

Gesellschaft für Anlagenund Reaktorsicherheit (GRS) mbH

Radionuclide transport modelling

Performance assessment of repositories in clays





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André Rübel Dirk-Alexander Becker Eckhard Fein

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Abstract

The main focus of research for deep disposal of nuclear waste repositories in Germany has been on salt formations so far. For clay formations, one had to fall back on the experiences developed in other European countries e.g. Switzerland. A decision to consider other host rock formations than salt for a potential waste repository for high level waste in Germany has lead to the necessity to acquire and enhance the knowledge about the safety-relevant processes in clay formations on a national level. In particular, computer codes to perform integrated performance assessment calculations existed in Germany up to that time only for salt and crystalline rock and had to be developed also for waste repositories in clay formations. The necessary computer programs were developed, tested and a first integrated performance assessment calculation for a generic repository in clay formations was performed within the project "Development of an instrument to calculate the radionuclide transport in clay formations", shorty titled "TONI", which was financed by the German Federal Ministry of Economics and Technology (BMWi).

The programs newly developed or improved are CLAYPOS, CHETMAD and r³t. The first two are codes make use of a one-dimensional geometry for the application in long-term safety assessments, while the third is a code with a three-dimensional geometry which is used mainly for detailed modelling. The programs were tested on the one hand by comparison with analytical solutions and on the other hand by modelling of insitu diffusion experiments and natural tracer profiles and comparing the results to those obtained by other groups.

The integrated performance assessment calculations were based on conceptual ideas developed by DBE Technology for the disposal of high level wastes in argillaceous media found in two different regions. The clay formations were chosen on the basis of a study carried out by BGR. The formations regarded are the Opalinus Clay that can be found in Southern Germany and the Lower Cretaceous Clays that can be found in Northern Germany.

Integrated performance assessment calculations were performed for the two mentioned clay formations; including a reference case and parameter variations of all main input parameters. Also a probabilistic calculation was performed.

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Both clay formations showed low radionuclide fluxes from the host rock and a low resulting annual radiation exposure compared to the regulatory limit of $3 \cdot 10^{-4}$ Sv·y⁻¹. A comparison between the results of the reference case and the parameter variations shows some remarkable issues:

- The diffusion coefficient is the most relevant parameter for the annual radiation exposure and the breakthrough time of the radionuclides through the clay formation.
 Other important parameters are the formation thickness, the distribution coefficients and solubility limits for some radionuclides.
- A high thickness of the clay formation like those found for the Lower Cretaceous Clays - can lead to a complete containment of the radionuclides in the clay formation within the safety relevant period of one million years.
- The maximum annual radiation exposure, which for both formations results from
 I-129 at times larger than one million of years is surprisingly nearly the same in
 both reference cases; despite the large difference in formation thickness.
- The influence of the parameter uncertainty on the annual radiation exposure is the lower, the higher the thickness of the formation. For clay formations of a large thickness, only the diffusion coefficient is of high importance for the annual radiation exposure. All other parameters are of minor importance.

For the Opalinus Clay, the results for the reference case being calculated with the onedimensional long-term assessment code CLAYPOS were compared to the results of a simulation with the code r³t which accounts for a more complex three-dimensional geometry. The difference in the results between both simulations was found to be unexpectedly high with CLAYPOS leading to higher radionuclide fluxes than r³t. The difference was identified to be mainly due to the simplification of the geometry by CLAYPOS. However, the high degree of simplification was however found to be necessary, since otherwise the computing times would be too high for a large number of parameter variations or probabilistic assessments.

Within this project a new instrument was developed to perform integrated performance assessment calculations for repositories in clay formations and was applied for the first time for a generic case.

Zusammenfassung

Bei der Forschung für die Endlagerung von radioaktiven Abfällen in tiefen geologischen Formationen wurden in Deutschland bisher vor allem Salzformationen als Wirtsgestein in Betracht gezogen. Für Endlager im Tongestein konnte aus deutscher Sicht bislang lediglich auf Erfahrungen in anderen europäischen Ländern, wie z.B. der Schweiz, zurückgegriffen werden. Wegen der Bestrebungen, zukünftig auch andere Wirtsgesteine als Salz verstärkt zu berücksichtigen, war es erforderlich, die im nationalen Rahmen vorhandene Kenntnisse bezüglich der sicherheitsrelevanten Prozesse im Tongestein zu vertiefen und zu erweitern. Insbesondere existierten in Deutschland umfassende langzeitsicherheitsanalytischen Modelle zur Berechnung des Radionuklidtransports nur für Salz und Kristallingesteine, nicht aber für Tongestein. Letztere wurde im Rahmen des vom Bundesministerium für Wirtschaft und Technologie (BMWi) geförderten Forschungsvorhabens "Entwicklung eines Instrumentariums zur Berechnung des Radionuklidtransports in Tonformationen (Kurztitel TONI)" entwickelt, getestet und für zwei generische Endlager im Tongestein angewendet.

Die neu entwickelten Programme sind CLAYPOS, CHETMAD und r³t. Die ersten beiden Programme sind für die Anwendung im Rahmen von langzeitsicherheitsanalytischen Rechnungen vorgesehen und verwenden eine eindimensionale Geometrie, während r³t eine drei-dimensionale Geometrie verwendet und für Detailbetrachtungen vorgesehen ist. Die Programme wurden getestet, zum einen durch den Vergleich mit analytischen Lösungen und zum anderen durch die Modellierung von in-situ Diffusionsexperimenten und natürlichen Spurenstoffprofilen und den Vergleich mit den Ergebnissen anderer Gruppen getestet.

Die langzeitsicherheitsanalytischen Rechnungen basieren auf einem Endlagerkonzept, welches von der DBE Technology für die Endlagerung von hochaktiven Abfällen in zwei unterschiedlichen Tonformationen entwickelt wurde. Die Tonformationen wurden auf Grund einer Studie der BGR ausgewählt. Die betrachteten Tonformationen sind der Opalinuston in Süddeutschland und die Unterkreidetone in Norddeutschland.

Für beide der genannten Tonformationen wurden langzeitsicherheitsanalytische Rechnungen durchgeführt. Diese schließen Rechungen für den Referenzfall, Parametervariationen und probabilistische Rechnungen mit ein.

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Für den Referenzfall ergeben sich für beide Formationen niedrige jährliche Strahlenexpositionen, die unter dem Schutzziel von 3·10⁻⁴ Sv·a⁻¹ liegen. Ein Vergleich für die Referenzfälle und Parametervariationen zeigt einige bemerkenswerte Ergebnisse:

- Der Diffusionskoeffizient ist im Bezug auf das Maximum der Strahlenexposition und dem Zeitpunkt der Ankunft der Radionuklide in der Biosphäre der wichtigste Parameter.
- Eine große Mächtigkeit der Tongesteinsformation kann zu einem praktisch vollständigen Einschluss der Radionuklide in der Tonformation innerhalb des Betrachtungszeitraums von einer Million Jahren führen.
- Der Einfluss der Parameterunsicherheit auf das Maximum der j\u00e4hrlichen Strahlenexposition ist geringer, je m\u00e4chtiger die Formation ist. Bei Tonformationen mit einer M\u00e4chtigkeit wie jener bei den Unterkreidetonen ist der Diffusionskoeffizient der einzige Parameter, der einen wesentlichen Einfluss auf den Verlauf der j\u00e4hrlichen Strahlenexposition hat. Alle anderen Parameter haben demgegen\u00fcber nur eine untergeordnete Bedeutung.

Die Ergebnisse der Rechnungen, die mit dem Programm CLAYPOS für den Referenzfall beim Opalinuston durchgeführt wurden, wurden mit Ergebnissen des Programms r³t verglichen. Während CLAYPOS eine stark vereinfachte, eindimensionale Geometrie betrachtet, wird in r³t eine dreidimensionale Geometrie berücksichtigt. Die Unterschiede zwischen beiden Rechnungen waren unerwartet groß, wobei CLAYPOS einen höheren Radionuklidstrom berechnet als r³t. Dieser Unterschied resultiert in erster Linie aus der Vereinfachung der Geometrie in CLAYPOS. Diese Vereinfachung ist jedoch notwendig, damit Rechnungen mit einer größeren Anzahl von Parametervariationen oder sogar probabilistische Rechnungen mit praktikablen Rechnerzeiten durchgeführt werden können.

In dem hier vorgestellten Projekt wurde ein neues Instrument zur Durchführung langzeitsicherheitsanalytischer Rechnungen für Endlager in Tonformationen entwickelt und zum ersten Mal auf ein generisches Endlager in Deutschland angewendet.

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1 Introduction

The assessment of the long-term safety of a repository for nuclear waste¹ requires a powerful and qualified instrument. The approach used for the safety assessment must meet national regulations on the one hand and should be internationally accepted on the other hand. Further it must be continuously adapted to the state of the art of science and technology. Computer codes used for safety assessments must be tested and verified and be designed for the prerequisites of a real waste repository system.

As one task in a long-term safety assessment, the release of radionuclides from the repository into the biosphere and the potential radiation exposure of the population have to be quantitatively determined. The simulations consider the full transport pathway of the radionuclides; the release out of the waste matrix, the transport through the technical and geotechnical near-field barriers, the transport through the geosphere consisting of the host rock and surrounding rock formations and the radioecological impact in the biosphere. The safety assessment calculations at GRS are carried out using a software package named EMOS [7, 65]. EMOS consists of different program modules, each of them representing one of the compartments of the repository system, which are: the near-field, the far-field and the biosphere. Dedicated program modules to calculate the radionuclide transport exist for different host rock types like salt (LOPOS) or granite formations (GRAPOS) and for different far-field rocks types like porous media (CHET) or fractured media (CHETMAD). To a large extent, the modules for each compartment are interchangeable with each other, thus providing a high degree of flexibility in modelling different host rock types and waste repository concepts. The whole instrument existing at GRS is continuously improved and applied for safety assessments, either for real repository sites like ERAM [64] and ASSE, or generic studies like SPA [34] for granite. Additionally, it is also permanently used for the judgement of questions of topical interest.

In Germany there exists extensive practical and theoretical experience regarding the storage of nuclear waste in salt formations. The essential processes are known, are mostly well understood and can be modelled adequately. There exist two program modules named LOPOS and REPOS to perform long-term safety assessment calcula-

¹ In the following the general term "waste repository" is used meaning a waste repository for nuclear waste

tions with EMOS. These two modules have been used within a variety of generic and real site studies e.g. [11, 24, 63, 64].

The relevant scenarios and processes for a waste repository in crystalline formations were discussed within the international project SPA [34]. Within this project the Modules GRAPOS and CHETMAD were developed by GRS as tools for the long-term safety assessment calculations and were tested for a generic repository in a granite formation.

In contrast to salt, before the start of this project, there existed only limited experience about waste repositories in clay formations in Germany. Therefore one had to rely on the experiences developed in other European countries e.g. [2, 37, 38, 42]. A discussion about the consideration of host rock types other than salt or granite for a potential waste repository in Germany has lead to the necessity to acquire and enhance the knowledge on a national level about the safety-relevant processes in clay formations. Particularly, no comprehensive instrument to perform long-term safety assessment calculations for a waste repository in clay formations existed in Germany before the start of this project. To close this gap, the project "Development of an instrument to calculate the radionuclide transport in clay formations"², short title "TONI" was started with the support of the German Federal Ministry of Economics and Technology (BMWi). The report in hand presents the outcome of that project.

The reason for developing a new instrument for a repository in a clay formation instead of using an existing one for another host rock type is the following: The migration of radionuclides in a clay formation shows some special characteristics compared to other media that have to be taken into account in the models. The permeability of a non-fractured clay formation is generally very low. As an example, the permeability of the Opalinus Clay formation at the location of Benken is about 10⁻²⁰ m². In such low-permeable porous media, diffusion is dominating over the advective radionuclide transport. Therefore the exact description of the diffusion within the model is of great importance.

The description of the diffusion in clay formations differs from that in other porous media. The very small pore radius in connection with the electrical charged clay surfaces

² German title: "Entwicklung eines Instrumentariums zur Berechnung des Radionuklidtransports in Tonformationen"

lead to an electromagnetic interaction between the clay matrix and the diffusing radionuclides. This interaction has the effect that the accessible porosity and the diffusion coefficient both depend on the diffusing species. The porosity is therefore called element-specific porosity and the diffusion coefficient is called element-specific diffusion coefficient, respectively. Another notable difference compared to other porous media is caused by the layered structure of clay formations resulting from the sedimentation process: the diffusion is anisotropic, i.e. the transport parallel to the bedding is faster than perpendicular to the bedding.

The transport codes which were available at GRS before the beginning of this project did not include this clay-specific peculiarities in such a way as required for the long-term safety assessment calculations. Therefore, new codes had to be developed or existing codes had to be extended to include these effects. Prior to the development, first the scientific basis had to be reviewed. After the development, the model approach and the newly developed codes had to be tested and qualified.

Typically, the models and codes are qualified either by calculating problems with known solutions, or by comparison with other, already qualified codes; sometimes also by comparison with results from laboratory experiments. Laboratory experiments however, cover only small timescales ranging from some weeks up to some years maximally. The long-term behaviour of a waste repository is in contrast controlled by processes that have to be accounted for over geological timescales of many thousands of years. Therefore, the modelling of natural analogues is also useful to validate the codes.

As a first step, this project regards for three different types of conceptual models of clay formations in respect of modelling. Within these concepts, it is not necessary to distinct between the near field and the far field, since the bentonite, which is used as near-field barrier, has properties very similar to those of the clay formation itself. Thus both compartments can be modelled together. The three conceptual models are:

 Homogenous, non-fractured clay formations: this type of clay formation has uniform transport properties throughout the whole examined domain. Diffusion is the only transport process that has to be considered and can be modelled as a onedimensional process.

- Clay formations with a single fracture: in this type of clay formation the radionuclides are assumed to be transported in the fracture from the container to the point of release into a more permeable formation or an aquifer.
- Clay formations with a complex geometry: this type of clay formation has a more complex geometry including inhomogeneous distribution of transport parameter values. The transport process has to be modelled in three dimensions taking the real geometry into account.

These three different conceptual models are covered by three different dedicated codes for the modelling of the radionuclide transport process in clay formations. The integrated performance assessment calculation including the consideration of uncertainties uses a 1D-code, whereas for the examination of complex geological situations a 3D-code is used. The 3D-code can also be used to clarify which processes have to be considered in the long-term safety calculation and to quantify the deviance originating from the abstraction to 1D. The three codes which were developed or improved within this project are:

- CLAYPOS, which accounts for the one-dimensional diffusive transport,
- CHETMAD, which accounts for the one-dimensional transport in a fracture with consideration of matrix diffusion and
- **r**³**t**, which accounts for the three-dimensional transport in complex geometries.

A detailed description of the three conceptual models and the relevant processes in a clay formation is given in chapter 3. A detailed description of the three dedicated transport codes is given in chapter 4. The qualification of the codes is described in chapter 5, and finally their application in an integrated performance assessment calculation is described in chapter 7.

2 Project approach

The aim of this project was to develop qualified instruments to perform long-term safety assessment calculations for a waste repository in a clay formation. To reach this goal the following sub-goals had to be achieved:

- development of suitable conceptual models,
- development of the computer codes,
- testing and qualification of these codes and finally
- application of the codes in an integrated performance assessment calculation.

The conceptual models including the relevant features, events and processes (FEPs) that influence the radionuclide transport are described in chapter 3. The conceptual models were already largely developed prior to the start of this project within the framework of the project WIGRU-4 [41].

2.1 Development of the computer codes

The new modules had to be created either by new developments or by enhancing existing codes to allow for the specific features of radionuclide transport in clay formations into account. These are mainly features in regard to the description of the diffusion process, e.g. that the diffusion-accessible porosity and the diffusion coefficients have to be considered as being element-specific.

- Based on the computer code GRAPOS the new module CLAYPOS has been developed to simulate the one-dimensional radionuclide transport through a clay formation and other adjacent impermeable formations into the closest nearby aquifer.
- The existing computer code CHETMAD has been enhanced to model the radionuclide transport in fractures. It takes matrix diffusion into account.
- The computer code r³t has been extended to simulate the three-dimensional radionuclide transport through heterogeneous clay formations.

A detailed description of the goals of the development and the implementation of the new features in the codes is given in chapter 4.

2.2 Qualification of the developed codes

Several steps have been undertaken to qualify the newly developed computer codes. Besides the calculation of problems for which analytical solutions exist, also the modelling of diffusion experiments and natural analogues - i.e. natural tracer profiles in clay formations - has been performed. The results of the modelling were compared on the one hand to the experimental results and on the other hand to the results achieved by other modelling groups.

In low-permeable clay formations natural tracer profiles are establishing over geological periods of time. The natural tracers are for example stable water isotopes, dissolved gases, or chlorine. These profiles are developing due to the fact that at some time in the geological past the concentrations of these tracers in the surrounding aguifers of the clay formation have changed compared to the concentrations in the clay formation itself. The resulting concentration gradient between the aquifer and the clay formation causes a transport of the natural tracers into or out of the formation and leads to a characteristic concentration distribution in the clay formation, which is conserved over long timescales due to the fact of the low permeability of the formation. The concentration distribution observed today allows one making conclusions about the type of transport process if the hydrogeological boundary conditions over time are known. The clay formation quasi records the changes in hydrogeological conditions and transport process over time. Thus, natural tracer distributions can be regarded as a natural analogue for the transport of contaminants in the clay formation over long timescales. Besides the qualification of the codes the modelling of the tracer profiles can be used to test the underlying model assumptions. The modelling of the natural tracer profiles is described in chapter 5.3.

The modelling of natural tracer profiles applies only to non-sorbing tracers. To test and qualify the modelling of sorption processes a simulation of in-situ borehole diffusion experiments was performed. Such diffusion experiments were carried out in the rock laboratory at Mont Terri in the following way: a solution of known chemical composition is filled in a packer interval down in a borehole and the concentration decrease of the tracers in the borehole is monitored over a long period of time. The exact procedure is described in section 0. In this type of experiments, the diffusion and retention properties of anionic and cationic species can be examined. Tracers that have been used in these types of experiments are e.g. Na-22, Cl-36, Cs-134 and H-3 [73]. Besides the

qualification of the codes the simulation of these experiments also yields valuable information about the transport and sorption parameter values in clay formations.

Some concepts for waste repositories include the storage of cemented waste forms like the concept of the Nagra in Switzerland [38], or use concrete linings to support the tunnel walls, as in the concepts of ANDRA in France [2] and NIRAS/ONDRAF in Belgium [42]. The pore water in the cement material is highly alkaline what can result in the propagation of an alkaline plume in the surrounding clay formation by diffusion of Hydroxide ions. The propagation of the alkaline plume modifies the pore water chemistry in the clay formation which can alter the sorption properties for the radionuclides. The coupling of r³t with the geochemical code PHREEQC was tested by modelling the propagation of an alkaline plume in a clay formation and the results were compared to the results of simulations with the transport feature of PHREEQC itself.

The different efforts undertaken to qualify the newly developed computer codes are described in detail in chapter 5.

2.3 Application of the developed codes

As the final step of the project the developed codes were used to perform an integrated performance assessment (PA) calculation for a generic waste repository in a clay formation. The aim of this step was to develop a reference case and to determine the resulting potential radiation exposure of the population.

The repository layout and concept on which the performance assessment is based was developed by DBE³ Technology within the research project GEIST [16] which dealt with the disposal of high-level waste in clay formations. Two different types of clay were taken into account in the GEIST project. One of them is the Opalinus Clay at a location in the southern part of Germany. A similar formation is also regarded in the Swiss programme "Entsorgungsnachweis" [38]. The other type is the Lower Cretaceous clay sequences found in the northern part of Germany.

³ German Company for the Construction and Operation of Waste Repositories (Deutsche Gesellschaft zum Bau und Betrieb von Endlagern)

Based on the repository concept, scenarios for the future development of the repository were deduced. As a basis, a reference scenario that represents the expected future development of the repository was defined. Another scenario takes into account deviations from the expected development, i.e. the occurrence of fractures resulting from geological events.

Using the developed codes, the potential radiation exposure resulting from both scenarios was calculated for a repository located in the Opalinus Clay and the Lower Cretaceous Clay formations. The required input data which is related to the layout and geometry of the repository was taken from the GEIST project. Transport and retention parameter values for the radionuclides were taken from the Swiss "Entsorgungsnachweis" for the Opalinus Clay and for the Lower Cretaceous Clay from the literature.

The relevant parameters which affect the radionuclide flux into the biosphere were determined by parameter variations and probabilistic calculations. The scenarios and the integrated performance assessment calculations are described in chapter 7.

3 Conceptual model for the radionuclide transport in clay formations

In the following chapter the features, events and processes (FEPs) that may influence the radionuclide transport within clay formations are discussed. The aim of this discussion is to identify the relevant FEPs that have to be taken into account in the models to calculate radionuclide migration out of a waste repository in a clay formation.

The radionuclide migration from the waste repository is modelled only as far as to the release point of the radionuclides into the next adjacent aquifer or into a fracture zone within the clay formation in which a fast advective transport to the adjacent aquifer occurs. In regard to the modelling of the radionuclide transport, three different configurations of clay formations are distinguished in the following discussions. These configurations are shown in figure 3.1 and are:

- A homogenous, fracture-free clay formation (figure 3.1a) is characterised by uniform transport properties within the whole domain. The radionuclide transport can be simulated using a one-dimensional geometry in direction of the shortest distance to the adjacent aquifer or a higher permeable formation.
- A clay formation with single fractures (figure 3.1b). These single fractures can result from geological events and may be hydraulically permeable over longer distances. They can be regarded as single planes with an aperture less than one millimetre and a trace length between several metres and some tens of metres. The radionuclide transport is modelled as one-dimensional transport in the fracture as far as to the intersection with the adjacent aquifer or a formation of higher permeability. Additionally, the penetration of radionuclides into the clay matrix has to be taken into account.
- A clay formation with a complex geometry or zones of joint (figure 3.1c). In clay formations which consist of different facies with heterogeneous transport properties, the main transport direction cannot easily be predicted anymore and a one-dimensional simulation of the transport is not adequate to correctly describe the radionuclide transport. In this case the radionuclide transport has to be modelled in three-dimensionally. The same applies to zones of joint which are bands with thicknesses in the range from metres to tens of metres and which are characterised by a kind of fissure network, i.e. a large amount of very small fractures which are not hydraulically connected. The zones of joint can be regarded as a macroscopic do-

main which has a spatial uniform, but higher permeability than the surrounding clay formation.



Fig. 3.1: Schematic representation of the different types of clay formations

Only those types of clay formations will be taken into account as host rock for a waste repository in a clay formation that show no fractures and are characterised by simple geological situations resulting in an almost uniform distribution of the transport properties over large scales. Additionally, the position of the repository in the host rock formation will be chosen to maximise the distance to adjacent water conducting formations. However, it cannot be completely excluded that undetected fractures exist in the formation or that new fractures are evolving after geological events.

Unconsolidated clay can relieve mechanical stress by plastic deformation and thus will prevent the generation of any fractures at all or existing fractures will close again within short time. Therefore, formations of plastic clay are always accounted as being non-fractured. In contrast to this, in formations of consolidated clay fractures may develop, e.g. by tectonic activities. Consolidated clays also have the ability that fractures in the formation are closing again with time [20]. This means that the fracture is typically still detectable as some kind of disturbance, but shows the same transport properties than the surrounding undisturbed clay formation. Formations with closed, inactive fractures are further regarded as being undisturbed and free of fractures. Examinations at the rock laboratory in Mont Terri [45] and at the location of Benken [39] show that in the geological past the Opalinus Clay at both locations had fractures, that have closed again and are inactive nowadays.

In the following sections, the FEPs that influence the radionuclide transport in clay formations are described. Unfortunately some of the terms which are of importance in the following are inconsistently defined in the literature. This mainly applies to terms which are related to diffusion and sorption processes. Where necessary, these terms are defined and the according German term is also given. Additionally, the typical values for the most important parameters for different clay formations are given.

3.1 Transport processes

The migration of radionuclides dissolved in the pore water of a clay formation is driven by three main transport processes: advection, diffusion and dispersion. The transport of radionuclides in the gaseous phase is not regarded in the following. Advection denotes the process of the movement of water in the clay formation. The movement can be either due to differences of pressure or water density or due to do the displacement of water as a result of gas production and flow. Diffusion and dispersion denote processes of the migration of dissolved radionuclides in the water due to radionuclide concentration gradients.

The permeability of non-fractured clay formations is typically very low and is for example of about 10^{-20} m² at the location Benken. In such low-permeable porous media the diffusive radionuclide transport is dominating over the advective transport of water. In addition to the transport of the dissolved radionuclides, the co-transport of radionuclides sorbed onto colloids has to be taken into account in the case colloids are present and mobile.

The corrosion of the emplaced waste, the containers, and the backfill can yield corrosion products which can affect the pore water chemistry in clay. The effects are the propagation of a redox-front in a HLW-repository and the propagation of an alkaline front in a waste repository for cemented, low-level wastes or in repositories where cement is used to support the tunnel walls. Due to the highly reducing conditions around the corroding containers and the high pH-buffer-capacity of the clay formation, it is assumed that both effects only have a local affect on the pore water chemistry and can be neglected for the main part of the formation [38].

Besides the transport processes mentioned above, there are five additional so called coupled transport processes. Coupled transport processes are those that cause a flux resulting from a gradient of a potential which is not directly related to the flux. An example is the flux of ions as a result of a temperature gradient, the so-called Soret-Effect. Mathematically one speaks of a flux depending on a non-conjugated force. The

coupled transport processes, their driving forces and the resulting fluxes are given in table 3.1. Over the long period of one million years taken into account in the long-term safety assessment, these processes have only minor influence on the radionuclide transport and therefore can be neglected [59, 60].

Process	Driving force	Transported quantity
Dufour-Effect	chemical gradient	heat
Chemical Osmosis	chemical gradient	pore water
Thermal Osmosis	temperature gradient	pore water
Soret-Effect	temperature gradient	dissolved substance
Hyperfiltration	hydraulic gradient	dissolved substance

 Tab. 3.1:
 Coupled transport processes

3.1.1 Diffusion

In a porous medium, diffusion practically takes place only in the pore water, not in the solid matter. Therefore, the diffusive flux in a porous medium is reduced in comparison to the one in free water. Accordingly, the diffusion-accessible porosity⁴ n_{diff} is relevant for the diffusive flux *j*. An additional effect is that the diffusing radionuclides are not able to propagate straightforward through the medium due to its crooked pore space. Hence, the diffusion coefficient in the pore water which is called pore diffusion coefficient⁵ D_p is further reduced by a geometrical factor *G* compared to that for free water D_0 . The one-dimensional form of Ficks first law in a porous media therefore can be written as

$$j = -n_{diff} D_P \frac{dc}{dx}.$$
(3.1)

It should be pointed out that other terms are used in the literature for the parameters porosity and diffusion coefficient and that these terms are even sometimes used inconsistently by describing different parameters with the same term. Therefore, the exact

⁴ Sometimes diffusion accessible porosity is also denoted as diffusion porosity [46]. The corresponding German term is "diffusionszugängliche Porosität".

⁵ In the following, "diffusion coefficient" is used for the "pore diffusion coefficient" if not stated otherwise.

definition of the diffusion coefficient and the porosity are of high importance when giving numbers. The diffusion-accessible porosity is often merged into the diffusion coefficient. The diffusion coefficient is than often called "effective diffusion coefficient". Also common is the term "apparent diffusion coefficient", which additionally includes the retardation factor⁶.

As is described in the following two sections, the diffusion-accessible porosity and the diffusion coefficient are specific for the diffusing substance. Although strictly speaking these two parameters are different for each species and should therefore be called "species-specific diffusion-accessible porosity" and "species-specific diffusion coefficient" the community performing long-term-safety assessments has established the term "element-specific" in their reports. This is mainly due to a lack of data as described below. To be consistent with the commonly used terms, this report also uses the term "element-specific" keeping in mind that in the future different values for the porosity and diffusion coefficient may be used for the same element in different speciation states.

3.1.1.1 Diffusion-accessible porosity

Only a fraction of the pore space is available for diffusion of the dissolved radionuclides in a clay formation. Therefore, the diffusion-accessible porosity n_{diff} is smaller than the total porosity n_{tot} , which denotes the fraction of the pore water volume in the total volume of the rock.

The reasons for the reduced diffusion-accessible porosity are interactions of the radionuclides with the clay matrix which are in particular pronounced in clay formations, due to their very small pore radii compared to other porous media. The mean pore radii in clay formations are typically only a few nanometres [25]. In the Opalinus Clay for example, 50% of the pores have a radius of less than 4 nm. The other half of the pores have a mean pore radius of about 8 nm [45]. In comparison to that, a monomolecular layer of water at the pore wall has a thickness of about 3 nm. Therefore, significantly less than 10 layers of water molecules can reside side by side in the bigger part of the pores.

⁶ The retardation factor (R) is a measure of the clay's ability to restrain the migration of the radionuclides. For its definition see section 3.2.3.

The radionuclides are expelled from parts of the pore water due to three different effects: the electrostatic interaction of the pore water with the clay matrix, the exclusion of the dissolved radionuclides from the Stern-Gouy-layer and the exclusion of the radionuclides from small pores due to their size:

- The clay matrix generates a negative electrical surface charge on its interface to the pore water since some of the lattice ions are replaced by other ions with a higher number of valence electrons. Anions which are dissolved in the pore water are repelled from the negatively charged clay surface and reside preferably in the central part of the pores. This reduction of the accessible porosity is called **anion exclusion**.
- The already mentioned electrical charge of the clay matrix at the interface to the pore water on the other hand leads to a strong binding of the water molecules at-tached to the interface. Substances which are dissolved in the pore water can hardly penetrate this so called **Stern-Gouy-layer**. Therefore, the pore space which is accessible for diffusion is reduced by the Stern-Gouy-layer. This effect also applies to non-charged diffusing substances, but it is small compared to the anion exclusion.
- Some of the substances dissolved in the pore water are too large to be able to enter the smaller pores in a clay formation. This effect is called **filtration** and primarily affects colloidal pollutant complexes.

Due to the insufficient data basis for different diffusing species, the diffusion-accessible porosity is commonly divided into not more than three to four different groups of substances. In general these groups are distinguished by their electrical charge and in particular cases also by the size of the species if special complexes are investigated.

In most cases, it can be assumed that the diffusion-accessible porosity for cations equals the total porosity. For anions however, one accounts for an anion exclusion effect and the diffusion-accessible porosity is assumed to be significantly lower than the total porosity. Experiments yield an anion exclusion of about 50% for iodine and bromide for different types of clay [13, 67]. For the Boom Clay at the Belgian Mol site, the diffusion-accessible porosity for anions is specified to be 0.12 compared to a total porosity of about 0.35 [36]. The size exclusion effect was also observed for the Boom Clay at the Mol site. For uranium complexes the diffusion-accessible porosity is specified to be only 0.1.

3.1.1.2 Diffusion coefficient

The diffusion coefficient for ions in free water D_{θ} is mostly well known and is e.g. for iodine at 25 °C in the range of 1 to $2 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ [12]. The diffusion coefficient in a porous medium is smaller compared to the one in free water due to the longer, meandering pathways of the diffusing ions in the pore space. It is called pore diffusion coefficient D_p and is defined by

$$D_P = G \cdot D_0. \tag{3.2}$$

The ratio of the pore diffusion coefficient and the diffusion coefficient in free water is the geometrical factor G. The geometrical factor takes two effects into account which are often mentioned in the literature; the so called tortuosity and the constrictivity. Due to the same effects as discussed with the diffusion-accessible porosity, also the diffusion coefficient is depending on the diffusing species.

The geometry factor is always smaller than unity and was determined e.g. for Hydrogen in the Boom Clay to be about $5 \cdot 10^{-3}$ [70], $6 \cdot 10^{-3}$ for Helium in the Opalinus Clay [52] and $4 \cdot 10^{-3}$ for Helium in the Callovo-Oxfordian [49], respectively. In general the geometry factor is not explicitly specified, but the pore diffusion coefficient is used.

Like for the diffusion-accessible porosity, the data basis of the pore diffusion coefficient depending on different species is rather weak. For this reason, the pore diffusion coefficient in long-term safety assessments is also only divided into two or three groups depending on the electrical charge of the diffusing species. Values for some pore diffusion coefficients, which were determined in experiments or which are used in long-term safety assessments for different clay formations are given in table 3.2.

As a result of the sedimentation process, clay formations are typically deposited in a layered structure. This structure results in anisotropic properties of the formation which also affects the diffusion coefficient. The diffusion coefficient parallel to the bedding is typically higher than perpendicular to the bedding. The anisotropy of the diffusion coefficient is independent of the diffusing species and was determined to be of a factor of 2 to 6 for the Opalinus Clay at the location of Benken [38] and about a factor of 2 for the Boom Clay at the location of Mol [13]. The values given in table 3.2 are for diffusion perpendicular to the bedding.

Formation	Location	Transported substance	D _P [m ² /s]	Ref.
Experimental deter	mined values			
Callovo-Oxfordian	Bure	НТО	1.4·10 ⁻¹¹	[1]
Opalinus Clay	Mont-Terri	Не	3.1·10 ⁻¹¹	[52]
		НТО	8.3·10 ⁻¹¹	[45]
		iodine	3.5·10 ⁻¹¹	
		НТО	4.0·10 ⁻¹⁰	
Boom Clay	Mol	iodine	2.7·10 ⁻¹⁰	[36]
		dissolved organic matter	1.3·10 ⁻¹¹	
Values used in safety assessments				
Opalinus	Bonkon	anions	2.5·10 ⁻¹¹	[30]
Opannus	Delikeli	other substance	5.0·10 ⁻¹¹	[[29]

 Tab. 3.2:
 Pore diffusion coefficient perpendicular to the bedding in different clay formations

The diffusive propagation of radionuclides can be illustrated by the following example: The concentration of radionuclides penetrating a clay formation by diffusion can be calculated as function of the distance from the source x and the time t to be [8]

$$C(x,t) = C_0 \cdot erf\left(\frac{x}{2\sqrt{Dt}}\right), \tag{3.3},$$

where C_0 denotes the initial radionuclide concentration at the source. The distance at which the concentration of the radionuclide is a bout half the initial concentration at the source is about⁷

$$x \approx \sqrt{Dt} \tag{3.4}.$$

With a diffusion coefficient of $D = 5 \cdot 10^{-11} \text{ m}^2/\text{s}$ equation 3.4 shows that in one million years the concentration in a distance of 40 m to the source rises from zero to approximately half of the initial concentration at the source.

 $^{^{7}}$ $\,$ The deviation from the correct value is less than 5% $\,$

3.1.2 Advection

Despite the low permeability of the clay formations advection can be relevant for the radionuclide transport in some particular cases. In these cases one has to distinguish between advection in the homogenous clay matrix and in fractures.

3.1.2.1 Driving forces

The driving forces for the advection are pressure gradients resulting from different effects. Figure 3.2 exemplarily shows the different pressure gradients that exist in a clay formation for a simplified one-dimensional geometry and a horizontal bedding of the clay formation.



Fig. 3.2: Hydraulic gradients in a horizontal bedded clay formation

The "natural" vertical hydraulic gradient i_h results from the differences of the hydraulic heads in the aquifers of the overlying and underlying beds of the clay formation. At the location of Benken for example the difference in hydraulic head between both aquifers above and below the Opalinus Clay formation was measured to be about 6 m. This results in a hydraulic gradient of about 0.06 m/m. To model the advective radionuclide transport, the hydraulic heads are used as boundary conditions in the aquifers.

In many clay formations, a pore water pressure is measured that does not correspond to the local hydrostatic pressure resulting in the additional hydraulic gradient i_{pw} . Therefore these pore pressures are called anomalous pore pressures. The origin of these anomalous pore pressures is not yet fully understood. A common explanation in the literature is that it is due to an alteration of the depth of burial. If the depth of burial is increasing, the lithostatic pressure is rising and the clay formation is compacted. Due to the low permeability of the clay formation, the pore water cannot leak from the formation as fast as the depth of burial is rising. This results in pore water pressures being above the local hydrostatic pressures as could be expected from the burial depth. If the burial depth is decreasing the reverse process is taking place. To consider the anomalous pore water pressures in the modelling of the advective radionuclide transport, the porosity of the clay formation, i.e. the storage capacity, has to be taken into account as a transient parameter.

For the Opalinus Clay at the location of Benken anomalous pore water pressures of 50 to 300 m above the local hydraulic head are measured [38]. The anomalous pore water pressure is dissipating over long periods of time by an advective flux out of the clay formation into the adjacent aquifers. Due to the low permeability of the clay formation a period of more than one million years can be necessary to return to local hydrostatic pressure [58].

The anoxic corrosion of metals leads to gas production and pressure build-up in the waste repository. If the produced gas enters the pore space of the clay formation it displaces pore water and thus a hydraulic gradient i_g can rise. More probable, however, is that the gas pressure leads to pathway dilation or micro-fissuring. These two processes lead to a gas pressure release without a displacement of greater amounts of pore water. The gas transport in clay formations is discussed in more detail in section 3.4. The gas production and the gas pressure are not taken into consideration in the model for the radionuclide transport in the water phase since their effect on the advective water flow is assumed negligible.

3.1.2.2 Permeability

Clay formations that are considered as host rock for waste repositories typically have very low permeabilities and are classified as aquicludes. Permeability values for three investigated locations are given in table 3.3.

Clay formation	Location	k [m²]	Ref.
Callovo-Oxfordian	Bure	5.0·10 ⁻²⁰	[2]
Opalinus	Benken	1.0·10 ⁻²⁰	[38]
Boom	Mol	4.1·10 ⁻¹⁹	[36]

 Tab. 3.3:
 Permeability of different clay formations

The permeability of the clay formations may be affected by the construction of the waste repository. The excavation of the repository in the formation can lead to disturbed rock zones along the constructed tunnel walls. These zones are called excavation disturbed zones (EDZ) which typically reach up to two meters deep into the formation. The EDZ shows an enhanced permeability compared to the undisturbed formation. This may lead to the generation of preferential pathways and hence to an augmented advective transport along the tunnels. Due to the self-healing capacity of the clay formations the EDZ is closing with time. This leads to a permeability close to that of the undisturbed formation [3]. For the performance assessment calculations it is usually assumed that the EDZ is sealed again before the containers fail. In this case the influence of the EDZ can be neglected.

If cemented wastes are emplaced in the repository or concrete is used to support the tunnel walls the corrosion of the cement in contact with water can lead to the propagation of an alkaline plume into the clay formation. The alkaline pore water can lead to a weathering of the clay matrix and to an increase of the permeability. In the studies for the Opalinus Clay it was determined that due to the high pH buffer capacity of the clay formation the propagation of the alkaline plume is limited to a distance of less than 10 m from the cement material. Furthermore, the precipitation of secondary minerals may even lead to a sealing of the pores. Due to both effects, an increase of the permeability of the clay formation by alkaline pore water is neglected [38]. It has to be verified for each single case that this applies also to other types of clay formations.

Like the diffusion coefficient, the permeability is anisotropic due to the layering of the clay formations. The permeability parallel to the bedding is higher than that perpendicular to the bedding. For the Opalinus Clay an anisotropy factor of 5 is determined. For the Boom Clay the value is 2 to 4 and for the Callovo-Oxfordian up to 10. In table 3.3 the higher permeability values parallel to the bedding are given.

3.1.2.3 Advection porosity

The pore space in which advective water transport occurs is called advection porosity and it is lower than the total porosity. This is due to the small pore diameters of a large fraction of the pores. If the pore radius is smaller than 2 nm it is assumed that no advective flow is possible through these pores due to the strong interaction of the water molecules with the pore wall [25]. No data for the so called advection porosity⁸ [46] exists for most of the clay formations, so the total porosity is used for the modelling.

3.1.2.4 Darcy's law

The advective flux density q of the water is described by Darcy's law

$$q = \frac{\rho \ g \ k}{\mu} \cdot i , \qquad (3.5)$$

where μ and ρ denote the viscosity and the density of the water, *g* the acceleration of gravity, *k* for the permeability of the formation and *i* for the pressure gradient.

In media with very fine pores, the pore water behaves as a non-Newtonian fluid which shows a non-linear relationship between the hydrostatic pressure and the flow velocity. This is caused by the viscosity which itself is a function of the flow velocity. In this case Darcy's law is not valid anymore. There are some indications that this effect may also exist in clay formations, however, while this effect is rather small and advection only plays a minor role in clay formations anyway, non-Newtonian flow is neglected, here.

⁸ Sometimes the "advection porosity" is also called "flow" or "advective transport" porosity.

The displacement velocity of the water v_a is linked to the flux density by

$$v_a = \frac{q}{n} \,. \tag{3.6}$$

Using data for the permeability k of 10^{-20} m², the porosity n of 0.12 and an assumed natural hydraulic gradient i of 1.0 m/m, one gets a distance velocity of about $5 \cdot 10^{-13}$ m/s, i.e. 25 m in one Million years.





Figure 3.3 shows the propagation of radionuclides in a low-permeable clay formation from a simplified one-dimensional model. The curves show the normalised concentration as function of the distance to the constant source after a time of one million years. The transport parameters permeability, diffusion coefficient and porosity were chosen as typical values for a low-permeable clay formation. According to equation 3.6, the advective front (shown as dashed line) propagates only 25 m into the clay formation in one million years. The diffusion profile after one million years from equation 3.3 is shown as solid line. At a distance of 50 m, diffusion leads to an increase of the concentration from initially 0 to 37% of the concentration at the source. This example illus-

trates that the advection of the water can be neglected compared to the diffusion process in very low-permeable clay formations.

3.1.2.5 Dispersion

The dispersion coefficient D_d is given by

$$D_d = v_a \cdot d \tag{3.7},$$

where *d* denotes the dispersion length. With the distance velocity calculated in the previous section and an estimated dispersion length of 0.1 m one obtains a dispersion coefficient of $5 \cdot 10^{-13}$ m/s. The dispersion in low-permeable clay formations is therefore very low due to the low distance velocity of the water. Compared to the diffusion coefficients given in table 3.2 the dispersion coefficient is lower by at least one order of magnitude. Therefore, the dispersion can be neglected in clay formations with low permeability.

3.1.3 Advection in fractures and zones of joint

The transport processes in zones of joint are the same as those described for nondisturbed clay formations. Only the different transport parameters have to be taken into account. These are particularly an enhanced permeability, porosity and diffusion coefficient. Also the retention properties may be affected. Due to the enhanced permeability in zones of joint, the advective flow maybe has to be taken into account.

For the radionuclide transport in single fractures the following transport processes have to be considered:

- advective transport due to the flow of water in the fracture,
- diffusive and dispersive transport along the direction of flow,
- diffusive transport perpendicular to the flow direction (matrix diffusion) and
- retardation in the matrix.

The radionuclide transport in a single fracture with matrix diffusion can be described in the same way as for other fractured formations as e.g. granite [34]. If many fractures

are present these are combined to a representative fracture and a value which quantifies the numbers of fractures per area unit. The representative fracture is characterised by only a few parameters in the model. First of all, these are aperture of the fracture, the porosity of the filling of the fracture and the total width of open flow channels per rock area. The diffusive transport from the container to the fracture can be modelled like for the undisturbed clay formation. As conservative assumption it may be assumed that the radionuclides are directly released into the fracture as was shown in figure 3.1b.

3.2 Sorption

The retardation of dissolved pollutants as consequence of its interaction with the clay matrix is determined by two processes: the surface complexation and the ion exchange. In the following, first the physical and chemical processes and second the modelling of the processes will be described.

3.2.1 Surface complexation

The surface complexation process is a reaction of dissolved species with functional groups at the surface of minerals to form surface complexes. Typical functional groups which are relevant for the sorption of contaminants in natural sediments are aluminol, silanol or other metal hydroxo groups. Depending on the pH-value, these groups can be charged positively or negatively. They are called "surface binding sites". In clay minerals the aluminol and silanol surface binding sites are predominant.

Besides pure ions like Ca^{2+} also dissolved complexes like $[UO_2OH]^+$ can be bound to the clay surface by surface complexation. The strength of the binding mainly depends on its type, i.e. whether the ion is directly bound to the surface or in a hydrated state. In the first case one speaks of specific adsorption and of the formation of an inner-sphere complex. This binding is of ionic and/or covalent nature and is as strong as a chemical binding. One also speaks of chemisorption. In the second case water molecules are interposed between the surface functional group and the ions it binds. In this case one speaks of unspecific adsorption and of the formation of an outer-sphere complex. This binding is of electrostatic nature and is weaker than that of an inner-sphere complex.

3.2.2 Ion exchange

Ion exchange is the process that replaces ions bound on surface sites of the mineral with dissolved ions from the pore water. The bindings are also surface complexes; however, ion exchange is distinguished from the surface complexation by the fact that the surface sites involved in ion exchange have a permanent charge which is independent of the pH-value.

These kinds of surface sites exist for example in interlayers of clay minerals. The surface charge results from the charges of the clay matrix. To compensate the negative charge of the surface, the interlayer sites are occupied by cations. Typical cations that are preferentially sorbed onto the interlayer sites are Cs, Rb, K, Na, Ba, Sr, Ca and Mg.

3.2.3 Sorption models

Different models exist to describe the sorption processes. These models either describe the sorption in a phenomenological way or they try to depict the sorption in a mechanistic way:

 Isotherms are a phenomenological way to describe the sorption. The Henry isotherm assumes a linear relationship between the concentration of the sorbed and the dissolved contaminants. The quotient of both concentrations is termed distribution coefficient or for short K_d-value. The Langmuir and the Freundlich isotherms assume a non-linear relationship between the sorbed and dissolved fractions of the contaminant.

In case of linear (Henry) equilibrium sorption, the retardation factor R_f is determined by

$$R_f = 1 + \frac{1 - n}{n} \rho K_d , \qquad (3.8)$$

where *n* denotes the porosity and ρ for the bulk density of the rock. R_f characterises the retardation effect of the sorption on the radionuclide transport. Surface complexation models are a mechanistic way to describe the sorption process. Reactions of surface sites like protonisation and deprotonisation of the functional group and the reaction with contaminants are taken into account in the following way:

$$XOH + H^{+} = XOH_{2}^{+} \text{ and}$$

$$XOH = XO^{-} + H^{+}, \quad (3.9)$$

$$XO^{-} + Cs^{+} = XOCs,$$

where XOH denotes a surface site. The reactions are described by the law of mass action, thus complexation coefficients are needed for each surface complex. Geochemical codes take into account competing reactions between mobile and immobile complexes by using appropriate complexation coefficients. In contrast to the commonly used complexation in solution, for surface complexation onto the clay matrix the contribution of the electrical field on the activity coefficient of the sorbed ion or complex is included by an exponential term in the law of mass action. For the reaction between a surface site and a Cs^+ ion given above, the law of mass action can be written as:

$$K = \frac{[\text{XOCs}]}{[\text{XO}^{-}]\{\text{Cs}^{+}\}}$$
(3.10)

with

$$\{Cs^+\} = [Cs^+]e^{-\Psi F/RT}$$
 (3.11)

The brackets denote the activity of the respective species. For the sorbed Cs^+ -ion the activity in solution [Cs^+] is extended by the exponential term which takes into account the contribution of the electrical field. The resulting activity is given in curly braces. The surface potential Ψ in the exponential term is depending on the surface charge density of the matrix. Accordingly, the surface potential is changing with the pH-value in the same way as the surface charge density.

 Ion exchange models are another mechanistic way to describe the sorption process. Reactions of the following type are taken into account:

$$XNa + Cs^{+} = XCs + Na^{+}$$
(3.12)

The sorption by ion exchange is described by a law of mass action using a so called selectivity coefficient

$$K_{\rm Na,Cs} = \frac{[\rm XCs][\rm Na^+]}{[\rm XNa][\rm Cs^+]}$$
 (3.13)

Sorption by ion exchange always replaces one cation by another. Hence, the surface charge remains unchanged in this reaction. Therefore, the influence of the electrical field on the activity of the sorbed ions does not have to be explicitly included in the mass action law. The ion exchange usually is examined by the use of geochemical codes. Competing reactions between the different components in solution can be taken into account in these codes additionally.

The phenomenological models are only valid for a well-defined water-sediment system. Strictly speaking, the model parameters have to be determined again each time the chemical properties of the sediment or the solution have changed. Since this procedure is practically not feasible, the same parameter values are used even if the system changes are not too dramatic, causing an uncertainty of the model. The mechanistic models however explicitly include the consequence of the chemical changes on the sorption process. The use of mechanistic models is therefore especially useful if the chemical conditions of the water-sediment system are changing with time. In a case where the chemical conditions of the solution are buffered by the sediment and also the sediment properties remain unchanged, phenomenological models are sufficient to describe the sorption process.

A general problem occurring with the use of surface complexation models is that detailed knowledge of the assembly of the surface in natural sediments is often lacking and therefore the exponential term in the law of mass action correcting for the electrostatic forces cannot be exactly determined.

All mentioned sorption models are equilibrium models. If the sorption process is slow compared to the transport process no equilibrium models can be used. In this case the kinetics of the reaction must be included in the model.
3.3 Colloid-facilitated transport

Colloids are by definition particles with diameters between 1 nm and 1 mm. They are ubiquitous in natural groundwater and are known to be able to influence radionuclide transport if the concentration is sufficiently high. The colloid-facilitated transport only plays a role in advective transport processes. In this case, colloids can potentially increase the transport velocity of radionuclides. Due to the small pore sizes, the colloids are larger than the majority of the pores of typical clays which restricts the mobility of colloids.

The total concentration of natural, organic colloids in clay formations can be comparatively high. However, there is only a small fraction of very small colloids which can be transported over larger distances through these narrow pores. Most likely, the majority of the colloids can only be transported in wider fractures. Analysis of water samples from the Opalinus Clay [45] show concentrations of organic colloids of about 0.64 ppm. However, the concentration of the colloid fraction with a sizes smaller than 10 nm amounts to only 0.03 ppb.

An additional source for colloids can be the dissolution of the waste matrix [17]. But filtration experiments show, that these colloids are not able to permeate a slice of compacted bentonite with a thickness of only a few millimetres [18]. Moreover, these types of colloids are not long-term stable in clay pore waters according to experiments by Schäfer et al. [56]. The colloids coagulate in a very short time forming larger particles. The same applies to colloids resulting from dissolution of the clay matrix itself.

Since advection plays only a minor role and the colloids are more or less immobile in homogenous clay formations, the colloid-facilitated transport in homogenous clay formations is also of minor importance and can be disregarded. In contrast to that, the colloid-facilitated transport by natural, organic colloids in fractures might have to be taken into account. The colloids are transported by advection, diffusion and dispersion. Additionally the sorption of the colloids onto the fracture walls has to be considered.

3.4 Gas transport

Three different processes can cause gas transport in a water saturated clay formation:

- dissolution of gas in the pore water and a subsequent diffusion,
- two-phase flow of gas and water and
- flow of gas on pathways created as consequence of the high gas pressure.

The driving force for the gas transport is the pressure build-up from gas generation. This is caused on the one hand by the anoxic corrosion of the metallic parts of the waste matrix and the waste containers and on the other hand by radiolysis of the water which penetrates into the waste containers. In the void volume in or around the container a gas pressure develops according to the amount of the generated gas.

A fraction of the gases can be dissolved in the pore water of the clay formation corresponding to the gas solubility. It can be transported by diffusion. In modelling, the diffusion coefficient and the accessible porosity for the dissolved gaseous species are usually chosen as for electrically neutral species. Since the gas production rates in most waste repository concepts for the storage of iron containers are usually too high [38], so that only a small fraction of the produced gases can be removed by diffusion.

For the advective transport in two-phase flow the gas has to partly or fully displace the pore water from the pore space. To displace the water the gas pressure has to exceed a threshold, the so-called gas entry pressure. The value of the gas entry pressure determines whether the gases actually can displace water from the pores or if fractures are produced in the clay formation. Fractures can only be generated if the pressure needed for their creation is lower than the gas entry pressure. Experiments carried out with Boom Clay indicate that the pressure needed to produce fractures is depends on the permeability of the clay.

Experiments carried out with Opalinus Clay from Benken [39] show that at this location a gas flux could already be established at gas pressures below the minimum principal stress. In the case of the Opalinus Clay at Benken two phase flow is expected if the maximum gas pressure is about 3 to 4 MPa below the minimum principal stress of about 12 to 15 MPa. At higher pressures, a first gas release by pathway dilation is expected until the gas pressure exceeds the threshold pressure of about 17.5 MPa needed to create gas fracs. For the repository concept described in the safety report of

the project Opalinus Clay it is expected that the gas pressure will exceed the pressure needed to create microscopic gas pathways (pathway dilation), but will not exceed the pressure to create macroscopic gas fracs [38]. Due to the anisotropy of the permeability and the principal stress, the gases flow preferentially occurs along the bedding planes.

It is assumed that the diameters of the microscopic gas pathways created by the gas pressure are smaller than 1 mm [43]. Since the gas pressure build-up due to corrosion is slow, the development of the gas pathways is presumably slow, too. As soon as the gas pathways are formed, the gas pressure will decrease due to the resulting gas flow. The penetration of the gases into the pore space is believed to cause only a minor desaturation of the pore space. Therefore, the gas pathways will be resealed as soon as the gas flow decreases and water resaturates the pore space [66].

Although some experiments and theoretical geomechanical modellings exist for the gas transport in clay formations, the mechanism is still not fully understood. Especially for compacted claystones there still exists no complete evidence that the process takes place as described and that the tightness of the clay formation is not affected by the gas flow. Since the gas transport process most likely is highly affected by the mineral composition of the clay and the degree of compaction, this evidence has to be shown for each potential waste repository site and for the appropriate clay type.

As long as the gas transport mechanisms are not completely understood the development of long-lasting micro fractures have to be taken into account. This may lead to the development of zones of higher permeability in the clay formation. For that an increased permeability in the clay formation due to a network of micro-fractures was for example considered in the safety analysis for the project Opalinus Clay as "what-if? case".

Experiments have shown that hydrogen gas in contact with a clay formation can be taken up by the clay formation or it is converted into other gases, leading to a decrease of hydrogen concentration along the transport pathways through the clay formation [43, 73, 70]. This also applies to the partial hydrogen gas pressure in a gas phase which is in contact with clay. The exact mechanism for this process is not yet known. However, there exist indications that the process is caused by a microbial conversion of the hydrogen with carbon dioxide to methane and water. This process results in a reduction of the amount of moles of molecules in the gas phase and consequently also

results in a reduction of gas pressure. This process has still to be further confirmed and quantified in more detail. Therefore, this process is not considered at the moment, which is a conservative assumption.

3.5 Résumé

Only homogenous non-fractured clay formations will be considered as host rock for a nuclear waste repository. The permeability of non-fractured clay formations is very low and is typically 10^{-20} m² or even less. With media of such little permeability, diffusive radionuclide transport is clearly dominant over advective transport. If fractures do exist in the formation, advection has to be taken into account as well as the colloid-facilitated radionuclide transport by natural organic colloids.

The diffusion of radionuclides in low-permeable clay formations is described by element-specific diffusion coefficients and element-specific diffusion-accessible porosities. Since the element-specific data basis for these two parameters is still rather weak; typically only three different values are used depending on the electrical charge of the pollutant: for anions, for cations and for electrical neutral species. In the majority of the cases the diffusion coefficient for the radionuclides in clay formations is anisotropic. The coefficient for diffusion parallel to the bedding plane is found to be higher than for the one perpendicular to the bedding plane. The advection depends on the permeabilities and the hydraulic gradients. In addition to the natural hydraulic gradients in some clay formations also so-called anomalous pore water pressures exist and have to be taken into account. However, for most clay formations which are considered as host formation for a waste repository, advection can be neglected compared to diffusion.

If the clay formation includes fractures or zones of joint the radionuclide transport can be dominated by the advective transport in these. Zone of joint can be regarded as a macroscopic domain which has a homogenous, but enhanced permeability compared to the undisturbed clay formation. In this case, the transport in zones of joint can be modelled in the same way as in the undisturbed clay formation.

The radionuclide transport in single fractures can be described in the same way as for other fractured rocks. The transport is advective, dispersive and diffusive along the fracture and the diffusive transport perpendicular to the flow direction, which is called matrix diffusion. The fracture itself is characterized by only a few parameters. First of all, these are the aperture of the fracture and the total width of the open flow channel. Due to the self-healing capacity of most clay formations it has to be considered that fractures will close with time. The fractures therefore are only hydraulically active during a limited period of time and the transport therein has to be described by models that use transient parameters. If fractures are present, colloid-facilitated transport may also play a role.

Two types of sorption processes are distinguished in clay formations. These are on the one hand the surface complexation and on the other hand the ion exchange. The surface complexation can be further sub-classified into the unspecific and specific sorption, depending on whether water molecules are interposed between the surface functional group and the ions it binds or not. In principal, these sorption processes also can be observed in other mineral types, but especially the specific sorption and the ion exchange do have a particular relevance for clays due to their pronounced surface charge. The description of the sorption processes in integrated models is typically done using isotherms. For the specific sorption and the ion exchange however, process level surface complexation models are more appropriate.

4 Program development

The development of programs to model the radionuclide transport in clays could have either been based on adapting transport modules for other host rock types that already existed before the start of this project to the special needs of modelling radionuclide transport in clay formations, or could have been achieved by creating new modules from the scratch. The program modules to come into question existing before the start of the project are:

- GRAPOS, which is a module of the EMOS package that simulates the onedimensional diffusive transport in a cylindrical geometry. This module was used to model the bentonite barrier in the near-field of a waste repository in a granite host rock.
- CHETMAD, which is a module of the EMOS package that simulates the transport in fractures taking matrix diffusion into account. This module was used to model the transport in a fractured hard rock like granite.
- r³t, which is a program for modelling the radionuclide transport in large regions of porous media. It deals with 2D and 3D geometries and includes a multitude of effects to model transport and retention. Along with the program d³f simulating the density driven flow, r³t was initially developed to model the radionuclide transport in the overburden of repositories in salt.

In low-permeable clay formations taken into consideration as host rock for waste repositories, diffusion dominates the radionuclide transport. Advection and dispersion only play a minor role and can be neglected in most cases. Due to this reason, it was decided that for the integrated performance assessment a code which accounts for diffusion only is sufficient and GRAPOS was used as a basis for the development of a new integrated module called CLAYPOS. For the few cases where advection may play a role, the 3D transport code r³t and the module CHETMAD to simulate the transport in fractures were considered to be sufficient this time. Therefore these two codes were to be enhanced to meet the new requirements.

In the following sections, the status of the modules prior to this project, the required developments to model the radionuclide transport in clay formations and the implementation of the changes is discussed for each of the three mentioned modules. Table 4.1 on page 45 summarises which effects were considered in the three modules before the start of this project and which developments were made.

In addition to the individual requirements for developments of each module some requirements are identical for all three modules. These are particularly the implementation of element-specific diffusion-accessible porosities and element-specific diffusion coefficients. The latter was already implemented in the program $r^{3}t$.

4.1 CLAYPOS

The module GRAPOS, which was the basis for the development of the module CLAYPOS simulates a single waste container for high level waste in low-permeable media. It makes use of a one-dimensional cylindrical geometry. GRAPOS was developed within the framework of the project SPA to model the near-field of a waste repository in granite which comprises a bentonite barrier. A detailed description of the module GRAPOS can be found in [34].

For the waste container two processes are modelled. First, the mobilisation from the waste matrix after the failure of the waste container is modelled for the three different compartments gas space, metal parts and waste matrix. For each compartment a different mobilisation rate is used. In the second place, the precipitation of radionuclides is taken into account upon transgression of solubility limits.

For the domain of the bentonite barrier the diffusive transport and the retention by linear sorption according to the Henry isotherm are modelled. The radioactive decay is modelled in the container as well as in the bentonite. On the outer boundary, the boundary condition is defined by the water flow around the bentonite barrier.

Description of the model

The aim of the new module CLAYPOS which is based on the existing module GRAPOS is to model the one-dimensional diffusive transport through the near-field barriers, the clay host rock and other adjacent impermeable formations into the closest nearby aquifer. The transport in the near-field and in the host rock should be modelled combined in one module. The near-field is represented by a bentonite barrier. To achieve this combined modelling it is necessary to allow the possibility of defining different materials that have different transport parameter values.

CLAYPOS simulates the release from a single waste container and the transport through the overlying column of bentonite and clay as a representative section of the whole repository. The flux from the whole repository is calculated by multiplying the flux from one section with the number of sections in the whole repository. As a conservative simplification the transport is simulated only in the upward direction. The decrease of the source inventory due to the flux of radionuclides in the downward direction is neglected. For those radionuclides that reach their solubility limits within the container, this simplification should make only a minor effect on the calculated radionuclide flux. For radionuclides whose concentration remains below their solubility limit within the container, the concentration in the source and the transport in direction of the aquifer are overestimated. The water volume determining whether the solubility limits are reached or not, has to be defined according to the void volume in the waste container.

The transport in CLAYPOS is modelled in one dimension. This implies that the concentration profile in the formation is calculated only at the position of the container in direction to the aquifer. This is the direction in the reference cell with the highest concentration gradient. The simplification of the one-dimensional model now implies that the maximum concentration gradient is assumed to be uniform in the whole modelled section. This involves - in contradiction to reality - that the flux from the formation is proportional to the cross-section of the model. Consequently the one-dimensional model overestimates the radionuclide flux the more, the higher the container distance is.

Two types of geometries were to be implemented in the new CLAYPOS module, which are schematically shown in the figure 4.1. These are a plane (4.1a) and a radial (4.1b) geometry. The figures show the representative section of the repository for a concept using storage in drifts. The cross-sectional area of the representative section is defined by the distances between the disposal drifts and the waste containers. The thickness of the column is defined by the distance from the waste container to the adjacent aquifer. The two domains I and II in figure 4.1 represent the bentonite barrier and the clay host rock. The transport in both materials is one-dimensional, but with different transport properties.

Figure 4.1a shows the plane geometry in CLAYPOS. The cross-sectional area equals the drift distance times the container distance and is constant over the whole thickness of the model. In the reality, the cross-sectional area of the contaminant plume is not constant over the whole thickness of the formation. This is the reason why the radial symmetric geometry was implemented in CLAYPOS.



- Fig. 4.1:
 Schematic representation of the model geometries in CLAYPOS

 a.) upper figure:
 plane geometry
 - b.) lower figure: radial geometry

Figure 4.1b shows the radial symmetric geometry in CLAYPOS. The cross-sectional area of the inner boundary is chosen equal to the half of the surface area of the waste container, while the outer cross-sectional area is the same as for the plane geometry. The transport is calculated in one-dimensional radial symmetric geometry what corresponds to a two-dimensional geometry in the orthogonal space.

Only one container in a representative section of the repository is modelled in CLAYPOS. It is necessary to implement the possibility to allow for different types of

containers with different lifetimes or for different emplacement areas of the repository which have different distances between containers and/or drifts. Both needs can be achieved by defining groups of containers. For each group of containers a different dataset is defined. This corresponds to an internally repeated application of the model for each group of containers. At the end the flux from the whole repository is calculated from the individual fluxes for each group of containers, weighted by the number of containers in each group.

For the outer boundary condition of the radionuclide flux, the water volume flow in the aquifer is explicitly entered in the model. Since the volume flow in the aquifer can be very high and the impossibility to exactly specify the volume flow in every case, an excessively high water flow may be entered into the model to simulate a zero concentration boundary condition. This is a conservative assumption.

To assess the uncertainty and the sensitivity of the long-term safety calculations, the module CLAYPOS had to be enabled to perform probabilistic calculations. For this purpose, program code was implemented in CLAYPOS for a coupling to the STATIST frame from the EMOS package, to accept the assignment of variables from and to pass the output to the STATIST frame.

Implementation

For the spatial discretisation, the model area is divided in N segments. If the concentration at the inner boundary is only slightly time-dependent, the solution will come close to the stationary one. Therefore, the distances between each of the N segments are chosen in a way that they correspond to constant concentration steps for the stationary solution.

For each time step the radioactive decay is calculated analytically for the dissolved / sorbed and the precipitated inventory and the diffusive transport of the radionuclides is solved numerically. An implicit solution algorithm is used with a fixed time step width given. That means that the variable parameters are inserted with their values at the end of the examined time step for higher stability of the algorithm, i.e. negative concentrations are automatically avoided. The time derivative is replaced by an upwind difference and the spatial derivative is replaced by the central difference between the segments.

For the inner boundary condition two cases are to be distinguished. Provided that the solubility limit has been reached (a), the boundary concentration is given, otherwise (b) a source is assumed. In order to represent also the gradient correctly at the inner and outer boundaries in the case of the stationary solution, the discretisation raster is extended into the inner/outer area and the boundary condition is extrapolated.

The algorithm and the underlying mathematical equations are similar to the ones in the old GRAPOS module. A detailed description of the technical implementation can be found in the GRAPOS documentation. Due to the new requirements of the model described above, the organisation of the input data as well as the number of needed input data has essentially changed. A complete description of the input and output files of CLAYPOS can be found in the appendix A.

4.2 CHETMAD

The advective radionuclide transport in fractures including the colloid-facilitated transport can be simulated with the CHETMAD module. This module takes into account advection, dispersion and diffusion of the radionuclides and the colloids in the fracture and additionally the diffusion of the radionuclides in the matrix. Further, the sorption of the radionuclides onto the colloids and of the colloids onto the fracture wall is included in the module. For the simulation of the radionuclide mobilisation and the transport from the container to the fracture the module CLAYPOS can be used.

Before the start of this project, the module CHETMAD already fulfilled all requirements to model the transport in a fracture in the clay formation, except the consideration of the element-specific diffusion-accessible porosity and the element-specific diffusion coefficient. These two issues were additionally implemented in the scope of this project.

The algorithm and the underlying mathematical equations are identical to the ones in the original CHETMAD module. A detailed description of the technical implementation can be found in the CHETMAD documentation [33]. The organisation of the input data as well as the number of needed input has only slightly changed. A description of the changes of the input files compared to the previous version of CHETMAD can be found in the appendix B.

4.3 r³t

The transport program $r^{3}t$ simulates the three-dimensional, advective, dispersive and diffusive transport in porous media. The geometry of the clay formation and the waste repository can be completely represented in the $r^{3}t$ model geometry. The effect of anisotropic advection was already included in $r^{3}t$ before the start of this project. $r^{3}t$ is able to simulate linear as well as non-linear sorption processes either in equilibrium or as kinetically controlled sorption processes. The solubility limits are taken into account in the whole model area. A detailed description of the program $r^{3}t$ and its capabilities can be found in [14].

Changes to the implementation of transport

To simulate the radionuclide transport process in a clay formation, some extensions had to be implemented in $r^{3}t$. These are:

- spatial variability of the diffusion coefficient
- anisotropy of the diffusion coefficient
- element-specific porosity.

To implement the anisotropic diffusion in $r^{3}t$ the diffusion coefficient D' in Fick's law which is given in three dimensions by the equation

$$\boldsymbol{j} = n_{\text{diff}} \boldsymbol{D'} \nabla \boldsymbol{c} \tag{4.1}$$

has to be defined as a tensor. A principal axis system can be defined in which the bedding of the clay formation is parallel to the axes of the reference system. In this case the tensors' elements on the main diagonal in x and in y direction are the diffusion coefficients parallel to the bedding and the element in z direction is the diffusion coefficient perpendicular to the bedding. All other elements are equal to zero. The tensor looks like

$$\mathbf{D'} = \begin{pmatrix} D'_x & 0 & 0\\ 0 & D'_y & 0\\ 0 & 0 & D'_z \end{pmatrix}$$
(4.2)

In a case where the principal axis system and the bedding of the clay formation are not parallel to each other, the system of the clay formation has to be transformed into the system of the principal axis. The rotation from the main axes system (without index) to the system of the clay formation (with index p) is described by the three Eulerian angles as shown in figure 4.2. The three angles describe

- a rotation around the z-axis by the angle Φ ,
- a rotation around the x'-axis by the angle Θ and
- a rotation around the z''-axis by the angle Ψ .



Fig. 4.2: The definition of the three Eulerian angles [23]

The rotations are than defined by the following three rotation matrices:

$$\mathbf{C} = \begin{pmatrix} \cos \Phi & \sin \Phi & 0 \\ -\sin \Phi & \cos \Phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$\mathbf{B} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \Theta & \sin \Theta \\ 0 & -\sin \Theta & \cos \Theta \end{pmatrix}$$
(4.3)
$$\mathbf{A} = \begin{pmatrix} \cos \Psi & \sin \Psi & 0 \\ -\sin \Phi & \cos \Psi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

And finally a vector from one system to the other can be transformed by

$$\vec{r}_{p} = \begin{pmatrix} x_{p} \\ y_{p} \\ z_{p} \end{pmatrix} = \mathbf{A} \cdot \mathbf{B} \cdot \mathbf{C} \ \vec{r} \ .$$
(4.4)

The changes on the input files of $r^{3}t$ to consider anisotropic diffusion and a description of the $r^{3}t$ pre-processor dialogs to enter the data for the anisotropic diffusion is described in appendix C.

The use of point, line, area and volume sources is possible in $r^{3}t$. Fluxes or concentrations of radionuclides can be given for the grid cells in which the point sources are located, or which are intersected by the line, area or volume source. $r^{3}t$ itself does not include a source term for the release of the radionuclides from the waste. As source term the appropriate output from the module CLAYPOS can be used that gives the mobilisation from the waste matrix. The $r^{3}t$ pre-processor is able to convert the data from CLAYPOS output format and units to the $r^{3}t$ input format and units. The precipitation of radionuclides due to exceeding of solubility limits is not accounted for in the CLAYPOS output, but is calculated by $r^{3}t$.

Coupling with PHREEQC

Additionally to the changes described above, it was foreseen in the scope of this project to include a more detailed description of the sorption processes to r³t, which means it was strived for a mechanistic description of the surface complexation and the ion exchange. To achieve this goal it was decided to couple r³t to an existing geochemical code. From the available computer programs, the program PHREEQC from Parkhurst was chosen, which is freely available from the internet [44]. The choice was made due to the reasons that PHREEQC is:

- a widely used geochemical code and therefore is well qualified,
- continuously further developed,
- already successfully coupled to transport codes by other groups e.g. by Parkhurst himself to the transport code HST3D resulting in the coupled code PHAST,
- written in the same programming language as r³t i.e. C++,
- open source software i.e. the complete source code of PHREEQC is available and the program is distributed for free and
- includes a large database for exchange coefficients.

At the beginning of the project it was planned to implement the coupling between r³t and PHREEQC by using the input and output files of PHREEQC. However, after a few tests it was clear that a coupling on a file basis is by far too slow and only a direct inmemory link between r³t and PHREEQC by directly including the PHREEQC code in r³t had a chance for a successful coupling. As result is was necessary to examine the PHREEQC source code and data structures in detail which was a much higher effort than expected in the beginning. For the coupling r³t now directly uses the PHREEQC data structures for data storage and retrieval and calls the PHREEQC procedures for the equilibrium calculation.

Figure 4.3 shows the flowchart of a coupled r³t-PHREEQC calculation. At the beginning r³t is initialised by reading its input files. r³t loads PHREEQC into memory and PHREEQC is initialised by reading the dedicated input file "phreeqc.in" given in appendix D. This initialises all values for determining the exchange reactions. All pollutants given in the input file "pollutant", "initial", "boundary" and "phreeqc.in" must match each other and must include the parameters pH, pe and water content (wm). In contrast to the usual r³t calculations all concentrations have to be given in moles per kilogram of water [Mol/kg_w]. This unit also has to be used in the PHREEQC input file.

After the variables are initialised, the calculation starts with the first the transport step done by r³t. After the transport step r³t transfers the concentrations to the PHREEQC data structures and the reaction step is executed. The concentrations after the reaction step are again retrieved from PHREEQC by r³t and are written to the output file. The output at the moment includes the concentrations in the solution, the amount and saturation index of the equilibrium phases and the amount of the exchangers.



Fig. 4.3: Flowchart of the coupled r³t-PHREEQC calculation

No transport of the charge imbalance is calculated presently. Therefore, the solutions always have to be charge balanced. To achieve this, the charge balance has to be calculated by PHREEQC by explicitly giving the code word "charge balance" behind the pH-value in the input file "phreeqc.in".

The simulations performed for the test cases have shown some not yet fully understood problems of convergence in the PHREEQC simulation causing the simulation to terminate. The reasons for these problems and possible measures have to be identified in the future. Furthermore, the coupling of r³t and PHREEQC as achieved at the moment does not yet include all desired features. Further development on the coupling has do be done in following projects for the consideration or improvement of

- surface complexation,
- multiple materials with different phase composition,
- isotopes and radioactive decay and
- calculation performance; the test cases have shown a reduction of performance of the coupled r³t version of about a factor of 60 against the uncoupled version.

4.4 Résumé

The development of the programs to model the radionuclide transport in this project was based on some codes which already existed before the start of this project. One program was nearly newly developed and two others were enhanced in the scope of this project. The first one is the program CLAYPOS which covers the one-dimensional diffusive transport. The second is the program CHETMAD which covers the advective, dispersive and diffusive transport in a fracture and diffusion into the matrix. Finally, the third is the program r³t that covers the three-dimensional advective, dispersive and diffusive transport including a multiplicity of retention processes. Table 4.1 shows the list of the processes needed to describe the radionuclide transport in a clay formation. It is indicated which processes are included in the programs (yes) and which processes were added during this project (new).

Tab. 4.1: List of FEPs included in the programs CLAYPOS⁹, CHETMAD and r³t¹⁰
 "yes" denotes that the effect was included before the start of this project,
 "new" denotes that the effect was included in the scope of this project and
 "no" denotes that this effect is currently not included

FEP	CLAYPOS	CHETMAD	r ³ t
Probabilistic calculations	new	no	no
Source term	yes	CLAYPOS	CLAYPOS
Solubility limits in source	yes	CLAYPOS	yes
Radionuclide transport in porous media	yes	yes	yes
Diffusion	yes	yes	yes
Element-specific accessible porosity	new	new	new
Element-specific diffusion coefficient	new	new	yes
Anisotropic diffusion	no	no	new
Advection	no	no	yes
Time dependent porosity			no
Anisotropic permeability			yes
Flow-porosity			yes
Dispersion	no	no	yes
Radionuclide transport in fractures	no	yes	no
Transmissivity of fracture		yes	
Fracture geometry		yes	
Matrix diffusion		see above	
"Lifetime" of fracture		no	

⁹ The newly developed code CLAYPOS was based on the existing code GRAPOS. The entries "yes" and "new" in the table refer to the comparison with GRAPOS 2.0

¹⁰ Coupling between r³t and PHREEQC not yet fully implemented

FEP	CLAYPOS	CHETMAD	r ³ t
Colloid-facilitated transport in fractures	no	yes	no
Colloid concentration		yes	
Colloid transport		yes	
Sorption of colloids		yes	
Filtration of colloids		no	
Sorption	yes	yes	yes
Linear adsorption isotherms	yes	yes	yes
Non-linear adsorption isotherms	no	no	yes
Surface complexation	no	no	PHREEQC
lon exchange	no	no	PHREEQC
Solubility limits in transport domain	no	no	yes
Radioactive decay	yes	yes	yes
Gas transport	no	no	no

5 Qualification

The three programmes CLAYPOS, CHETMAD and $r^{3}t$ were developed or enhanced within this project, respectively. The following chapter describes in which ways these three programmes were tested and qualified.

The implementation of the element-specific diffusion coefficients and element-specific porosities in CHETMAD were tested in a very simple way: It was checked whether calculations performed with the original version of CHETMAD - in a way that several independent calculations were performed for each radionuclide with a dedicated parameter set - agreed with a single calculation with the new code including all radionuclides and an element-specific parameter set. As the results were consistent, the new code was verified against the old code.

CLAYPOS and r³t were tested in different ways by the modelling of:

- test cases with known analytical solutions,
- in-situ diffusion experiments carried out under well-known boundary conditions and
- in-situ diffusion profiles developed over geological times in clay formations.

The last two items included the modelling of results from the DI-A diffusion experiment that was performed at Mont Terri and the modelling of an in-situ profile from Benken. Both modelling works were also performed by other groups using their own tested codes, giving the opportunity to compare the results of $r^{3}t$ and CLAYPOS to their results. Some of the work presented in this chapter was performed within the European project FUNMIG¹¹ which was partly co-financed by this project. This work is or will be also described in FUNMIG internal or public reports in almost the same manner. The following sections describe the different calculations which were performed to qualify the developments on CLAYPOS and $r^{3}t$.

¹¹ Fundamental processes of radionuclide migration; Contract FP6-516514

5.1 Analytical test cases

The calculation of diffusion-controlled transport phenomena is of great importance in multiple disciplines of physics, especially in thermodynamics, but also in geosciences. Due to this fact, analytical solutions for diffusion problems for special geometries and boundary conditions are searched for since a long time. The solutions are published in the relevant literature [8, 9, 30] and are used to qualify the codes.

5.1.1 One-dimensional plane geometry



Fig. 5.1: Schematic representation of the one-dimensional plane geometry

The diffusion in a one-dimensional plane geometry with fixed boundary conditions was used as first test case to verify the programs CLAYPOS and $r^{3}t$. This geometry is shown in figure 5.1. The solution for the concentration C(x,t) at time *t* and position *x* is given by:

$$C(x,t) = C_1 + (C_2 - C_1)\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{l} \exp \frac{-Dn^2 \pi^2 t}{l^2} + \frac{4C_0}{\pi}\sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \frac{(2m+1)\pi x}{l} \exp \frac{-D(2m+1)^2 \pi^2 t}{l^2}$$
, (5.1)

where C_1 und C_2 denote the concentrations at the surfaces and *l* denotes the length of the domain. For long times this equation is converging against the linear concentration profile of the steady state:

$$C(x) = \frac{x}{l} (C_2 - C_1) + C_1.$$
(5.2)



Fig. 5.2: Concentration profile for the one-dimensional plane geometry calculated by the programs r³t and CLAYPOS and the analytical solution for 100, 1 000, 10 000 and 100 000 years

Figure 5.2 shows the calculated concentration profiles calculated with CLAYPOS, $r^{3}t$ and the analytical solution for the one-dimensional plane geometry for four selected times. The length of the domain was chosen to be l = 50 m and the diffusion coefficient to be $D = 5 \cdot 10^{-10}$ m²·s⁻¹. It can be seen that the curves from CLAYPOS and r³t are exactly fitting the curve of the analytical solution. For 100 000 years the steady-state described by equation 5.2 is already reached.

To calculate the radionuclide fluxes at the right boundary of the domain, the gradient of the concentration is needed. The flux Q out of the domain with a cross-section of 1 m² using a fixed concentration of $C_2 = 0$ and an initial concentration of $C_0 = 0$ can be calculated from the following analytical solution:

$$Q(t) = \frac{DC_1}{l} + \frac{2DC_1}{l} \sum_{n=1}^{\infty} (-1)^n \exp(-Dn^2 \pi^2 t / l^2).$$
 (5.3)

For $t \rightarrow \infty$ equation 5.3 is converging against

$$Q = \frac{DC_1}{l} \,. \tag{5.4}$$



Fig. 5.3: Flux out of the one-dimensional plane domain versus time

Figure 5.3 shows the flux out of a one-dimensional plane domain versus time as result of calculations with CLAYPOS and r³t as well as the analytical solution after equation 5.3. All fluxes are normalised to the flux which results from the asymptotic value given by equation 5.4. As can be expected from the concentration profiles, the fluxes calculated numerically and the analytical solution fit very well. Additionally, for long times the calculated fluxes trend towards the expected asymptotic value.



Fig. 5.4: Schematic representation of the one-dimensional hollow cylinder geometry

Besides the plane geometry, the program CLAYPOS can also calculate twodimensional geometries having hollow-cylinder symmetry. This problem can be reduced to a one-dimensional problem using cylindrical coordinates. This kind of geometry is shown in figure 5.4. The analytical solution of the concentration in dependence of the time *t* and the radius *r* is given in cylinder-coordinates by:

$$C(x,t) = C_0 + (C_1 - C_0) \left[1 + \frac{2}{\pi} \int_0^\infty \exp(-Du^2 t) \frac{J_0(ur)Y_0(ur_i) - Y_0(ur)J_0(ur_i)}{J_0(ur_i)^2 + Y_0(ur_i)^2} \frac{du}{u} \right], (5.5)$$

where C_1 denotes the concentration at the inner surface, C_0 depicts the initial concentration in the domain and $r_i = d_i/2$ depicts the radius at the inner surface. Furthermore, J_0 and Y_0 represent the first and second kind Bessel functions of integer order.



Fig. 5.5: Concentration profile for the one-dimensional hollow cylinder geometry of CLAYPOS and the analytical solution in one dimension as well as of r³t for the two-dimensional representation

Figure 5.5 shows the concentration profiles calculated with CLAYPOS and the analytical solution for the one-dimensional geometry with cylindrical symmetry for three selected times. The analytical calculations were performed with the program Matlab[®]. Additionally, figure 5.5 shows the concentration profiles calculated with $r^{3}t$. Besides CLAYPOS which uses a one-dimensional geometry in cylindrical coordinates, the program $r^{3}t$ uses a two-dimensional geometry in Cartesian coordinates.

A very good agreement can be observed between the results of the two numerical models and the analytical solution. However, the effort of the computing time for the simulation is very different. The transformation of the underlying radial geometry in Cartesian coordinates requires a high accuracy in the spatial and temporal discretisation. Consequently, this high accuracy requires extended computing times in the order of a day in r³t compared to computing times of less than a minute needed to simulate the same problem using CLAYPOS.

5.2 In-situ diffusion experiments

The aim of in-situ diffusion experiments is to test whether the diffusion coefficients measured on small core samples in the laboratory can be transferred to describe the diffusion process on a larger scale in the formation. This is a kind of up-scaling experiment from the centimetre to the metre scale. In short, the diffusion experiments are carried out in the following way: first, a solution of known chemical composition is filled in a packered section in a borehole drilled into the formation. The concentration decrease of the tracers in the borehole is monitored over a long time. After termination of the diffusion experiment an over-core is drilled with a large diameter and the tracer distribution is determined from measurements on the obtained over-core material. Both experiments in combination allow determining the in-situ diffusion coefficient and porosity.

5.2.1 DI-A experiment

The in-situ diffusion experiment DI-A was performed at the underground laboratory of Mont Terri in the Opalinus Clay by Nagra and the Mont Terri Consortium from 2002 until 2003 [72]. In a borehole with diameter of 76 mm an interval with a length of one metre was isolated with a packer system. This interval, which is further called test chamber had a volume of $4.54 \cdot 10^{-3}$ m³. An external volume was connected to the test chamber, summing up to a total volume of the system of $1.09 \cdot 10^{-2}$ m³. The system was filled with a solution similar to that of the Opalinus Clay pore water. This solution was equilibrated with the clay at the borehole wall. After reaching equilibrium a cocktail of four different tracers was injected into the test chamber. The layout of the diffusion experiment is schematically shown in figure 5.6.

The tracers diffuse through the outer wall of the test chamber into the clay formation. The flux into the formation leads to a concentration decrease of the tracers in the test chamber. The temporal evolutions of the concentrations in the test chamber are monitored by analysing water samples. After termination of the experiment an over-core was drilled with a large diameter and the tracer distribution in the formation can be measured on the obtained over-core material. The temporal evolution of the concentration together allow for a simultaneous determination of both the diffusion coefficient and the diffusion-accessible porosity. If only one set of concentrations is measured, either in the test chamber or in the over-core, only one of both parameters can be determined depending on the estimate of the other parameter.



Fig. 5.6: Schematic representation of the layout of the in-situ diffusion experiment DI-A [73]

In the first phase of the DI-A experiment four tracers were injected into the system: HTO, Na-22, Caesium in the form of CsCI and Iodine in the form of NaI. Figure 5.7 shows the measured temporal evolution of the concentrations in the test chamber as symbols. A more detailed description of the experiment and the modelling carried out within the DI-A experiment can be found in [72, 68]. As described in these publications, for the modelling the programs GIMRT and HYDRUS-2D were used. The parameters were derived from the results of laboratory experiments. The values of the input data used for the modelling in [72] are listed in table 5.1 and the results of the modelling are shown as lines in figure 5.7. For iodine, anion exclusion was assumed reducing the diffusion-accessible porosity by a factor of two. For tritiated water and for iodine no sorption was supposed. The sorption of Na-22 is modelled with linear and caesium with non-linear sorption isotherms.



Fig. 5.7: Temporal evolution of the normalised tracer concentration in the DI-A experiment and modelled data from [73]

	НТО	Na-22	CsCl	Nal
Injected tracer amount	1.7 MBq	22 kBq	1.835 g	16.34 g
Quantity of substance [mol]	1.58·10 ⁻⁹	4.33·10 ⁻¹²	1.09·10 ⁻²	1.09·10 ⁻¹
Concentration [mol/m ³]	1.45·10 ⁻⁷	3.97·10 ⁻¹⁰	1	10
Half-life [a]	12.323	2.603	-	-
Diffusion coefficient [m²/s]	3.18·10 ⁻¹⁰	3.47·10 ⁻¹⁰	5.88·10 ⁻¹⁰	3.47·10 ⁻¹⁰
Porosity [-]	0.17	0.17	0.17	0.085
Sorption model	-	linear Henry	non-linear Freundlich	-
Sorption parameter	-	K _D = 7.1·10 ⁻⁵ m³/kg	a = 3.72·10 ⁻⁴ mol m³/kg b = 0.53	-

Tab. 5.1: Transport parameter values for the modelling of the DI-A experiment [72]

To test the developments made on the programs CLAYPOS and r³t, the temporal evolution of the concentrations in the test chamber and the concentration distributions in the formation were modelled. The results were compared with the experimental data and to the modelling results for the DI-A experiment. The modelling with CLAYPOS was performed using one-dimensional cylinder geometry while the modelling with r³t was performed using a two-dimensional Cartesian geometry, similar to the case presented in the previous section. In contrast to the constant concentration in the test chamber was assumed, here the amount of substances is constant leading to a decreasing concentration.



Fig. 5.8: Temporal evolution of the normalised tracer concentration squared dots: experimental data presented in [73] dashed lines: modelling with CLAYPOS solid lines: modelling with r³t

The results of the modelling of the temporal evolution of the concentrations with CLAYPOS and $r^{3}t$ are shown in figure 5.8. The profile for Caesium could only be modelled with $r^{3}t$, since non-linear sorption is not implemented in CLAYPOS. It can be seen that there exists a good agreement between the measured data from the experiment and the modelled data. There is also a good agreement between the modelling with CLAYPOS and $r^{3}t$ and the modelling presented in [72] and shown in figure 5.7. The deviations between results of $r^{3}t$ and CLAYPOS are due to different inner boundary conditions and are rated not to be relevant.

Figure 5.9 shows the normalised model results of the concentration profiles in the formation after 0.8 years. The results of CLAYPOS and $r^{3}t$ match each other well. A small difference can be seen for the tracer HTO and a distance larger than 0.16 m. This deviation is due to the difference in the outer boundary conditions and the size of the modelled domain. In $r^{3}t$ a domain size of 0.5 m with a closed boundary condition was used. Since the profile of HTO reaches to the outer boundary already after 0.8 years, the closed boundary condition here leads to an increase of the concentration at the outer boundary.



Fig. 5.9: Modelled tracer distribution in the formation versus distance to the borehole dashed lines: modelling with CLAYPOS solid lines: modelling with r³t

Since the individual tracers showed different penetration depths into the formation, the size of the modelled domain has to be chosen according to the tracer with the greatest penetration depth. However, the grid width, i.e. the resolution of the modelling domain has to be chosen according to the tracer with the smallest penetration depth. This leads to the need of large and very highly resolved modelling domains what can exceed memory capacity of the computing system or lead to unacceptable high computing times. This problem can only be overcome in splitting the calculations into different computer runs in which the model geometry is optimized for each tracer. The modelling of caesium with r³t has been performed with a smaller model size of 14 cm, while the other tracers were modelled with a model size of 50 cm

The modelled curves from both programs for HTO, I and Na fit well to the measured concentration distributions that were determined after over-coring of the diffusion chamber and sampling of the core material. The measured data of these samples is presented in [68] and is shown in figure 5.10. For the modelling with CLAYPOS and $r^{3}t$, the transport parameter values from table 5.1 [72] were used, which slightly differ from the ones used in [68], which explains the small differences to the modelling presented there.



Fig. 5.10: Tracer distribution in the rock [68] For lodine two different data sets being calculated with different water contents are shown

Like for the modelling presented in [68], the profile of Cs does not match very well to the measured data, which however shows a high scattering. Nevertheless, the curve for Cs in figure 5.9 shows a shape as expected for a non-linear Freundlich isotherm sorption: the concentration shows a kind of concentration front. On the left to the front the sorption sites are saturated. The dissolved and the sorbed tracer fractions are in equilibrium. Within a short distance, the concentration drops very quickly down to almost zero. As result of the modelling of the DI-A diffusion experiment it is shown that the modelling with both programs CLAYPOS and r^3t was performed successfully. The

results fitted well to the experimental data and to modelling results obtained by other groups with different programs.

5.2.2 DR experiment

The DR experiment was performed by the Nagra within the framework of the European FUNMIG project. The modelling work of the experiment presented in the following was performed by GRS and was co-funded by this project. Therefore the results are also presented in the FUNMIG internal report [54].



Fig. 5.11: Schematic drawing of the borehole equipment of the DR experiment [15] In blue the three intervals are shown (two tracer intervals and one auxiliary interval for hydraulic observations at the bottom)

Figure 5.11 illustrates the setup of the DR experiment. The borehole was drilled at an angle of 45° with respect to the tunnel bottom, such that the bedding is almost perpendicularly intersected. Three test intervals were installed. The one at the bottom serves as an auxiliary interval for the observation of the hydraulic pressure during the experiment. The surface equipment including the reservoir tanks of approximately 20 I each was installed and filled with artificial pore water between March 7 and 9, 2006. On March 16, 2006, the circulation of the artificial pore water through the test intervals was started. Tracer cocktails were injected into the two circuits on April 19, 2006. First, the valves to the test intervals were closed in order to mix the tracers within the surface equipment. On April 20, samples were taken from each circuit, before the valves to the

test intervals were opened. The fluid circulates continuously, such that the water in the tank and in the bottom hole is always well mixed.

The main differences of the DR experiment compared to the DI-A experiment are a shorter test interval and a higher volume of the reservoir tank. These changes were introduced to enable to study the anisotropy of the diffusion and to achieve a higher penetration depth of the strongly sorbing tracers into the formation. Since the test interval is shorter, it cannot be assumed as being long compared to its diameter. Hence it was expected that the limited length of the interval affects the temporal evolution of the tracer distribution and that a correct simulation cannot be performed in a two-dimensional geometry like for the DI-A experiment. Therefore, the DR experiment was modelled by r³t using a three-dimensional geometry.

The geometrical parameter values of the DR experiment are given in table 5.2. In contradiction to the data given in the table, a volume of 20 litres was assumed for the fluid circuit for both intervals in the first prediction calculations. The amount of the tracers injected is given in table 5.3 and the transport parameter values are given in table 5.4. The diffusion coefficient for propagation perpendicular to the bedding was taken 4 times smaller than the one for propagation parallel to bedding; hence the anisotropy ratio was 4.

The non-linear Freundlich isotherm for the sorption of Cs⁺ in table 5.4 is defined in the form $S = a \cdot c^b$, where the parameter *a* has the unit [l^b mol^{1-b} kg⁻¹]. In r³t however, the Freundlich isotherm is defined somewhat different in the form $S = a^* \cdot c^{b-1}$, where the parameter a^* has the unit [m³ kg⁻¹]. The parameter a^* needed as input parameter for r³t can be calculated from the parameters *a* and *b* by

$$a^* = (1 \cdot 10^{-3})^b \cdot a. \tag{5.6}$$

The parameter b is identical for both cases.

Property		Value
Borehole radius	[mm]	38.0
Local dip angle	[°]	45
Dip angle w/r to borehole	[°]	0
Borehole length to upper interval	[m]	8.27
Length of upper tracer interval	[m]	0.15
Distance between upper and lower interval	[m]	0.40
Length of lower tracer interval	[m]	0.15
Distance between lower and auxiliary interval	[m]	0.40
Length of auxiliary interval	[m]	0.13
Volume of circuit fluid for upper interval	[1]	20.583
Volume of circuit fluid for lower interval	[1]	20.174

 Tab. 5.2:
 Geometrical parameter values of the DR experiment

Tab. 5.3: Amount of tracers injected in the DR experiment

Eu-152, Se-75, and O-18 shall be added at a later stage. It seems that Br was added at a lower concentration than previously planned.

Interval	Tracer		Concentration
Upper	Co-60	[Bq·l ⁻¹]	4.09·10 ²
	Ba-133	[Bq·I ⁻¹]	8.69·10 ²
	Cs-137	[Bq·l ⁻¹]	3.05·10 ²
	HDO	[‰]	+155.5
Lower	Na-22	[Bq·I ⁻¹]	1.16·10 ³
	Sr-85	[Bq·l ⁻¹]	3.93·10 ³
	Cs	[mg·l ⁻¹]	24.7
	Br	[mol·l ⁻¹]	9.44·10 ⁻⁴
	I	[mol·l ⁻¹]	8.88·10 ⁻⁴
	НТО	[Bq·l ⁻¹]	1.24·10 ⁵

Tab. 5.4: Transport parameter values for scoping calculations of the DR-experiment estimated from previous laboratory or field experiments, D_p is the pore diffusion coefficient, $D_e = n \cdot D_p$ the effective diffusion coefficient, n the accessible porosity, K_d the solid/liquid distribution coefficient, τ the half-life

Tracer	D _p [m ² ·s ⁻¹]	D _e [m ² ·s ⁻¹]	n [-]	K _d [m ^{3.} kg ⁻¹]	τ [a]
HDO	3.33·10 ⁻¹⁰	5.0·10 ⁻¹¹	0.15	0	stable
HTO	3.33·10 ⁻¹⁰	5.0·10 ⁻¹¹	0.15	0	12.323
F	2.00·10 ⁻¹⁰	1.6·10 ⁻¹¹	0.08	0	stable
Na-22⁺	4.67·10 ⁻¹⁰	7.0·10 ⁻¹¹	0.15	2.048·10 ⁻⁴	2.602
Sr-85 ²⁺	4.67·10 ⁻¹⁰	7.0·10 ⁻¹¹	0.15	1.30·10 ⁻³	0.1777
Ba-133 ²⁺	4.67·10 ⁻¹⁰	7.0·10 ⁻¹¹	0.15	1.30·10 ⁻³	10.5
Cs-137 ⁺	2.00·10 ⁻⁰⁹	3.0·10 ⁻¹⁰	0.15	0.55	30.17
Cs⁺	2.00·10 ⁻⁰⁹	3.0·10 ⁻¹⁰	0.15	S = 0.186 C ^{0.53}	stable
Co-60 ²⁺	2.00·10 ⁻⁰⁹	3.0·10 ⁻¹⁰	0.15	0.55	5.272

The geometry and the grid of the $r^{3}t$ model are shown in figure 5.12. The grid is nonuniform with a higher density around the test interval to enhance numerics. The grid has about 183 000 nodes and 1 051 450 elements. Due to the high number of grid elements one calculation last about one to three weeks, depending on the number and type of tracers considered. The calculation for non-linearly sorbing tracers is even more time consuming than for linearly sorbing ones.

Figure 5.13 shows a cross-section of the propagating tracer plume. The anisotropic diffusion of the tracer can be clearly seen. As expected, the extension of the plume perpendicular to the drilling is much larger than parallel to the drilling. The predicted temporal evolution of the tracer concentrations in the borehole is shown in figure 5.14. The sequence of the different tracers is the same as in the DI-A experiment. Iodine is the tracer with the lowest concentration decrease in the borehole. The non-linearly sorbing Cs is decreasing somewhat faster than the linearly sorbing one. The fastest decrease can be observed for Sr-85 due to the small half-live of the tracer. Sr-85 is predicted to have nearly vanished after only one and a half years. The influence of the radioactive decay can also be seen for the two tracers HTO and HDO, which have the same transport properties, but HTO has a half-life of about 12.3 years, while HDO is stable. As mentioned before, the short length of the test interval was believed to influence the temporal evolution of the tracer concentration in the borehole. This was the reason why a three-dimensional model was used in the $r^{3}t$ simulations. To study the effect of the short borehole length on the evolution of the concentration an additional simulation was performed using a two-dimensional model. The comparison of the results from both simulations for four selected tracers can be seen in figure 5.15. As one expects, the decrease in the concentration is always faster in the three-dimensional model than in the two-dimensional one. This is due to the additional diffusion in the z-direction of the three-dimensional model.

However, the difference is not very large and is even below 10% after two years of diffusion time. At the current stage of the project it can be doubted that the accuracy of the experimental data will allow to resolve this difference. The reason that there is only a small difference found between both models is the experimental alignment of the borehole, which is perpendicular to the bedding. Due to this setting, the main direction for the diffusion is in radial direction relative to the borehole. The diffusion in z-direction of the borehole - which causes the difference between both models - is lower by a factor of five. A borehole parallel to the bedding therefore should have led to a higher effect. However, the favourable setup of the borehole parallel to the bedding was not possible because of technical reasons, since this would maybe have lead to a collapse of the borehole.


Fig. 5.12: Geometry and grid of the r³t model



Fig. 5.13: Shape of the propagating tracer plume in the DR experiment



Fig. 5.14: Predicted temporal evolution of the borehole concentration



Fig. 5.15: Comparison of the borehole concentration received by the 2D and 3D models dotted lines: 2D model solid lines: 3D model

5.3 Natural tracer profiles

In low-permeable clay formations characteristic profiles of natural tracers have developed in the pore water over the geological past. Corresponding profiles of H-2, O-18, Cl⁻, Cl-36 and He-4 have been measured in the Opalinus Clay at the locations of Mont Terri [45, 52] and Benken [39, 22]. These profiles result from the fact that over the geological past the concentration of these tracers in the groundwater of the adjacent aquifers has changed compared to the concentration in the pore water of the clay formation. According to the concentration gradient a diffusive flux is established, transporting the tracer into or out of the clay formation. The result is a mixture of the formation water initially present and the water penetrating from the adjacent formations. The shape of the profile is determined by the transport process and its boundary conditions.

Accordingly, the concentration profiles observed today allows to draw conclusions on the type of transport process and on the transport parameters, if the hydrogeological boundary conditions are sufficiently well known. The natural tracer profiles therefore can be used as natural analogue for the transport of contaminants in the clay formation over long timescales. The tracer profiles are again some kind of "natural" up-scaling experiment from the scale of one metre in the in-situ diffusion experiments up to several tens of metres on the formation scale. The modelling of the tracer profile can yield a large scale diffusion coefficient averaging all small scale heterogeneities.

To test the program $r^{3}t$, the profiles of the dissolved Helium concentration and the concentrations of the stable water isotopes H-2 and O-18 in the pore water of the Opalinus Clay at the locations of Benken and Mont Terri were modelled. This work was partly performed within the project FUNMIG which was co-financed by this project and is presented in the same way, there [55]. Besides testing $r^{3}t$, an additional goal was to test, whether a higher complexity in the model provides a better agreement of the simulation with the measured data.

The Opalinus Clay is a marine sediment which has been deposited in the Aalenium, about 180 million years before present. By compaction and consolidation the Opalinus Clay formation was altered and presently possesses a thickness of 80 to 120 m [45]. This formation is considered as potential host rock for a waste repository for long-lived and high-level nuclear waste [38]. Additional information about the Opalinus Clay is also given in section 7.3.

5.3.1 Benken

Benken is located in the Züricher Weinland, about 6 km south of Schaffhausen. This site was studied by the Nagra in the "Project Opalinus Clay" to demonstrate the principal disposal feasibility of high-level waste in the Opalinus Clay [38]. As one part of the project, an exploration drilling was carried down to examine the geological und hydrogeological boundary conditions and to perform borehole tests. Figure 5.22 shows a small section out of the full lithological sequence as it was found at the location of the



Fig. 5.22: Geology at the location of Benken after [39].

drilling, where the Opalinus Clay as potential host rock was found to be located in depths between 539 to 652 m and having a thickness of 113 m.

Among other examinations, also measurements of the isotope content of the pore water were performed on drill-core samples from the section of this drilling shown in figure 5.22. Additionally, measurements of the isotope content of the groundwater that stems from the aquifers of the Malm and Sandsteinkeuper have been performed [39, 51].

The profiles measured in these studies were simulated by Gimmi et al. [21, 22] to determine the transport process for contaminants dissolved in the pore water of the Opalinus Clay. It was found that the transport in the Opalinus clay is exclusively diffusive. The measured isotope profiles and the modelling performed within the framework of the Project Opalinus Clay are used in the following to do a comparison with the modelling using the program r^3t .

The isotope ratios of O-18 to O-16 and H-2 to H-1 in the water molecule are often examined in hydrogeological studies and are well know under the term "stable isotopes". The isotope content of the water is given in per mil deviation relative to the isotope content of the standard mean ocean water (SMOW). As constituent of the water molecule, the stable isotopes take part in the hydrological cycle. The isotope content is affected by the climatic conditions during the groundwater recharge. According to the changes in climatic conditions and the changes from marine to meteoric conditions or vice versa, the isotope content in the groundwater of the aquifers adjacent to the Opalinus Clay is changing and the isotopes are diffusing in or out of the Opalinus Clay pore water. This results in a characteristic isotope concentration profile in the pore water of the Opalinus Clay reflecting the climatic changes in the past.





Figure 5.17 shows as symbols the measured depth profile of the isotope concentration in the pore water of the Opalinus Clay formation at the location of Benken. In the inner part of the formation (layers A2 - A5) the value for the isotope concentration is higher than in the aquifers of the Malm (A1) and Sandsteinkeuper (A8) above and below the formation. This can be explained as remains of old formation waters present in the formation. At the boundary to the aquifers a transition profile is evolving which results from the ongoing transport of heavy isotopes out of the formation to the aquifers and of lighter isotopes from the aquifers into the formation. Besides the measured data, figure 5.17 also shows the results from the modelling with $r^{3}t$. In these modelling only diffusion was considered as transport process for both isotopes using a diffusion coefficient of D = $1 \cdot 10^{-10} \text{ m}^{2} \cdot \text{s}^{-1}$. The modelled profiles fit best to the measured data for a model time of 0.5 million years for H-2 and for a model time of one million years for O-18. The modelled profiles for both isotopes agree very well with the results of the modelling performed by another group [22].





Figure 5.18 shows the results of a modelling examining the influence of an advective flow through the Opalinus Clay perpendicular to the bedding. The curves are plotted for a model time of 0.5 million years. The simulation varies on both, the advective flow velocity the flow direction. Negative values of flow velocities indicate a flow directed upwards. An advective flow velocity of only $2 \cdot 10^{-12} \text{ m} \cdot \text{s}^{-1}$ already leads to a significant deformation of the profile. Therefore, the advective flow velocity at the location of Benken is believed to be smaller than this value. An assumed flow velocity one order of magnitude higher than in the previous simulation leads to a nearly complete replacement of the heavier isotopes in the formation by lighter isotopes from the aquifer. These simulations also agree very well with the simulations presented in [22].

5.3.2 Mont Terri

The Mont Terri rock laboratory is located in north-western Switzerland, in the Swiss Jura. It is situated in a side gallery of a motorway tunnel of the A16 that intersects an overthrust anticline of the Folded Jura between the cities St. Ursanne and Courgenay. The formation of interest is the Opalinus Clay.

Due to the movement of the Alps in the late Miocene (upper tertiary) the upper sediment layers of the alpine foreland und the Jura were shifted northwards over the immobile basis. In the area of the Folded Jura, the northern front overthrusted the Tabular Jura what resulted in the development of the Mont Terri anticline. During this process the layers of the Opalinus Clay were sheared and tilted, resulting in a dip of the Opalinus Clay strata of about 45° towards southeast in the area of the underground laboratory. The anticline was heavily eroded in the area of the Mont Terri during the geological past, so the Opalinus Clay and the adjacent formation crop out at the surface nowadays. A geological cross-section of the Mont Terri is shown in figure 5.19.



Fig. 5.19: Simplified geological cross-section through the Mont Terri after [45]

In the following sections, the profiles of the natural tracer concentration of Helium and the stable isotopes in the pore water of the Opalinus Clay at Mont Terri are examined and modelled. This is done to test the program $r^{3}t$, but furthermore to test whether an enhancement of the complexity of the model results in a better understanding of the profiles.

5.3.2.1 Helium

During groundwater recharge, in the unsaturated zone the atmospheric Helium is dissolved according to its solubility in the groundwater. The Helium concentration in young groundwater is in the order of $5 \cdot 10^{-8}$ cubic centimetres of dissolved He-4 per gram pore water (ccSTP⁴He·g⁻¹) [71]. As soon as the groundwater is transported into deeper horizons, it is isolated from the atmosphere and hence the dissolved atmospheric Helium component remains constant. Additionally to this atmospheric Helium component, Helium from other sources can be accumulated in the deeper groundwater horizons.

One common source is radiogenic Helium, i.e. Helium that stems from radioactive decay. The main sources for radiogenic Helium in the underground are the Uranium and Thorium isotopes which are ubiquitous in all rock material. Helium atoms are generated by the α -decay of Uranium and Thorium and some of their daughter products which are released from the rock matrix into the ground- and pore water, increasing the Helium concentration in the water. The maximum Helium concentration in the pore water is depending both, on accumulation time, i.e. the residence time of the water and consequently on the advective transport velocity of the water and on the diffusive transport of the Helium itself. The Helium produced in the clay and its accumulation in pore water permits conclusions about the type of transport process in the formation. This can be regarded as natural analogue for contaminants which are released from a waste repository in the clay formation.

Figure 5.20 shows the measured Helium concentration in the pore water of the Opalinus clay versus the position in the rock laboratory tunnel. Additionally, this figure shows a fitted model curve. The profile was described in [52] as a steady-state between the in-situ production of Helium in the formation and its diffusive loss into the adjacent aquifers: Due to the accumulation of the produced Helium its concentration in the pore water is increasing. In the adjacent aquifers young groundwater is circulating with Helium content close the atmospheric solubility equilibrium. As result of the increasing concentration gradient between the pore water in the Opalinus Clay and the groundwater in the adjacent aquifers, Helium is diffusing out of the clay into the aquifers. At a certain time, steady-state is reached between the production in the formation and the loss into the aquifers. From that moment on, the profile does not change anymore. The Helium profile found at Mont Terri has already reached this steady-state. In

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this case, the profile can be described under the assumption of a formation with homogenous transport properties [6] by:

$$C(x) = \frac{A}{2D} \left(Lx - x^2 \right) + C_0, \qquad (5.7)$$

where $A = 1.1 \cdot 10^{-11} \text{ ccSTP} \cdot \text{g}^{-1} \cdot \text{y}^{-1}$ denotes the production rate of Helium in the formation, $C_0 = 5 \cdot 10^{-8} \text{ ccSTP} \cdot \text{g}^{-1}$ denotes the Helium concentration in the adjacent aquifers and L = 189 m denotes half of the transport distance. As can be seen in figure 5.19 the Opalinus Clay formation is inclined relative to the tunnel, so the thickness of the formation is smaller than the measured distance in the tunnel. For the one-dimensional model according to equation 5.7 a constant angle of incline of 45° was assumed resulting in an effective transport distance for the diffusion perpendicular to the bedding of about $2^{-1/2}$ times the distance in the tunnel. A parabolic fit on the data according to equation 5.7 yields a diffusion coefficient of $D = (3.5 \pm 1.3) \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ [52].





In reality, the angle of incline of the formation relative to the tunnel is not constant throughout the whole formation. To take this into account, the profile of the Helium concentration was modelled with $r^{3}t$ for a two-dimensional geometry. In figure 5.21, the ge-

ometry used is shown schematically. The formation is divided into different facies each having a specific angle of incline relative to the tunnel. The angle of incline is stepwise changing from a value of 55° at the transition of the Dogger to the Opalinus Clay at a tunnel position of 781 m to a value of 30° in the Lias at a tunnel position of 1 100 m.



Fig. 5.21: Geometry for r³t to model the Helium profile (not to scale)

In the first step, the transport parameter values were chosen to be uniform for the whole model. The diffusion coefficient was taken as $D = 3.5 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ and the porosity as 0.16. Figure 5.22 shows the Helium concentration along the tunnel calculated with r³t under the assumption of homogenous transport parameter values as blue curve (1). The boundaries of the model were assumed to be located at 755 m and 1 126 m of the tunnel position. The value of 755 m differs somewhat from the value received by the parabolic regression. This causes a small shift of curve (1) relative to the black curve of the 1D model. The maximum of the curve (1) is located at about 915 m. All subsequent curves calculated with r³t in the following have to be compared to curve (1).

Curve (1) in figure 5.22 shows a small asymmetry which is due to the variable angle of incline of the formation. Figure 5.23 shows a two-dimensional representation of the Helium distribution in the model area. From this figure it can be seen that due to the variable angle of incline, the Helium concentration isosurfaces are not parallel to the boundaries of the model causing the asymmetry of the simulated concentration profile.





- (1) homogenous transport parameter values
- (2) variable porosity, isotropic diffusion
- (3) variable porosity, anisotropic diffusion

In a second step, the specific porosities of the different facies were considered. The porosity for each of the facies was assigned the mean value of the data from [52] and some of the values given in [45]. These mean values are compiled in table 5.5. The numbers of the materials given in table 5.5 correspond to the ones in figure 5.21. The green curve (2) in figure 5.22 shows the result of the simulation with facies-dependent porosities. The main differences between the simulations with homogenous (1) and facies-dependent (2) porosities are a higher maximum value and a kink at the transition between the facies M5 and M6. The higher maximum is due to the lower porosity in the outer layers of the model which results in a slower transport. The kink in the curve corresponds to a discontinuity in the porosity value at this position.

As third step of the modelling with $r^{3}t$, anisotropic diffusion was accounted for besides the facies-dependent porosities. The anisotropy ratio was chosen to be 5 according to the value determined for the Opalinus Clay [38]. Furthermore, the diffusion coefficient was chosen in a way that for an angle of incline of 56° the effective diffusion coefficient in x-direction of the model area corresponds to the diffusion coefficient chosen for modelling the isotropic case with a value of $3.5 \cdot 10^{-11} m^{2} \cdot s^{-1}$. Both assumptions give a diffusion coefficient parallel to the bedding of the Opalinus Clay of $1.5 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ and perpendicular to bedding of $3.0 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$.



Fig. 5.23: Two-dimensional representation of the Helium distribution in the model a-rea

The result of this simulation is shown as orange curve (3) in figure 5.22. Taking the anisotropic diffusion into account causes another modification of the shape of the modelled curve. While the position of the maximum of the curve is shifted only slightly, the shape of the left side of the curve is changed remarkably. The reason for this change can be seen from the two-dimensional distribution of the Helium concentration shown in figure 5.24. The anisotropy with a higher diffusion coefficient parallel to the bedding compared to that perpendicular to the bedding leads to the fact that the surfaces of equal Helium concentration now are aligned more parallel to the bedding as without regarding the anisotropy as shown in figure 5.23. Since the angle of incline is changing at most on the left side of the model this effect mainly affects the curve at this position and leads to an asymmetric shift of the left part of the curve.



Fig. 5.24: Two-dimensional representation of the Helium distribution in the model area with taking anisotropy into account

Tab. 5.5: Porosity of the different facies

Material	Name	Porosity [%]
MO	Lower Dogger	7.9
M1	OPA Sandy	13.5
M2	OPA Shaly	17.1
M3	OPA carbonate-rich	15.3
M4	Main fault	-
M5	Jurensis Marl	16.4
M6	Posidonia Shale	12.6
M7	Obtusus Clay	12.8
M8	Gryphaea Limestone	18.3

The numbers of the materials correspond to the ones in figure 5.21

A comparison of all four simulations for the Helium profile shows that the simplest one, the one-dimensional model delivers the best fit to the measured data. The simulation with variable porosity shows the largest deviation from the measured data, while the consideration of anisotropic diffusion smoothes out the effect of facies-dependent porosity. For the modelling of the Helium profile, a higher complexity of the model did neither lead to a better agreement of the modelled curve and the measured data nor to a better insight into the transport parameter values of the formation.

5.3.2.2 Stable Isotopes

The modelling of the stable isotope profile is much more difficult to manage than the modelling of the Helium profile. While the boundary conditions of the Helium profile are more or less well defined by the solubility of Helium in the young surface groundwater, for the modelling of the stable isotope profiles the palaeohydrogeological background has to be known much better. In most cases this background, however, is not well known.

At the Mont Terri, marine conditions have prevailed between 30 and 10 million years before present [45]. It is assumed that this period was sufficient to impress the isotopic signature of the seawater on the existing pore water in the Opalinus Clay. Therefore, an isotopic signature of 0 ‰ for both isotopes is assumed as initial value after this period of time. In the following ten million years the region around Mont Terri was

slowly uplifted and the overlying formations were eroded. It is not completely defined when the change from marine to meteoric conditions occurred.

For the modelling of the stable isotope profile it is assumed in the first case that in both aquifers above and below the Opalinus Clay formation meteoric conditions prevailed from ten million years before up to present time. The differences in the climatic conditions like the change between warm and glacial periods are not taken into account. It is rather assumed that over the whole ten million years the same isotopic signature like today prevailed in both aquifers.





triangles: measured O-18 data plotting on right axis

squares: measured H-2 data plotting on left axis

- 1D = one-dimensional analytical solution of diffusion profile
- (1) = $r^{3}t$ simulation with homogenous transport parameter values
- (2) = $r^{3}t$ simulation with facies-dependent porosity and isotropic diffusion
- (3) = $r^{3}t$ simulation with homogenous porosity, different boundary condition
- (4) = $r^{3}t$ simulation with facies-dependent porosity and anisotropic diffusion

Figure 5.25 shows the measured stable isotope content in the pore water of the Opalinus Clay at Mont Terri. All concentration values found are isotopic heavier than those of modern groundwater which are indicated by the blue line. The concentrations of the isotopes in the samples are the higher the distant from the borders of the Opalinus Clay formation. In [52] the profile is explained as a result of mixing of the formation water initially present in the pore water and the meteoric waters penetrating from the adjacent formations.

Figure 5.25 shows the result of a one-dimensional analytical model according to equation 5.1 as black line. As boundary condition at distances of 725 and 1 122 m the isotope content was held constant at the Holocene isotope signature. In contrary to the Helium profile, there is no source of stable isotopes in the inner of the formation. The transport is going on until in the steady-state the profile shows a constant Holocene signature everywhere. Until now, the pore water of the Opalinus clay has lost about 75 % of its initial content of heavy isotopes.

Using the program $r^{3}t$ four additional cases were modelled. The first two correspond to the ones of the modelling of the Helium profile. The first simulation accounts for homogenous porosity (1) and the second simulation for facies-dependent porosity (2). Like for the Helium profile it can be seen that the facies-dependent porosity leads to a slower transport and consequently leads to a higher maximum of the profile.

The third simulation (3) accounts for homogenous porosity, but different boundary conditions. Instead of the Holocene isotope content that of two water samples from 721 and 1 120 m, which show a small deviation from the Holocene isotope signature were used as boundary condition. The result shown as curve (3) in figure 5.25 shows a better agreement between the model and the measured data at the boundaries.

The last simulation which is shown as curve (4) accounts for facies-dependent porosity, for anisotropic diffusion and for the different boundary conditions. Like for the Helium profile this curve shows that the anisotropy leads to an asymmetric deformation of the profile shape. This is expressed in a higher deviation of the curve from the measured data in comparison with the curve for the case with neglected anisotropy.

For the stable isotopes, none of the simulations can be valued to better fit the data than another curve. Like for the simulation of the Helium profile, a higher complexity of the model neither gives a better fit to the data nor does it provide a better understanding of the real transport process.

5.4 Alkaline plume

Some concepts for waste repositories include the storage of cemented waste forms as e.g. the concept of the Nagra in Switzerland [38] or use concrete linings to support the emplacement tunnel walls as e.g. the concepts of Andra in France [2] and NIRAS/ONDRAF in Belgium [42]. The pore water in the cement is highly alkaline what can result in the propagation of the alkaline water into the surrounding clay formation by diffusion of hydroxide ions. The alkaline plume causes a change of the pore water chemistry in the clay formation. This may also alter the sorption of the radionuclides. The coupling of r^3t with the geochemical code PHREEQC was tested by modelling the propagation of an alkaline plume in a clay formation. The objective of this modelling was not to achieve new scientific results like in the previous sections, but to verify r^3t by demonstrating that the result from the standalone application PHREEQC and the coupled program r^3t are in agreement.



Fig. 5.26: Schematic representation of the one-dimensional geometry for the propagation of the alkaline plume

Figure 5.26 shows the schematic representation of the one-dimensional geometry used to model the propagation of the alkaline plume. The composition of the alkaline water at the left boundary was assumed to be constant (solution 0) and the initial composition of the pore water (solution 1) to be uniform in the whole model area. The right side of the model was chosen as closed boundary condition. The chemical compositions of solution 0 and solution 1 are given in table 5.6.

The length of the model area is 5 m. The area is divided in a rectangular grid and the length of each grid cell is 0.125 m leading in a total number of 40 cells. PHREEQC

uses a real one-dimensional model, while $r^{3}t$ uses a two-dimensional model with constant transversal properties. The width of the $r^{3}t$ model is 1 m.

The composition of the alkaline water (solution 0) was chosen according to the concrete pore water given in [19]. The composition of solution 1 was chosen according to the Opalinus Clay reference water as given in [10]. The equilibrium phases were chosen according to the definition in [19], while the exchange species and exchange rates were chosen according to [10]. The full PHREEQC input file giving the exchange data is given in Appendix D. As thermodynamic database the standard PHREEQC database "Ilnl.dat" was used with the amendments defined in [19].

Two different cases were studied for the comparison between PHREEQC and the coupled r³t; the first cases accounts for simple advective flow, while the second accounts for simple diffusive flux. Both cases were simulated with r³t and with the PHREEQC internal transport code. The results were compared by means of the pH-value profiles in the model area.

	Solution 0	Solution 1
рН	12.5	7.24
ре	4.0	-2.83
AI	0.0	1.78·10 ⁻⁸
С	0.0	0.0
Са	2.19·10 ⁻²	1.05·10 ⁻²
CI	3.03·10 ⁻²	1.63·10 ⁻¹
Fe	0.0	4.33·10 ⁻⁵
К	2.21·10 ⁻²	5.65·10 ⁻³
Mg	0.0	7.48·10 ⁻³
Na	8.02·10 ⁻³	1.69·10 ⁻¹
S	1.20·10 ⁻⁴	2.40·10 ⁻²
Si	3.01·10 ⁻⁵	1.78·10 ⁻⁸
Sr	0.0	3.04·10 ⁻⁴

 Tab. 5.6:
 Chemical conditions [-] and concentrations [mol/kgw] in the solutions for the test case of the propagation of an alkaline plume

Advective flow

In this test case an advective flow was assumed from the left to the right hand side of the model. The transport velocity was chosen such that the Courant number is 1, i.e. the value of the flow velocity is defined by the length of the grid cell of the grid divided by the length of the time step width. In this case, dispersion is neglected. This means that the liquid content of each grid volume of the grid is fully replaced by that of its left neighbour in each time step. Within PHREEQC advective flow is calculated that way if the codeword "advection" is used. Additionally the code word "transport" is used to define the advective flow in an alternative simulation. The appropriate input files for PHREEQC are given in the Appendix D.

The pH-value profiles in the pore water after the three different calculations are shown in figure 5.27 for 10 and 100 time steps. The result from r³t exactly matches the result of PHREEQC with the "advection" option. This shows that the coupling between r³t and PHREEQC works like expected. The difference to the PHREEQC calculation using the code word "transport" is mainly due to the fact that the result is given for a different position, there.



Fig. 5.27: Comparison of profiles of pH-value calculated with r³t and PHREEQC for the test case regarding advective flow

Diffusive flux

The second case accounts for simple diffusive transport. For that, no exact agreement between the simulation results of r³t and PHREEQC can be expected due to principle differences in the implementation of the transport in the codes; r³t uses an implicit and PHREEQC an explicit algorithm to calculate the diffusive flux. The time step width used within PHREEQC code to calculate diffusion is determined by

$$\Delta t = \frac{(\Delta x)^2}{3D},\tag{5.8}$$

where *x* denotes the length of the grid cell and *D* for the diffusion coefficient. Using a diffusion coefficient of $1 \text{ m}^2 \cdot \text{s}^{-1}$ and a grid width of 0.125 m a time step of about $5 \cdot 10^{-3}$ seconds is calculated. The time step width used for the simulation with r^3 t is about one order of magnitude longer.

The boundary condition on the left boundary was chosen differently in both simulations. PHREEQC uses a boundary condition of the first kind, also called Diriclet boundary condition, where the concentration is held constant for all times in a virtual 0th cell. The concentration in the first cell of the domain is calculated by mixing the 0th cell and the 1st cell resulting in the value at the left border varying slightly. In r³t a boundary condition of the third kind, called leaching boundary condition in the r³t documentation, was used where the flux at the left boundary is proportional to ($C - C_{ref}$), where C_{ref} denotes the desired concentration at the boundary.

The pH-value profiles in the pore water for four different numbers of time steps obtained by the two programs are directly compared in figure 5.28. Figures 5.29 and 5.30 additionally show the results of the two programs separately. For distances from the boundary greater than about half a metre, the results of both programs match each other very well. The difference for distances less than half a metre are due to the different boundary condition. The chemical buffering reaction dominates over the diffusive flux, pulling down the pH-value after each reaction step. An output of the data after the transport step would lead to higher pH-values at the left boundary in figure 5.30. After the buffering capacity in the clay is exceeded, the pH-value increases to the expected values.



Fig. 5.28: Profiles of pH-value calculated with PHREEQC and r³t for the test case regarding diffusive flux solid lines: r³t dashed lines: PHREEQC



Fig. 5.29: Profiles of pH-value calculated with PHREEQC for the test case regarding diffusive flux



Fig. 5.30: Profiles of pH-value calculated with r³t for the test case regarding diffusive flux



Fig. 5.31: Profiles of Gypsum content in the equilibrium phase calculated with PHREEQC and r³t for the test case regarding diffusive flux solid lines: r³t dashed lines: PHREEQC

Figure 5.31 shows the profiles of the Gypsum content in the equilibrium phase calculated by $r^{3}t$ and PHREEQC. The black horizontal line shows the initial Gypsum content of about 0.1 mol·g⁻¹. Gypsum is dissolved by the propagating alkaline plume. In regions of an increased pH-value, the Gypsum content in the equilibrium phase is found to be zero. For the time step 5 the alkaline plume has propagated up to about 2 m as can be seen in figure 5.28. Accordingly, the Gypsum content is found to be zero at distances less than 2 m and is slowly increasing up to the initial value for larger distances. For long times, the PHREEQC simulation shows that in the steady state Gypsum is completely dissolved in the steady state in the whole area. For the $r^{3}t$ simulation an increase of the content at the left boundary can be seen resulting in a steady-state value of about 0.03 mol·g⁻¹. The reason for this precipitation of Gypsum at the left boundary is not clear without ambiguity and has to be further studied in the future. It might be either related to the different boundary condition or to a numerical instability of the coupling.

5.5 Résumé

Both of the codes CLAYPOS and r³t were compared to analytical solutions for test cases with plane and cylindrical geometry. For all cases it could be shown an exact agreement between both programs and to the analytical solution of the spatial and temporal evolution of the concentration distributions. The fluxes of the contaminants were found to agree with the analytical solutions, too.

Additionally, both codes were used to model two in-situ diffusion experiments performed by Nagra at the Mont Terri underground laboratory. These are the DI-A and the DR experiments. In the case of the DI-A experiment a good agreement of the simulations with the experimental data was found as well with the simulations obtained by other groups. The DR experiment was not completed at the time when this report was written. The modelling is not compared to experimental data, but it could be shown that the simulation of the DR experiment is possible in principle and the differences between a 2D- and a 3D-simulation were shown.

The modelling of the profiles of stable isotopes from Benken shows a good agreement between the results of $r^{3}t$ and codes used by other groups. The investigation of the natural tracer profiles in the pore water of the Opalinus Clay at Mont Terri shows that a modelling with $r^{3}t$ is generally possible. However, the modelling shows that a higher

degree in complexity does not improve the agreement between the simulations and the experimental data. At the time being, two explanations for that can be given:

- On the one hand it is possible that the model on which the simulations are based on is still not complex enough and that the most relevant influences on the profile are still not included in the model. These might be for example the variability of the Helium production rate or the palaeohydrogeological history of the stable isotopes. However, for the Benken site the Helium production rate was found to be almost uniform.
- On the other hand it is possible that the complexity of the model is too high and does not correspond with the level of detail and the quality of the input data. This may generate artefacts in the profiles which do not correspond to reality. This for example could apply to the angle of incline, which is well known in the underground laboratory and in the region around the tunnel, but only poor information exists about its extension into the inner parts of the clay formation.

We currently trend to the second explanation. The main reason for this decision is the good agreement of the simple, one-dimensional models and the measured data. The high heterogeneity of the transport properties (on a small scale however) and the high anisotropy tends to flatten out the variability on a larger scale.

The coupling of $r^{3}t$ with the geochemical code PHREEQC was not finished within the bounds of this project. The current development state was tested by modelling the propagation of an alkaline plume into a clay formation. In most cases, the results of the coupled version of $r^{3}t$ were found to acceptably agree with that of PHREEQC. Some differences were found that were due to fundamental differences in the implementation of the boundary conditions. The simulation performed for the test cases also revealed some problems of convergence in the PHREEQC simulation which are not fully understood and caused the calculation to terminate. The reasons for these problems and possible measures have to be identified in the future. However, the principal feasibility of the coupling between $r^{3}t$ and PHREEQC could be successfully demonstrated by these examples.

6 Model geometry

The modelling of the radionuclide transport from a waste repository performed within the framework of a long-term safety assessment requires a high level of abstraction and simplification. This applies in particular to the geometrical realisation of the long-term safety assessment model. However, it always has to be proven that the simplification leads to a conservative result, i.e. that the radionuclide fluxes are never underestimated by the simplified model. The possible degree of detail of a three-dimensional model is restricted on the one hand by the available memory of the computing system. An inadequate high degree of detail additionally leads to inefficient long computing times. In a long-term safety assessment a large number of simulations have to be performed. Starting from a few different calculations for parameter variations, one may need up to one thousand computing runs for probabilistic calculations. Due to the necessary abstraction to reduce the computing times, the calculations for the long-term-safety assessment are performed with the one-dimensional program CLAYPOS, while r³t is used to verify the reference case and to examine special questions.



Fig. 6.1: Schematic representation of the radionuclide transport in a waste repository in a clay formation

Figure 6.1 shows the schematic representation of the diffusive radionuclide transport from the containers to the overlying aquifer. To reduce the complexity of the model an advantage is taken from the symmetry of the container arrangement in the waste repository. This can be achieved by not modelling of only a small subset; a representative section of the repository instead of all containers in the whole waste repository. In a repository concept envisaging drift storage as shown in figure 6.1, the representative section may consist of only one single container and a related host rock region. However, there are different ways to transfer the real geometry in a one-dimensional abstraction.

Figure 4.1 on page 36 shows the two geometries implemented in CLAYPOS for the diffusive transport from the container to the overlying aquifer. In both geometries, the height of the column is the distance from the container to the aquifer, but the crosssection for diffusion and the area of the source are different. The first CLAYPOS geometry is the plane geometry. It can account for different materials with different parameter values for transport properties like the diffusion-accessible porosities, but the cross-section in the whole model is constant. The radionuclide source is distributed over the whole area. This is expected to overestimate the diffusive flux which is proportional to the cross-section.

The other geometry implemented in CLAYPOS is the cylindrical-symmetric geometry. The cross-section for diffusion is constantly growing from the inner towards the outer part of the model region. The cross-section at the inner boundary corresponds to half of the surface of the waste container times the distance between two containers. The cross-section at the outer boundary is the same as for the plane geometry. In the domain between these two boundaries the transport in radial direction is simulated. The apex angle of the cylindrical cutout can be calculated from the width of the two boundary cross-sections and their distance.

As mentioned above, it has to be shown that the simplification of the geometry leads to a conservative estimation of the calculated radionuclide flux. By comparing the results from simulations with CLAYPOS with those of $r^{3}t$, it is examined in the following which of the two geometries in CLAYPOS is the better approximation of a two-dimensional simulation with $r^{3}t$. For this purpose, the transport of a stable tracer through a clay formation with a thickness of 50 m was examined. The concentration of the tracer in the container was assumed to be constant with time as it holds for solubility limited contaminants. The distance between two containers was chosen to be 20 m.



 Fig. 6.2:
 Model geometry for the program r³t

 left:
 line sources on the border

 right:
 square area sources at the border

For $r^{3}t$ two variants have been used with different implementation of the source in the model. The first variant uses line sources at the border of the model domain with a length of 1 m and the second uses square area sources of 1 m x 1 m placed directly at the border of the model domain. Both variants are shown in figure 6.2. The second case seems to be more realistic regarding the actual geometry of the container. The dark gray area shown in figure 6.2 depicts the representative section modelled with CLAYPOS.

Figure 6.3 shows the concentration profiles for four cases: two simulations with the different geometries of CLAYPOS and two simulations with the different implementations of the source in r³t. The model-time for which the curves apply to is 21 000 years. A comparison of the two calculations performed with r³t shows that the concentration in the simulation using the area source (red line) is always higher than in the simulation using the line source (purple line). This is clearly related to the larger source surface in the case of the area source as in the case of the line source by a factor of 3 m versus 1 m. Therefore the flux of the contaminant into the formation is also higher by a factor of three. Since in reality the waste container has a certain spatial extension, the case with the area source is assumed to be more realistic. For the comparison with CLAYPOS in some of the following figures only this case is shown.



Fig. 6.3: Concentration profiles for different geometries used in CLAYPOS and r³t



Fig. 6.4: Flux out of the formation for different geometries used in CLAYPOS and r³t

If one compares the result of the simulation of $r^{3}t$ with the two simulations with CLAYPOS it can be clearly seen, that the concentration calculated by the CLAYPOS simulation using the plane geometry is higher than the one from $r^{3}t$, while the CLAYPOS simulation using the radial geometry results in a lower concentration than the one with $r^{3}t$. This also affects the radionuclide flux.

Figure 6.4 shows the flux out of the upper model boundary for the same four cases. Compared to the simulation with $r^{3}t$, the simulation with CLAYPOS using the plane geometry yields a higher and the simulation with the radial geometry a lower flux. It is assumed that the simulation by $r^{3}t$ is more realistic for the presented situation. Since the flux must in no case be underestimated in a calculation for a long-term safety assessment, only the plane geometry is allowed to be used, even if the radionuclide flux may be overestimated.

The relative factor between $r^{3}t$ and CLAYPOS in this case is about three, but it can be much higher in other cases, i.e. if the distance between the containers is larger. This is due to the fact that the radionuclide flux calculated by CLAYPOS grows proportional to the cross-section for diffusion. This means that the flux grows linear with the distance of the containers or even quadratic if both container and drift distance are increased. In reality and in the $r^{3}t$ simulation however, the flux does not or only slightly grow if the cross-section is larger since it is limited to the small flux near the container. This effect can be seen in figure 6.5 showing the fluxes calculated with CLAYPOS and $r^{3}t$ for a container distance raised by a factor of three to 60 m. The drift distance was kept the same. Therefore the cross-section grows also by a factor of three. In this case the relative factor between CLAYPOS and $r^{3}t$ is about 5.7.



Fig. 6.5: Flux out of the formation for different geometries used in CLAYPOS and r³t for a container distance of 60 m



Fig. 6.6: Concentration profiles for different geometries used in CLAYPOS and r³t for a sorbing contaminant



Fig. 6.7: Concentration profiles for different geometries used in CLAYPOS and r³t for a single waste container

The contaminant regarded in the preceding simulations shown in figure 6.3 was nonsorbing. Figure 6.6 shows the corresponding concentration profiles for the same geometry (20 m container distance) and the time, but for a contaminant sorbed with linear sorption. The K_d-value used is 0.1 m³·kg⁻¹. For the sorbing contaminant all three curves are closer together than in the case with a non-sorbing contaminant and the curve for the simulation of CLAYPOS using the plane geometry shows nearly the same result as the calculation using r³t.

In the preceding simulations with r³t shown in this section, it was always assumed that several adjoining containers would fail simultaneously and that therefore a representative section can be defined as shown in figure 6.2. This kind of assumption is also the basis for the model CLAYPOS. This assumption implies that there is no flux of radionuclides at the boundaries in horizontal direction, since the concentration in the neighbouring segment is the same. But if the containers do not fail simultaneously, this assumption is wrong. An extreme situation would be that only one single container fails at a certain time. Then, the loss of radionuclides in lateral direction is maximal. This case is examined in the following.

Figure 6.7 shows how the profiles change if only a single container fails. Additionally to the curves for the simultaneous failure of several containers already shown in figure 6.3, curve (2) shows the concentration profile due to the release from a single container into isotropic medium. Curve (3) shows the concentration profile due to the release from a single container into an anisotropic medium in which the diffusion coefficient in x-direction is higher by a factor of five relative to the one in y-direction.

As one would expect, the concentrations from the release of one container shown as curve (2) are lower than those obtained for the release from several containers. This can be explained by the fact that for the case with several containers the concentration in horizontal direction is nearly uniform. This is similar to a case with one horizontal widely extended source. The gradient and therefore the flux in x-direction is nearly zero, resulting in a higher flux in y-direction. For a single container, the concentration gradients in x-direction and in y-direction are equal. Even after long times the concentration distribution is equal to those of a point source. This circumstance is visualized in figure 6.8. In this figure, the two-dimensional concentration distributions calculated by r³t are shown after a model-time of 100 000 years for several containers on the left hand side and for a single container on the right hand side.



Fig. 6.8: Spatial distribution of a contaminant calculated by r³t for several (left) and for one container (right) after a time of 100 000 years

As shown in figure 6.9 an anisotropic medium with a higher diffusion coefficient in xdirection compared to the one in y-direction, leads to a concentration distribution which is more similar to the one shown in figure 6.8 on the left hand side for several containers. This is the reason why the curve (3) in figure 6.7 lies above than curve (2), but it is still below curve (1).

As résumé of the simulations with CLAYPOS and r³t in regard of the implemented geometries in CLAYPOS, the conclusion can be drawn that for calculations for long-term safety assessment with CLAYPOS the plane geometry has to be used to achieve a conservative estimation of the radionuclide flux. The radial geometry may lead to an underestimation of the radionuclide flux and is therefore is not acceptable. The use of the plane geometry may lead to a notable overestimation of the radionuclide flux.



Fig. 6.9: Spatial distribution of a contaminant calculated by r³t for one container in an anisotropic medium after a time of 100 000 years

7 Integrated performance assessment calculation

The newly developed programs were used to perform integrated performance assessment calculations for a generic waste repository in a clay formation. The repository concepts used in the following are based on the concepts developed by DBE Technology in the framework of the two research projects GEIST and GENESIS [16, 28] and are briefly summarised in section 7.2. The concepts are designed for the disposal of high level wastes in two different clay formations at two different locations in Germany. These formations were selected on the basis of a study by the BGR¹² [26]. A map of the potentially suitable clay formations in Germany is shown in figure 7.1. The formations regarded in the following are the Opalinus Clay which can be found in Southern Germany and the Lower Cretaceous Clays which can be found in Northern Germany.

In the first section of this chapter, the scenarios for the reference case and for one alternative evolution are described. The reference scenario underlies all calculations for the performance assessment calculation presented in the sections 7.3 for the Opalinus Clay and 7.4 for the Lower Cretaceous Clays including the parameter variations and the probabilistic calculations.

A lot of site specific input data is needed for the integrated performance assessment calculations. The input data regarding the geometry and layout of the repository is taken as far as possible from the reports for the studies GEIST and GENESIS. The data for the transport parameter values to model the radionuclide transport had to be taken from the literature. The availability of transport parameters values for the Lower Cretaceous Clays is rather poor. For the Opalinus Clay there exists a large amount of data from the study performed by the Nagra for the Benken site [38]. However, the transferability of this data to the location in Southern Germany is doubtful due to the differences in geology. From the high uncertainty of the data basis it follows that the goal of the performance assessment calculation presented in the following cannot be to characterize the safety of a waste repository concept at a given location, but to obtain a principle understanding about the main processes and about the importance of the different parameters for the repository system as a whole.

¹² Federal Institute for Geosciences and Natural Resources (Bundesanstalt f
ür Geowissenschaften und Rohstoffe)



Fig. 7.1: Potential host rock formations in Germany [4]

Blue: Salt domes

Green: Cretaceous and Jurassic clay formations with a thickness larger than 100 m and a depth between 100 and 1 000 m below surface To reach this goal, parameter variations of the main transport parameter values were performed and their influence on the radionuclide fluxes is presented in the following for both clay formations. The range of the available data can rather be seen as an indication of their actual bandwidth. Additionally, a probabilistic calculation with 1 000 simulations was performed to verify and also to support the conclusions drawn from the parameter variations. The potential annual radiation exposure¹³ will be presented as a result from all calculations for an easier comparison among each other.



7.1 Scenarios

Fig. 7.2: Schematic representation of the reference scenario

The performance assessment calculations presented in the following are based on scenarios for the evolution of the waste repository. Simplified sketches of the repository system and the reference scenario for a waste repository in a clay formation are shown in figure 7.2. The containers can either be emplaced in tunnels or in boreholes. The void spaces around the containers are backfilled; either with bentonite or bentonitesand mixtures. The bentonite and those parts of the host-rock that may have been desaturated during the construction of the repository will be resaturated within a few tenths to hundreds of years after closure. In the reference case it is assumed that the

¹³ In the following "annual exposure" is used in the text for the term "potential annual radiation exposure".

resaturation causes a swelling of the bentonite and consequently a pressure build-up. All pathways in the bentonite and the excavation disturbed zone (EDZ) are closed due to self-sealing processes before the time the first container fails.

The clay formation provides sufficient water to fully corrode the steel containers [53]. Therefore, the corrosion process is not limited by the availability of water, but by the corrosion rate of the steel. Before the failure of the containers, the activity of the radionuclides changes only due to radioactive decay or ingrowth. Afterwards, the radionuclides are mobilised and transported. A barrier effect by the container or the cladding is not taken into account; the release into the geosphere starts immediately after failure of the container.

The radionuclides become dissolved in the water volume inside the failed container. Some radionuclides may be precipitated if they reach their solubility limits within the container volume. Neither temporal change nor lateral differences in chemical conditions are taken into account. Therefore, radionuclides will only reach their solubility limits within the container and nowhere else.

The mobilised radionuclides are transported through the geotechnical bentonite barrier and through the host rock by diffusion only. The diffusion properties like diffusion coefficient or diffusion-accessible porosities in the bentonite and in the clay formation may be different. Additional to the host rock, other low-permeable rock formations may overlie the host rock, where the transport may also occur only by diffusion. The radionuclides are transported to the next aquifer, where the radionuclides are diluted. The further transport in the aquifer is mainly by advection. A retention of the radionuclides in all compartments results from sorption of the radionuclides. Due to the transport of the radionuclides into the aquifer, the groundwater gets contaminated. If the groundwater is used as drinking water or for the production of food, it comes to a potential radiation exposure of the population. While dilution is taken into account, transport and retention in the aquifer are neglected in the integrated performance assessment calculations presented in the following to focus the conclusions on the host rock formation.

The reference scenario described above underlies all integrated performance assessment calculations presented in the sections 7.3 for the Opalinus Clay and 7.4 for the Lower Cretaceous Clays including the parameter variations and the probabilistic calculations. In addition to the reference scenario one disturbed evolution scenario is examined in section 7.3.6. It accounts for a fracture in the host rock formation that directly in-

tersects one container. After the container failure, the radionuclides are released directly from the container into the fracture. The radionuclides are transported in the fracture by advection, dispersion and diffusion. Additionally, the radionuclides also diffuse into the rock matrix. Like for the reference case, the radionuclides are directly released from the host rock into the biosphere.

7.2 Repository concept

This section gives a short summary of the repository concept developed by DBE Technology. The details discussed in this summary are only related to the data of the geometric layout, which is needed as input for integrated performance assessment calculation. A detailed description of all other details can be found in the documentation of the two projects GEIST and GENESIS [16, 28, 48].



Fig. 7.3: Schematic representation of the repository concept (after [48])

A schematic representation of the repository concept is shown in figure 7.3. The repository concept is based on the disposal of the containers in vertical boreholes which are 50 m in length inclusive the borehole seal. The left hand side of the figure 7.3 shows the side view of one borehole. The borehole is between 1.0 and 1.4 m in diameter. The BSK-3 containers for spent fuel have a diameter of 0.43 m and a length of 4.90 m. The ring opening around the containers in the borehole has a width of at least 0.3 m and is filled with compacted bentonite.
Optionally, a layer of sand or a bentonite/sand mixture of variable thickness is inserted as heat spreader next to the container to reduce the temperature load of the bentonite. This optional layer of sand is the reason for the variable borehole diameter given above. As an alternative or additionally to the sand layer, graphite can be added to the bentonite to enhance the thermal conductivity of the bentonite.

The top of each borehole is sealed with a borehole seal made out of compacted bentonite of about 2 m in length. The drift above the borehole is supposed to have a height of about 8 m. This height is needed for technical reasons to be able to transport the containers and also to be able to turn the containers into an upright position. The drift will also be filled with bentonite after closure. Concrete may be used to support the tunnel walls. At the time when this report was written, it was not defined in the stage of the projects GEIST and GENESIS, if any part of the concrete may be dismantled prior to closure of the repository or if all concrete might be left in the repository. An influence of the concrete on the transport, e.g. by the propagation of an alkaline plume, was not considered at this point in time.

The right hand side of figure 7.3 shows the top view of a part of the repository. The boreholes are arranged in a hexagonal geometry. This arrangement was chosen since it is the most favourable in regard of the temperature evolution and required space. The distances of the drifts and the boreholes were chosen in a way to receive a regular array of boreholes. The drift distance is therefore $\sqrt[3]{}_2$ times the borehole distance. The actual values for the borehole distance and the number of containers in each borehole, i.e. the container distance, were calculated by the DBE from the thermal constraint that the maximum temperature in the bentonite should not exceed 100°C. Due to differences in the properties like the thermal conductivity or the burial depth, these values are specific to the considered formation.

The concept of the DBE was designed for containers for high-level vitrified waste and for BSK-3 containers for spent fuel. For the performance assessment calculation in this study, only BSK-3 containers with spent fuel are regarded in order to be allow comparison with similar calculations made in the framework of the project WIGRU-4 for repositories in salt and granite [31]. The BSK-3 is a steel container designed to hold up to three spent fuel elements with about 1 600 kg heavy metal in total.

7.3 Opalinus Clay formation in Southern Germany

The Opalinus Clay is a marine sediment which has been deposited in the Aalenium, about 180 million years before present. At that time, the middle of Europe was mostly covered by the Jurassic sea, a mainly shallow sea with some deeper basins. An overview of the palaeohydrogeological situation of Europe at the time of the Jurasic Sea is shown in figure 7.4. Land areas were made up of some isolated massifs. These massifs were the sources for fine-grained sedimentary detritus which formed the Opalinus Clay sediments. A few centimetres of sediments were deposited each 100 years while at the same time the sea-floor lowered, resulting in a rather constant depth of the sea.



Fig. 7.4: Palaeohydrogeological situation of Europe in the Jurassic [39]

The Opalinus Clay formation was covered and buried in the following millions of years by claystones and limestones. By compaction and consolidation, the Opalinus Clay formation was altered and has a thickness of 80 to 120 m, today. The spatial distribution of the thickness of the Opalinus Clay as it is found today in Southern Germany is shown in figure 7.5. The model area chosen by the DBE is indicated in the same figure. It is found south-east of Ulm. The criteria to choose this model area were mainly the thickness of the formation, the depth of burial and the distance to zones of seismic activity [28].



Fig. 7.5: Thickness of the Opalinus Clay formation in Southern Germany after [28] The grey area indicates the model area



Fig. 7.6: Cross-section of the model area in Southern Germany [48]

Figure 7.6 shows a cross-section through the model area. In this area, the Opalinus Clay is found in a depth of -756 m to -877.5 m below surface and has a thickness of 121.5 m. No data for the transport parameter values exist for this location. Therefore, data from the Nagra study about the Opalinus Clay in the Züricher Weinland had to be used. Although the clay formation found in the area of Ulm is also an Opalinus Clay,

the transferability of the data from the area of the Züricher Weinland to the area of Ulm is doubtful. The reason for this can be seen from figure 7.4. While the region of Zürich lay near the Alemannic Islands during the Jurassic, the region of Ulm lay more in the deeper basin. Therefore, the area of Ulm was more influenced by the Bohemian massif, resulting in a somewhat different composition of the clay. For example, a higher occurrence of sand layers is expected in this area. However, since no boreholes exist in this area to confirm the geology, no information is available which is more precise.

7.3.1 Input data

This section describes the input data needed for the calculation of the reference case of the integrated performance assessment calculation. The bandwidths of the parameter values for variations or probabilistic calculations are described in the appropriate sections. The input data is arranged in five different categories:

- geometry,
- source-term,
- near-field,
- host-rock and
- biosphere.

The far-field transport in the aquifer is neglected; therefore no data is given for this compartment. The biosphere is only considered to be able to calculate an annual exposure which will be presented as an indicator for the results of the calculations. An indicator like the exposure makes it easier to compare the different simulations than comparing the radionuclide fluxes.

7.3.1.1 Geometry

The geometry data is mainly taken from the repository concept developed by the DBE. The borehole distance and the maximum numbers of containers per borehole were determined from calculations of the temperature evolution in the formation under the restriction of a maximum temperature of 100°C in the bentonite [28]. For the case using sand as heat spreader (case B-rB) a borehole distance of 50 m with three containers in

each borehole was calculated. This borehole distance results in an area of the hexagonal reference cell of 2 165.1 m². Using a square cross-section like in the CLAYPOS model, this gives a width of the model of 46.53 m.

The transport distances in the geotechnical barrier, i.e. the bentonite, and in the host rock are calculated from the thickness of the host rock and the repository layout under the assumption that the repository is located exactly in the middle of the Opalinus Clay layer. The three containers of each borehole are merged together at the position of the topmost container in the CLAYPOS model and are regarded as one container with three times the inventory. Therefore, the transport distances are the same for all containers. The geometry input data is given in table 7.1.

Parameter		Value
Borehole length	[m]	50
Numbers of containers per borehole	[-]	3
Area of the hexagonal reference cell	[m²]	2 165.06
Width of the CLAYPOS model	[m]	46.53
Transport length in the bentonite	[m]	10
Transport length in the host rock	[m]	30

Tab. 7.1: Geometry input data for the Opalinus Clay

7.3.1.2 Source term

The source term data regarding the inventory and the release of the radionuclides from the inventory were chosen according to a study performed for salt and granite in the framework of the project WIGRU-4 [31]. The reason was to obtain comparable results to this study. The radionuclide inventory given in table 7.3 is calculated for burned UO_2 and MOX fuel with a burn-up of 50 GWd/t_{HM} and an interim storage time of 10 years. From the calculations by the DBE, a minimum interim storage time of 73 years was calculated to meet the temperature requirements in the repository under the assumed geometry [28]. Therefore, an additional interim storage time of 63 years has to be considered in the model calculations.

The data for the whole inventory is based on the assumption that 8 550 tonnes heavy metal (t_{HM}) are going to be produced in Germany. To simplify matters, the differences between the types of high-level wastes produced are neglected and it is assumed that

all waste is present as spent fuel. For the data in table 7.3 it is neglected that the spent fuel has different interim storage times due to the different unload times from the reactor. It is rather assumed that all fuel is unloaded from the reactor at the same time. It is further assumed that each container is loaded with 1.6 t_{HM} resulting in a total number of 5 350 containers.

In the program CLAYPOS, the three different containers of each borehole are merged together at the position of the topmost container and are regarded as one container. Therefore, the inventory of one modelled container in a simulation with CLAYPOS has three times the inventory of a container as given in table 7.3.

The container is of the type BSK-3 made from steel. The container geometry is given in table 7.2. The thickness of the container wall is 0.05 m. Due to the corrosion of the steel by the saline pore water of the clay, the container is failing after some time. The corrosion rates for TStE 3555 steel in salt water were measured by Smailos et al. [57] to be $5 \,\mu\text{m}\cdot\text{y}^{-1}$ at 90°C and 46 $\mu\text{m}\cdot\text{y}^{-1}$ at 170°C. Therefore, the corrosion rate at 100°C was assumed to be about 10 $\mu\text{m}\cdot\text{y}^{-1}$. If only surface corrosion occurs this rate results in a time-span until the complete corrosion of the container of 5 000 years. It is further assumed that the container will collapse under the rock pressure if half of the thickness of the container wall is corroded. Therefore, a container life-time of 2 500 years was used. Conservatively, it was further assumed that all containers in the repository fail at the same time.

After the container has failed, the radionuclides are released from the spent fuel. The radionuclides are contained in three different compartments of the fuel and the radionuclides are released from these compartments with different rates. The following three different compartments are considered; the

- gas space from which the nuclides are released instantaneously after container failure, which is therefore also called instant release fraction,
- metal parts of the fuel element from which mainly activation products are released within several hundreds of years and
- fuel matrix from which the radionuclides are released very slowly over a period of several hundreds of thousands of years.

The release rates from the different compartments are given in table 7.4. The distribution of the elements on the three compartments in the fuel is given in table 7.5 in per cent of the total inventory.

After the radionuclides are released from the fuel they are dissolved in the water volume inside the container. Some radionuclides may be precipitated if they reach their solubility limits within the container volume. Since three containers are merged in the CLAYPOS model, the water volume is also three times the void volume of a single container. The data for the solubility limit for each element is taken from the Nagra study for the Opalinus Clay [38] and is given in table 7.6. The minimum and maximum values for the solubility limits give an impression of the uncertainty of the solubility limit data.

Parameter		Value
Length	[m]	4.90
Diameter	[m]	0.43
Wall thickness	[m]	0.05
Void volume	[m ³]	0.30
Mass	[kg]	1 660
Inventory	[t _{HM}]	1.6
Life-time	[y]	2 500

Tab. 7.2:BSK-3 container data

Nuclide	Half-life [y]	Container [Bq]	Repository [Bq]
C-14 ¹⁴	5.730·10 ⁺³	3.020·10 ⁺¹⁰	1.616·10 ⁺¹⁴
CI-36	3.000·10 ⁺⁵	5.493·10 ⁺⁰⁸	2.939·10 ⁺¹²
Co-60	5.272·10 ⁺⁰	1.634·10 ⁺¹⁴	8.743·10 ⁺¹⁷
Ni-59	7.500·10 ⁺⁴	9.626·10 ⁺¹⁰	5.150·10 ⁺¹⁴
Ni-63	1.000·10 ⁺²	1.371·10 ⁺¹³	7.333·10 ⁺¹⁶
Se-79 ¹⁵	1.100·10 ⁺⁶	2.796·10 ⁺¹⁰	1.496·10 ⁺¹⁴
Sr-90	2.864·10 ⁺³	3.756·10 ⁺¹⁵	2.009·10 ⁺¹⁹
Zr-93	1.500·10 ⁺⁶	1.341·10 ⁺¹¹	7.172·10 ⁺¹⁴
Nb-94	2.000·10 ⁺⁴	1.013·10 ⁺⁰⁵	5.421·10 ⁺⁰⁸
Mo-93	3.500·10 ⁺³	7.148·10 ⁺⁰⁷	3.824·10 ⁺¹¹
Tc-99	2.100·10 ⁺⁵	4.066·10 ⁺¹¹	2.175·10 ⁺¹⁵
Sn-126	2.345·10 ⁺⁵	4.964·10 ⁺¹⁰	2.656·10 ⁺¹⁴
I-129	1.570·10 ⁺⁷	3.222·10 ⁺⁰⁹	1.724·10 ⁺¹³
Cs-135	2.000·10 ⁺⁶	3.481·10 ⁺¹⁰	1.863·10 ⁺¹⁴
Cs-137	3.017·10 ⁺¹	6.324·10 ⁺¹⁵	3.383·10 ⁺¹⁹
Sm-151	9.300·10 ⁺¹	1.092·10 ⁺¹⁴	5.844·10 ⁺¹⁷
Ra-226	1.600·10 ⁺³	1.691·10 ⁺⁰⁴	9.048·10 ⁺⁰⁷
Th-229	7.880·10 ⁺³	1.032·10 ⁺⁰⁴	5.519·10 ⁺⁰⁷
Th-230	7.540·10 ⁺⁴	6.280·10 ⁺⁰⁶	3.360·10 ⁺¹⁰
Th-232	1.405·10 ⁺¹⁰	8.118·10 ⁺⁰⁰	4.343·10 ⁺⁰⁴
Pa-231	3.276·10 ⁺⁴	2.029·10 ⁺⁰⁶	1.085·10 ⁺¹⁰
U-233	1.592·10 ⁺⁵	5.795·10 ⁺⁰⁶	3.100·10 ⁺¹⁰
U-234	2.455·10 ⁺⁵	6.609·10 ⁺¹⁰	3.536·10 ⁺¹⁴
U-235	7.038·10 ⁺⁸	7.969·10 ⁺⁰⁸	4.263·10 ⁺¹²
U-236	2.342·10 ⁺⁷	1.348·10 ⁺¹⁰	7.210·10 ⁺¹³

Tab. 7.3: Radionuclide inventory

¹⁴ It has been discussed recently, in which chemical form C-14 is present in spent fuel [29]. As conservative assumption it was assumed in this study that all C-14 is in organic form, resulting in lower retention parameters.

¹⁵ The half-life of Se-79 has been revised several times. Initially, a value of 65 000 years was given in the nuclide charts. The value used here was determined in 1997, but was revised in 2001 to be only 295 000 years [61, 62]. To be conservative and because of the uncertainty which of the values is correct, the higher value has been used in safety assessments until now. New data which was still unpublished at the time of this report seems to support a value between 300 000 and 400 000 years.

Nuclide	Half-life [y]	Container [Bq]	Repository [Bq]
U-238	4.468·10 ⁺⁹	1.953·10 ⁺¹⁰	1.045·10 ⁺¹⁴
Np-237	2.144·10 ⁺⁶	2.153·10 ⁺¹⁰	1.152·10 ⁺¹⁴
Pu-238	8.774·10 ⁺¹	4.747·10 ⁺¹⁴	2.540·10 ⁺¹⁸
Pu-239	2.411·10 ⁺⁴	3.465·10 ⁺¹³	1.854·10 ⁺¹⁷
Pu-240	6.563·10 ⁺³	8.160·10 ⁺¹³	4.366·10 ⁺¹⁷
Pu-241	1.435·10 ⁺¹	1.387·10 ⁺¹⁶	7.419·10 ⁺¹⁹
Pu-242	3.750·10 ⁺⁵	6.035·10 ⁺¹¹	3.229·10 ⁺¹⁵
Am-241	4.322·10 ⁺²	3.277·10 ⁺¹⁴	1.753·10 ⁺¹⁸
Am-242m	1.410·10 ⁺³	3.228·10 ⁺¹²	1.727·10 ⁺¹⁶
Am-243	7.37·10 ⁺³	5.740·10 ⁺¹²	3.071·10 ⁺¹⁶
Cm-243	2.91·10 ⁺¹	1.447·10 ⁺¹²	7.741·10 ⁺¹⁵
Cm-244	1.810·10 ⁺¹	8.996·10 ⁺¹⁴	4.813·10 ⁺¹⁸
Cm-245	8.500·10 ⁺³	3.484·10 ⁺¹¹	1.864·10 ⁺¹⁵

Tab. 7.4: Mobilisation rates for different fuel compartments

		Fuel Matrix	Metal parts	Gas Space
Mobilisation rate	[y ⁻¹]	1.0·10 ⁻⁶	3.6·10 ⁻³	instantaneous

Tab. 7.5: Relative inventory in the different fuel compartments in per cent

Element	Metal parts	Fuel Matrix	Gas Space
С	72.20	26.41	1.39
CI	0.00	94.00	6.00
Ni, Mo, Nb	99.50	0.47	0.03
Sn	0.00	98.00	2.00
I, Se	0.00	97.00	3.00
Cs	0.00	96.00	4.00
Rb, H	0.00	95.00	5.00
Sr, Sm, Pb	0.00	99.90	0.10
Zr	9.40	86.07	4.53
Тс	0.10	99.89	0.01
Pd, Cm, Am, Pu, Pa, U, Th, Ac, Np, Ra	0.00	99.99	0.01

Element	reference	minimum	maximum
н	high	high	high
Be	1·10 ⁻⁶	1·10 ⁻⁶	high
C _{org}	high	high	high
CI	high	high	high
Са	1·10 ⁻²	1·10 ⁻²	1·10 ⁻²
Ni	3·10 ⁻⁵	1·10 ⁻⁵	8·10 ⁻⁵
Se	5·10 ⁻⁹	2·10 ⁻¹¹	1·10 ⁻⁵
Sr	2·10 ⁻⁵	3·10 ⁻⁶	1.10-4
Zr	2·10 ⁻⁹	3·10 ⁻¹¹	2·10 ⁻⁹
Nb	3·10 ⁻⁵	1·10 ⁻⁸	1·10 ⁻⁴
Мо	1·10 ⁻⁶	1·10 ⁻⁶	1·10 ⁻⁵
Тс	4·10 ⁻⁹	1·10 ⁻⁹	1·10 ⁻⁸
Pd	5·10 ⁻⁸	1·10 ⁻¹⁰	2·10 ⁻⁷
Ag	3·10 ⁻⁶	1·10 ⁻¹⁰	3·10 ⁻⁶
Sn	1·10 ⁻⁸	5·10 ⁻⁹	1·10 ⁻⁷
I	high	high	high
Cs	high	high	high
Sm	5·10 ⁻⁷	3·10 ⁻⁷	9·10 ⁻⁷
Но	5·10 ⁻⁷	3·10 ⁻⁷	9·10 ⁻⁷
Pb	2·10 ⁻⁶	2·10 ⁻⁸	8·10 ⁻⁵
Po	high	high	high
Ra	2·10 ⁻¹¹	4·10 ⁻¹²	5·10 ⁻⁸
Ac	1·10 ⁻⁶	5·10 ⁻⁸	3·10 ⁻⁵
Th	7·10 ⁻⁷	2·10 ⁻⁷	3·10 ⁻⁶
Ра	1·10 ⁻⁸	1·10 ⁻⁸	1·10 ⁻⁵
U	3·10 ⁻⁹	3·10 ⁻¹⁰	5·10 ⁻⁷
Np	5·10 ⁻⁹	3·10 ⁻⁹	1.10-8
Pu	5·10 ⁻⁸	3·10 ⁻⁹	1·10 ⁻⁶
Am	1.10-6	5·10 ⁻⁸	3·10 ⁻⁵
Cm	1.10-6	5·10 ⁻⁸	3.10⁻⁵

Tab. 7.6:Solubility limits in [mol·l⁻¹]"high" denotes no solubility limit

7.3.1.3 Near-field

The near-field geometry was already described in section 7.3.1.1. The transport length in the bentonite is 10 m. It is assumed that the drifts are filled with bentonite with a dry density of $\rho = 2.760 \text{ kg} \cdot \text{m}^{-3}$. This value is also assumed for the borehole seals. The data for the element-specific transport parameter values were taken from the Nagra study for the Opalinus Clay [38] and are listed in table 7.7. The diffusion coefficient given in table 7.7 is the effective diffusion coefficient. The pore diffusion coefficient D_p needed as input value for CLAYPOS can be calculated from the effective diffusion coefficient D_{eff} by division by the porosity *n*:

$$D_p = \frac{D_{eff}}{n} \tag{7.1}$$

For the sorption values in the near-field, the reference value given was used in the calculation for the reference case. The minimum and maximum values which are also given reflect the uncertainty of the sorption values.

Element	K _d ref. [m ³ ·kg⁻¹]	K _d min. [m ³ ·kg⁻¹]	K _d max. [m³⋅kg⁻¹]	D _{eff} [m ² ⋅s ⁻¹]	n [-]
Н	0	0	0	2·10 ⁻¹⁰	0.36
Ве	0.2	0.009	5	2·10 ⁻¹⁰	0.36
C _{org}	0	0	0	2·10 ⁻¹⁰	0.36
CI	0	0	0	3·10 ⁻¹²	0.05
Са	0.003	5·10 ⁻⁴	0.02	2·10 ⁻¹⁰	0.36
Ni	0.2	0.009	5	2·10 ⁻¹⁰	0.36
Se	0	0	0	3·10 ⁻¹²	0.05
Sr	0.003	5·10 ⁻⁴	0.02	2·10 ⁻¹⁰	0.36
Zr	80	1	4 000	2·10 ⁻¹⁰	0.36
Nb	30	1	900	2·10 ⁻¹⁰	0.36
Мо	0	0	0	3·10 ⁻¹²	0.05
Тс	60	0.5	600	2·10 ⁻¹⁰	0.36
Pd	5	0.2	100	2·10 ⁻¹⁰	0.36
Ag	0	0	0	2·10 ⁻¹⁰	0.36
Sn	800	1	10 000	2·10 ⁻¹⁰	0.36

Tab. 7.7: Near-field transport parameter values

Element	K _d ref. [m ³ ·kg⁻¹]	K _d min. [m ³ ·kg⁻¹]	K _d max. [m ³ ·kg⁻¹]	D _{eff} [m ² ⋅s⁻¹]	n [-]
I	5·10 ⁻⁴	5·10 ⁻⁵	0.005	3·10 ⁻¹²	0.05
Cs	0.1	0.03	0.3	2·10 ⁻¹⁰	0.36
Sm	4	0.1	100	2·10 ⁻¹⁰	0.36
Но	4	0.1	100	2·10 ⁻¹⁰	0.36
Pb	7	0.5	100	2·10 ⁻¹⁰	0.36
Po	0.06	0.008	0.5	3·10 ⁻¹²	0.05
Ra	0.002	3·10 ⁻⁴	0.01	2·10 ⁻¹⁰	0.36
Ac	20	1	300	2·10 ⁻¹⁰	0.36
Th	60	10	200	2·10 ⁻¹⁰	0.36
Pa	5	0.2	100	2·10 ⁻¹⁰	0.36
U	40	2	400	2·10 ⁻¹⁰	0.36
Np	60	6	600	2·10 ⁻¹⁰	0.36
Pu	20	1	300	2·10 ⁻¹⁰	0.36
Am	20	1	300	2·10 ⁻¹⁰	0.36
Cm	20	1	300	2·10 ⁻¹⁰	0.36

7.3.1.4 Host rock

The geometry data for the host-rock was already described in section 7.3.1.1. The transport length in the host-rock is 30 m. The Opalinus Clay at the location in Southern Germany is bedded with an angle of incline of 1.3° . This is not relevant for the one-dimensional calculations with CLAYPOS and is also neglected in the three-dimensional calculations with r³t. No advection is considered in the calculations, therefore no data about the hydraulic gradient and hydraulic permeability of the host rock is given. The density of the Opalinus Clay is 2 400 kg·m⁻³. All other values for the element-specific transport parameter values for the host-rock were taken from the Nagra study for the Opalinus Clay [38] and are listed in table 7.8. The pore diffusion coefficient D_p needed as input value for CLAYPOS can be calculated from the effective diffusion coefficient D_{eff} by division by the porosity *n* as shown in equation 7.1.

For the distribution coefficients in the near-field, the reference value given was used in the calculation for the reference case. The minimum and maximum values which are also given indicate the uncertainty of the distribution coefficients.

Element	K _d ref. [m ^{3.} kg ⁻¹]	K _d min. [m ³ ·kg⁻¹]	K _d max. [m ^{3,} kg⁻¹]	D _{eff} [m²⋅s⁻¹]	n [-]
Н	0	0	0	1·10 ⁻¹¹	0.12
Ве	0.9	0.03	20	1·10 ⁻¹¹	0.12
C _{org}	0	0	0	1·10 ⁻¹¹	0.12
CI	0	0	0	1·10 ⁻¹²	0.06
Са	0.001	1.10-4	0.007	1·10 ⁻¹¹	0.12
Со	0.4	0.01	20	1·10 ⁻¹¹	0.12
Ni	0.9	0.03	20	1·10 ⁻¹¹	0.12
Se	0	0	0	1·10 ⁻¹²	0.06
Sr	0.001	1.10-4	0.007	1·10 ⁻¹¹	0.12
Zr	10	0.3	300	1·10 ⁻¹¹	0.12
Nb	4	0.1	100	1·10 ⁻¹¹	0.12
Мо	0.01	0.001	0.2	1·10 ⁻¹²	0.06
Тс	50	0.5	500	1·10 ⁻¹¹	0.12
Pd	5	0.2	100	1·10 ⁻¹¹	0.12
Ag	0	0	0	1·10 ⁻¹¹	0.12
Sn	100	0.2	1 000	1·10 ⁻¹¹	0.12
1	3·10 ⁻⁵	3·10 ⁻⁶	4·10 ⁻⁴	1·10 ⁻¹²	0.06
Cs	0.5	0.09	3	1·10 ⁻¹¹	0.12
Sm	50	5	600	1·10 ⁻¹¹	0.12
Eu	50	5	600	1·10 ⁻¹¹	0.12
Но	50	5	600	1·10 ⁻¹¹	0.12
Pb	2	0.02	300	1·10 ⁻¹¹	0.12
Po	0.1	0.04	0.7	1·10 ⁻¹²	0.06
Ra	7·10 ⁻⁴	1·10 ⁻⁴	0.005	1·10 ⁻¹¹	0.12
Ac	10	1	200	1·10 ⁻¹¹	0.12
Th	50	10	200	1·10 ⁻¹¹	0.12
Ра	5	0.2	100	1·10 ⁻¹¹	0.12
U	20	0.5	200	1·10 ⁻¹¹	0.12
Np	50	5	500	1·10 ⁻¹¹	0.12
Pu	20	1	300	1·10 ⁻¹¹	0.12
Am	10	1	200	1·10 ⁻¹¹	0.12
Cm	10	1	200	1·10 ⁻¹¹	0.12

 Tab. 7.8:
 Opalinus Clay transport parameter values

7.3.1.5 Biosphere

The potential radiation exposure of a grown-up individual was calculated with the module EXCON using dose conversion factors. A ground water flow of $10^5 \text{ m}^3 \cdot \text{y}^{-1}$ was assumed in the module CLAYPOS to convert the radionuclide flux from the clay formation to concentration values. With a horizontal extension of the total repository of about 2 000 m this value corresponds to an aquifer thickness of 50 m and a groundwater velocity of $1 \text{ m} \cdot \text{y}^{-1}$. The dose conversion factors were chosen according to a study performed in the framework of the project WIGRU-4 for salt and granite [31] and are given in table 7.9. The reason was to receive comparable results to this study.

The biosphere model to calculate the dose conversion factors [47] is in accordance to the German regulations and includes the following pathways:

- consumption of contaminated drinking water,
- consumption of fish from contaminated lakes,
- consumption of plants irrigated with contaminated water,
- consumption of milk and meat from cattle, which were watered and fed with contaminated fodder and
- exposure due to habitation on the contaminated land.

Table 7.10 additionally gives the dose coefficients for ingestion [5] used to calculate the radiotoxicity from the radionuclide flux. The dose coefficients are a measure for the damage to a human being by the ingestion of 1 Bq of a given radionuclide within 50 years after ingestion. This includes all damage resulting from the daughter nuclides produced in the body. Daughter nuclides that are produced before the ingestion have to be regarded separately. Therefore, the dose coefficients of short-lived daughter nuclides which are not explicitly included in the calculation are added to their mothers under the assumption of radioactive equilibrium. Those radionuclides that include the dose coefficients of some daughter nuclides are indicated by a plus sign after their name in table 7.10.

Activation and fission products		Th- and Np- series		U- and Ac-series	
Nuclide	DCF	Nuclide	DCF	Nuclide	DCF
C-14	4.6·10 ⁻⁸	Cm-248	5.0·10 ⁻⁶	Cm-246	8.0·10 ⁻⁷
CI-36	3.5·10 ⁻⁸	Pu-244	3.0·10 ⁻⁶	Pu-242	9.4·10 ⁻⁷
Ca-41	2.0·10 ⁻⁹	Cm-244	3.8·10 ⁻⁷	AM-242	7.6·10 ⁻⁷
Co-60	3.9·10 ⁻⁶	Pu-240	9.6·10 ⁻⁷	U-238	7.1·10 ⁻⁷
Ni-59	4.9·10 ⁻⁹	U-236	5.6·10 ⁻⁷	Pu-238	7.5·10 ⁻⁷
Ni-63	1.1·10 ⁻⁹	Th-232	1.1·10 ⁻⁴	Th-234	4.8·10 ⁻⁹
Se-79	3.4·10 ⁻⁷	Ra-228	2.4·10 ⁻⁶	U-234	1.4·10 ⁻⁶
Rb-87	1.3·10 ⁻⁷	U-232	5.4·10 ⁻⁶	Th-230	3.7·10 ⁻⁵
Sr-90	1.8·10 ⁻⁷	Th-228	1.3·10 ⁻⁶	Ra-226	3.0·10 ⁻⁵
Zr-93	3.7·10 ⁻⁸	Cm-245	1.4·10 ⁻⁶	Pb-210	2.3·10 ⁻⁶
Mo-93	3.2·10 ⁻⁷	Pu-241	1.8·10 ⁻⁸	Po-210	4.9·10 ⁻⁶
Nb-94	3.1·10 ⁻⁶	Am-241	8.0·10 ⁻⁷	Cm-247	2.9·10 ⁻⁶
Tc-99	8.8·10 ⁻⁹	Np-237	4.7·10 ⁻⁶	Am-243	2.0·10 ⁻⁶
Pd-107	1.9·10 ⁻⁹	U-233	3.9·10 ⁻⁶	Pu-239	9.8·10 ⁻⁷
Sn-126	1.6·10 ⁻⁵	Pa-233	8.8·10 ⁻⁹	U-235	3.3·10 ⁻⁶
I-129	5.6·10 ⁻⁷	Th-229	1.7·10 ⁻⁵	Pa-231	4.0·10 ⁻⁵
Cs-135	5.7·10 ⁻⁸	Ra-225	1.1·10 ⁻⁷	Ac-227	1.0·10 ⁻⁵
Cs-137	9.5·10 ⁻⁷	Ac-225	3.7·10 ⁻⁸	Th-227	1.9·10 ⁻⁸
Sm-151	3.2·10 ⁻¹⁰			Ra-223	1.1·10 ⁻⁷

Tab. 7.9: Dose conversion factors (DCF) in $Sv \cdot y^{-1} / Bq \cdot m^{-3}$

Tab. 7.10:Dose coefficients for ingestion in Sv/Bq to calculate the radiotoxicityA plus sign after the nuclide name indicates that the dose coefficient for thisnuclide includes the dose coefficient for all daughter nuclides up to the nextone given in the table

Activation and fission products		Th- and Np- series		U- and Ac-series	
Nuclide	Dose coefficient	Nuclide	Dose coefficient	Nuclide	Dose coefficient
C-14	5.80E-10	Cm-244	1.20E-07	Pu-242 +	4.30E-07
CI-36	9.30E-10	Pu-240	2.50E-07	Am-242 +	1.23E-08
Co-60	3.40E-09	U-236 +	3.77E-07	Pu-238	2.30E-07
Ni-59	6.30E-11	Th-232	2.30E-07	U-238 +	4.89E-08
Ni-63	1.50E-10	Ra-228 +	8.34E-07	U-234	4.90E-08
Se-79	2.90E-09	Cm-245	2.10E-07	Th-230	2.10E-07
Sr-90	3.07E-08	Pu-241	4.80E-09	Ra-226 +	2.80E-07
Zr-93	1.22E-09	Am-241	2.00E-07	Pb-210	6.91E-07
Nb-94	1.70E-09	Np-237 +	1.11E-07	Am-243 +	2.01E-07
Mo-93	3.22E-09	U-233	5.10E-08	Pu-239	2.50E-07
Tc-99	6.40E-10	Th-229 +	6.13E-07	U-235 +	4.73E-08
Sn-126	5.07E-09			Pa-231	7.10E-07
I-129	1.10E-07			Ac-227 +	1.21E-06
Cs-135	2.00E-09				
Cs-137	1.30E-08				
Sm-151	9.80E-11				

7.3.2 Reference case

Using the model, the repository concept and the input data described in the preceding sections, an integrated performance assessment calculation was performed using the modules CLAYPOS and EXCON. To present the results of the calculations, figures of the radionuclide fluxes and of the annual exposure are shown in the following. The abscissa of those figures gives the time measured from closure of the repository. Although the safety relevant time period mostly regarded in long-term safety assessments is one million years, a longer period of time is shown in most of the figures. This is due to the fact, that some of the curves show interesting details even beyond that period of time. To reflect that this period is normally not regarded in long-term safety assessessments, the background is shaded in grey for times later than one million years.

The radionuclide fluxes from the container into the near-field are shown in figure 7.7. The most relevant nuclides are Pu-240 for times before 10^4 years, Pb-210 for times later than $6 \cdot 10^4$ years and Pu-239 in between. Pb-210 is not part of the initial inventory of the waste, but stems from the radioactive decay of the Uranium series. Other radionuclides with high fluxes from the container are Pu-242 and Th-229. Those radionuclides that dominate the flux from the clay formation are shown as thick solid lines in figure 7.7. These however are not relevant for the flux from the container.

The flux from the Opalinus Clay is shown in figure 7.8. This flux is dominated by C-14 for times before $8 \cdot 10^4$ years, I-129 for times later than $8 \cdot 10^5$ years and by Cl-36 and Se-79 in between. All those radionuclides that have the highest fluxes from the container are effectively retained by the clay formation. Those radionuclides that play the major role in the flux from the clay formation are all such elements that are assumed not to sorb on the clay, like Carbon, Chloride and Selenium, or only have a small sorption coefficient, like lodine. Neglecting any sorption for Carbon is a conservative assumption in this calculation on the basis that a high percentage of the Carbon may exist in organic form.

The highest flux from the clay formation is C-14 at about 28 000 years showing a flux of 710 Bq·y⁻¹. After this time the C-14 flux is decreasing due to radioactive decay. Se-79 is the only radionuclide to reach a steady state between the fluxes into and out of the clay formation. At times later than about one million years both fluxes are constant over a long period of time with an influx into the formation of about 200 Bq·y⁻¹ and an outflow

from the formation of about 100 $Bq \cdot y^{-1}$. Thus Se-79 looses about half of its activity during its travel through the clay formation.



Fig. 7.7: Radionuclide fluxes from the container per reference section solid lines: radionuclides that dominate far-field flux dotted lines: other radionuclides



Fig. 7.8: Radionuclide fluxes from the Opalinus Clay per reference section

The resulting annual exposure versus time is shown in figure 7.9. The exposure is dominated by the radionuclides C-14, Se-79 and I-129 and in the second order also by CI-36. However, due to the uncertainties regarding the half-life of Se-79 as discussed with the inventory, the exposure by Se-79 might be overestimated. The maximum annual exposure is caused by I-129 with about $5.3 \cdot 10^{-8} \text{ Sv} \cdot \text{y}^{-1}$ and reached at $2.25 \cdot 10^{6}$ years, which is later than the period usually considered in a long-term-safety assessment. The maximum annual exposure within one million years is also caused by I-129 with about $2.26 \cdot 10^{-8} \text{ Sv} \cdot \text{y}^{-1}$, which is about a half of the maximum value.

Although the cases are not directly comparable, these are the same four radionuclides which also play the dominant role in the Nagra study for the Züricher Weinland. However, CI-36 is of higher and Se-79 of lower importance there. The reasons are differences in the source-term. In the Nagra study, the release rate of CI-36 is assumed to be about three orders of magnitude higher than that of Se-79 at the beginning and is decreasing to that of Se-79 after about 40 000 years [38], while in this study the release rates are rather the same starting from the beginning.

To verify the calculation performed with CLAYPOS and the curve shown in figure 7.9, a three-dimensional calculation with r³t was performed for comparison. This calculation is presented in the following section.



Fig. 7.9: Annual exposure versus time for the Opalinus Clay

7.3.3 Reference case verification with r³t

A more detailed simulation of the reference case was performed with the program $r^{3}t$ for comparison to the CLAYPOS simulation. In CLAYPOS a simplified reference section was used where the hexagonal structure was replaced by a square one and the three containers in each borehole were abstracted to one. Additionally, the transport was examined only in one dimension. In contrast to this, $r^{3}t$ regards for a representative section of the repository reflecting the real geometry including the hexagonal structure and for independent containers. The representative section regarded in the $r^{3}t$ model is shown as blue area in figure 7.10.



Fig. 7.10: Representative section of the waste repository modelled in r³t

Figure 7.11 additionally shows the three-dimensional geometry of the r³t model from a diagonal top view. The geometry of r³t represents a rectangular parallelepiped with a height (z-direction) according to the thickness of the formation of 121 m. The depth (y-direction) of the model is 100 m which is two times the borehole distance and the width (x-direction) of the model is 173 m which is $\sqrt{3}$ times the depth, according to the hexagonal structure of the geometry. The model represents one complete hexagonal section in a way that this structure can be seamlessly continued in both directions. One representative section includes the inventory of eight boreholes i.e. five complete boreholes in the inner and four halved boreholes at the sides and another four quartered boreholes at the edges. The eight boreholes altogether contain the inventory of 24 containers.

The data for the radionuclide fluxes from the containers was taken from the CLAYPOS calculation shown in figure 7.7, but only for one single container instead of three. In the simulation with $r^{3}t$, the containers are represented by point sources. The source strength was divided by a factor of two or four for the containers at the sides and edges, respectively. The position of the sources is shown as the yellow ellipsoids in figure 7.11.



Fig. 7.11: Three-dimensional representation of the r³t model of the repository in the Opalinus Clay formation

The same values for the transport parameters and the same assumptions were used in the simulation with $r^{3}t$ as in the simulation with CLAYPOS with the exception of the following differences:

 The geotechnical bentonite barrier is not modelled in r³t. The whole model has uniformly the transport parameter values of the Opalinus Clay.

- The diffusion was modelled anisotropic in r³t with a diffusion coefficient parallel to the bedding (in x- and y-direction) being five times higher than perpendicular to the bedding (in z-direction) for all radionuclides. The diffusion coefficient perpendicular to the bedding is the same as in the CLAYPOS model.
- The solubility limits were not considered in the container as in CLAYPOS, but r³t accounts for the solubility limits in the pore water of the clay formation in the whole modelled domain.
- Due to calculation time constraints, only the four radionuclides C-14, Cl-36, Se-79 and I-129, which already proved to be the most relevant radionuclides in the CLAYPOS calculation, were regarded in the r³t simulation.

The influence of the anisotropic diffusion can be seen from the three cross-section plots shown in figure 7.12. In the horizontal cross-section (a) the radionuclide plumes are distributed symmetrically around the point sources. In the vertical cross-sections (b) and (c) it can be seen that the propagation is faster in the horizontal direction than in the vertical direction resulting in an elliptic shape of the plume. The effect of the sources hexagonal borehole layout can also be seen from the cross-sections (b) and (c); the radionuclides released from the sources in cross-section (b) can be seen as light blue spots in cross section (c) and vice versa.

The figures 7.13 and 7.14 show the results of the simulations with r³t and CLAYPOS in terms of radionuclide fluxes from the host rock in Becquerel per year. The arrival times of the radionuclide fluxes are about the same in both simulations, which becomes obvious from figure 7.14. However, the absolute values of the radionuclide fluxes are much higher in the CLAYPOS simulation compared to those calculated with r³t. The relative factors for the maximum values are about 1 000 for C-14 and I-129, 12 800 for Cl-36 and 21 000 for Se-79.

It has to be explicitly pointed out that this does not imply that the result from the $r^{3}t$ simulation is more realistic and that the result from CLAYPOS is overestimating the true radionuclide fluxes by a factor of 1 000. In fact, both simulations are only models and the simulation by $r^{3}t$ might underestimate the true fluxes by not taken additional effects in account, like the enhanced horizontal radionuclide distribution along the repository tunnels. Therefore, only the reason for the differences between both programs can be investigated in the following, not the question which is more realistic.







Fig. 7.13: Comparison between radionuclide fluxes from calculations with CLAYPOS and r³t on a logarithmic scale



Fig. 7.14: Comparison between radionuclide fluxes from calculations with CLAYPOS (left axis) and r³t (right axis) on a linear scale

The reason for the difference between the results of both programs is examined in the following and the potential effects which may influence the calculated fluxes in a way to explain the difference are listed below. Three different types of effects are discussed and are distinguished in the list by their type of bullet point: first, general differences between both programs which are not related to the model (o); secondly, those types of effects which lead to an underestimation of the flux by $r^{3}t$ (-) and thirdly, those types of effects which lead to an overestimation of the flux by CLAYPOS (+).

• **Code implementation**¹⁶: The transport parameters in the transport equation might be differently implemented in the two programs. An example is the usage of pore diffusion coefficients vs. effective diffusion coefficients.

However, this kind of difference would not only result in different diffusive fluxes, but also in different travel times of the radionuclides. The good agreement of the shape and position of the C-14 and I-129 peaks in figure 7.14 indicates that the differences in the height of the peak are not due to the transport process, but due to other model assumptions. Furthermore, principal differences between both programs should have been already recognised during qualification in chapter 5.

• **Different representation of solubility limits**: While CLAYPOS accounts for solubility limits within the container, r³t accounts for the solubility limits in the whole formation, but in the container.

First of all, Se-79 is the only solubility limited radionuclide of the four relevant ones. Also for Se-79, no influence on the radionuclide flux is expected due to the different representation of the solubility limits, since the actual radionuclide concentration in the water - which acts as boundary concentration at the source - is the same in both representations. Therefore, the influence of the different representation of the solubility limits was not studied further.

Source geometry: The sources in the r³t model are represented by point sources.
 In chapter 6, the geometry of the source was found to influence the strength of the diffusive flux. The influence of the source geometry on the calculated flux in the reference case was tested by comparing the results from three calculations with

¹⁶ Legend of bullets:

o general difference between r³t and CLAYPOS

effect which leads to an underestimation of the flux by r³t

⁺ effect which leads to an overestimation of the flux by CLAYPOS

different source size: one case with a point source and two cases with volume sources having five and ten metres width. The size of the source was found to have only a negligible influence on the calculated flux. This is mainly due to two reasons: firstly, the anisotropy of the diffusion, which leads to a fast concentration equalisation in horizontal direction, independent of the source width and secondly, the mesh width of the grid of the r³t model. In all calculations, the mesh width was between 1.5 m and 2.5 m. The flux from the point source is distributed equally over one grid element, resulting in an equivalent source volume, large enough to effectively spread the flux.

 Near-field representation: While the CLAYPOS model distinguishes between both compartments, the model for the r³t simulation uses the same transport parameter values for the bentonite in the near-field and for the Opalinus Clay. This was done to simplify the construction of the r³t model.

The influence of the near-field was tested by performing a CLAYPOS simulation where the near-field transport parameters values were identical to those of the Opalinus Clay. The results are shown in figure 7.15 as dashed line in comparison to the reference case. For C-14, Cl-36 and Se-79 the application of Opalinus Clay transport parameter values in the near-field results in lower radionuclide fluxes, while for I-129 the radionuclide flux is higher. This is due to the transport parameters. Carbon, Chloride and Selenium have lower diffusion coefficients in the Opalinus Clay than in the bentonite, resulting in lower fluxes if the Opalinus Clay parameter values are used. Iodine on the other hand has a higher distribution coefficient in the bentonite than in the Opalinus Clay resulting in higher fluxes, when Opalinus Clay parameter values are used.

For C-14, the effect of using Opalinus Clay parameter values for the near-field in CLAYPOS results in a lower flux by a factor of 2.4. A higher flux by a factor in the same order of magnitude is expected if bentonite transport parameter values were used in the near-field in the r³t model.

Boundary conditions: The boundary condition for the top of the clay formation is determined by the radionuclide concentration in the aquifer. For numerical reasons, the water flow in the aquifer was assumed to be much lower in the r³t simulation than in the CLAYPOS simulation, what might result in higher radionuclide concentrations and therefore in a reduced radionuclide flux.

Test calculations with CLAYPOS have shown that the concentration in the aquifer is low enough in both cases to have no effect on the concentration gradient. Hence, a higher water flow in the aquifer of the r³t simulation would have no effect on the radionuclide flux.

Model dimension: CLAYPOS uses a one-dimensional model, whereas r³t uses a three-dimensional one. This implies that CLAYPOS calculates the concentration at the position of the source and assumes that it is uniform in the horizontal direction. The same applies to the concentration gradient controlling the radionuclide flux. In contrast to this, the concentration (and also the radionuclide flux) in the r³t model decreases with the horizontal distance from the source.

The vertical concentration profiles from the position of the source to the aquifer are shown for three radionuclides in figure 7.17 for both codes. These concentration profiles nicely agree to each other. The model dimension therefore has only a negligible effect on the vertical concentration distribution.

This is completely different for the horizontal concentration distribution, which is assumed to be uniform in the CLAYPOS model. The horizontal concentration profile in the $r^{3}t$ simulation is shown in figure 7.18 on the example of C-14 as normalised concentration versus horizontal distance from the source for different points in time. In the $r^{3}t$ model the concentration at horizontal distances more than 10 m from the source does not reach more than 80% of the concentration at the source.

The effect of the model dimension was further studied by performing an additional two-dimensional $r^{3}t$ simulation. The results for C-14 are shown in figure 7.16. If compared to the CLAYPOS simulation using Opalinus Clay near-field parameter values, the two-dimensional $r^{3}t$ simulation results in a radionuclide flux by a factor of 20 lower than in the CLAYPOS simulation. The three-dimensional $r^{3}t$ -simulation is again lower by a factor of about 20 than the two-dimensional simulation. Thus, for the repository layout used here, every reduction of the complexity of the model by one dimension results in an overestimation of the flux by a factor of 20, i.e. the one-dimensional CLAYPOS model overestimates the flux compared to the three-dimensional $r^{3}t$ -model by a factor of about 400.

The effect of the model geometry is inherent to the CLAYPOS model and was already described in section 4.1. It was expected that the simplification would lead to an overestimation of the radionuclide flux.

Legend of bullets:

o general difference between r³t and CLAYPOS

⁻ effect which leads to an underestimation of the flux by r³t

⁺ effect which leads to an overestimation of the flux by CLAYPOS

+ **Layout of cross-section area:** In CLAYPOS a square geometry, whereas in r³t the real hexagonal geometry is used.

The square geometry has a lower width-to-area ratio than the hexagonal geometry. This effect is already included in the numbers calculated to compare the model dimension in the preceding paragraph. However, the hexagonal layout of the repository even pronounces the overestimation from the use of a one-dimensional geometry. A calculation for a waste repository with a square layout would most probably lead to an effect somewhat lower than for the layout used here.

Container representation: CLAYPOS simulates one container with three times the inventory while r³t simulates all three containers at the correct positions. At least for the simulations carried out here no influence on the radionuclide fluxes was found to result from to the different container implementations in CLAYPOS and r³t. The radionuclide flux from the two lowermost containers in the r³t simulation does not contribute to the overall flux out of the formation, but is shielded by

the flux from the topmost container. This is due to the fact that only diffusion is taken into account as transport process and there is no concentration gradient from the two lowermost containers towards the topmost one. Therefore, the two lowermost containers are irrelevant for the simulation and this simplification does not affect the calculated fluxes.

Downwards directed flux: CLAYPOS does simulate the radionuclide flux only in the upward direction and neglects the flux directed downwards.
 Neglecting of the downward flux can lead to a slower decrease of the radionuclide concentrations in the source and thus to an overestimation of the radionuclide fluxes. For the inventory and the repository layout regarded in this model, this does not play a role; at least for the four radionuclides relevant for the exposure. Therefore, this simplification was found not to influence the result in this case.

The preceding analysis can be summarised as follows: The difference between the radionuclide fluxes calculated with r³t and CLAYPOS was found to be caused by two differences in the applied complexity of the model. The main difference is due to the simplification in the representation of the model geometry as a one-dimensional model in CLAYPOS compared to the three-dimensional r³t model. The second simplification that was found to affect the simulation results is a difference in the near-field representation. While the CLAYPOS model uses different transport parameter values for the nearfield and the far-field, the r³t model uses identical transport parameter values for both compartments. For C-14 the two effects were quantified to be about a factor of 20 for the reduction in each model dimension, resulting in the flux of C-14 from the one-dimensional CLAYPOS model to be higher by a factor of 400 compared to the three-dimensional $r^{3}t$ model. Another factor of 2.4 is due to the underestimation of the flux by $r^{3}t$ and results from the difference in the near-field representation. The overall factor from these two effects is therefore found to be 960 explaining nicely the actual difference found. For the other three relevant radionuclides the same principal reasons are applicable, however the factors for both effects are different.

The high difference in the calculated radionuclide fluxes can raise the question whether the simplification in the model geometry of CLAYPOS is already too rigorous and hence a more complex code like r³t should be used also for the performance assessment calculation. The answer to this question is twofold: first, the simplified code clearly defends from the risk of underestimating the radionuclide fluxes in the safety assessment as it may occur for the more detailed code in case important transport effects might be not considered, e.g. a faster horizontal radionuclide dispersion along the EDZ of the repository tunnels, which was taken into account in the r³t simulation.

Second, the simplification of the model geometry is crucial for the performance assessment in terms of calculation times. The CLAYPOS simulation for the reference case regarding 41 radionuclides takes about 70 seconds computing time for 10^6 years simulation time and about 30 minutes for 10^8 years simulation time. In contrast to that, the r³t simulation for the reference case takes about two days computing time for 10^6 years simulation time regarding only four radionuclides. For a tenfold of radionuclides r³t would also need at least computing times ten times higher, i.e. about 20 days. Computing times that long prohibit performing a larger number of parameter variations and even make it impossible to perform probabilistic calculations with several hundreds of computing runs.

Therefore, a high degree of simplification is necessary to be able to perform the performance assessment calculations in convenient times. However, in the future it could be worth to reconsider the underlying model of the CLAYPOS code, whether a reduction of the conservativeness in the model is possible or not. One potential improvement could be achieved by using a one-dimensional model on a curvilinear coordinate system which is adapted to the contour lines of the diffusive propagation.



Fig. 7.15: Influence of the near-field parameter values on the radionuclide flux calculated by CLAYPOS





(1) CLAYPOS reference case with bentonite near-field parameter values

(2) CLAYPOS with Opalinus Clay near-field parameter values

- (3) r³t with two-dimensional geometry
- (4) r³t with three-dimensional geometry



Fig. 7.17: Comparison of vertical concentration profiles through the host rock from calculations with CLAYPOS and r³t



Fig. 7.18: Horizontal concentration profiles of C-14 calculated with r³t for different points in time

7.3.4 Parameter variations

To examine the influence of the different input parameters on the result of the integrated performance assessment calculation for a repository in the Opalinus Clay formation, parameter variations have been performed varying the main model parameter values in reasonable bandwidths. The results are presented in the following figures 7.19 to 7.29. An overview of all parameter variations, the most relevant nuclides and the maximum annual exposures are given in table 7.11 and are shown in figure 7.29.



7.3.4.1 Geometry parameters

Fig. 7.19: Parameter variation of geometry: thickness of the formation

Figure 7.19 shows the parameter variation of the formation thickness. Actually, not the formation thickness was varied, but the parameter value for the transport distance in the formation. Under the assumption that the repository is located exactly in the middle of the formation, the variation in the formation thickness would be two times the variation shown in the plots.

The transport distance was chosen once 10 m less and once 10 m more than the reference value of 30 m. Unless the geology of a site is normally well known, some uncertainty of the transport distance can arise from disturbing effects like the EDZ or the propagation of the alkaline plume, which both may lower the thickness of the undisturbed host rock. A higher transport distance can result from a slow transition to the adjacent rock formation. The variation of the formation thickness results in a change of the travel time of the radionuclides. Within the bandwidth of the parameter variation, always the same radionuclides are the most relevant ones. These are C-14, Se-79 and I-129. Due to its relatively short half-life, C-14 is affected the most by a variation of the formation thickness.



Fig. 7.20: Large scale variation of formation thickness

Figure 7.20 shows an additional variation of the formation thickness within a wider range. This variation is not to test the influence of a parameter uncertainty, but to demonstrate the effect of the formation thickness when comparing formations with similar transport properties at different locations and of different thickness. The transport distance is varied between 10 m and 300 m. As in the parameter variation before, the main influence on the variation of the exposure in a timeframe up to 10^5 years is from C-14 which is reduced by radioactive decay the more the higher the travel times.

If the transport distance exceeds 100 m C-14 does not play any role for the exposure anymore. For the case with a transport length of 100 m, Se-79 is the radionuclide dominating the annual exposure in the timeframe up to one million years. For an even higher transport distance of 300 m, the exposure decreases significantly and there is only a negligible exposure prior to one million years. For clay formations of such thickness one can speak of a complete containment of the waste within the formation.

The low amount of radionuclide release from the repository can be also demonstrated by looking at the temporal evolution of the radiotoxicity released from the repository. The radiotoxicity is a measure for the potential damage of a mixture of different radionuclides. It is calculated from the inventory or radionuclide flux by multiplication with the dose factors given in table 7.10.



Fig. 7.21: Radiotoxicity of the inventory of the repository

Figure 7.21 shows the temporal evolution of the radiotoxicity of the inventory of the repository. The radiotoxicity at the beginning is $1.6 \cdot 10^{12}$ Sv and decreases by radioactive decay down to $1.5 \cdot 10^{11}$ Sv at the time of 2 500 years where the containers fail. At one million years the radiotoxicity has dropped to $1.2 \cdot 10^{9}$ Sv.

Figure 7.22 shows the cumulative radiotoxicity released from the repository. Even for the case with the lowest thickness of the clay formation, only about 10^5 Sv are released from the repository within one million years; more than six orders of magnitude below the initial inventory. The reason for this is that the actinides which mainly determine the radiotoxicity of the waste are efficiently retained in the clay formation by sorption. The radiotoxicity of the four radionuclides relevant for the exposure is about $2.4 \cdot 10^6$ Sv at the beginning. This value is indicated in figure 7.22 as horizontal green line. This shows that the retention of those four nuclides is much lower.

Figure 7.23 finally shows the percentage of C-14 and I-129 released from the repository for different formation thicknesses. If the transport length exceeds 50 m, the released fraction of I-129 is lower than 1‰ of the initial inventory.







Fig. 7.23: Release of the radionuclides C-14 and I-129 from the Opalinus Clay for different formation thicknesses in per cent

7.3.4.2 Source-term parameters

The varied source-term parameters are the container lifetime shown in figure 7.24 and the solubility limits shown in figure 7.25. The uncertainty in the container lifetime is due to the uncertainty of the chemical conditions and consequently of the corrosion rate. The container lifetime was varied up and down by a factor of two. The container lifetime directly determines the beginning of the radionuclide release from the waste; as stated before, any other retention by the container was neglected in the calculations.

As one would expect, the influence of the container lifetime on the annual exposure can be seen only for earlier times. For later times, the difference in the starting time of the radionuclide release is small compared to the travel times of the radionuclides. Consequently, the effect of the variability in the container lifetime can only be seen in the exposure resulting from C-14. But also for C-14, the change in the container lifetime only slightly influences the maximum annual exposure. Even an instantaneous failure of the containers does not significantly increase the maximum annual exposure and lowers the breakthrough-time of C-14 in the biosphere by only less than a factor of two. The container lifetime therefore is a less important parameter within the varied bandwidth.


Fig. 7.24: Parameter variation of source-term: container lifetime



Fig. 7.25: Parameter variation of source-term: solubility limit

For the solubility limits three different cases were calculated. The first two cases regard for a variation of the solubility limit of all radionuclides up and down by a factor of ten and in the third case no solubility limits were taken into account at all. The only radionuclide of the four relevant radionuclides of the reference case which is solubility limited is Se-79. It reaches its solubility limit directly after container failure. The differences of the variations relative to the reference case in figure 7.25 are only due to the change in the solubility limit of Se-79 which becomes the most relevant nuclide if the solubility limit is higher than in the reference case.

The increase in the annual exposure is nearly two orders of magnitudes in the case with no solubility limits compared to the reference case. Other solubility limited radionuclides also show an increase of their contribution to the annual exposure due to lower solubility limits, however these radionuclides are not relevant for the exposure in the reference case and do not become relevant even if no solubility limits are applied at all. The solubility limit is therefore on the one hand an important parameter if one of the relevant radionuclides is solubility limited, like Se-79 in this case, but on the other hand is not important in regard of the exposure for all the other solubility limited radionuclides which have only a small contribution to the exposure in the reference case.

7.3.4.3 Transport parameters

Three transport parameters have been varied all of which have a direct influence on the transport velocity of the radionuclides and therefore on the travel times through the host rock. These are the diffusion coefficient (results shown in figure 7.26), the distribution coefficient for linear sorption (figure 7.27) and the diffusion-accessible porosity (figure 7.28). The transport parameter values were varied in the same way for the bentonite barrier and for the Clay formation.

The element-specific diffusion coefficient was varied up and down by one order of magnitude. The variation has a high impact on the resulting annual exposure. A diffusion coefficient one order of magnitude higher leads to an early breakthrough of the radionuclides through the clay formation already 500 years after the container failure. As stated before, a shorter travel time has a high influence on the annual exposure resulting from C-14 due to the small half-life of C-14 of only 5 730 years. With a diffusion coefficient ten times higher, the maximum of the C-14 peak arrives in the biosphere at about 7 000 instead of 30 000 years, which is a difference of four times the half-life of

C-14. Therefore, an increase by only a factor of about 16 would be expected due to the difference in radioactive decay. The increase found is however by a factor of about 470. This means that there is an additional increase by about a factor of 55 due to the smaller dispersion of the radionuclides during the shorter travel time through the clay formation.

A decrease of the diffusion coefficients by one order of magnitude results in a very strong reduction of the exposure. The annual exposure can be seen in figure 7.26 only for times later than 500 000 years. C-14 has completely decayed at this point in time. The most relevant nuclide for this case is Se-79. The variation of the diffusion coefficient shows the highest impact on the annual exposure from all the variations performed within reasonable bandwidths.

Figure 7.27 shows the variation of the distribution coefficients (K_d -values) for linear sorption. The K_d -values were varied up and down by one order of magnitude. Iodine is the only one of the four most relevant radionuclides in the reference case which is sorbed at all. The variation that can be seen for a K_d smaller or higher by a factor of ten is only due to the changes of the transport of I-129. A smaller K_d results in an increase of the annual exposure resulting from I-129 by up to a factor of twelve. A higher K_d results in the annual exposure from I-129 dropping below that from Se-79. Yet higher K_d -values therefore do not result in a further decrease of the exposure, since already in the case with the distribution coefficients being increased by a factor of ten, only non-sorbing radionuclides dominate the exposure.

One additional case was examined where no sorption was regarded at all. This results in a very strong increase of the annual exposure throughout the whole period and the maximum annual exposure increases to about $2.1 \cdot 10^{-3}$ Sv·y⁻¹ at about 600 000 years resulting from the radionuclides Th-230 and Ra-226. At earlier times, the annual exposure is dominated by Pu-239. The sorption therefore can be regarded as important parameter to hold back the actinides. However, within reasonable values the variation of the distribution coefficient plays no important role for the exposure.

The last parameter varied is the diffusion-accessible porosity, which was varied up and down by a factor of two. The variation of the diffusion-accessible porosity only affects Se-79 and I-129. C-14 and CI-36 show no dependency on the diffusion-accessible porosity. This is the reason why the annual exposure does not change at early times.



Fig. 7.26: Parameter variation of transport parameters: diffusion coefficient



Fig. 7.27: Parameter variation of transport parameters: distribution coefficient



Fig. 7.28: Parameter variation of transport parameters: diffusion-accessible porosity

The fact that the radionuclides react differently on the change of the diffusionaccessible porosity is astonishing at first, since the porosity is a direct parameter in the transport equation. The reason for this behaviour is described in the following. The radionuclides can be divided into three different groups on how they are affected by the diffusion-accessible porosity:

- Solubility limited radionuclides: Radionuclides which reach their solubility limit have a fixed concentration in the source, independent on the diffusion-accessible porosity. The diffusive flux however, will change in a linear way relative to the change of the diffusion-accessible porosity according to equation 3.1.
- Sorbing radionuclides: The retardation factor *R* of a radionuclide *i* is depending from the porosity *n* as given by:

$$R^{i} = 1 + \frac{1 - n^{i}}{n^{i}} \rho K_{d}^{i}, \qquad (7.2)$$

where ρ denotes the density of the rock. Therefore, the diffusive flux of a sorbing radionuclide depends on the porosity in a non-linear way.

- Neither solubility limited nor sorbing radionuclides: Since the release of the radionuclides from the waste form is independent of the porosity, radionuclides which neither sorb nor do reach a solubility limit have a higher concentration in the pore water the lower the porosity and vice versa. Therefore, the porosity affects on the one hand the concentration gradient in a way that a lower porosity results in a higher gradient, i.e. a higher radionuclide flux. On the other hand the porosity directly affects the diffusive flux in a way that a lower porosity results in a lower radionuclide flux. Both effects are just balancing each other resulting in the fact that the total diffusive flux is independent of the diffusion-accessible porosity.

From the parameter variation it follows that the diffusion-accessible porosity plays no role for non-sorbing, non retarded radionuclides and only a minor role for all other radionuclides.



Fig. 7.29: All parameter variations for the Opalinus Clay

Figure 7.29 resumes the curves from all parameter variations shown before. The yellow area indicates the bandwidth of the annual exposure obtained by the parameter variations within reasonable values. The results from the parameter variations are also tabulated in table 7.11.

As a result from the parameter variations it is found that the diffusion coefficient is the most important of the examined parameters. Other important parameters are the formation thickness, the distribution coefficients and with some limitations also the solubility limits.

Tab. 7.11: Results of parameter variations for the Opalinus ClayResult of the reference case is given for comparisonMaximum annual exposure is given within the period of 10⁶ yearsAn index i denotes a an element-specific parameter

			Important	Maximum annual exposure			
Parameter Case Value radionuclide		radionuclides	nuclide	time [y]	value [Sv·y⁻¹]		
Reference ca	se		C-14, Se-79, I-129	I-129	1.0·10 ⁶	2.2·10 ⁻⁸	
	high	40 m	C-14, Se-79, I-129	I-129	1.0·10 ⁶	8.0·10 ⁻⁹	
	low	20 m	C-14, Se-79, I-129	C-14	17 870	6.1·10 ⁻⁸	
thickness of		10 m	C-14, Se-79, I-129	C-14	10 500	7.7·10 ⁻⁷	
formation		50 m	C-14, Se-79, I-129	I-129	1.0·10 ⁶	4.1·10 ⁻⁹	
		100 m	Se-79	Se-79	1.0·10 ⁶	4.9·10 ⁻¹¹	
		300 m	I-129	no relevar	nt exposure	up to 10 ⁶ y	
	high	5 000 y	C-14, Se-79, I-129	I-129	1.0·10 ⁶	2.2·10 ⁻⁸	
container lifetime	low	1 250 y	C-14, Se-79, I-129	I-129	1.0·10 ⁶	2.2·10 ⁻⁸	
	no	0 y	C-14, Se-79, I-129	I-129	1.0·10 ⁶	2.2·10 ⁻⁸	
	low	S _i /10	C-14, Cl-36, I-129	I-129	1.0·10 ⁶	2.2·10 ⁻⁸	
solubility limit	high	S _i ·10	C-14, Se-79	Se-79	1.0·10 ⁶	6.7·10 ⁻⁸	
	no	0 mol·l⁻¹	C-14, Se-79	Se-79	1.0·10 ⁶	1.3·10 ⁻⁶	
diffusion	low	D _i /10	Se-79, CI-36	Se-79	1.0·10 ⁶	1.4·10 ⁻¹¹	
coefficient	high	D _i ·10	C-14, Se-79, I-129	C-14	8 750	2.7·10 ⁻⁶	
	high	K _{Di} ·10	C-14, Se-79	Se-79	1.0·10 ⁶	5.9·10 ⁻⁹	
distribution coefficient	low	K _{Di} /10	C-14, I-129	I-129	1.0·10 ⁶	2.6·10 ⁻⁷	
	no	0 m ³ ·kg⁻¹	Pu-239, Th-230	Th-230	5.6·10⁵	2.1·10 ⁻³	
norosity	low	n _i /10	C-14, Se-79, I-129	Se-79	1.0·10 ⁶	7.3·10 ⁻⁹	
porosity	high	n _i ·10	C-14, Se-79, I-129	I-129	1.0·10 ⁶	8.2·10 ⁻⁸	

7.3.5 Probabilistic calculations

To verify the results about the influence of the parameter uncertainty obtained from the parameter variations, a probabilistic assessment by the Monte Carlo method has been performed with 1 000 simulating runs using the STATIST and STATOUT codes of the EMOS package. Each single simulation was performed using the same codes as for the calculation of the reference case.

The same parameters as those used for the parameter variations have also been used as random variables in the probabilistic assessment, except for the thickness of the formation which could not be varied since this feature is not implemented in the current version of CLAYPOS. This results in a set of eight independent random variables which are listed in table 7.12 together with their bandwidths and the distribution functions used. Except for the container lifetime, the parameter values are all element-specific. For element-specific parameters, only one element was varied independently as lead element, while all other elements were varied in the same manner as the lead element.

The distributions of the random variables were chosen as uniform distribution functions since no information about preferential values of the parameters was available, so each of the values within the bandwidth has the same likelihood to be used in the calculation. Except for the container lifetime, for parameter values which are varying by more than one order of magnitude, logarithmic distribution functions were used.

Tab. 7.12:	Random variable	es, bandwidths a	and distribution functions
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both for the bentonite	and the clay f	forma	ation.				
for the probabilistic a	assessment.	The	transport	parame	eters	were	varied

Parameter		Band	Distribution	
r ai a		lower limit upper limit		function
	Container lifetime	1 y	5 000 y	uniform
eld	Solubility limits	ref. value / 10	ref. value · 10	log. uniform
Near-fi	Diffusion coefficients	ref. value / 10	ref. value · 10	log. uniform
	Distribution coefficients	ref. value / 10	ref. value · 10	log. uniform
	Porosities	ref. value / 2	ref. value · 2	uniform
pla	Diffusion coefficients	ref. value / 10	ref. value · 10	log. uniform
Ir-fie	Distribution coefficients	ref. value / 10	ref. value · 10	log. uniform
Ц	Porosities	ref. value / 2	ref. value · 2	uniform

7.3.5.1 Uncertainty analysis

All 1 000 Monte Carlo simulations resulted in a radionuclide release from the clay formation and therefore in a exposure in the biosphere. All calculated annual exposures are below the regulatory limit of $3 \cdot 10^{-4}$ Sv·y⁻¹ within one million years. One simulation reaches a annual exposure of $3.4 \cdot 10^{-4}$ Sv·y⁻¹, but for 10^8 years. An overview of the ten simulations yielding the highest exposures is shown in table 7.13. Each line of the table gives the information about one simulation. The lines are sorted in the order of decreasing maximum annual exposure. The first three columns are the simulation number, the maximum exposure and the point in time at which the maximum exposure occurred. The remaining six columns give those three nuclides which have the largest contribution to the exposure at this point in time and their contribution to the annual exposure.

All ten simulations listed in table 7.13 reach their maximum exposure at the end of the simulation, at 10⁸ years by Ra-226. All those simulations are characterized by high diffusion coefficients and low distribution coefficients leading to a low retention and fast transport of actinides from the Uranium and Thorium decay chains. As an example, the values of the transport parameters used in simulation 4 are given in table 7.14 as factors relative to the values used in the reference case.

	Maxi	mum	Most relevant nuclides						
Nr.	expo	sure	1		2.		3.		
	Value [Sv·y⁻¹]	Time [y]	Name	Value [Sv·y⁻¹]	Name	Value [Sv·y⁻¹]	Name	Value [Sv·y⁻¹]	
4	3.4·10 ⁻⁴	9.9·10 ⁺⁷	Ra-226	3.4·10 ⁻⁴	Ra-228	5.6·10 ⁻⁰⁸	Pb-210	1.7·10 ⁻⁰⁸	
210	5.2·10 ⁻⁵	9.9·10 ⁺⁷	Ra-226	5.2·10 ⁻⁵	Pb-210	1.8·10 ⁻⁰⁹	Ra-228	4.6·10 ⁻¹⁰	
5	5.1·10 ⁻⁵	9.9·10 ⁺⁷	Ra-226	5.1·10 ⁻⁵	Pb-210	1.9·10 ⁻⁰⁹	Ra-228	3.7·10 ⁻¹⁰	
512	2.8·10 ⁻⁵	9.9·10 ⁺⁷	Ra-226	2.8·10 ⁻⁵	Pb-210	9.6·10 ⁻¹⁰	Ra-228	1.3·10 ⁻¹⁰	
185	2.4·10 ⁻⁵	9.9·10 ⁺⁷	Ra-226	2.4·10 ⁻⁵	Pb-210	6.5·10 ⁻¹⁰	Ra-228	6.9·10 ⁻¹²	
837	1.5·10 ⁻⁵	9.9·10 ⁺⁷	Ra-226	1.5·10 ⁻⁵	Pb-210	5.3·10 ⁻¹⁰	Ra-228	4.8·10 ⁻¹¹	
827	1.4·10 ⁻⁵	9.9·10 ⁺⁷	Ra-226	1.4·10 ⁻⁵	Pb-210	6.7·10 ⁻¹⁰	Pa-231	8.2·10 ⁻¹¹	
514	1.4·10 ⁻⁵	9.9·10 ⁺⁷	Ra-226	1.4·10 ⁻⁵	Pb-210	4.2·10 ⁻¹⁰	Ra-228	1.1·10 ⁻¹¹	
85	8.6·10 ⁻⁶	9.9·10 ⁺⁷	Ra-226	8.6·10 ⁻⁶	Pb-210	2.3·10 ⁻¹⁰	Ra-228	1.3·10 ⁻¹²	
565	8.1·10 ⁻⁶	9.9·10 ⁺⁷	Ra-226	8.1·10 ⁻⁶	Ra-228	6.4·10 ⁻¹⁰	Pb-210	3.7·10 ⁻¹⁰	

Tab. 7.13: Simulations with the highest annual exposure

Tab. 7.14: Values of the random variables in simulation 4

Factors are given relative to the reference values

Parameter		Factor
	Container lifetime	1.1
ple	Solubility limits	3.1
ar-fi	Diffusion coefficients	7.8
Ne	Distribution coefficients	0.2
	Porosities	2.0
Ir-field	Diffusion coefficients	9.5
	Distribution coefficients	0.15
Ц	Porosities	1.8

When all simulations are ordered according to their maximum annual exposure, the first simulation reaching its maximum annual exposure within one million of years is on 14^{th} place with a value of $4.9 \cdot 10^{-6} \text{ Sv} \cdot \text{y}^{-1}$ and is also dominated by Ra-226. The first simulation that is not dominated by Ra-226 at its maximum annual exposure is on 19^{th} place being dominated by C-14 with a value of $2.8 \cdot 10^{-6} \text{ Sv} \cdot \text{y}^{-1}$. The maximum annual exposure of each simulation and the point of time of its occurrence are shown in figure 7.30 with the dominant radionuclide being colour-coded.



Fig. 7.30:Time and value of the maximum annual exposureThe dominant radionuclide is colour-coded

There exist three accumulation points in figure 7.30; one for early times around 10^4 years being dominated by C-14, one for times later than 10^6 years mainly being dominated by I-129 and one for the simulation end being dominated by Ra-226. In only a few simulations Se-79 dominates the maximum exposure. For a probabilistic assessment, the annual exposure is characterized by a frequency distribution of exposures, not by a single number. The frequency distribution is characterised by the statistical indicators given in table 7.15. The indicators are listed for the time of the maximum annual exposure and for four additional points in time.

The mean value given in table 7.15 is an estimate of the expected maximum annual exposure. The quality of this estimate is characterized by the confidence interval, which refers to a confidence of 95%. There is a probability of 95% that the actual maximum annual exposure is within the confidence interval reaching from 0.0 to $2.4 \cdot 10^{-6}$ Sv·y⁻¹. Figure 7.31 shows the cumulative frequency distribution of the maximum annual exposure and the confidence limits, while figure 7.32 shows the frequency density distribution of the maximum annual exposure as bar chart. The mean value for the maximum annual exposure is $8.3 \cdot 10^{-7}$ Sv·y⁻¹ which does not correspond to the centre of the distribution shown. Since the frequency distribution does not represent a normal distribution, the confidence interval is calculated by the Chebyshev's inequality as given in [35]. Using this method, the confidence interval is decreasing with the square root of the sample size and is found to be sufficiently small in this case. The grey lines in figure 7.31 show the frequency distribution for one million of years. This distribution does not differ very much from the one for 10⁸ years indicating that most of the simulations reach their maximum annual exposure before or not very much later than one million of years. The temporal evolution of the mean annual exposure, the confidence interval, the median and the 95%-quantile are shown in the figures 7.33 and 7.34.

		10 ⁴ y	10 ⁵ y	10 ⁶ y	10 ⁷ y	Max.
Mean value		1.7·10 ⁻⁰⁷	8.4·10 ⁻⁰⁸	2.3·10 ⁻⁰⁷	1.2·10 ⁻⁰⁷	8.3·10 ⁻⁰⁷
Standard deviation		4.7·10 ⁻⁰⁷	1.4·10 ⁻⁰⁶	2.2·10 ⁻⁰⁶	1.9·10 ⁻⁰⁶	1.1·10 ⁻⁰⁵
Confidence interval	upper limit	2.3·10 ⁻⁰⁷	2.8·10 ⁻⁰⁷	5.3·10 ⁻⁰⁷	3.9·10 ⁻⁰⁷	2.4·10 ⁻⁰⁶
	lower limit	1.0·10 ⁻⁰⁷	0.0	0.0	0.0	0.0
Median		1.3·10 ⁻¹²	6.8·10 ⁻¹¹	1.5·10 ⁻⁰⁸	1.6·10 ⁻⁰⁸	6.0·10 ⁻⁰⁸
95%-quantile		1.2·10 ⁻⁰⁶	1.2·10 ⁻⁰⁷	6.4·10 ⁻⁰⁷	3.3·10 ⁻⁰⁸	1.4·10 ⁻⁰⁶
Maximum		4.3·10 ⁻⁰⁶	4.2·10 ⁻⁰⁵	6.6·10 ⁻⁰⁵	6.0·10 ⁻⁰⁵	3.4·10 ⁻⁰⁴

Tab. 7.15: Statistical indicators for the annual exposure for different times in $[Sv \cdot y^{-1}]$



Fig. 7.31: Complementary cumulative frequency of the maximum annual exposure The coloured lines represent the frequency distribution for 10⁸ years while the grey lines represent the one for 10⁶ years.



Fig. 7.32: Frequency density of the maximum annual exposure



Fig. 7.33: Mean value and confidence interval of the annual exposure



Fig. 7.34: Maximum, median and 95%-quantile of the annual exposure

7.3.5.2 Global sensitivity analysis

While the uncertainty analysis described in the previous section gives the variability of the exposure due to the variability of the input data, the sensitivity analysis tries to quantify the contribution of each input parameter to the variation of the result. This section describes a global sensitivity analysis in which all input parameters are varied at once based on the Monte Carlo method. The sensitivity of the results was calculated by the Spearman-Test. The Spearman correlation coefficient, which is used in the following, was calculated on the basis of ranks. The values of the random variable are replaced by their rank, i.e. by their position in a sorted list of the values. The rank transformation results in a linear correlation between the input parameter and their value, enhancing the significance of the method.

The results of the Spearman test are shown for 10^4 , 10^5 , 10^6 and 10^7 years and for the time of the maximum annual exposure in table 7.16. The numbers given denote the importance of the parameter at the given point in time for those parameters whose rank was identified in the hypothesis testing with a significance of 5%. Differences in rank of the other parameters are regarded as insignificant. Orange shaded fields indicate parameters yielding a correlation coefficient greater than 0.1. Correlations lower than 0.1 may occur by random correlation and are regarded as not relevant.

Tab. 7.16: Ranking of random variables by Spearman test for different points in time Max denotes the point in time of the maximum annual exposure. Ranks are given for those parameters which were identified in the hypothesis testing with a significance of 5%.

Para	meter	10⁴y	10⁵y	10 ⁶ y	10 ⁷ y	Max.
Near-field	Container lifetime			7		
	Solubility limits		3	3		4
	Diffusion coefficients	2	2	4		5
	Distribution coefficients			2	3	2
	Porosities					
Ir-field	Diffusion coefficients	1	1	1	1	1
	Distribution coefficients			5	2	6
Ц	Porosities			6	4	3

Orange shaded fields indicate a correlation coefficient greater than 0.1.

The most important parameter for all times is the diffusion coefficient of the radionuclides in the clay formation. The diffusion coefficient in the near-field is important for times up to 10^5 years and looses importance for later times. The distribution coefficient of the clay formation is only important for very late times, while the distribution coefficient of the near-field is the second important parameter at 10^6 years. The influence of the distribution coefficient has been examined with the parameter variations in section 7.3.4.3, showing a variation of about one order of magnitude in the annual exposure at 10^6 years. The sensitivity analysis now surprisingly shows that this effect is due to the near-field distribution coefficient, not the one in the clay. This is confirmed by additional parameter variations in which the distribution coefficient in each compartment has been varied individually. The result of these parameter variations are shown in figure 7.35, confirming that the variation already shown in figure 7.27 results by 85% from the nearfield distribution coefficient. This is due to the distribution coefficient of lodine being nearly one order of magnitude higher in the near-field than in the clay formation.

The influence of the diffusion coefficient and the distribution coefficient in the clay formation on the annual exposure is further illustrated in the figures 7.36 and 7.37. While there can be seen a clear relationship between a higher diffusion coefficient and a higher annual exposure in figure 7.36, no relationship is observed in figure 7.37 between the distribution coefficients and the annual exposure.



Fig. 7.35: Parameter variation of distribution coefficients broken down into near-field and clay formation



Fig. 7.36: Influence of diffusion coefficients in the clay formation on the maximum annual exposure in terms of ranks



Fig. 7.37: Influence of distribution coefficients in the clay formation on the maximum annual exposure in terms of ranks

7.3.6 Disturbed evolution scenario: fracture

In the following section a disturbed evolution scenario is examined regarding a continuous fracture from the two aquifers over- and underlying the clay formation. In the worst case the fracture intersects the whole formation, the bentonite near-field and the container in a way that the radionuclides are directly released from the container into the fracture. This is the situation that was shown schematically in figure 3.1b. As alternative a situation was examined where the fracture intersects only the host rock and bypasses the container in a distance of 5 m.

A hydraulic gradient of $1 \text{ m} \cdot \text{m}^{-1}$ between the both aquifers is assumed, which is a rather high value. The transmissivity of the fracture was assumed to $10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$. The width of the fracture *b* can be estimated from the transmissivity *T* by the cubic law

$$T = \frac{\rho g}{\mu} \frac{b^3}{12},$$
 (7.3)

where ρ denotes the density and μ for the viscosity of the fluid and g denotes the gravity. The values which were assumed for the other data describing the geometry of the fracture are given in table 7.17. The residence time of the water in the fracture can be estimated by $t = (L \cdot b)/(T \cdot I)$ to be less than one year.

Tab. 7.17: Geometry input data for the fracture scenario

Parameter		Symbol	Value
Transmissivity	[m ² ·s⁻¹]	Т	10 ⁻¹⁰
Trace length of fracture	[m]	x	10
Width of open flow channel per rock area	[m·m⁻²]	W	5·10 ⁻³
Width of the fracture	[m]	b	6·10 ⁻⁶
Hydraulic gradient	[m·m⁻¹]	Ι	1
Volume flow in the fracture	[m ³ ·y ⁻¹]	Q	3·10 ⁻²
Transport pathway length	[m]	L	40

The radionuclide flux from the container has been calculated with the program CLAYPOS as in the reference case, but only for one single container. The transport in the fracture was calculated with the program CHETMAD. It denotes the advective flow in the fracture and the matrix diffusion, i.e. diffusion of the radionuclides into the clay

formation, where the radionuclides can be sorbed. The same element-specific diffusion coefficients and distribution coefficients for the radionuclides in the Opalinus Clay have been chosen as in the reference case.

The results from the calculation are shown in terms of radionuclide fluxes in figure 7.38 and as annual exposure in figure 7.39. It can be seen from the fluxes that the release from the Opalinus Clay shown as dashed lines in figure 7.38 is only slightly retarded relative to the release from the container shown as solid lines. This shows that the retention by matrix diffusion is rather low. The positive characteristic of the clay formation - that the diffusion coefficients of the radionuclides in the formation are low - leads in the case of the disturbed evolution by a single fracture to a low retention of the radionuclides.

The scenario of a single fracture leads to an almost constant annual exposure versus time of about 10^{-5} Sv·y⁻¹. The most relevant radionuclides are Pu-240, Pu-239 and Ra-226. A release of radionuclides through a single fracture over such a long time is however not realistic. As said before, clay formations tend to self-seal fractures. The transmissivity of the fracture therefore is decreasing with time, like is the annual exposure sure. To model this effect in a realistic way, a program which uses transient parameters would be needed.

Two other situations have been examined within the calculations, which are briefly discussed in the following: on the one hand that the fracture does not intersect directly the container but there remains about 5 m of intact bentonite and on the other hand that the hydraulic gradient is one order of magnitude lower. In the first case, the exposure is reduced for early times by two orders of magnitude and for later times by one order of magnitude. This effect however is only due to the retention in the five meters of bentonite. In the second case, the radionuclides are somewhat more retarded as in the case shown in figure 7.38, but the retardation is still too small that it has a significant influence on the resulting exposure.



Fig. 7.38: Mobilisation and release from the container as well as release from the Opalinus Clay for the scenario of a continuous fracture dotted lines: mobilisation solid lines: release from the container dashed lines: release from the Opalinus Clay formation



Fig. 7.39: Annual exposure for the scenario of a continuous fracture

7.4 Lower Cretaceous Clay formation in Northern Germany

The second type of clay formation that was considered by the DBE in the framework of the research project GENESIS for the disposal of high level wastes is the Apt, which is part of the Lower Cretaceous Clays in Northern Germany. The Lower Cretaceous Clay formations were deposited in the Lower Saxon Basin within a period of 45 million years and are between 144 and 99 million years old.



Fig. 7.40: Palaeogeographical situation of the Lower Saxon Basin at the time of the Hauterive after [32]

The long sedimentation period of the Lower Cretaceous Clays resulted in a rather complex system which is typically divided into 6 stages:

- Wealden (144 to 137 million years),
- Valangain (137 to 132 million years),

- Hauterive (132 to 127 million years),
- Barrême (127 to 121 million years),
- Apt (121 to 112 million years) and
- Alb (112 to 99 million years).

Due to differences in sediment thickness and lithology, the Lower Saxon Basin is spatially divided into three parts, the West, Central and East part. The Lower Saxon basin with its three parts and the adjacent land and swell areas at the time of the Hauterive is shown in figure 7.40. The Lower Saxon Basin was rather small with a length of 280 km and a mean width of 80 km. The water depth is estimated to a few hundred meters and the sedimentation rates were high. The basin was separated by a mainly submarine swell, the Pompeckj' Swell, from the cretaceous North Sea. However, the uplift and depression (epirogeny) of the area resulted in a changing degree of separation over the long time, influencing the sedimentation process. During the Apt and the Alb, the Pompeckj' Swell lost its separating function of the Lower Saxon Basin to the North Sea and regions that had been land surface before became flooded [32]. The situation of the southeast part of the Lower Saxon Basin during the Apt is shown in figure 7.41.

The region northeast of Hannover has been chosen by the DBE as model area for a generic waste repository in the Lower Cretaceous Clays. The complete cross-section of the model area is shown in figure 7.42. The Apt as the potential host formation is found in a depth between -250 and -470 metres below surface level and has a thickness of 220 metres. The main reasons to choose the Apt was on the one hand because of the low depth what eases the construction of the tunnels and on the other hand because of low organic carbon and pyrite contents.

The Hauterive is also described in the literature as a very homogenous and suitable formation, but is buried at a very large depth what makes it much more difficult to construct the repository due to high rock pressure and temperature. However, it has to be kept in mind that the formation of glacial channels during cold climate periods has occurred in Northern Germany. In Gorleben for example, the sediments were eroded up to a depth of 200 to 250 m. In respect thereof, a repository in a deeper formation than the Apt would be more favourable.



Fig. 7.41: Southeast part of the Lower Saxon Basin at the time of the Apt after [32]
A = Thickness of Apt < 100 m; B = Thickness of Apt > 200 m;
C = Land or shallow water sediments eroded; D = Swell areas



Fig. 7.42: Cross-section of the model area in Northern Germany [48]

7.4.1 Input data

Quite some of the input data, especially regarding the source term and the biosphere, are the same in the model for the Lower Cretaceous Clays as in the model for the Opalinus Clay. In these cases, only references to the respective preceding sections will be given in the following.

7.4.1.1 Geometry

The geometry layout of the repository was determined by the DBE from calculations of the temperature evolution. Due to the lower burial depth of the Apt in comparison to the Opalinus Clay also the temperature of the rock in the repository depth is lower, which is about 22° C in the Apt compared to 43° C in the Opalinus Clay. Therefore, a higher heat input from the repository into the formation is permissible before the critical temperature of 100° C is reached in the bentonite and the containers can be stored closer to each other in the repository. A borehole distance of 47 m was calculated with five containers in each borehole. This borehole distance results in an area of the hexagonal reference section of about 1 913 m² and a width of the square CLAYPOS model of 43.74 m.

The transport distances in the host rock are calculated under the assumption that the repository is located exactly in the middle of the Apt formation. Additionally, the Alb was considered as low-permeable barrier with an additional thickness of 250 m.

Parameter		Value
Borehole length	[m]	50
Numbers of containers per borehole	[-]	5
Area of the hexagonal reference section	[m²]	1 913.05
Width of the CLAYPOS model	[m]	43.74
Transport length in the bentonite	[m]	10
Transport length in the Apt	[m]	80
Transport length in the Alb	[m]	250

Tab. 7.18: Geometry input data for the Lower Cretaceous Clays

7.4.1.2 Source term

Nearly all source term data was chosen for the Lower Cretaceous Clays as in the model for the Opalinus Clay given in section 7.3.1.2 on page 104. The only difference is the interim storage time, which was calculated by the DBE due to thermal constraints to 30 years. Since the inventory was calculated for an interim storage time of 10 years an additional 20 years were taken into account in the model.

Another potential difference in the source term related input data could be the values for the solubility limits, since the pore water of the Lower Cretaceous Clays is expected to be more saline than the pore water of the Opalinus Clay. The influence of saline water on the solubility limits in bentonite geotechnical barriers has been studied in connection with repositories in granite formations. In [69] the influence of saline water on the solubility limits is expected to be rather low with a tendency on slightly higher solubility limits for some radionuclides like Strontium or Radium. Since the actual pore water composition or actual solubility limits are not known, the same solubility limits as in the model for the Opalinus Clay were used.

7.4.1.3 Near-field

The transport parameter values in the geotechnical bentonite barrier in the near-field were chosen the same as in the model for the Opalinus Clay given in section 7.3.1.3 on page 110. Like for the source term parameter values, there might be an influence due to potentially higher saline pore water in the Lower Cretaceous Clays. In [69] an influence of saline water on the diffusion coefficient of C, Cl, Ni, Se, Sr, I and Ra was considered with a tendency of higher values and an influence on the distribution coefficients of Ni, Sr, Cs and Ra with the tendency of lower values. However, since the actual pore water composition and its influence on the transport parameter values are not known, the same values as in the model for the Opalinus Clay were used.

7.4.1.4 Far-field

The transport length in the host rock, which is the Apt formation, is 80 m. Overlying the Apt is the Alb with an additional transport length of 250 m. For the Apt and for the Alb the same transport properties are assumed in the following. There exists only very few data for the transport parameter values of these two formations. Most values were de-

rived on samples of the cored drilling Konrad 101 which was sunk as part of the research programme related to the Konrad waste repository site, where these two formations are found in the overburden [40].

A literature study for porosity data derived eight values for the Alb with a mean value of 0.155 and one value for the Apt of 0.167. Therefore a value of 0.16 was used for both formations for all radionuclides except Chloride, Selenium, Molybdenum and Iodine. For these four elements an anion exclusion by a factor of two was assumed and consequently a porosity of 0.08 was used.

No diffusion coefficients are available for both formations. Table 7.19 gives an overview of the diffusion coefficients found for neutral species in five different types of clay formations ranging from very old consolidated claystones like the Opalinus Clay to Quaternary unconsolidated clays like the Lauenburger Clay. The range of the pore diffusion coefficients is about one order of magnitude. As cautious assumption, the highest value of $2.6 \cdot 10^{-10}$ m²·s⁻¹ was used for all radionuclides.

The values for the distribution coefficients are given in table 7.20. They were determined on samples from the Alb und Hauterive; for Technetium and Palladium on samples of Oxford Marls [40]. All other elements which are not listed are assumed not to sorb ($K_d = 0$).

Tab. 7.19: Diffusion coefficient for different clay formations for neutral species
 Some values are calculated from D_e and the porosity given by equation 7.1.
 All values given are perpendicular to the formation.

Formation	Location	D _p [m ² ⋅s ⁻¹]	n	Tracer	Ref.
Opalinus Clay	Mont-Terri	3.1·10 ⁻¹¹		He	[52]
Opalinus Clay	Benken	7.1·10 ⁻¹¹	0,14	НТО	[39]
Callovo-Oxfordian	Bure	1.3·10 ⁻¹⁰	0,18	НТО	[2]
Boom Clay	Mol	2.2·10 ⁻¹⁰		НТО	[13]
Lauenburger Clay	Gorleben	2.6·10 ⁻¹⁰		Не	[50]

Element	K _d [m ³ /kg]	Element	K _d [m ³ /kg]	Element	K _d [m ³ /kg]
Тс	5·10 ⁻⁴	С	2·10 ⁻²	U	0.012
Se	5·10 ⁻⁴	Sr	2·10 ⁻⁴	Ra	3·10 ⁻³
Zr	8·10 ⁻²	Np	6·10 ⁻²	Ni	1·10 ⁻³
Nb	1	Pu	0.5	Th	8·10 ⁻²
Cs	5·10 ⁻²	Am/Cm	0.5	Ра	1
I	0	Pb	6·10 ⁻⁴	Ac	4·10 ⁻²

Tab. 7.20: Distribution coefficients for the Lower Cretaceous Clays

7.4.1.5 Biosphere

The same parameter values and assumptions for the biosphere were used in the model for the Lower Cretaceous Clays as in the model for the Opalinus Clay given in section 7.3.1.5 on page 113 and also a ground water flow of $10^5 \text{ m}^3 \cdot \text{y}^{-1}$ was assumed in the module CLAYPOS to convert the radionuclide flux from the clay formation to concentration values.

7.4.2 Reference case

Using the input data described in section 7.4.1, an integrated performance assessment calculation was performed using the modules CLAYPOS and EXCON. While figure 7.43 shows the radionuclide flux from the Lower Cretaceous Clays, figure 7.44 shows the resulting annual exposure. The annual exposure is mainly determined by I-129. CI-36 plays a minor role while in contrast to the model for the Opalinus Clay Se-79 does not play any role at all. This is due to the small, but non-zero distribution coefficient assumed for Selenium in the model for the Lower Cretaceous Clays in combination with the long transport length.

The maximum annual exposure within one million years is about 10^{-9} Sv·y⁻¹ and the maximum flux is about 20 Bq·y⁻¹ both resulting from I-129. The maximum annual exposure in the whole regarded time-span is about $5 \cdot 10^{-8}$ Sv·y⁻¹ and the maximum flux is about 850 Bq·y⁻¹ both resulting from I-129 at about 4.5 million years.

When the curve for the annual exposure shown in figure 7.44 is compared to the curves in figure 7.20 given for the variation of the formation thickness for the Opalinus Clay, it can be seen that for the Lower Cretaceous Clays the exposure in the biosphere even occurs earlier than for the Opalinus Clay with a thickness of 100 m. This is due to the diffusion coefficient being three times higher, here. This effect is even more pronounced since the annual exposure in the case of the Opalinus Clay with a thickness of 100 m is mainly due to Se-79 until 10^6 years, while Selenium does not play a role for the Lower Cretaceous Clays. The annual exposure resulting from lodine is only reaching a maximum of 10^{-12} Sv·y⁻¹ within one Million years for the Opalinus Clay. This comparison again pronounces the importance of the diffusion coefficient for the radionuclide transport.

Comparing the radionuclide flux to the ones in the reference case of the Opalinus Clay, it is obvious that the fluxes are arriving significantly later in the biosphere for the Lower Cretaceous Clays than for the Opalinus Clay. However, the maximum value of the flux for the radionuclide I-129 is in the same order of magnitude in both cases. This is due to the long half-life of I-129. I-129 turns out to be the most relevant radionuclide for the repository systems studied here.



Fig. 7.43: Radionuclide fluxes from the far-field of the model area in Northern Germany



Fig. 7.44: Annual exposure versus time for the model area in Northern Germany

7.4.3 Parameter variations

The same parameter variations as for the Opalinus Clay have been performed for the Lower Cretaceous Clays. Figure 7.45 shows the temporal evolution of the annual exposure for all of the parameter variations. The yellow area indicates the bandwidth of the annual exposure by the parameter variations within reasonable values. It seems unlikely that the diffusion coefficient in the Lower Cretaceous Clay formation might be even one order of magnitude higher than the already high value assumed. In this case the diffusion coefficient would be in the range of that in free water which is e.g. for He-lium $5.5 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ [27]. To pronounce this, the area below the curve of the high diffusion coefficient has not been included in the yellow shaded area.



Fig. 7.45: All parameter variations for the model area in Northern Germany

Apart from the variation of the diffusion coefficient, all other variations lie within a comparatively narrow band. Altogether it can be stated that the variation of all parameters apart from the diffusion coefficient shows a much lower impact on annual exposure than for the Opalinus Clay. Even the curve neglecting any sorption does not lead to very high annual exposures and stays below 10^{-6} Sv·y⁻¹ for all times. This effect is due to the high thickness of the formation in the case of the Lower Cretaceous Clays.

Like in the case for the Opalinus clay, also for the Lower Cretaceous Clays the variation of the diffusion coefficient shows the highest impact on the annual exposure. The impact however is mainly on the time of breakthrough of the radionuclides from the clay formation, and less on the maximum annual exposure. This leads to a most remarkable conclusion for a repository in a clay formation of a thickness like the Lower Cretaceous Clays, in the reference case: within realistic bandwidths of their values, none of the transport parameters is of crucial importance for the safety of the repository.

7.4.4 Probabilistic calculations

As for the Opalinus Clay formation, a probabilistic assessment with 1 000 Monte Carlo simulations has been performed for the Lower Cretaceous Clays. The same eight independent random variables, bandwidths and distribution functions have been used here as described in table 7.12. This also applies to the diffusion coefficient in the clay formation, although a diffusion coefficient one order of magnitude higher than the reference value is an unrealistic assumption as already pointed out for the parameter variations. This leads to an overestimation of the annual exposures. The results are briefly discussed in the following in comparison to those described in section 7.3.5 for the Opalinus Clays.

7.4.4.1 Uncertainty analysis

In comparison to the Opalinus Clay, fewer simulations resulted in a radionuclide release from the Lower Cretaceous Clays formation. No radionuclide release was observed prior 10 000 years for any simulation, which denotes a complete containment of the radionuclides prior this time; independent from the parameters. At 100 000 and 1 000 000 years, 552 respectively 50 simulations resulted in no radionuclide release. At one million years about 50% of the simulations resulted in an annual exposure below $10^{-14} \text{ Sv} \cdot \text{y}^{-1}$, which is a value which still could be referred to as complete containment. All calculated annual exposures are at least three orders of magnitude below the regulatory limit of $3 \cdot 10^{-4} \text{ Sv} \cdot \text{y}^{-1}$. The maximum annual exposure obtained in simulation 4 is $2.7 \cdot 10^{-7} \text{ Sv} \cdot \text{y}^{-1}$. An overview of the ten simulations yielding the highest annual exposure is shown in table 7.21.

The maximum exposure is caused by I-129 in all simulations and occurs later than one million years. The second important radionuclide is CI-36 and in a few cases Se-79. No other radionuclides play a significant role for the maximum annual exposure in any simulation. As for the Opalinus Clay, the highest annual exposure found is reached in

simulation 4. However, the order of the other simulations in table 7.21 differs from that for the Opalinus Clay. The maximum annual exposures for all 1 000 simulations and the point of time of their occurrence is shown are figure 7.46.

	Maximum annual exposure		Most relevant nuclides						
Nr.			1.		2.		3.		
	Value [Sv·y⁻¹]	Time [y]	Name	Value [Sv·y⁻¹]	Name	Value [Sv·y⁻¹]	Name	Value [Sv·y⁻¹]	
4	2.7·10 ⁻⁷	1.5·10 ⁺⁶	I-129	2.7·10 ⁻⁷	CI- 36	1.2·10 ⁻¹⁰	Se- 79	3.5·10 ⁻¹¹	
993	2.4·10 ⁻⁷	1.8·10 ⁺⁶	I-129	2.4·10 ⁻⁷	CI- 36	5.5·10 ⁻¹¹	Se- 79	8.3·10 ⁻¹⁴	
512	2.2·10 ⁻⁷	2.2·10 ⁺⁶	I-129	2.2·10 ⁻⁷	CI- 36	2.0·10 ⁻¹¹	Se- 79	1.9·10 ⁻¹¹	
565	2.2·10 ⁻⁷	1.8·10 ⁺⁶	I-129	2.2·10 ⁻⁷	CI- 36	5.3·10 ⁻¹¹	Se- 79	1.1·10 ⁻¹²	
5	2.1·10 ⁻⁷	1.8·10 ⁺⁶	I-129	2.1·10 ⁻⁷	CI- 36	5.3·10 ⁻¹¹	Se- 79	1.6·10 ⁻¹¹	
210	1.9·10 ⁻⁷	1.8·10 ⁺⁶	I-129	1.9·10 ⁻⁷	CI- 36	4.8·10 ⁻¹¹	Se- 79	1.5·10 ⁻¹⁵	
998	1.8·10 ⁻⁷	2.2·10 ⁺⁶	I-129	1.8·10 ⁻⁷	CI- 36	2.0·10 ⁻¹¹	Se- 79	8.4·10 ⁻¹⁵	
823	1.8·10 ⁻⁷	1.8·10 ⁺⁶	I-129	1.8·10 ⁻⁷	CI- 36	5.3·10 ⁻¹¹	Se- 79	2.3·10 ⁻¹⁷	
185	1.8·10 ⁻⁷	1.8·10 ⁺⁶	I-129	1.8·10 ⁻⁷	Se- 79	1.2·10 ⁻¹⁰	CI- 36	5.5·10 ⁻¹¹	
390	1.7·10 ⁻⁷	2.2·10 ⁺⁶	I-129	1.7·10 ⁻⁷	CI- 36	1.7·10 ⁻¹¹	Se- 79	8.5·10 ⁻¹⁴	

Tab. 7.21: Simulations with the highest annual exposure



Fig. 7.46: Time and value of the maximum annual exposure The dominant radionuclide is I-129 for all simulations

The frequency distribution of the annual exposure is characterised by the statistical indicators given in table 7.22. The indicators are listed for the time of the maximum radiation exposition and for four additional points in time. The mean value given in table 7.22 is an estimate of the expected maximum annual exposure. The quality of this estimate is characterized by the confidence interval, which refers to a confidence of 95%. There is a probability of 95% that the actual maximum annual exposure is within the confidence interval reaching from $1.3 \cdot 10^{-8}$ to $2.2 \cdot 10^{-8}$ Sv·y⁻¹, which is a very narrow interval.

Figure 7.47 shows the cumulative frequency distribution of the maximum annual exposure and the confidence limits, while figure 7.48 shows the frequency density distribution of the maximum annual exposure as bar chart. The centre of this distribution is at about 10^{-8} Sv·y⁻¹. The frequency distribution is lower, but wider than the one received for the Opalinus Clay which is due to a more pronounced tailing of the distribution towards the lower annual exposures. The grey lines in the plot for cumulative frequency show the frequency distribution for one million of years. This distribution is significantly lower than the one for 10^{-8} years, indicating that most of the simulations reach their maximum of exposure much later than 10^{-6} years. About 50% of the simulations do not exceed a maximum annual exposure of 10^{-14} Sv·y⁻¹ before one million of years. The temporal evolution of the mean annual exposure, the confidence interval, the median and the 95%-quantile are shown in the figures 7.49 and 7.50.

		10⁴y	10 ⁵ y	10 ⁶ y	10 ⁷ y	Max.
Mean value		0.0	6.5·10 ⁻¹⁵	2.1·10 ⁻⁰⁹	8.4·10 ⁻⁰⁹	1.8·10 ⁻⁰⁸
Standard deviation		0.0	9.4·10 ⁻¹⁴	1.1·10 ⁻⁰⁸	1.1·10 ⁻⁰⁸	3.4·10 ⁻⁰⁸
Confidence interval	upper limit	0.0	2.0·10 ⁻¹⁴	3.6·10 ⁻⁰⁹	9.9·10 ⁻⁰⁹	2.2·10 ⁻⁰⁸
	lower limit	0.0	0.0	5.1·10 ⁻¹⁰	6.9·10 ⁻⁰⁹	1.3·10 ⁻⁰⁸
Median		0.0	0.0	8.3·10 ⁻¹⁵	1.8·10 ⁻⁰⁹	3.3·10 ⁻⁰⁹
95% Percentile		0.0	5.2·10 ⁻¹⁵	8.4·10 ⁻⁰⁹	3.0·10 ⁻⁰⁸	8.9·10 ⁻⁰⁸
Maximum		0.0	2.9·10 ⁻¹²	1.7·10 ⁻⁰⁷	3.7·10 ⁻⁰⁸	2.7·10 ⁻⁰⁷

Tab. 7.22: Statistical indicators for the annual exposure for different times in $[Sv \cdot y^{-1}]$



Fig. 7.47: Complementary cumulative frequency of the maximum annual exposure The coloured lines represent the frequency distribution for 10⁸ years while the grey lines represent the one for 10⁶ years.



Fig. 7.48: Frequency density of the maximum annual exposure



Fig. 7.49: Mean value and confidence interval of the annual exposure



Fig. 7.50: Maximum, median and 95%-quantile of the annual exposure

7.4.4.2 Global sensitivity analysis

As for the Opalinus Clay, the sensitivity analysis is evaluated on the basis of the Spearman-Test. Table 7.23 shows the result of the global sensitivity analysis for 10^4 , 10^5 , 10^6 and 10^7 years and for the point in time of the maximum annual exposure. The numbers given denote the importance of the parameter at the given point in time for those parameters whose rank was identified in the hypothesis testing with a significance of 5%. Differences in rank of the other parameters are regarded as insignificant. Orange shaded fields indicate parameters yielding a correlation coefficient greater than 0.1. Correlations lower than 0.1 may occur by random correlation and are regarded as not relevant.

The most important parameter for all times is again the diffusion coefficient of the radionuclides in the clay formation. No other relevant parameter was identified to influence the annual exposure for times smaller than one million of years. For times longer than one million of years, three other parameters could be identified: the distribution coefficients in the far- and the near-field and the diffusion-accessible porosity in the farfield. However, even for very large times, these three parameters have a much lower influence on the resulting annual exposure than the diffusion coefficients in the far-field. This emphasizes the result received from the parameter variations that the influence of the parameter uncertainty decreases with increasing formation thickness.

Tab. 7.23: Ranking of random variables by Spearman test for different points in time Max denotes the point in time of the maximum annual exposure.
Ranks are given for those parameters which were identified in the hypothesis testing with a significance of 5%.

Orange shaded fields indicate	a correlation coeffic	cient greater than 0.1.
-------------------------------	-----------------------	-------------------------

Parameter		10 ⁵ y	10 ⁶ y	10 ⁷ y	Max.
Near-field	Container lifetime	2	3	5	
	Solubility limits				
	Diffusion coefficients				
	Distribution coefficients			3	3
	Porosities				
Far-field	Diffusion coefficients	1	1	1	1
	Distribution coefficients		2	2	2
	Porosities			4	4

7.5 Résumé

A large number of integrated performance assessment calculations have been performed for two different clay formations. In both cases, these calculations included a reference case, parameter variations of all main input parameters and a probabilistic calculation with 1 000 simulations.

For both clay formations simulations showed low radionuclide fluxes out of the formation and low resulting annual exposures compared to the regulatory limit of $3 \cdot 10^{-4}$ Sv·y⁻¹. This is all-too-true, because the performance assessment calculations performed with the program CLAYPOS trend to overestimate the radionuclide fluxes from the repository as shown with a comparison to the code r³t. The radionuclides relevant for the exposure are C-14, Cl-36, Se-79 and I-129. The relevance of Se-79 might have been overestimated in this study by assuming a too high half-life.

A comparison between the results of the reference case and the parameter variations for the Opalinus Clay and for the Lower Cretaceous Clays shows some remarkable issues:

- A large thickness of a clay formation like it is found for the Lower Cretaceous Clays - can lead to a complete containment of the radionuclides in the clay formation within the safety relevant period of one million years.
 For the Lower Cretaceous Clays for example, the longer travel time leads to a complete decay of C-14. Since the lack of site specific data, very conservative values for the diffusion coefficients have been used for the Lower Cretaceous Clays. More realistic diffusion coefficients would have led to a complete containment of all ra-
- The maximum annual exposure, which for both formations results from I-129 at times later than one million years, is surprisingly of the same order of magnitude in both cases. I-129 turns out to be the most relevant radionuclide for both formations.

dionuclides during one million of years.

- The diffusion coefficient is the most relevant parameter for the annual exposure and the time of arrival of the radionuclides in the biosphere. Other important parameters are the formation thickness, the distribution coefficients and for a few radionuclides also the solubility limits.
- The influence of the parameter uncertainty of the transport parameter values on the annual exposure is the lower, the higher the thickness of the formation. For clay
formations of a large thickness like the Lower Cretaceous Clays, the diffusion coefficient is the only parameter that significantly affects the annual exposure. All other parameters are of minor importance e.g. the solubility limits and the distribution coefficients. Even neglecting any sorption of the radionuclides in the clay formation does not lead to annual exposures higher than 10^{-6} Sv·y⁻¹ for all times.

First and foremost, the low influence of the parameter uncertainty on the resulting annual exposure leads to the conclusion that a higher thickness of the Clay formation is more favourable. Because of the low burial depth of the Apt formation and the possible influence of future glacial channels it should however be considered if another, deeper buried formation within the sequence of the Lower Cretaceous Clays would also be suitable for the construction of a waste repository, like for example the Hauterive.

The results of the probabilistic assessment calculations support those from the parameter variations: the most important parameter is the diffusion coefficient of the radionuclides in the clay formation. For a thick clay formation like the Lower Cretaceous Clays this was found to be even the only parameter to influence the annual exposure within the safety-relevant period of one million of years.

For the Opalinus Clay, the results for the reference case being calculated with CLAYPOS were compared to the results of a simulation with r³t. While CLAYPOS used a simplified one-dimensional geometry, the r³t code uses a more complex threedimensional geometry. The difference in the results from both simulations was found to be unexpectedly high: Compared to the r³t simulation, the ones with CLAYPOS lead to higher radionuclide fluxes of C-14 and I-129 by about a factor of 400. The difference was identified to be mainly due to the simplification of the geometry by CLAYPOS, but also to some extend by simplifications in the r³t model. Nevertheless, the high degree of simplification is necessary; on the one hand to defend from the risk of underestimating the radionuclide fluxes and on the other hand to limit the computing times to be able to perform a large number of parameter variations or probabilistic assessments. However in the future, it could be worth to reconsider the underlying model of the CLAYPOS code, whether a reduction of the conservativeness in the model is possible or not.

8 Résumé and outlook

This report presents the results of the project "Development of an instrument to calculate the radionuclide transport in clay formations", short title "TONI", which was financed by the German Federal Ministry of Economics and Technology (BMWi). Within this project a model concept for the radionuclide transport in clay formations was developed which was then implemented into computer codes for long-term safety analysis. The developed computer codes were tested and a first integrated performance assessment calculation for a generic repository in a clay formation was performed. The three developed or improved programs are:

- CLAYPOS to calculate the one-dimensional diffusive radionuclide transport as far as to the closest aquifer,
- CHETMAD for the calculation of the radionuclide transport in fractures and
- r³t to calculate the three-dimensional advective/diffusive radionuclide transport in heterogeneous clay formations including the mechanistic description of sorption by establishing a coupling with the geochemical code PHREEQC.

The main focus of the program development was set on the reference case scenario which represents the expected, undisturbed evolution of the clay formation. The three codes were qualified by the modelling of several test cases, including cases with analytical solutions, in-situ diffusion experiments and in-situ diffusion profiles. All programs met the requirements that were defined at the beginning. The coupling of the code $r^{3}t$ with PHREEQC could not be fully completed within this project, but the principal concept and the so far implemented steps have been shown to work.

Integrated performance assessment calculations for two different clay formations in Germany were performed in order to improve the understanding of the system behaviour and the relevance of the various model parameters. Parameter variations and probabilistic assessments helped to better quantify the relevant processes and effects that influence the release and transport of radionuclides. The results shown low radionuclide fluxes from the formation and low resulting annual exposures for the reference case.

For thick clay formations as the Lower Cretaceous Clays found in Northern Germany, a complete containment of the radionuclides within one million of years seems to be a

realistic option. The influence of the parameter uncertainty was found to be decreasing with an increasing formation thickness. Within realistic bandwidths of their values, none of the transport parameters is of crucial importance for the reference case of a repository in a clay formation of a thickness like the Lower Cretaceous Clays.

The work performed and the results achieved in this project still leave some open issues that have to be tackled or reconsidered in future activities. Among these issues are to

- repeat the calculations for the integrated performance assessment calculation using site specific data,
- reconsider the possible options for an additional improvement of the onedimensional code for long-term safety assessment CLAYPOS to reduce the conservatism,
- proceed with working on the coupling of r^3 t with the geochemical code PHREEQC,
- study gas production and gas transport processes in clay formations and
- develop a new code to model transport processes in the EDZ and in fractures using transient transport parameters.

The work on the coupling of $r^{3}t$ with PHREEQC is currently continued within the project¹⁸ "Enhancements on the safety related methods for the preparation of a safety case in Germany" short title WESAM, which started in October 2006 and which is also financed by the BMWi.

Within the presented project, a new instrument to perform integrated performance assessment calculations for repositories in clay formations was successfully developed and applied for the first time for a generic waste repository in Germany. This new instrument could now be applied for a real site analysis and assessment.

¹⁸ German title: "Weiterentwicklung sicherheitstechnischer Methoden zur Vorbereitung eines Safety Case in Deutschland" identification number 02 E 10276.

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Appendix

A Description of CLAYPOS input and output files

This section describes the structure of all CLAYPOS input files and the meaning of the output files. The format information given below is as Fortran 77 format statements.

Input file: Module specific data (*.med)

This file is used to control the program flow. It includes the pathnames of the input files and different control parameters. The file is organised as follows:

CLAYPOS3 Comment		A10 *
**CGR_ELDA	eldapath	A10,A120
**CGR_ABDA	abdapath	A10,A120
**CGR_CODA	codapath	A10,A120
**CGR_REDA	redapath	A10,A120
****NNG	nng, iswsum	A10,2I5
***CNG-ING	(cnl(k), inl(k), k=1, nng)	A10,6(4X,A2,1X,I3)
****CNTHR	(cthr(k), ithr(k), k=1,6)	A10,6(4X,A2,1X,I3)
****CNNPR	(cnpr(k), inpr(k), k=1, 6)	A10,6(4X,A2,1X,I3)
*****CNUR	(cur(k), iur(k), k=1,6)	A10,6(4X,A2,1X,I3)
****CNAMR	(camr(k), iamr(k), k=1,6)	A10,6(4X,A2,1X,I3)
****TE	te, dtstart, dtd, nout	A10,3E10.3,I10
*****NDIS	ndis	A10,I5
****IFAIL	ifail	A10,I5
*****UNITS	cunit	2A10
***TIMEOUT	ntime	A10,I5
(xtime(k),k=	=1,ntime)	10X,6E10.0
**SPACEOUT	nspace	A10,I5
(tspace(k),k ************ STOP	=1,nspace)	10x,6E10.0 A10 A10

The variables have the following meaning:

eldapath	Full path of the file containing the element-specific data (*.elda)
abdapath	Full path of the file containing the waste specific data (*.abda)
codapath	Full path of the file containing the container specific data (*.coda)
redapath	Full path of the file containing the domain specific data (*.reda)
nng	Number of radionuclides to calculate

iswsum	Not used	
cnl, inl	Nuclide names composed of element name in uppercase and mass	
	number e.g.: CS-137 (possible additional lines)	
cthr, ithr	Names of the selected nuclides of the Thorium-series, for which mass	
	totals are to be calculated (4n)	
cnpr, inpr	Names of the selected nuclides of the Neptunium-series, for which	
	mass totals are to be calculated (4n+1)	
cur, iur	Names of the selected nuclides of the Uranium-series, for which	
	mass totals are to be calculated (4n+2)	
camr, iamr	Names of the selected nuclides of the Americium-series, for which	
	mass totals are to be calculated (4n+3)	

The variables *cthr, ithr, cnpr, inpr, cur, iur, camr, iamr* foreseen to calculate total masses are not used at the moment and can be left open.

te	End time of the calculation		
dtstart	Initial time step width		
dtd	Control parameter used to determine the time discretisation. Larger values result in a finer discretisation. A value of 10 is usually sufficient. CLAYPOS uses two different time step widths, an inner for the calculation of the diffusion and an outer one to control the calculation. The inner time step width is a whole number fraction of the outer one. The time step widths are controlled by <i>dtd</i> in the following way:		
	 The outer time step width must not be larger than the shortest half-life of the regarded radionuclides, while only those radionuclides are regarded, those mobilised inventory is larger than 1% of the initial inventory. The outer time step width must not be larger than 1+ 0.01/√<i>dtd</i> times the preceding time step width. The outer time step width must not be larger than 10⁴/<i>dtd</i>. The outer time step width must not be larger than 10⁴/<i>dtd</i>. The number of the inner time steps is the next whole number larger than <i>dtd</i> 		
nout	Number of output points in time for each decade		
ndis	Number of spatial discretisation elements		
ifail	Not used		

cunit	Unit of the inventory data, either:		
	' BEQ' Or		
	' MOL'		
ntime	Number of positions for which a time depended output of the concen-		
	trations is written to the output file gzk		
xtime	Positions for which a time-depended output of the concentrations is		
	written to the output file gzk. These values are adapted to the spatial		
	discretisation and therefore are likely to be slightly changed.		
nspace	Number of points in time for which a place-dependent output of the		
	concentrations is written to the output file gok.		
tspace	Points in time for which a place-dependent output of the concentra-		
	tions is written to the output file gok. These values are adapted to the		
	time discretisation and therefore are likely to be slightly changed.		

Input file: Element-specific data (*.elda)

This file contains all type of data which is specific to the elements. Files of the type *.elda are also used in other EMOS modules and are documented elsewhere e.g. [65]. The element-specific file for CLAYPOS must at least contain the following data for all elements:

- Solubility
- Mobilisation rates from the waste for the three compartments metal parts, gas space and matrix
- Relative fraction of the element inventory in the waste for the three compartments metal parts, gas space and matrix
- Distribution coefficients (*K*_d-values) for all materials
- Element-specific porosity for all materials
- Element-specific diffusion coefficients for all materials

Input file: Waste specific data (*.abda)

This file defines the composition of the different wastes and gives the radionuclide inventory either in Mol or Becquerel. Files of the type *.abda are also used in other EMOS modules and are documented elsewhere e.g. [65].

Input file: Container specific data (*.coda)

This input file contains all data related to the waste containers like geometrical alignment, time of container failure, mobilisation rates etc. The coda file is organised as follows:

Comment	*
distc, rleff	2E10.0
totnc	E10.0
ncont, icout	215
i, pcont(i), rlenc(i), tlife(i), cwname(i), (iel(i,k)	, k=1,8)13,3E10.0,1x,A10,8I4

The last line has to be repeated for each group of containers (i=1,...,ncont). The variables have the following meaning:

distc	Container distance. For full radial symmetry use 0.0
rleff	Effective distance. For the plane geometry the concentration at the
	boundary is reduced by <i>rleff/distc</i> reduziert. This parameter should
	always be set to <i>distc</i> . For the radial geometry this parameter is not
	used.
totnc	Number of containers as floating point number
ncont	Number of groups of containers. All containers within each group
	have the same properties and are failing at the same point in time.
i	Counter for each group of containers. The order has to be followed.
pcont(i)	Relative fraction of the group of containers i from the total number of
	containers. If the sum of all fractions is not equal to one each number
	is scaled automatically. So also the absolute number of containers in
	each group might be given.
rlenc(i)	Length of a container in the group <i>i</i>

- *tlife*(*i*) Life-time of a containers in the group *i*. All containers in each group fail at the given point in time.
- *cwname(i)* Name of the waste in a container of the group *i* as defined in the waste specific data input file (*.abda)

The numbers iel(i,k), k = 1, ..., 8 give the numbers of the column in the element-specific data input file *.elda-Datei:

iel(i,1)	Solubility
iel(i, 2)	not used
iel(i, 3 5)	Mobilisation rate for the three compartments metal parts, gas space
	and waste matrix
iel(i, 6 8)	Relative inventory in the three compartments metal parts, gas space
	and waste matrix

Input file: Domain specific data (*.reda)

This file contains all data defining the different regions or domains through which the diffusion occurs like the distances and the properties of each domain. The file is organised as follows:

Comment	*
volf, flnc	2E10.0
cgeom	A10
rinn	E10.0
nregion	I5
i, rout(i), rhomat(i), ieldi(i), ielpo(i), ielkd(i)	I3,2E10.0,3I4

The last line has to be repeated for each domain (i=1,...,nregion).

The vatiable have the following meaning:

volf	Volume flow in the overburder	Volume flow in the overburden						
flnc	Uncontaminated fraction of th	Uncontaminated fraction of the volume flow						
cgeom	Type of geometry; either: `	PLANAR ' or '	RADIAL'					
rinn	Distance of the inner boundar	Distance of the inner boundary. For the radial geometry this is the in-						
	ner radius of the cylindric domain. For the plane geor							

	gives the distance between origin of the coordinate system and the
	beginning of the formation. For the plane geometry this does not af-
	fect the calculation, but only changes the coordinate.
nregion	Number of domains
i	Counter for each domain
rout(i)	Distance of the outer boundary of domain i to the origin of the coordi-
	nate system
rhomat(i)	Density of the material in the domain <i>i</i>

The parameters ieldi(i), ielpo(i), ielkd(i) give the column number of the elementspecific data for the domain *i* in the input file *.elda:

ieldi(i)	Diffusion coefficient
ielpo(i)	Porosity
ielkd(i)	Distribution coefficient

Input file: Nuclide specific data (nuda.dat)

The nuclide specific input file is used in all other EMOS modules and is documented elsewhere e.g. [65]. The path of the nuclide specific input file is given in the script file.

Input file: Script file

EMOS-calculations are controlled by a csh script file which calls all modules. Some values are stored in string variable which are stored as environment variables during runtime. These variables are read by the program modules. The script file is usually generated by the pre-processor. The following lines have to be adopted for CLAYPOS:

```
setenv TEXT 'Comment'
...
set NAME_RECHENLAUF = runname
set PFAD_RECHENLAUF = runpath
set PFAD_AUSGABE = outpath
set PFAD1 = medpath
set NAME_MEDA_CLAYPOS3 = medname
...
```

set MODUL1	= execpathname
··· setenv NAME_BENUTZER	username
 setenv NAME_DATENBASI	s <i>nudapathname</i>
 cat <i>scriptpathname</i> >>	• \$NAME_PBD

The variables have the following meaning:

comment	Comment in single quotes
runname	Name of the calculation (=Name of the script file)
runpath	Path of the script file without filename
outpath	Path of the output files
medpath	Path of the module specific input file *.med without file name
execpathname	Full path of the program executable
username	Name of the user
nudapathname	Full path of the nuclide specific data basis
scriptpathname	Full path of the script file

Input files for probabilistic calculations (*.stuv and *.stda)

Currently five different variables can be used in CLAYPOS as random variables. The variables, the dimension of the variable to be defined in the stuv-file and the meaning of the indices to be defined as first two parameters for each variable in the stda-file are:

tlife	Life-time of the container group i (one-dimensional field).
reg	Element specific data of radionuclide i and parameter j
	(two-dimensional field).
volf	Volume flow in the overburden (scalar)
flnc	Uncontaminated fraction of the volume flow (scalar)
rhomat	Density of the material <i>i</i> (one-dimensional field)

Parameters three to five in the stda-file are the type of the probabilistic density function, and the lower and upper boundary of the distribution.

Output files

The CLAYPOS calculation creates the following output files:

*.out	General information and balance sheets
*.pbd	Information about problems during calculation
*.gvs	Data description file. This file defines the format of the other output
	files and is used by the post-processor to interpret the other output
	files.
*.gim	Time-dependent nuclide inventories in the different compartments: to-
	tal, container, precipitated and host rock summed over all containers
	given in Mol
*.gns	Nuclide fluxes from each container given according to the switch
	UNITS in Mol/y or Bq/y.
*.gok	Place-dependent concentrations for the points in time defined in the
	module specific input file *.med
*.gsk	Fluxes into and concentrations in the overburden as used by modules
	following in the calculation chain
*.gws	Nuclide fluxes from the waste matrix according to the switch UNITS in
	Mol/m ³ or Bq/ m ³
*.gzk	Time-dependent concentrations at positions defined in the module
	specific input file *.med

The output files can be converted to xy-column format or TECPLOT format by the EMOS post processor.

B Description of the changes to the CHETMAD input files

This section specifies the changes made to the modules CHETMAD2 and CHETMADC1 to take element-specific porosity and element-specific diffusion coefficients into account. As new input parameters, the element-specific porosities and diffusion coefficients are needed. This data is entered as columns in the element-specific data file (ELCH).

The values for the porosity and diffusion coefficient in the material specific data file (MACH) denote a uniform porosity and diffusion coefficient for all elements, if the given number is greater zero (enter 0.5 if the uniform value for all elements is 0.5) and denote the column number of the according element-specific data in the ELCH-file if the number is lower than zero (enter -5 if the column number of the element-specific data in the ELCH-file is 5).

Changes to the file structure of the input files

MED-file

The code word in the first line of the med-file is changed from CHETMAD2 / CHETMADC1 to CHETMAD3 / CHETMADC2:

1. Line: CHETMAD3 / CHETMADC2 Code word in the format A10 right justified.

Mach-file

The meaning of the values of the code words "Matrixporosität" and "Matrixdiffusion" was changed. If you enter a positive number (greater zero) for "Matrixporosität" or "Matrixdiffusion", CHETMAD will use the value as uniform value for all elements. Example:

Matrixporosität 0.5

results in a uniform porosity of 0.5 for all elements. If you enter a negative number (less than zero) for "Matrixporosität" or "Matrixdiffusion", CHETMAD will take the absolute of the value and use it as the column number in the ELCH-file for the element-specific data. Example:

Matrixporosität -4

results in column 4 in the ELCH-file to be taken as element-specific porosity values.

ELCH-file

The element-specific porosity values and diffusion coefficients are entered as additional columns in the ELCH-file.

C Description of the r³t input file "retention" and of the pre-processor dialogs to enter the material specific parameters

In this section, the input of the parameters for the new anisotropic diffusion and element-specific porosity into the r³t pre-processor and the representation of the parameters in the input files are described. All the parameters are located in the configuration file **retention**. The hydrological units are combined to materials as usual in the input files of d³f and r³t. The properties of each material have to be defined in the retention file. The window of the pre-processor to define the material properties now looks like:

X Set Material OO					
WEST					
diffusion					
anisotropic					
🗌 element specific					
porosity					
🗌 element specific					
pore water					
🗌 immobile					
Ok Back Help					

The following nine combinations of the material properties should be possible:

	1	2	3	4	5	6	7	8	9
diffusion									
anisotropic		$\mathbf{\nabla}$	$\mathbf{\nabla}$	$\mathbf{\nabla}$	$\mathbf{\nabla}$				
element-specific			M		M	M	V		
element-specific porosity				\checkmark	$\mathbf{\nabla}$		\mathbf{V}	\mathbf{V}	
immobile pore water									V

This means that all combinations of diffusion and porosity can occur. Immobile pore waters however can only be modelled in an isotrope medium without elementspecific diffusion coefficients and without element-specific porosities. The input dialogs of all nine combinations and their representation in the retention file are shown in the following.

1.) Isotropic medium, no element-specific diffusion, no element-specific porosity, no immobile pore water

This is the default combination of parameters. This case is still the same as it has been before the enhancement of $r^{3}t$. This leads to the following queries:

🗙 🗝 WEST Specific Prope 💶 🔳				
rock density [kg/m³] 2500.0				
porosity [-]	0.2			
diffusion [m²/s] 1.0E-9				
alpha_L [m]	1.0			
alpha_T [m]	0.1			
Ok Back Help				

X-∺ Set Elem	ent Parameter	s for WEST	• 🗆 🗙
MOBILE PHASE	E		
	🖲 equilibrium	\odot kinetic controlled \odot speciation \odot Henry \bigcirc Henry function \bigcirc Langmuir \bigcirc Freundlich	
	stochastic	🗌 solubility 🗌 solubility function	
-IMMOBILE PH/	ASE		
		equilibrium \bigcirc Henry \bigcirc Henry function \bigcirc Langmuir \bigcirc Freundlich	
MOBILE PHAS	SE		
	🖲 equilibrium	\odot kinetic controlled \odot speciation ${ m lackstyle Henry}$ \odot Henry function \odot Langmuir \odot Freundlich	
ть			
	stoch astic	🗌 solubility 🔲 solubility function	
-IMMOBILE PH	IASE		
		equilibrium \bigcirc Henry \bigcirc Henry function \bigcirc Langmuir \bigcirc Freundlich	
<u></u>			
		Ok Back Help	

\mathbf{X}	-• WEST Elem	ent Parameters -	U	• • ×
	MOBILE			
U	equilibrium	Henry	K_D [m≋/kg]	0.0020
		Ok Back	Help	

This is depicted in the file retention as follows:

```
WEST
rock_density 2500.0 porosity 0.2 porosity_im 0.0 g 1.0 diffusion 1.0E-9
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
U
mobile
equilibrium Henry 0.0020
mobile end
U end
```

```
Th
mobile
equilibrium Henry 0.2
mobile end
Th end
WEST end
```

2.) Anisotropic medium, no element-specific diffusion, no element-specific porosity, no immobile pore waters

The angles defining the anisotropy are always material dependent, but not dependent on the element. This leads to the following queries:

X	WEST Spe	cific Properties	000	
rock density [kg/m³] porosity [-]		NaN NaN		
anisotropy [arc] diffusion [m²/s]	Phi NaN diff_x NaN	Theta 0.0 diff_y NaN	Psi 0.0 diff_z NaN	
alpha_L [m] alpha_T [m]		NaN NaN		
Ok Back Help				

X	-∺ Set Elemei	nt Parameters	s for WEST					• • ×
	MOBILE PHASE							_
		equilibrium	\odot kinetic controlled	\bigcirc speciation	Henry	\bigcirc Henry function	\odot Langmuir \odot Freundlich	
U								
		stochastic				solubility	solubility function	•
	IMMOBILE PHASE							
			equilibrium 🔾	Henry 🔿 Henry	function (🔿 Langmuir 🔿 Freu	ndlich	
	-MOBILE PHASE							
		🖲 equilibrium	O kinetic controlled	O speciation	Henry	⊖ Henry function	🔿 Langmuir 🔿 Freundlich	
Пт	n							
		stochastic 🗌				🗆 solubility	solubility functio	n
	IMMOBILE PHAS	6E						
			equilibrium O	Henry O Henry	function	🔿 Langmuir 🔿 Frei	undlich	
								~
				0k	Back	Help		

X -> WEST Elem	ent Parameters -	U	• • ×
U _{equilibrium}	Henry	K_D [m≋/kg]	0.0020
	Ok Back	Help	

This is depicted in the file retention as follows:

```
WEST
rock_density 2500.0 porosity 0.2 porosity_im 0.0 g 1.0
anisotropic diffusion phi 90.0 theta 0.0 psi 0.0
diff_x 1.0E-9 diff_y 1.0E-12 diff_z 1.0E-12
```

```
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
U
mobile
equilibrium Henry 0.0020
mobile end
U end
Th
mobile
equilibrium Henry 0.2
mobile end
Th end
WEST end
```

3.) Anisotropic medium, element-specific diffusion, no element-specific porosity, no immobile pore waters

The angles defining the anisotropy are always material dependent, but not dependent on the element. The values for the diffusion coefficient are element-specific. This leads to the following queries:

X	WEST Specific Properties			
rock density [kg/m³]		NaN		
porosity [-]		NaN		
anisotropy [arc]	Phi NaN	Theta 0.0 Psi 0.0		
alpha_L [m]		NaN		
alpha_T [m]		NaN		
Ok Back Help				

X	⊣¤ Set Elemer	nt Parameters	for WEST			• • ×	
	MOBILE PHASE					_	
		I equilibrium	\odot kinetic controlled \odot speciation ${ullet}$	Henry 🔿 Henry function	🔿 Langmuir 🔿 Freundlich		
U							
		stochastic		🗌 solubility	solubility function		
	-IMMOBILE PHASE						
			equilibrium O Henry O Henry fun	ction O Langmuir O Freu	ndlich		
	MOBILE PRASE	a			o o		
		• equilibrium	O Kinetic controlled O speciation (Henry O Henry function	O Langmuir O Freundlich		
Т	h						
		stochastic		🗌 solubility	solubility function		
		_ stornastic		solubility			
	IMMOBILE PHAS	E					
			equilibrium 🔿 Henry 🔿 Henry fur	nction O Langmuir O Freu	ndlich	_	
	Ok Back Help						

X		WEST Element Parameters - U	0	\bigcirc	•
U	MOBILE equilibrium K_D [m²/kg] diffusion [m²/s]	Henry NaN diff_x NaN diff_y NaN diff_z NaN			
		Ok Back Help			

This is depicted in the file retention as follows:

```
WEST
rock_density 2500.0 porosity 0.2 porosity_im 0.0 g 1.0
anisotropic diffusion phi 90.0 theta 0.0 psi 0.0
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
U
Mobile
diff_x 1.0E-9 diff_y 1.0E-12 diff_z 1.0E-12
equilibrium Henry 0.0020
mobile end
U end
Th
Mobile
diff_x 1.0E-10 diff_y 1.0E-14 diff_z 1.0E-14
equilibrium Henry 0.2
mobile end
Th end
WEST end
```

4.) Anisotropic medium, no element-specific diffusion, element-specific porosity, no immobile pore waters

The angles defining the anisotropy are always material dependent, but not dependent on the element. This leads to the following queries:

X	WEST Specific Properties	$\bigcirc \bigcirc \bigcirc \bigcirc$		
rock density [kg/m ^s]	NaN			
anisotropy [arc] diffusion [m²/s]	Phi NaN Theta diff_x NaN diff_y	O.0 Psi O.0 NaN diff_z NaN		
alpha_L [m] alpha_T [m]	NaN NaN			
Ok Back Help				

X-	⊭ Set Element Parameters for WEST	• 🗆 🗙
	MOBILE PHASE	_
	$lacksquare$ equilibrium $igcap$ kinetic controlled $igcap$ speciation $\ lacksquare$ Henry $igcap$ Henry function $igcap$ Langmuir $igcap$ Freundlich	
_		
	stochastic solubility solubility function	
ſ	IMMOBILE PHASE	
	equilibrium \bigcirc Henry \bigcirc Henry function \bigcirc Langmuir \bigcirc Freundlich	
	MOBILE PHASE	
	● equilibrium ○ kinetic controlled ○ speciation ● Henry ○ Henry function ○ Langmuir ○ Freundlich	
Th	n	
	Stochastic	
	IMMOBILE PHASE	
	equilibrium () Henry () Henry function () Langmuir () Freundlich	
	Ok Back Help	



This is depicted in the file retention as follows:

```
WEST
rock_density 2500.0 porosity_im 0.0 g 1.0
anisotropic diffusion phi 90.0 theta 0.0 psi 0.0
diff_x 1.0E-9 diff_y 1.0E-12 diff_z 1.0E-12
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
U
mobile
porosity 0.2
equilibrium Henry 0.0020
mobile end
U end
Th
mobile
porosity 0.25
equilibrium Henry 0.2
mobile end
Th end
WEST end
```

5.) Anisotropic medium, element-specific diffusion, element-specific porosity, no immobile poren waters

The angles of the anisotropy are always material dependent, but not dependent on the element. The values for the diffusion coefficient are element-specific. This leads to the following queries:

X	WEST Specific Properties			
rock density [kg/mª]		NaN		
anisotropy [arc]	Phi NaN	Theta 0.0	Psi 0.0	
alpha_L [m] alpha_T [m]		NaN NaN		
Ok Back Help				

X	X -∺ Set Element Parameters for WEST							
	MOBILE PHASE							_ _
		• equilibrium	\bigcirc kinetic controlled	\bigcirc speciation	Henry	O Henry function	🔿 Langmuir 🔿 Freundlich	
U								
		stochastic				solubility	solubility function	
	-IMMORILE PHASE							
			equilibrium 🔿	Henny O Henny	function (Langmuir 🔿 Freu	ndlich	
	MOBILE PHASE					<u></u>		
		• equilibrium	O KINETIC CONTROLLED	\bigcirc speciation	Henry	O Henry function	O Langmuir O Freundlich	
T	h							
		stochastic				solubility	solubility function	
							_ ·	
	IMMOBILE PHAS	E						
			equilibrium 🔿	Henry O Henry	function	🔿 Langmuir 🔿 Freu	Indlich	
1-								
				Ok	Back	lelp		

X		WEST Element Parameters - U	000
U	MOBILE equilibrium K_D [m ³ /kg] porosity [-] diffusion [m ² /s]	Henry NaN NaN diff_x NaN diff_y NaN diff_z NaN	
		Ok Back Help	

This is depicted in the file retention as follows:

```
WEST
rock_density 2500.0 porosity_im 0.0 g 1.0
anisotropic diffusion phi 90.0 theta 0.0 psi 0.0
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
```

```
U
Mobile
diff_x 1.0E-9 diff_y 1.0E-12 diff_z 1.0E-12
porosity 0.2
equilibrium Henry 0.0020
mobile end
U end
Th
Mobile
diff_x 1.0E-10 diff_y 1.0E-14 diff_z 1.0E-14
porosity 0.25
equilibrium Henry 0.2
mobile end
Th end
WEST end
```

6.) Isotropic medium, element-specific diffusion, no element-specific porosity, no immobile pore waters

This case is still the same as it has been before the enhancement of $r^{3}t$. This leads to the following queries:

🗙 🗝 WEST Specific Prope 💷 💌		
rock density [kg/m³] 25 00.0 porosity [-] 0.2		
alpha_L [m] alpha_T [m]	1.0 0. 1	
Ok Back Help		

Χ-	X -∺ Set Element Parameters for WEST •■×				
Г	MOBILE PHASE	_			
	● equilibrium ○ kinetic controlled ○ speciation ● Henry ○ Henry function ○ Langmuir ○ Freundlich				
					
	solubility solubility solubility function				
	equilibrium O henry O henry function O Langmuir O Freunulich				
	MOBILE PHASE				
	● equilibrium ○ kinetic controlled ○ speciation ● Henry ○ Henry function ○ Langmuir ○ Freundlich				
Th					
	Estachastic Establish				
	IMMOBILE PHASE				
	equilibrium \bigcirc Henry \bigcirc Henry function \bigcirc Langmuir \bigcirc Freundlich				
	Ok Back Help				

X	X → WEST Element Parameters - U			
U	diffusion [m²/s] equilibrium	1.e-9 Henry	K_D [m³/kg]	0.0020
		Ok Back	Help	

This is depicted in the file retention as follows:

```
WEST
rock_density 2500.0 porosity 0.2 porosity_im 0.0 g 1.0
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
U diffusion 1.0E-9
mobile
equilibrium Henry 0.0020
mobile end
U end
Th diffusion 1.0E-10
mobile
equilibrium Henry 0.2
mobile end
Th end
WEST end
```

7.) Isotropic medium, element-specific diffusion, element-specific porosity, no immobile pore waters

The angles of the anisotropy are always material dependent, but not dependent on the element. The values for the diffusion coefficient are element-specific. This leads to the following queries:

X WEST Specific Properties $\bigcirc \bigcirc \bigcirc$						
rock density [kg/m ^s]	NaN					
alpha_L [m]	NaN					
alpha_T [m]	NaN					
OkB	ack Help					
X-	X -려 Set Element Parameters for WEST	• D ×				
------	---	-------------------	--	--	--	--
	MOBILE PHASE	_				
	● equilibrium ○ kinetic controlled ○ speciation ● Henry ○ Henry function ○ Langmuir	O Freundlich				
U	0					
	solubility sol	ubility function				
II r	IMMOBILE PHASE					
	equilibrium \bigcirc Henry \bigcirc Henry function \bigcirc Langmuir \bigcirc Freundlich					
	MOBILE PHASE					
	\odot equilibrium \bigcirc kinetic controlled \bigcirc speciation \odot Henry \bigcirc Henry function \bigcirc Langmuir	○ Freundlich				
Th	Th					
	Solubility Solubility	lubility function				
	IMMOBILE PHASE					
	equilibrium 🔿 Henry 🔿 Henry function 🔿 Langmuir 🔿 Freundlich					
	Ok Back Help					



This is depicted in the file retention as follows:

```
WEST
rock_density 2500.0 porosity_im 0.0 g 1.0
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
U
Mobile
diffusion 1.0E-9
porosity 0.2
equilibrium Henry 0.0020
mobile end
U end
Th
Mobile
diffusion 1.0E-10
porosity 0.25
equilibrium Henry 0.2
mobile end
Th end
WEST end
```

8.) Isotropic medium, no element-specific diffusion, element-specific porosiy, no immobile pore waters

Diffusion is material dependent, but not element-specific. There is an element-specific porosity. This leads the following queries:

rock density [kg/m ^s]	NaN
diffusion [m²/s]	NaN
alpha_L [m]	NaN
alpha_T [m]	NaN

X	여 Set Elemen	t Parameters	for WEST					- - ×
	MOBILE PHASE							_
		equilibrium	\bigcirc kinetic controlled	\bigcirc speciation	Henry	O Henry function	🔿 Langmuir 🔿 Freundlic	h
U								
		stochastic				solubility	solubility function	in 🕴
	IMMOBILE FRASE							
			equilibrium ()	Henry () Henry	function) Langmuir () Freu	Indlich	
	MOBILE PHASE							
		🖲 equilibrium	\bigcirc kinetic controlled	\bigcirc speciation	Henry	\bigcirc Henry function	🔿 Langmuir 🔿 Freundlig	h
Tł	r							
		stochastic				solubility	solubility functi	on
	-IMMOBILE PHAS	E						
			aquilibrium ()	Hanny A Hann	function		undlich	
			equilibrium ()	nemy O nemy	Tunction			_
	Ok Pack Hein							

X	X WEST Element Par						
U	equilibrium K_D [m³/kg] porosity [-]	Henry NaN NaN					
	Ok Back	Help					

This is depicted in the file **retention** as follows:

```
WEST
rock_density 2500.0 porosity_im 0.0 g 1.0 diffusion 1.0E-9
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
U
Mobile
porosity 0.2
equilibrium Henry 0.0020
```

```
mobile end
U end
Th
Mobile
porosity 0.25
equilibrium Henry 0.2
mobile end
Th end
WEST end
```

9.) Isotropic medium, no element-specific diffusion, no element-specific porosity, immobile pore waters

This case is the same as for immobile pore waters before. This leads to the following queries:

🗙 🖙 WEST Specific Prope 🔹 🗆 🗙				
, rock density [kg/m³]	2500.0			
porosity [-]	0.2			
porosity_im [-]	0.05			
g [-]	0.8			
diffusion [m²/s]	1.0E-9			
alpha_L [m]	1.0			
alpha_T [m]	0.1			
Ok Back Help				

X	🗝 Set Elemer	t Parameters	for WEST					• • ×
	MOBILE PHASE							<u> </u>
		🖲 equilibrium	\bigcirc kinetic controlled	\bigcirc speciation	Henry	\bigcirc Henry function	\bigcirc Langmuir \bigcirc Freundlich	
U								
		stochastic				solubility	solubility function	
	IMMOBILE PHASE							
			equilibrium 🔘	Henry 🔿 Henry	function (🖯 Langmuir 🔿 Freu	ndlich	
	-MORILE PHASE-							
	MOBILE THASE	equilibrium	○ kinetic centrelled		A Hanny			
		© Equilibrium		O speciation	@ nemy			
IT I	I							
		stoch astic				solubility	solubility function	
			equilibrium 🖲	Henry 🔿 Henry	function	🔿 Langmuir 🔿 Frei	undlich	_
				UK	васк	негр		

	(→ WEST Element Parameters - U					
	equilibrium	Henry		K_D [m³/kg] 0.0020		0
U	IMMOBILE					
	equilibrium	alpha [1/s]	0.5	K_D [n	n®/kg]	.0030
		Ok	Back	Help		

This is depicted in the file retention as follows:

```
WEST
rock_density 2500.0 porosity 0.2 porosity_im 0.05 g 0.8 diffusion 1.0E-9
alpha_L 1.0 alpha_T 0.1
# element-specified definition of retention
U
mobile
equilibrium Henry 0.0020
mobile end
immobile
alpha 0.5
equilibrium Henry 0.0030
immobile end
U
end
Th
mobile
equilibrium Henry 0.2
mobile end
immobile
alpha 0.06
equilibrium Henry 0.0040
immobile end
Th
end
WEST end
```

D Input files for coupled r³t-PHREEQC simulation

The coupled r³t-PHREEQC simulation needs two additional input files compared to the conventional r³t simulation. These are "phreeqc.in" and "phreeqc.dat" which both have to be located in the main directory of the simulation. "phreeqc.in" defines the chemical species and phases in the same way as in a normal PHREEQC simulation. "phreeqc.dat" gives the thermodynamic database. The standard PHREEQC thermodynamic database "Ilnl.dat" was used in the test simulations with the additions given in [19].

This section gives the input files "phreeqc.in", "initial" and "boundary" which were used for the coupled $r^{3}t$ -PHREEQC simulation of the propagation of an alkaline plume. The other input files are the same as in a usual $r^{3}t$ simulation. The transport properties were defined identical for all pollutants in the input file "retention". No advective flow and no sources were used. To activate the coupled simulation in $r^{3}t$, the switch PHREEQC = 1 hast to be defined at the beginning of the script file "r3t.scr" as shown in this cut-out of a script file as example:

executable script file

phreeqc.in

PHREEQC code words are printed in bold. In contradiction to the standard PHREEQC input format, the section EXCHANGE must not contain the variable X.

TITLE TONI: Ausbreitung alkalische Front.

SOLUTION 1

pH 7.24 charge
 pe -2.83
 temp 25.0
 units mol/kgw
 density 1.000
Na 1.69E-01
Ca 1.05E-02
Sr 3.04E-04
Mg 7.48E-03
K 5.65E-03
Al 1.78E-08
S 2.40E-02

Cl 1.632537E-01 Si 1.78E-04 Fe 4.33E-05 C 0.0

EQUILIBRIUM_PHASES 1

CO2(g)	-2.2	10
Montmorillonite-Na	0.0	9.2
Cristobalite	0.0	7.5
Calcite	0.0	0.63
Gypsum	0.0	0.16
Pyrite	0.0	6E-5

EXCHANGE_MASTER_SPECIES

х х-

EXCHANGE_SPECIES

```
X- = X-
log_k = 0.0
X- + Na+ = NaX
log_k = 0.0
2x- + Ca+2 = CaX2
log_k = 0.37
X- + K+ = KX
log_k = 4.0
2x- + Mg+2 = MgX2
log_k = 0.31
2x- + Sr+2 = SrX2
log_k = 0.37
X- + H+ = HX
log_k = 1.0
```

EXCHANGE 1

NaX 3.005 CaX2 0.149 KX 0.060 MgX2 0.0905 SrX2 0.0 HX 0.0

PRINT

-reset false

```
END
```

boundary

The input file "boundary" should reflect the concentrations as would be given for solution0 of a PHREEQC calculation.

```
time independent end validity all end
validity Ca
time independent
surface 3 dissolution alpha 10.0 cref 2.19E-2
  time independent end
validity Ca end
validity Cl
time independent
     surface 3 dissolution alpha 50.0 cref 3.03E-2
  time independent end
validity Cl end
validity K
  time independent
     surface 3 dissolution alpha 50.0 cref 2.21E-2
  time independent end
validity K end
validity Na
time independent
    surface 3 dissolution alpha 50.0 cref 8.02E-3
time independent end
validity Na end
validity S
time independent
  surface 3 dissolution alpha 50.0 cref 1.20E-4
time independent end
validity S end
validity Si
time independent
surface 3 dissolution alpha 50.0 cref 3.01E-5
  time independent end
validity Si end
validity ph
time independent
    surface 3 dissolution alpha 50.0 cref 12.5
  time independent end
validity ph end
validity pe
  time independent
     surface 3 dissolution alpha 50.0 cref -2.83
  time independent end
validity pe end
boundary end
```

initial

The input file "initial" should reflect the concentrations as given for solution1 in the phreeqc.in.

```
version plume2d-d
liquid
validity all
global const 0.0
validity all end
validity Na
global const 1.69E-1
validity Na end
validity K
global const 5.65E-03
validity K end
validity Ca
global const 1.05E-02
validity Ca end
validity pe
global const -2.83
validity pe end
validity ph
global const 7.24
validity ph end
validity Sr
global const 3.04E-04
validity Sr end
validity Mg
global const 7.48E-03
validity Mg end
validity Al
global const 1.78E-08
validity Al end
validity S
global const 2.40E-02
validity S end
validity Cl
global const 1.632537E-01
validity Cl end
validity Si
global const 1.78E-04
validity Si end
validity Fe
global const 4.33E-05
validity Fe end
validity wm
global const 1.0
validity wm end
liquid end
initial end
```

E PHREEQC input files for uncoupled simulation

This section gives the input files for the uncoupled PHREEQC simulations which have been performed for comparison to the coupled simulations. The Simulation calculates the propagation of an alkaline plume in a clay formation. PHREEQC code words are printed in bold while comments are printed in grey text.

The first section gives the complete input file for the diffusive propagation of the plume. The second section gives those changes of the input file in the first section which are necessary to calculate the test case regarding for advection.

Diffusive propagation of alkaline plume

TITLE TONI: Ausbreitung alkalische Front.

Solution 0

Concrete pore water after Gaucher et al. (Appl. Geochem. 2004)

pH 12.5 pe 4.0 temp 25.0 units mol/kgw density 1.0

Na 8.02E-3 K 2.21E-2 Ca 2.19E-2 Si 3.01E-5 S 1.20E-4 Sr 0.0 Cl 3.03E-2 Al 0.0 C 0.0 Fe 0.0 Mg 0.0

SOLUTION 1-100

Clay pore water concentrations after Nagra NTB02-09 und NTB02-03

pH 7.24
pe -2.83
temp 25.0
units mol/kgw
density 1.000
Na 1.69E-01
Ca 1.05E-02
Sr 3.04E-04
Mg 7.48E-03
K 5.65E-03
Al 1.78E-08
S 2.40E-02
Cl 1.632537E-01
Si 1.78E-04
Fe 4.33E-05
C 0.0

EQUILIBRIUM_PHASES 1-100

MX80 clay after Gaucher et a. (Appl. Geochem. 2004)
and Nagra NTB02-09 (S/W 4.5, pc02)

```
CO2(g) -2.2 10

Montmorillonite-Na 0.0 9.2

Cristobalite 0.0 7.5

Calcite 0.0 0.63

Gypsum 0.0 0.16

Pyrite 0.0 6E-5
```

EXCHANGE_MASTER_SPECIES

х х-

EXCHANGE_SPECIES

Nagra NTB 02-09 Appendix D-1

X- = Xlog_k = 0.0 X- + Na+ = NaX log_k = 0.0 2X- + Ca+2 = CaX2 log_k = 0.37 X- + K+ = KX log_k = 4.0 2X- + Mg+2 = MgX2 log_k = 0.31 2X- + Sr+2 = SrX2 log_k = 0.37 X- + H+ = HX log_k = 1.0

EXCHANGE 1-100

```
# Nagra NTB 02-09 p.13
# C = equiv.fraction / valency * CEC * s/w-ratio
# equiv. fractions: Na+=0.848, Ca2+=0.084, Mg2+=0.051, K+=0.017
# CEC=0.787 s/w=4.5032
```

X 0.0 NaX 3.005 CaX2 0.149 KX 0.060 MgX2 0.0905 SrX2 0.0 HX 0.0

TRANSPORT

-cells	40
-length	40*0.125
-shifts	40
-time_step	1
-flow_direction	diffusion_only
-boundary_cond	constant closed
-diffc	1.0
-disp	0.0
-punch_cells	1-40
-punch_frequency	1
-print_frequency	1

SELECTED_OUTPUT

-file	plume.dat
-reset	false
-step	true
-distance	true
-time	true
-high_precision	true
-рН	true
-pe	true
-water	
-totals	Al C Ca Cl K Mg Na S Si Sr Fe
-molalities	NaX CaX2 KX MgX2 SrX2 HX
-equilibrium_phases	CO2(g) Montmorillonite-Na Cristobalite Calcite Gypsum
	Pyrite
-saturation_indices	CO2(g) Montmorillonite-Na Cristobalite Calcite Gypsum
	Pyrite

Advective propagation of alkaline plume

In the following, those changes to the preceding input file are given to describe the transport in PHREEQC for the test case regarding advection. In PHREEQC the advective transport process can be described in two ways. The first description uses the code word advection. The following block replaces the block transport above:

ADVECTION

-cells	40
-shifts	100
-punch_cells	1-100
-punch_frequency	1
-print_cells	1-100
-print_frequency	1

The second description also uses the code word transport. The following block replaces the block transport above:

TRANSPORT

-cells	40	
-length	0.125	
-shifts	100	
-time_step	3.15E7	
-flow_direction	forward	
-boundary_cond	constant	closed
-diffc	0.0	
-disp	0.0	
-punch_cells	1-100	
-punch_frequency	1	
-print_frequency	1	

END

Gesellschaft für Anlagenund Reaktorsicherheit (GRS) mbH

Schwertnergasse 1 50667 Köln Telefon +49 221 2068-0 Telefax +49 221 2068-888

Forschungsinstitute **85748 Garching b. München** Telefon +49 89 32004-0 Telefax +49 89 32004-300

Kurfürstendamm 200 **10719 Berlin** Telefon +49 30 88589-0 Telefax +49 30 88589-111

Theodor-Heuss-Straße 4 **38122 Braunschweig** Telefon +49 531 8012-0 Telefax +49 531 8012-200

www.grs.de