabilities of the phillipsite end-member were adjusted to meet experimental observations, namely that zeolite phases are absent in Opalinus Clay in bentonite systems, but may potentially be stabilized at slightly elevated pH (Traber & Mäder 2006).

Effingen Member

We reproduced the "low salinity reference pore water" defined in Mäder (2009a). As in the case of Opalinus Clay discussed above, the montmorillonite phase should represent all the cation exchange capacity present in the Effingen Member. Therefore, its amount does not fully match the amounts of smectite and illite/smectite mixed layer present in the Effingen Menber. To compensate the difference, we set the illite content in such a way that the sum of montmorillonite and illite corresponds to the sum of illite, illite/smectite mixed layer, smectite and chlorite.

We noticed two differences to the setup of Mäder (2009a):

- Mäder (2009a) defined the pore water without a phase for cation exchange. In order to be consistent with the other clay containing materials, we assumed that the cation exchange capacity (CEC) is roughly equal to the value given in Nagra (2010), which can be interpreted as a rough measure for CEC. As for the Opalinus Clay setup, we again associated all cation exchange phases with the montmorillonite solid solution.

- With this setup for cation exchange we are not able to exactly reproduce the total concentration of K in solution. Our concentrations are lower by a factor of about two. As discussed for the Opalinus Clay setup, concentrations of K are influenced by the exchange constants implemented in the montmorillonite model and the stability of the illite phase. However in order to have a consistent setup for all clay-containing materials we decided to use the same thermodynamic setup as for the Opalinus Clay and for the moment we accepted the difference in K^+ concentrations.

Helvetic Marls

In this setup we reproduce the Na-Cl reference pore water from Mäder (2009b). This pore water is based on the cation exchanger system (X-"ligand"), which Mäder (2009b) took from Baeyens & Bradbury (1994). Again, the montmorillonite solid solution represents all the cation exchange capacity that is present in the Helvetic Marls and its amount does therefore not perfectly match the amount of illite and/or illite/smectite mixed layer in the Helvetic Marls. Regarding exchange constants for K and the related solubility of illite, the same setup as for the Opalinus Clay was used.

Mäder (2009b) used PHREEQC to define the Helvetic Marls reference waters; the present work uses the GEMS/PSI code to calculate thermodynamic equilibria.

In principle, both works describe the same geochemical system. However, due to operational differences the actual numbers of the calculated equilibrium concentrations, especially for Mg and C, differ slightly as indicated in the fact sheet of the pore water composition below.

The main reasons for these differences are as follows:

- Mäder (2009b) used the solid phase assembly calcite, siderite, pyrite and quartz. The GEMS/PSI calculation considers in addition dolomite, illite, kaolinite, montmorillonite and barite. These additional solid phases are responsible for differences in K and Mg.

- Mäder (2009b) fixes the pCO_2 and, consequently, fixes the pH via the calcite equilibrium and the ionic strength. GEMS/PSI cannot "set" a pCO_2. pCO_2 and pH are the results of the calculation and have to be "set" by adding corresponding amounts of acid (i.e. HCl) or base (i.e. Na_2CO_3) to the chemical system.

- Mäder (2009b) uses a substantial excess of ion exchange sites to establish the system ion exchange properties. GEMS/PSI uses the previously mentioned montmorillonite solid solution model consisting of several montmorillonite end-members to establish the system ion exchange properties.

The chemical setup discussed above was specifically calibrated for the Opalinus Clay system and may be used for the other host rocks with moderate changes. Moderate, but less significant differences between the prescribed reference systems and our model calculations are only present in the setup for the Helvetic Marls. It is possible to adapt the chemical/thermodynamic setup for better matching the Helvetic Marls system, but this would be at the cost of the presently well-balanced representation of the Opalinus Clay system. Work to improve the geo-chemical setup is in progress.

Concrete materials

The mineral composition and the pore water chemistry of a CEM I 52.5 N HTS hydrated cement described by Lothenbach and Wieland (2006) is used as a starting point for the concrete compartment. The setup is based on the most recent CEMDATA07 thermodynamic database, which includes several ideal solid solutions for hydrated cement minerals consistent with the Nagra/PSI thermodynamic databases 01/01 and 12/07. The concrete setup is described in detail in Berner (2009).

A2 Reactive transport simulations

Sections 3.3.2 to 3.3.4 utilize information from reactive transport calculations. The calculations are described in detail in Kosakowski & Berner (2011a, 2011c, 2011d) and the thermodynamic and transport setups, as well as selected results are published in Berner et al. (2013) and Kosakowski & Berner (2011b). In this appendix we give only the most important features of the reactive transport setup (Section 5.2), and summarize the results (Section 5.3).

The reactive transport of chemical components is simulated with the multi-component reactive transport code OpenGeoSys-GEM. This code employs a sequential non-iterative approach to couple the mass transport code OpenGeoSys (http://www.opengeosys.org) with the Gibbs Energy Minimization (GEM) code GEMS3K (http://gems.web.psi.ch/) for the thermodynamic modelling of geochemical systems. For each time step, the advection-dispersion equation is first solved for all dissolved species, and the changed composition of the phase assemblage is passed to the chemical solver, which calculates the new local equilibrium at each grid node. The concentrations of dissolved chemical species are then taken as the result for this time step and used as the initial condition for the next transport step. Details regarding code development and verification can be found in Shao et al. (Shao et al. 2009a, 2009b), Hayek et al. (2011, 2012) and Kosakowski & Watanabe (2014).

A common model for reactive diffusive transport in clay containing media is not yet established. Experimental results from tracer diffusion tests in clay media give indications that anions and cations are constrained in different parts of the pore space (González Sánchez et al. 2008, Glaus et al. 2011). Typically, about half of the pore space seems accessible to anions in clay rocks like Opalinus Clay, whereas in bentonite systems the anion accessible porosity might become much lower.

Commonly up to three different water compartments in the pore space can be discriminated: free (outer) pore water, surface water and (for swelling clays) also interlayer water (Gimmi & Kosakowski 2011).

For swelling clay minerals like smectites the clay interlayer contains the cations that compensate the negative charges of the clay surfaces and up to several layers of water molecules. The interlayer hydration is a function of interlayer cation population, temperature, pressure and (outer) water chemistry (Norrish 1954, Slade et al. 1991). Very often it is assumed that negatively charged ions are strongly hindered from entering the interlayer space (Rotenberg et al. 2007, Kosakowski et al. 2008), although other authors come to different conclusions (Karnland et al. 2007).

The outer surfaces of clay minerals are commonly negatively charged which changes the water structure and dynamics near such surfaces (Rotenberg et al. 2010). The partitioning of dissolved species between free pore space and a diffuse double layer near surfaces was considered by Appelo et al. (2010) to explain the diffusion of several tracers in Opalinus Clay.

The model we used for assessing the effects of diffusive transport in clay media assumes that the interlayer hydration of montmorillonite is constant and the water is incorporated into the mineral structure as chemically bound water. In the host rock models this chemically bound interlayer water contributes to about half of the (volumetric) overall water content.

The montmorillonite system setup additionally includes a surface complexation model (Berner et al. 2013) which differs from that model of Appelo et al. (2010). Nevertheless, as indicated in Berner et al. (2013), small amounts of water and parts of Na^+ and Cl^- are removed from the free water phase and remain associated to a separate surface complexation phase.

The remaining system water is associated with a (free) fluid phase which is in thermodynamic equilibrium with the minerals. The host rock models were set up such that the volume fraction of this fluid phase matches the measured anion accessible porosity (Nagra 2002b, 2010). Consequently, hydraulic and transport porosity are also associated with the volume fraction of this fluid phase.

Transport of solutes is calculated in the free fluid phase for all dissolved species. Diffusion in the interlayer and along outer surfaces is not considered, as effects like so-called "surface diffusion" are mainly relevant for solutes at trace concentrations (Gimmi & Kosakowski 2011).

A2.1   Conceptual setup

Figs. A2.1 and A2.2 provide the model setup and dimensions for the cases with diffusive and advective transport. In order to minimize the code execution time, the 2D geometry of the near-field was simplified into an axisymmetric 1D model. In an interval of ±0.5 m around all interfaces, the distance between the finite element nodes was held constant at 0.01 m. This constant equidistant mesh makes it possible to compare the system evolution for the different cases near the interfaces. Towards the boundaries, the node distance was gradually enlarged in order to minimize the number of calculation nodes. As the calculations are very time-consuming, and since the CPU time needed is linearly related to the number of nodes, a minimization of node numbers is an effective way to reduce calculation times.
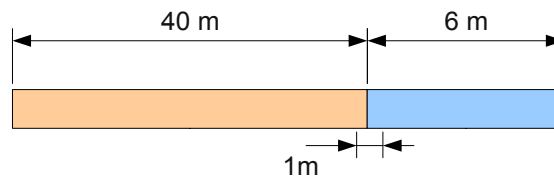

Fig. A2.1:   Dimensions of the one-dimensional conceptual models for diffusive transport.

The cement compartment is coloured in blue (right) and the orange compartment is clay material (left).
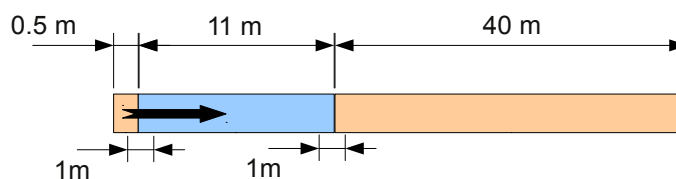

Fig. A2.2:   Dimensions of the one-dimensional conceptual models for advective transport.

The cement compartment is coloured in blue (middle) and the orange compartments are clay material (host rocks). The arrow indicates the direction of water flow.

All calculations were carried out at standard T-P conditions (25 ºC, 1 bar). The groundwater flow equation was solved at the beginning of the simulation.

For the diffusive cases, hydraulic heads were set to a value of 10 m (1 bar) at the (left) host rock boundary. The right boundary (concrete) was assumed to be impermeable, which causes the fluid velocities (and advective transport) to be zero. Initial pore water concentrations for

dissolved species were set to be in thermodynamic equilibrium with the solid phases. Concentrations at the left (host rock) boundary were held constant and the right boundary was assumed to be impermeable. The corresponding systems for all materials are given in Kosakowski & Berner (2011a).

For cases that simulate advective transport, a constant Darcy flux was set at the inflow boundary and solute concentrations were set according to pore water definitions. A fixed head boundary condition was set at the outflow boundary, which allowed free outflow of fluid.

A2.2 Material properties

Porosities

Porosities of unaltered materials were defined in accordance with Nagra (2010). Material and host rock setups are summarized in Section 5.1 and more details are given elsewhere (Berner et al. 2013, Kosakowski & Berner 2013).

Hydraulic conductivities

For the diffusion-dominated calculations, material parameters such as hydraulic conductivities and dispersion lengths were not needed. We set hydraulic heads to constant values in the whole domain, which resulted in zero fluid velocities for models that simulate diffusive transport only.

The advective cases did not utilize a full coupling between porosity changes and mass transport since the porosity was not updated according to the mineralogical changes. The idea was to force a constant flow of water into the system, independent of possible clogging processes. In one dimensional geometry, clogging will always stop the water flow in the system in the case of full coupling between hydraulics, transport and chemistry. Two or three-dimensional models would avoid this, but would still need the additional input as to how porosity and hydraulic conductivity are related.

Diffusion coefficients

A species-independent effective diffusion coefficient D_e [m^2/s] for all aqueous species is used for calculating the diffusive transport within OpenGeoSys-GEM. It is calculated using Archie's relation from the porosity n [-] and the free water diffusion coefficient D_w [m^2/s]

$$D_e = D_w n^m \qquad (A2.1)$$

Here m is an exponent which can vary for different kinds of porous media (rock types) from 1.3 (unconsolidated sediments, e.g. sand) up to 2 in well cemented (clay-free) sediments and between 1.5 and 2.5 in cement pastes and mortars (Tumidajski et al. 1996). However, for clay rocks Van Loon (personal communication) estimated a mean value of m = 2.5 and used the following modified relation:

$$D_e = 2.10^{-9} n^m + 2.10^{-11} n^{0.85} . \qquad (A2.2)$$

The diffusion coefficient in free water for electrolyte solutions varies between 1.1×10^{-9} m^2/s and 2.1×10^{-9} m^2/s (see Table 6.2-2 from Flury & Gimmi 2002).

For our simulations we choose Eq. 3.21 with the following parameters as "average" values for all the different materials: m = 2.0, $D_w = 1.5 \times 10^{-9}$ m^2/s, (value for 0.1 mol/L – 1.0 mol/L NaCl, Tab. 6.2-2 from Flury & Gimmi 2002).

The values for D_e from Eq. A2.1 are within the lower and upper limits given in (Nagra 2010) for materials that contain clays (host rocks, sand/bentonite mixture) and compare well with the harmonic mean of the anionic and cationic effective diffusion coefficients.

For some materials such as sand or highly porous mortars, the diffusion coefficients are too low by factors of 2 – 5. This discrepancy cannot be avoided, as we use only a single porosity – diffusivity relationship to describe all the different materials in our setup. Porosity – diffusivity relationships are empirical laws that need to be measured for each specific material. In addition, in the course of the simulations, material compositions and porosities near the interfaces may change completely. For the altered material compositions, the dependence of D_e on porosity is not known *a priori*.

A3   Summary of results of reactive transport calculations

Kosakowski & Berner (2011c) and Kosakowski & Berner (2011d) described in detail the numerical calculations on the geochemical evolution of host rock – concrete interfaces. Here we give a summary of the results. Concrete – clay interactions for sand-bentonite tunnel backfill and for three possible host rock types investigated: Opalinus Clay (includes 'Brown Dogger'), Effingen Member and Helvetic Marls.

For each clay – concrete interface three cases were calculated:

1. diffusive transport with full feedback of porosity changes on transport

2. diffusive transport without feedback of precipitation/dissolution of mineral phases on porosity and transport parameters

3. advective transport of the corresponding host rock pore water first through the concrete compartment and then advective transport of altered water through the host rock

Diffusive cases 1 (with porosity feedback on transport)

- The spatial discretization strongly influences the calculated clogging time (rule of thumb: a factor of 10 in discretization is a factor of 100 in clogging time), so that finer discretization produces faster clogging, whereas coarser discretization delays clogging.

- The system evolution slows down considerably or even stops when the porosity falls below 0.001.

- Diffusion across the clogged interface is minimal and the altered zones can equilibrate with the adjacent chemical system (host rock, concrete, bentonite) on the corresponding side of the interface.

  - the progress of dissolution/precipitation fronts stops

  - the advance of the pH – plume stops

Diffusive cases 2 (without porosity feedback)

- The basic assumption is that transport properties (effective diffusion coefficients) do not change with time. As the effective diffusion coefficient is calculated from the porosity via Archie's relation, the porosity (in the transport equation) is set to a constant value, although the volume fraction of the fluid phase in the full system might change.

- The mineral volume is allowed to exceed the reference volume. This indicates zones of strong porosity reduction.

- The absolute amount of water does not change; solid/water ratio may change since the amount of solids is variable.

- The progress of dissolution/precipitation fronts is proportional to $\sqrt{D_a t}$, where D_a is an apparent diffusion coefficient.

- D_a can be used for a rough estimation of maximum progress of dissolution/precipitation fronts and the extent of pH plume.

Advective cases 3 (without porosity coupling)

- The porosity coupling is switched off, because with porosity coupling the 1D models would either become numerically unstable (flow boundary conditions) or flow would stop in the case of clogging (pressure boundary condition; see also influence of diffusive models with porosity feedback on mass transport across interface).

- Dissolution/precipitation/pH fronts progress linearly with the water flow. For constant flow conditions, the fronts move linearly with time. This allows a rough estimate to be made for the progress of dissolution/precipitation/pH fronts.

- Mineralogical changes in the host rock compartment on the inflow side are a numerical/ conceptual artefact of the simulation, as this is caused by hydrodynamic dispersion (enhanced diffusion) against the direction of flow.

- In case of superposition of advective and diffusive changes at an interface, clogging at the inflow interface is possible (not a conceptual/numerical artefact).

- For the case where the inflow interface clogs (diffusive – advective transport), the flow across the interface is reduced. The flow field in the host rock will change in such a way that water flow is around the tunnel, which implies that the degradation of cement due to advective water flow is slowed down.

- Clogging at the outflow interface may lead to cases which are more complicated. One can expect a redirection of flow towards the backfilled access tunnels. It is unclear for this case whether the degradation of cement is faster or slower.

- The models that investigate the dimensionality effects (2D models of cement/host rock interfaces) are currently under development (Hoch et al. 2009). They show clogging at the tunnel interfaces.

Equilibrium chemistry vs. kinetic control of mineral precipitation/dissolution

For all three cases we use equilibrium chemistry, as in the long term the slow transport (diffusion) of solutes is the main control of reaction rates. Introduction of kinetic control of precipitation/dissolution reactions may change the mineral assembly and the extent of the alteration zones, but the work of Traber & Mäder (2006) shows that the differences are small. Introduction of kinetic control will change clogging times towards longer times (Marty et al. 2009).

The introduction of kinetic introduces uncertainties. Many parameters in the kinetic laws, such as reaction constants and reactive surface areas, are not well known. The introduction of kinetics has no significant influence on the advance of mineral reaction fronts (commonly associated with the pH plume) into the host rock, because the mineral reactions are mainly transport controlled under the investigated diffusive transport regimes. The advancement of a zone with slightly elevated pH (8-9) in the host rock is not associated with major mineralogical changes is mainly controlled by cation exchange and surface complexation (compare Kosakowski & Smith 2014).

Comparison of the different scenarios

Tab. A3.1: Comparison of diffusive scenarios 1 with porosity feedback on transport after clogging.

Materials	Sand-bentonite	Concrete	Opalinus Clay	Concrete	Effingen Member	Concrete	Helvetic marls	Concrete
Scenario	diffusive transport (10'000 years, min. Porosity: 0.0025)		Diffusive transport (2'428 years, min. Porosity: 0.0020)		Diffusive transport (2'147 years, min. Porosity 0.0012)		Diffusive transport (3'833 years, min. Porosity 0.00064)	
Alteration extension	0.20 m montmorillonite dissolution	0.15 m portlandite dissolution	0.01 montmorillonite dissolution	0.02 portlandite dissolution	<0.01 montmorillonite dissolution	<0.01 portlandite dissolution	<0.01 montmorillonite dissolution	<0.01 portlandite dissolution
pH plume at the end of simulation (after clogging)	2 m continuous increase from pH 8 to pH 10.5 extended zone with pH ~7.8 in sand/bentonite	12.7 pH constant	<0.01 m no increase in host rock	12.9 pH constant	<0.01 m pH 7.3 - 7.45 in host rock	<0.01 m pH 13.02 in concrete	0.02-0.3 m 8 <pH <8.6 0.01 m pH 9.9	0 - 0.3 m pH 12.8 >0.3 m pH >12.9
Mineralogy (precipitates only)	Na-, (K-,Ca-) phillipsite, illite, calcite, hydrotalcite, hydro-magnetite	C-S-H, ettringite	Na- (Ca-, K-) phillipsite, illite, calcite, hydro-magnetite	Ettringite, C-S-H, calcite	Na-, K- phillipsite, illite, calcite, hydrotalcite	C-S-H, ettringite, calcite, hydro-magnetite	Na-, K- phillipsite, calcite, hydrotalcite, hydro-magnetite	C-S-H, ettringite, calcite
Porosity decrease	Strong tendency to clog. 0.01 after 1720 years, 0.005 after 4793 years		Strong tendency to clog. 0.01 after 244 years, 0.005 after 890 years 0.002 after 2428 years		Strong tendency to clog. 0.01 after 72 years 0.005 after 193 years 0.002 after 896 years		Strong tendency to clog: 0.005 after 60 years 0.002 after 440 years	
Initial porosity	0.23	0.2	0.06	0.2	0.04	0.2	0.01	0.2

Tab. A3.2: Comparison of diffusive scenarios 2 calculated for up to 10'000 years without porosity feedback on transport.

Materials	Sand-bentonite	Concrete	Opalinus Clay	Concrete	Effingen Member	Concrete	Helvetic marls	Concrete
Maximum simulation time	10'000 years		10'000 years		10'000 years		10'000 years	
Alteration extension	0.76 m montmorillonite dissolution	0.66 m portlandite dissolution	0.11 m montmorillonite dissolution	0.58 m portlandite dissolution	0.11 m montmorillonite dissolution	0.48 m portlandite dissolution	0.03 m montmorillonite dissolution	0.28 m portlandite dissolution
pH plume	2.5 m (pH >8) 1.5 m (pH >10) 0.5 m (pH >11.5)	12.6 pH 0.05 m (pH <12)	0.16 m (pH >8) 0.1 m (pH >10)	12.6 pH 0 m (pH <12)	0.2 m (pH >8) 0.14 m (pH >10) 0.04 m (pH >12)	12.6 pH	1.27 m (pH >8) 0.21 m (pH >10) 0.02 m (pH >11.5)	12.65 -12.7 pH 0 m (pH = 12.64)
Mineralogy (precipitates only)	Na-, K- phillipsite, illite, calcite, C-S-H, hydrotalcite, hydro-magnetite, gypsum	C-S-H, ettringite, calcite, hydro-magnetite	Na-, K- phillipsite, illite, montmorillonite, calcite, hydro-magnetite, C-S-H, gibbsite, ettringite, strätlingite, hydrotalcite	C-S-H, ettringite, strätlingite, hydrotalcite, calcite	C-S-H, monocarbonate, hydrotalcite, strätlingite, Na-, K- phillipsite, illite, pyrite, hydro-magnetite, gibbsite, calcite	C-S-H, mono-carbonate, ettringite, calcite	Na-, K- phillipsite, calcite, hydrotalcite, calcite, quartz, hydro-magnetite	C-S-H, calcite
Porosity decrease	Strong tendency to clog. Due to C-S-H (clay/interface) and ettringite (concrete/interface) precipitation		Strong tendency to clog. Due to phillipsite (clay) and strätlingite, C-S-H (interface,cement) precipitation		Strong tendency to clog. Due to phillipsite (clay) and monocarbonate, C-S-H (interface,cement) precipitation		Strong tendency to clog. Due to phillipsite (clay) and C-S-H, hydrotalcite (interface,cement) precipitation	
Remarks	Advance of dissolution fronts are ~ sqrt(t*D)		Precipitation of montmorillonite "behind" dissolution front		Precipitation of illite "behind" dissolution front			

Tab. A3.3: Comparison of advective scenarios 3 without porosity feedback on transport.

Materials	Sand-bentonite (outflow interface)	Concrete (outflow interface)	Opalinus Clay (outflow interface)	Concrete (inflow interface)	Effingen Member (outflow interface)	Concrete (inflow interface)	Helvetic marls (outflow interface)	Concrete (inflow interface)
Scenario*	Advective transport (315 m^3 concrete water flowing from all emplacement tunnels into one tunnel) driven by gas production		$v_D = 1 \times 10^{-13}$ m^3/m^2 s total fluid volume per m^2 rock/concrete in 1e5 years: Q = 0.315576 m^3		$v_D = 1 \times 10^{-12}$ m^3/m^2 s total fluid volume per m^2 rock/concrete in 1e5 years: Q = 3.15576 m^3		$v_D = 4 \times 10^{-12}$ m^3/m^2 s total fluid volume per m^2 rock/concrete in 1e5 years: Q = 12.62304 m^3	
Alteration extension	1.4 m montmorillonite dissolution	<0.1 m portlandite dissolution	0.01 montmorillonite dissolution	<0.01 m portlandite dissolution	0.25 m montmorillonite/kaolinite dissolution	0.1 m portlandite dissolution	0.08 m montmorillonite dissolution	0.2 m portlandite dissolution
Mineralogy (precipitates only)	(K-, Na-) phillipsite, hydrotalcite, C-S-H, hydro-magnetite	C-S-H, ettringite, monocarbonate, hydrotalcite	Illite, (Na-, K-) phillipsite, calcite, hydro-magnetite	Ettringite, calcite	Na-, K-phillipsite, hydrotalcite, C-S-H, illite, calcite	Brucite, hydrotalcite, quartz	K-, Na-phillipsite, hydrotalcite, C-S-H, calcite, illite	Hydrotalcite, ettringite, brucite, calcite
Porosity decrease	Slight increase in alteration zone	Slightly decreased	Porosity decrease	Nearly no change	Strong porosity decrease	Slight porosity increase	Very Strong porosity decrease	Porosity decrease
pH plume	28 m (pH 9 - 10)	pH 13.1	<0.03 m (pH>10) <3 m (pH~8.42) <6 m (pH>7.3)	<2.5 m (pH 12.5 - 13.0)	0.2 m (pH >9) <40 m (pH 6.5 -8.6) >40 m (pH 8-9)	0.1 m (pH <12.16) pH = 12.16	<15 m (pH >9-10) <25 m (pH 7.5-8.5) >25m pH 8-9	pH 12.5 - 12.6

* The Q value for the bentonite-sand interface is taken from Kosakowski & Berner (2011a, 2011d). The Darcy flux v_D values for flow in the host rocks were chosen according to Nagra (2010) (see also (Kosakowski & Berner 2011a)).

A4   Concrete systems and pore waters

This paragraph lists the concrete systems and their pore waters defined for the different concrete degradation stages, as outlined in Section 2.4.

Tab. A4.1:   Concrete degradation Stage A.

For the freshly hydrated concrete the HTS reference system according to page 13 in Berner (2009) is relied upon (25 ºC).

System		2'252.5 g	1'000 cm^3	
Inert solids		1'645.5 g	621.4 cm^3	Sand, gravel
Hydrated cement phases		405.8 g	178.5 cm^3	
Pore solution		201.2 g	200.1 cm^3	
pH		13.10		
Eh		-529.9 mV		
IS		0.168 m		
log(pCO$_2$)		-13.1		
Porosity		20.0 %		
Solutes (total concentrations)	[mol/kg H$_2$O]	[mol/L]	**Species contributing > 1 % to total**	
Na	97.10×10^{-3}	96.83×10^{-3}	Na^+, $NaOH_{(aq)}$	
K	72.94×10^{-3}	72.74×10^{-3}	K^+, $KOH_{(aq)}$	
Ca	2.440×10^{-3}	2.434×10^{-3}	Ca^{2+}, $CaOH^+$, $Ca(H_2SiO_4)_{(aq)}$	
S	0.6252×10^{-3}	0.6235×10^{-3}	SO_4^{2-}, $K(SO_4)^-$, $Na(SO_4)^-$, $Ca(SO_4)_{(aq)}$	
Sr	0.2640×10^{-3}	0.2633×10^{-3}	Sr^{2+}, $SrOH^+$	
Cl	0.2469×10^{-3}	0.2462×10^{-3}	Cl^-	
C	44.73×10^{-6}	44.61×10^{-6}	CO_3^{2-}, $Na(CO_3)^-$, $CaCO_{3(aq)}$	
Si	43.56×10^{-6}	43.44×10^{-6}	$Ca(H_2SiO_4)_{(aq)}$, $H_2SiO_4^{2-}$, $H_3SiO_4^-$	
Al	26.14×10^{-6}	26.07×10^{-6}	$Al(OH)_4^-$	
Ba	2.66×10^{-6}	2.65×10^{-6}	Ba^{2+}, $BaOH^+$, $Ba(SO_4)_{(aq)}$	
Fe	0.212×10^{-6}	0.211×10^{-6}	$Fe(III)(OH)_4^-$	
Mg	2.91×10^{-9}	2.91×10^{-9}	$MgOH^+$, Mg^{2+}, $Mg(H_2SiO_4)_{(aq)}$,	
OH	*1.738×10^{-3}*	*1.733×10^{-3}*	*OH^-, $NaOH_{(aq)}$, $KOH_{(aq)}$*	

Tab. A4.1:   (continued)

Solids	[g]	[mmol]	Comments:
Solid solutions			**Solid solution end-members**
C-S-H	212.26	1'007.9 148.1	Jennite Tobermorite-II
Ettringite	35.74	28.48 3.4×10^{-5}	Al-ettringite Fe-ettringite
Monocarbonate	44.75	43.91 30.72	Al-monocarbonate Fe-monocarbonate
OH-hydrotalcite	7.65	10.09 6.33	Al-hydrotalcite Fe-hydrotalcite
Single phases			
Gibbsite	--	--	
Barite	0.0093	0.04	
Calcite	3.39	33.83	
Portlandite	101.3	1'367.0	
Hydro-magnetite	--	--	Just saturated
$Fe(OH)_3$-micr.	--	--	
Illite	--	--	
Quartz	--	--	Non-reactive SiO_2 included in component "inert"
Strontianite	0.70	4.76	
Celestite	--	--	
Inert	1'645.5	27'386	Assumed to have physical properties of quartz

Tab. A4.2: Concrete degradation Stage B, termed portlandite stability stage.

It was decided to use the Stage A system after 10'000 years of diffusive exchange with the basic Opalinus Clay system to represent Stage B (Berner & Kosakowski 2011, Kosakowski & Berner 2011b for more details) (25 °C).

System		2'251.6 g	1'000 cm^3	
Inert solids		1'645.5 g	621.3 cm^3	Sand, gravel
Hydrated cement phases		405.9 g	178.6 cm^3	
Pore solution		200.3 g	200.1 cm^3	
pH		12.54		
Eh		-498.1 mV		
IS		0.0983 m		
log (pCO$_2$)		-13.1		
Porosity		20.0 %		
Solutes (total concentrations)	[mol/kg H$_2$O]	[mol/L]	**Species contributing > 1 % to total**	
Na	42.27×10^{-3}	42.14×10^{-3}	Na$^+$, NaOH$_{(aq)}$	
Cl	37.50×10^{-3}	37.39×10^{-3}	Cl$^-$	
Ca	18.07×10^{-3}	18.01×10^{-3}	Ca^{2+}, CaOH$^+$	
K	3.309×10^{-3}	3.299×10^{-3}	K$^+$, K$^+$	
Sr	2.487×10^{-3}	2.479×10^{-3}	Sr^{2+}, SrOH$^+$	
S	47.14×10^{-6}	47.00×10^{-6}	SO$_4^{2-}$, Ca(SO$_4$)$_{(aq)}$, Na(SO$_4$)$^-$, Sr(SO$_4$)$_{(aq)}$	
Si	34.32×10^{-6}	34.21×10^{-6}	Ca(H$_2$SiO$_4$)$_{(aq)}$, H$_3$SiO$_4^-$, H$_2$SiO$_4^{2-}$,	
Ba	26.62×10^{-6}	26.53×10^{-6}	Ba^{2+}, BaOH$^+$	
C	8.065×10^{-6}	8.040×10^{-6}	CaCO$_{3(aq)}$, CO$_3^{2-}$, Na(CO$_3$)$^-$, SrCO$_{3(aq)}$	
Al	6.911×10^{-6}	6.890×10^{-6}	Al(OH)$_4^-$	
Fe	5.59×10^{-8}	5.576×10^{-8}	Fe(III)(OH)$_4^-$	
Mg	1.11×10^{-8}	1.10×10^{-8}	MgOH$^+$, Mg^{2+}	
OH$^-$	*49.08×10^{-3}*	*48.93×10^{-3}*	*OH$^-$, CaOH$^+$, NaOH$_{(aq)}$,*	

Tab. A4.2:   (continued)

Solids	[g]	[mmol]	Comments:
Solid solutions			**Solid solution end-members**
C-S-H	212.3	1'007.8 148.1	Jennite Tobermorite-II
Ettringite	35.74	28.47 *(3.4 × 10⁻⁵)*	Al-ettringite Fe-ettringite
Monocarbonate	44.75	43.90 30.72	Al-monocarbonate Fe-monocarbonate
OH-hydrotalcite	7.65	10.10 6.32	Al-hydrotalcite Fe-hydrotalcite
Single phases			
Gibbsite	--	--	
Barite	0.01	0.044	Secondary product
calcite	3.39	33.83	
portlandite	101.3	1'367.1	
Hydro-magnetite	0.09	0.32	
$Fe(OH)_3$-micr.	--	--	
Illite	--	--	
Quartz	--	--	Non-reactive SiO_2 included in component "inert"
Strontianite	0.70	4.76	
Celestite	--	--	
Inert	1'645.5	27'386	Assumed to have physical properties of quartz

Tab. A4.3:   Concrete degradation Stage C, termed low-pH stage.

In order to remain consistent with the concrete system used in the HLW near-field (Bradbury 2014) it was decided to select the low-pH shotcrete system as defined in Kosakowski & Berner (2011b), pages 6 – 15 and 49 – 50 (25 ºC).

System		2'276.8 g	1'000 cm^3	
Inert solids		1'701.3 g	642.4 cm^3	Sand, gravel, 0 – 8 mm
Hydrated cement phases		395.4 g	178.2 cm^3	
Pore solution		180.1 g	179.4 cm^3	
pH		11.07		
Eh		-180.7 mV		
IS		0.150 m		
log (pCO$_2$)		-9.65		
Porosity		18.0 %		
Solutes (total concentrations)	[mol/kg H$_2$O]	[mol/L]	**Species contributing > 1 % to total**	
Cl	124.3×10^{-3}	123.2×10^{-3}	Cl$^-$	
Na	104.9×10^{-3}	104.0×10^{-3}	Na$^+$, Na(SO$_4$)$^-$	
K	25.71×10^{-3}	25.48×10^{-3}	K$^+$, K(SO$_4$)$^-$	
S	7.881×10^{-3}	7.811×10^{-3}	SO$_4$$^{2-}$, Na(SO$_4$)$^-$, Ca(SO$_4$)$_{(aq)}$, K(SO$_4$)$^-$	
Ca	5.394×10^{-3}	5.346×10^{-3}	Ca^{2+}, Ca(SO$_4$)$_{(aq)}$, Ca(H$_2$SiO$_4$)$_{(aq)}$	
Sr	0.4079×10^{-3}	0.404×10^{-3}	Sr^{2+}, Sr(SO$_4$)$_{(aq)}$,	
Si	0.3479×10^{-3}	0.345×10^{-3}	H$_3$SiO$_4$$^-$, Ca(H$_2SiO_4$)$_{(aq)}$, SiO$_{2(aq)}$, H$_2SiO_4$$^{2-}$,	
Al	0.1159×10^{-3}	0.115×10^{-3}	Al(OH)$_4$$^-$	
C	16.82×10^{-6}	16.68×10^{-6}	CO$_3$$^{2-}$, Na(CO$_3$)$^-$, HCO$_3$$^-$, SrCO$_{3(aq)}$	
Ba	0.220×10^{-6}	0.218×10^{-6}	Ba^{2+}, Ba(SO$_4$)$_{(aq)}$	
Mg	0.123×10^{-6}	0.122×10^{-6}	Mg^{2+}, MgOH$^-$, Mg(H$_2$SiO$_4$)$_{(aq)}$, MgSO$_{4(aq)}$ Mg(H$_3$SiO$_4$)$^+$	
Fe	3.89×10^{-8}	3.86×10^{-8}	Fe(III)(OH)$_4$$^-$,Fe(II)(OH)$_{2(aq)}$	
OH$^-$	*1.634×10^{-3}*	*1.619×10^{-3}*	*OH$^-$, NaOH$_{(aq)}$, CaOH$^+$*	

Tab. A4.3: (continued)

Solids	[g]	[mmol]	Comments
Solid solutions			**Solid solution end-members**
C-S-H	309.43	19.94 2'335.8	Jennite Tobermorite-II
ettringite	37.06	29.53 $(6. \times 10^{-8})$	Al-ettringite Fe-ettringite
monocarbonate	--	-- --	Al-monocarbonate Fe-monocarbonate
OH-hydrotalcite	10.78	24.28 0.026	Al-hydrotalcite Fe-hydrotalcite
Single phases			
Gibbsite	1.39	17.78	
Barite	3.12	13.35	Secondary product (exchange of K^+ by Ba^{2+})*
Calcite	10.07	100.6	
Portlandite	5.1×10^{-3}	0.019	
Hydro-magnetite	6.93	64.8	Secondary product
$Fe(OH)_3$-micr.	16.60	43.2	Secondary product
Illite	--	--	Non-reaktive SiO_2 included in component "inert"
Quartz	--	--	
Strontianite	--	--	
Celestite	4.1×10^{-3}	2.25×10^{-5}	
Inert	1'701.3	28'316	Assumed to have the physical properties of Quartz

* See also Kosakowski & Berner (2011a), Section 2: Modelled concentrations of K^+ and SO_4^{2-} significantly deviate from experimental findings (Lothenbach & Winnefeld 2009), probably due to missing knowledge on the solubility determining solid phase(s). This was corrected by exchanging 2 K^+ by 1 Ba^{2+} and subsequent precipitation of barite.