Kaunas University of Technology

Faculty of Mathematics and Natural Sciences

Modelling of Radionuclide Migration from Solid Radioactive Waste Under Different Environmental Conditions

Master's Final Degree Project

Povilas Balčius

Project author

Doc. Dr. Vytautas Stankus

Supervisor

Dr. Dalia Grigaliūnienė
Consultant

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Doc. Dr. URBONAVIČIUS Benas Gabrielis

Reviewer

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Summary

Radioactive waste is generated due to modern human activities mainly from the energy sector and various medical applications. As such, this dangerous class of waste must be properly managed and disposed of. One of the most common methods of radioactive waste conditioning is cementation in a concrete matrix and disposal in repositories with appropriate engineered barrier system to prevent radionuclide leaching into the surrounding environment.

Naturally, concrete slowly degrades as it is exposed to various environmental conditions such an agressive chemical environment and water flow through the material. This requires for a thorough investigation on the potential effects of concrete degradation on the capability to keep the radionuclides retained in the concrete. This work is going to investigate how different environmental conditions could affect concrete alteration and consequently radionuclide release from the repository.

To achieve this, 3 seperate cases of different water (rainwater, rainwater with additional CO_2 partial pressure and groundwater) flow through the engineered barriers and waste matrix, and it's impact on the capability of the bottom concrete barrier to retain radionuclides and prevent their leaching out into the environmet are investigated. Addtionally, a case was modelled when the sorption value was selected regardless of the chemical evolution in the local environment. This was done to create a benchmark case for comparison.

Relative radionuclide flux out of the bottom barrier into the environment was compared between each case, it was found, that the highest radionuclide flux was in the case with groundwater flow causing degradation of concrete barriers.

Santrauka

Radioaktyvios atliekos yra pastovi problema, atsirandanti dėl įvairių žmonijos veiklų, tokių kaip energetikos sektoriaus veikla arba įvairių medicininių/pramoninių sričių veikla. Ši pavojingų atliekų klasė turi griežtus tvarkymo, saugojimo ir šalinimo reikalavimus. Vienas dažniausiai naudojamų radioaktyviųjų atliekų apdorojimo būdų yra, atliekų sucementavimas ir patalpinimas į specialiai įrengtus radioaktyviųjų atliekų atliekynus su atitinakamai įrengtais inžineriniais barjeraism tokiu būdu sumažinant radionuklidų patekimą į aplinką.

Dėl natūralių procesų, tokių, kaip aplinkos cheminės sąlygos ir vandens srautas per cemento matricą, betonas palaipsniui degradauoja. Norint tinkamai sutvarkyti radioaktyviasias atliekas, reikalinga atlikti tyrimus, apie galimus betono degradacijos efektus radionuklidų sulaikymui. Šis darbas skirtas išanalizuoti metodologiją, reikalingą teisingai atlikti šią analizę ir atlikti vieną tokių tytimų.

Šiame darbe bus atliekamas tyrimas apie aplinkos poveikį betono degradacijai ir radionuklidų sklaidai iš atliekyno, kai per atliekyną sunkiasi 3 skirtingų rūšių vanduo (lietaus vanduo, lietaus vanduo su didesniu CO_2 parcialiniu slėgiu ir gruntinis vanduo) ir bus stebimas apatinio betoninio barjero degradacija ir gebėjimas sulaikyti radionuklidus. Taip pat, kaip etalonas, bus sukuriamas modelis, kai į betono cheminę evoliuciją nėra atsižvelgiama.

Matuojamas santykinis radionuklidų srautas iš apatinio betono barjero ir kiekvienas atvejis yra palyginamas vienas su kitu. Pastebėta, kad gruntinis vanduo turėjo didžiausią įtaką radionuklidų migracijos padidėjimui.

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Abbreviations:

C-S-H: Calcius-silica-hidrates

IAEA: International atomic energy agency

LILW – low and intermediate level radioactive waste

CRP – coordinated research project (subsidized by IAEA)

NSARS – near-surface radioactive waste disposal safety assessment reliability study

K_d – Distribution coefficient

Introduction

Human activity leads to various consequences for the natural environment and humans living in said environment. One of more impactful activities are various, where hazardous waste is generated, including materials containing radioactive isotopes, be it for energy purposes, medical purposes or various industrial processes. To limit the negative radioactive waste impact on the environment and human health, it is necessary to manage it properly and to dispose of safely. For this purpose, radioactive waste is cemented into a solid cement matrix, placed into containers and disposed of in an appropriate repository, therefore increasing the ease of storage and disposal and reducing its capability to interact and contaminate the environment. In order to ensure adequate isolation of the radioactive waste it is necessary to evaluate the potential impact of environmental conditions on the concrete used to contain it. As such, for the Master's thesis „Modelling of Radionuclide Migration from Solid Radioactive Waste Under Different Environmental Conditions" the following goal is selected: to evaluate the potential migration of radionuclides from solid radioactive waste under various environmental conditions.

To achieve this it is necessary to understand the peculiarities of water flow through porous medium and radionuclide retention in cement. As water flows through the cement matrix many various chemical reactions can occur during this process (e.g. calcium leaching, sulphate attac, carbonation, etc.) and can lead to various damaging effects on the concrete matrix (e.g. decreasing of sorption capacity, cracking, etc.). This could impede it's capability to retain various contaminants inside and lead to radionuclide leaching out of the cement matrix, contaminating the surroundings with radioactive material.

In order to give confidence on the safety of the disposal facility, it is necessary to evaluate potential impact of water flow through concrete. This involves modelling of water flow through cemented radioactive waste and concrete barriers assuming different potential water chemical compositions. For the purpose of this work, concrete leaching with three types of water was analysed. The first type of water was assumed to be the regular rainwater in Lithuania. The second type was assumed to be the same rainwater, that would also gain additional CO_2 partial pressure due to various microbiological processes that could occur in the soil above the waste repository, while the water flows. Finally, degradation of concrete was modelled assuming leaching with groundwater. For evaluation of impact of different water types on concrete degradation and radionuclide migration, a group of objectives are formulated:

1) To get acquinted with the methods of disposing of radioactive waste and the cementitous materials used for such a task;

2) To investigate the chemical processes that could potentially occur in the cement matrix during exploitation and the modelling of such processes;

3) To create a conceptual and mathematical models for the purposes of this evaluation;

4) To investigate the acquired results.

1. Literature review

The literature review and analysis is going to focus on the classification of different types of radioactive waste, and disposal with the greatest attention to the disposal of low and intermediate level short lived radioactive waste in near surface repositories including radioactive waste cementation in concrete matrix and concrete barriers.

Furthermore, identification of the composition of concrete used in such bariers and the chemical processes in them, when water solutions pass through.

Lastly, the process of evaluating concrete barrier degradation will be described and how the chemical reactions occuring in the concrete impact the capability of said concrete to retain the radionuclides in it.

1.1. Radioactive waste management

1.1.1. Classification of waste

The main issue that arises when dealing with radioactive waste is its management, as a lot of radioactive materials can pose great danger to human health and the environment for thousands of years [1]. Thus, waste of different classification has to be stored differently as it could have different impact on the environment.

Radioactive waste can be classified in two ways: according to its physical state and according to radiological characteristics [2] Based on physical state radioactive waste is classified as solid, liquid and gasseous waste.

Gasseos state radioactive waste is various aerosols that form during the process of nuclear fission. It can be various gasses that form during fission or dust, infused with radionuclides [3].

Liquid radioactive waste is generally the technological water, that can be used in nuclear reactors for various purposes, such as the cooling of nuclear reactors. This contaminated water can further be classified by the activity of the radionuclides dissolved in it into: low level, the activity of such water is below $4*10^5$ Bq/l or intermediate level, when the water activity is $4*10^5$ Bq/l and above [3].

Solid radioactive waste can arise during nuclear power plant operation and decommissioning activities, maintenance work, etc and it's activity can vary greatly depending on the source of this waste.

Solid radioactive waste can further be classified by it's activity and half-life of the radionuclides in the waste. By activity, radioactive waste in Lithuania is calssified into A to G categories. A category waste is very low level and short-lived waste, B class low level and short-lived, C category waste is short-lived but of intermediate level waste. Class D radioactive waste is long-lived, but low level. Class E waste is intermediate level and long-lived waste.

Class F radioactive waste is spent radiation sources of various purposes (usually medical) and can be of high activity [1][2][3].

Finally, high-level radioactive waste is spent nuclear fuel or various products of reprocessing of spent nuclear fuel. This type of waste is of high-activity as it contains a large amount of fissile materials and is long-lived, due to containing radionuclides of long half-lives [1][2][3].

Furthermore, solid waste can be classified into flammable, inflammable, compressable, incompressable, unprocessable and more, depending on how the solid state waste was generated.

1.1.2. Radioactive waste treatment, storage and disposal

Radioactive waste disposal depends on the activity and half life (class) of the radioactive waste.

Aerosolised (gasseos) waste is usually released into the environment, determining the maximum limit of allowed waste in the environment [3][4]. Filtration is done when possible to reduce released amounts of radionuclides and is highly dependent on the type of radionuclides present

Liquid radioactive waste is held in leak-tight tanks. Liquid radioactive waste is processed with the aim to reduce its volume by the seperation of bulky liquid material, which radionuclide activity concentrations allow to discharge this liquid into environment. The rest of the liqui radioactive waste is eventually solidified during its conditioning by using binding materials. Solidified radioactive waste is placed in containers meeting the acceptance criteria for storate and or disposal [2][5][6].

Solid radioactive waste is stored, conditioned and disposed of depending on the class of the waste. Very low level waste (class A) can be stored until the dacay of short-lived radionuclides (radionuclides with a half-life of Cs-137 or less), when radiation protection controls are no longer necessary or can be disposed of in a repository with simpler engineered barriers. Solid radioactive waste of classes B, C, D and E are subject to conditioning. Short-lived low and intermediate level waste is usually disposed of in a near surface repository while low and intermediate level waste containing long-lived radionuclides are redirected to a deep geological repository [2][3][4].

Class F waste, spent sealed sources of ionising radiation shall be managed and stored separately from other radioactive waste. If it is possible, after use sealed sources are sent back to the manufacturer. If that is impossible, these materials are stored separately from other waste and subsequently disposed of in near surface or deep geological repositories [2][3][4].

Class G waste is high level radioactive waste and it is disposed of in a deep geological repository.

After the shut down of the Ignalina nuclear power plant, most of the waste generated during operation and being generated during decommisioning is of class A to E. It is foreseen that very low level waste will be disposed of in a Landfill type repostory while low and intermediate level short lived radioactive waste will be disposed of in a near surface repository, which consist of above ground vaults [7].

All radioactive waste repositories rely on multibarrier systems which consist of various engineered and natural barriers, reducing/preventing water flow through the waste. An example of such system is provided below:
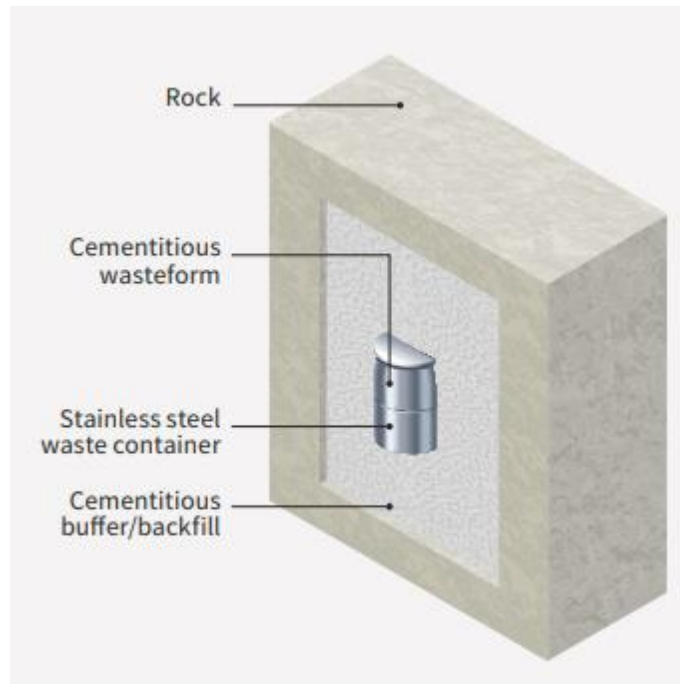
Fig. 1. Multibarrier radioactive waste containment system for intermediate activity radioactive waste.[8]

As can be seen in **Fig. 1**, concrete is an important part of the waste disposal units[8].

Cementitious materials are used to immobilise waste into a stable matrix to achieve as high radionuclide retention in the material as possible. Cementitious backfill and concrete constructions are also very common in the design of the repositories as they have low permeability and good radionuclide retention capacity. In addition to this, concrete is a very common construction material, making it quite cheap, as well as quite durable [9][10].

1.2. Chemical composition of concrete barriers

Concrete for regular construction purposes is usually composed of a mixture of 10% cementitious materials, 20% air and water, and the rest being filament, like sand and gravel. This gives structural concrete its relatively cheap cost and great durability [11]. The main component in cementitious material Portland cement. This material mainly consists of 3 chemical components: Lime (CaO) Silica (SiO_2) with various amounts of other oxides such as Aliuminium oxide (Al_2O_3) or Iron oxide (Fe_2O_3). These materials during the curing process interact with water creating a matrix of calcite ($CaCO_3$) with various other mixed in materials forming a concrete skeleton. Typical composition of CEM I cement, commonly used for radioactive waste disposal is presented in **Table 1** [12]:

Table 1. Composition CEM I cement used for waste repositories.

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	P_2O_5	CO_2	Total
% of weight	20,9	3,2	4,6	65,1	0,6	2,76	0,1	0,6	0,6	1,1	99,56

After cement hydration (reaction with water), different minerals are formed. The main components formed are various C-S-H minerals and Portlandite ($Ca(OH)_2$). The chemical composition of hydrated concrete is provided in **table 2** [13].

Table 2. Hydrated concrete composition[13].

Hydrate	Amount kmol/m^3 concrete
C$_3$FH$_6$	0,1008
C3AH6	0,02397
Monosulphate	0,09613
Ettringite	0
CSH-gel	1,225
Portlandite	1,036
Brucite	0,06079
KOH	0,04607
NaOH	0,007903
CaCO3	0,06295

To properly prevent radionuclide leaching a different, more dense formula is required to reduce the porosity in the concrete. This increases the requirement for the cementitious material. Generally, a higher fraction of Portland cement is added to create a denser type of concrete that would be of better properties to prevent water leaching, such as porosity [13]. This usually means that the filament mass is reduced and Portland cement content is increased, leading to a less porous material. This of course increases costs, and various recipes for this structural barrier concrete are being investigated to potentially reduce costs without decreasing the structural integrity of the cement matrix[14].

1.3. Chemical degradation of concrete barriers during water flow

Once cured, concrete matrix in ideal circumstances does not interact with any remaining water solute in the pores of the concrete. However, to properly predict any leaching of radionuclides from a concrete matrix, it is important to model the non-ideal scenarios as in such scenarios, the concrete matrix slowly degrades, potentially increasing the leaching from the concrete barrier [15].

In natural environments water composition can vary widely with it being inclined to being slightly acidic due to atmospheric content of carbon dioxide and other materials, which could solve in rainfall, that eventually infiltrates into concrete [16]. This provides a basis for the concrete barrier to degrade, as new components are introduced.

The main processes that have a negative impact on concrete are: decalcification, sulphate attack, chloride attack, carbonation, etc [12][13].

To properly describe these processes, it would be difficult to manually calculate every potential chemical reaction. As such, thermodynamic databases of cement reactions with various materials are catalogued to reliably predict hydrated cement phase assemblages and chemical compositions [19].

The use of thermodynamic databases allows for an accurate representation of various mineral phases that form during concrete degradation and allows for a dynamic look into the changes that occur to the capability to retain radionuclides incorporated in the concrete barriers. Such results should be

carefully considered, as they are only an accurate description of what is most likely to occur chemically in the concrete barrier, but due to potential changes in physical and chemical characteristics may change. In this work, only concrete decalcification will be considered, as well as radionuclide leaching due to water flow.

The chemical composition of water that flows through concrete and the composition of concrete itself impacts the potential reactions that occur in the concrete. While many of them could be potentially irrelevant to the concrete capacity of retaining radionuclides degradation of calcium-silica-hidrates can lead to a reduction in sorption of contaminants and lead to leaching. [18] The decalcification of these materials (washing out the calcium component out of the concrete matrix) leads to less sorbants in the concrete matrix, reducing the sorption capacity in concrete, which in turn increases radionuclide leaching.

While the reduction of CSH based materials is the most important factor in determining the suitability of concrete to retain radionuclides, there are many other processes that can happen both before and after this process. The reduction in calcium happens in multiple stages [19]. Potentially, important processes of leaching with water are: alkali leaching, portlandite leaching and CSH phases leaching [13]. As calcium is washed out of the repository barriers, the chemical conditions change and the cement matrix continuously loses its capability to retain contaminants. This can be exascerbated through physical imperfections in the concrete structure, such as a crack in the waste matrix, leading to an increased water flow through it and, in turn, increased rate of decalcification. [20] This can be seen in **Fig. 2** below, the crack in the cement acts as a medium of increased water flow, leading to faster reaction times in the concrete matrix, causing a washing out of calcium at a faster rate. However, in this work, we will only look into a case, where concrete imperfections do not exist.
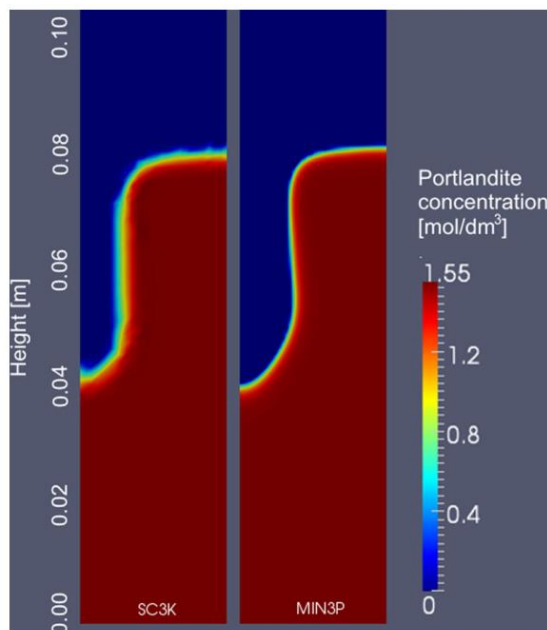
Fig. 2. Reduction in Portlandite, the main component of concrete, with a physical imperfection (a crack) in the concrete matrix, leading to increased leaching .[20]

However, chemical degradation takes time to occur and first of all much more reactive elements in the concrete matrix are going to react [19]. This can be tracked through various chemical parameters

of concrete, as well as, the concentration of elements in concrete pore water. One of these parameters is pH. With concrete having a high pH value as soon as it is created, due to various sodium and potassium compounds present in the matrix making it a very basic material (initial pH value can be close to 14 in concrete) [23]. Once these high base materials are washed out the pH value slowly drops, and other materials begin to interact with the water flowing through it, leading to the decalcification happening in multiple stages [22]. As can be seen in **Fig. 3**, the pH value in concrete matrix drops in stages. Firstly, the sodium and potassium compounds get washed out due to high reactivity with various solute materials flowing through the concrete.
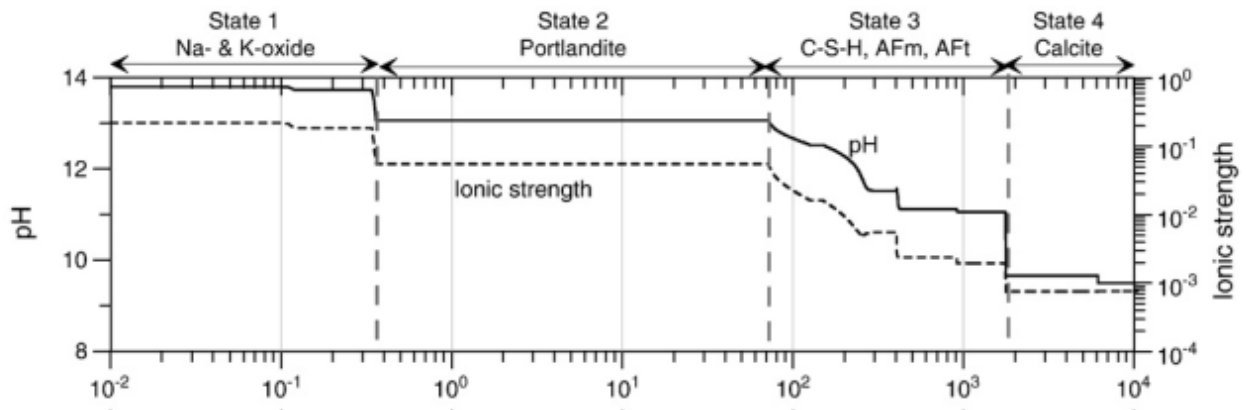
Fig. 3 The change of pH value of the concrete due to water flow through concrete washing out various elements. [21]

As potassium and sodium are washed out, the solute begins interacting with other materials, usually for stage 2, portlandite, as it is more reactive than C-S-H. This leads to an increase in porosity of the bulk material [22]. This porosity change can be seen in **Fig. 4**.
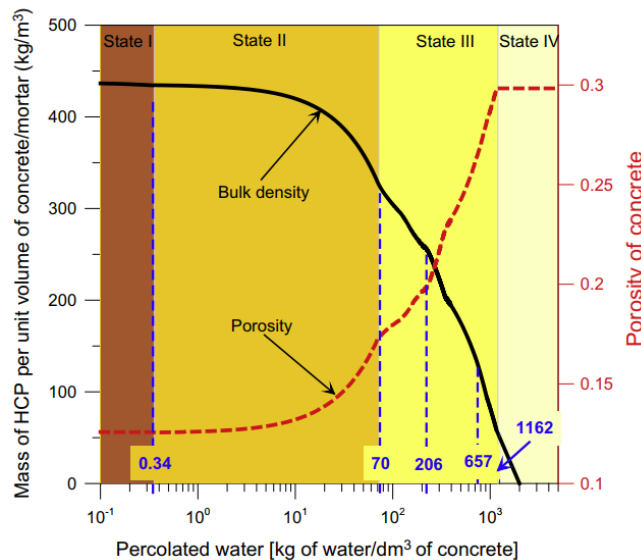
Fig. 4 Porosity change in concrete as it degrades due to aggressive water flow through it. [22]

When porosity changes, the water solution starts flowing faster through concrete, leading to an increased rate of decalcification.

The third stage of decalcification occurs when all of the portlandite has been washed out and C-S-H materials begin to dissolve. These two stages are the most important in waste matrix evolution as they

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lead to the highest changes in the physical characteristics of the concrete. In the final stage, calcite begins to be washed out, although, this does little to change radionuclide retention. Once the concrete matrix evolves past stage 2, radionuclide sorption can reduce quite drastically, leading to increased leaching. However, in the final stage of concrete degradation, stage 4 only filament aggregates remain in the concrete matrix, leading to a massive reduction in sorption, as the only sorbents left are the said filaments.

1.3.1. Thermodynamic databases

Modelling of these different reactions can be a daunting task, furthermore as the number of different materials increases, so does the difficulty in modelling them. To ease this task and avoid input of chemical reactions for each new model, thermodynamic databases are developed [17]. They contain a large number of chemical reactions with thermodynamical parameters, which can be to reliably predict hydrated cement phase assemblages and chemical compositions due to both different compositions of concrete and different environmental conditions such as acidic water or increased partial pressure of CO_2, for example.[23]

These databases are used to increase the accuracy of prediction of various phases in cement and ease modelling work. One of such databases is CEMDATA, developed particularly to predict changes in chemistry that occur during hydration of Portland cement or dissolution/precipitation of cement phases. This database is based on the mass action law and allows to predict changes in concrete composition.

1.4. Modelling of concrete barrier degradation

Cement and concrete are usually not in thermodynamic equilibrium with the surroundings where they are located. These barriers will experience water infiltration and movement of water solutions. This can potentially change the pore water in the concrete leading to change in the solubility and sorption of contaminants in the concrete matrix [21].

Leaching of calcium from concrete is very slow process that can take thousands of years. When modelling radionuclide release from the near surface repositories the time scale usually extends up to 1e+5 years. Therefore, the only way to evaluate potential evolution of the concrete barriers is numerical modelling.

There are two approaches to modelling of calcium leaching. The first one is modelling chemical evolution of concrete using only thermodynamic databases to model the change of the chemical composition of concrete and was used a team from the Belgian Nuclear Research Centre, in the work "Modelling chemical degradation of concrete during leaching with rain and solid types" [21]. The aim of this work was to determine the change in porosity due to mineralogical change in concrete.

This was done by adding water into the concrete to simulate water flow and thermodynamically equilibrating both parts of the chemical composition. The used water would be discarded and new water of the same composition would be added, but the concrete composition would be saved internally in the programs used. This process is shown in **Fig. 5**.
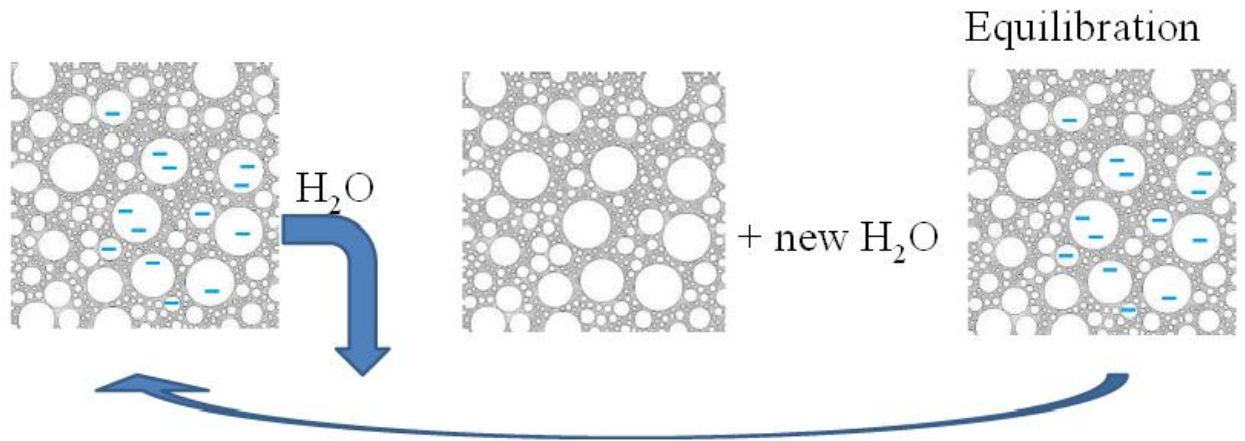
Fig. 5 Water change in thermodynamic equilibration process.

5 types of water were evaluated, with a notable exception of rainwater with increased CO_2 partial pressure, due to microbiological processes that could occur in topsoil. This increase in carbon dioxide led to an increase in carbonate in the water, that caused quicker concrete degradation, as compared to the initial cases with regular rainwater [21].

Reactive modelling can lead to more accurate results of concrete degradation evaluation, due to the fact that the model is not assumed to be a simple cube where water is constantly replaced, but a 2- or 3-dimensional structure with a set initial chemical composition and constant input of water solute of some composition. As the modelled structure is at least 2 dimensional this leads to a concentration gradient of various chemical elements, as the entire structure does not degrade at the same time all at once. The input water reacts with the upper layers of the concrete barrier first making it chemically passive. As water flows through the modelled barrier, chemically aggressive water makes its way to the other parts of the barrier, leading to a staggered degradation. Of course, this leads to a much larger demand on computational resources either leading to a vastly increased computation time, as large amounts of data and many datapoints need to be evaluated or to a simplification of model.

This approach has been used by Lars Olof Höglund in an attempt to evaluate the effects and processes of fracture formation, due to shrinking, drying, contraction due to cooling, groundwater flow, and corrosion of steel reinforcements on geological waste repository concrete barriers [13]. What has been found, that, in addition to physical processes causing increased leaching due to degradation of concrete, groundwater flow increased these problems significantly, by quickening the pace at which concrete barriers were decalcified.

Reactive transport modelling was further explored in the work "Decalcification of cracked cement structures" by J.Perko [20], where multiple teams were tasked with modelling of calcium leaching out of a cement slab with a crack in the middle. This was done in an attempt to compare different reactive transport models for systems with complex transport conditions (in this case with existing cracks in the model). What was discovered, that even though the computer programs used for the analysis were different, with potentially different thermodynamic databases and different reactive transport models, the results were largely similar. Even more so when simulating long-term concrete integrity, contaminant migration and risk assessment [20].

Reactive transport modelling, even though is computationally intensive or requires simplified models, can lead to accurate depiction of potential processes that can occur in the concrete matrix during degradation. Using this it can be possible to account for radionuclide migration inside and, if necessary, out of the system.

2. Task and methodology

2.1. Modelling of radionuclide migration from solid radioactive waste under different environmental conditions

2.1.1. Topic of this work

Radioactive waste is generated during operation and decommissioning of nuclear power plants as well as using radioactive materials in industry, medicine and research. In order to avoid any negative impact of radioactive material on the environment, it is necessary to manage this waste in a way, that would prevent radionuclide migration into the environment or at least reduce it to acceptable limits.

The purpose of this Master's thesis is to evaluate potential radionuclide migration from solid radioactive waste (cemented radioactive waste) under various environmental conditions. One of the factors that significantly affect radionuclide migration is distribution or sorption (depending on literature) coefficient (K_d). This coefficient is different for all radioactive elements. In addition, this coefficient depends on the material on which the radionuclides are absorbed (clay, sand, concrete etc.) and it can change, depending on the condition of the absorbing material. For example, concrete degradation due to aggressive water flow, can impact on how well it is capable to retain radionuclides in the concrete matrix. In this work, it is investigated how radionuclide leaching changes when due to water flow through the repository, the concrete barriers chemically degrade and subsequently changes radionuclide sorption. To assess this, various numerical methods are used to model water flow and mass transfer through porous material processes.

2.2. Radionuclide migration assessment methodology

Proper radioactive waste management needs to be carried out in a manner that would be of acceptable level of safety and which could demonstrate compliance to the established regulatory requirements [24]. To achieve this various national and international waste disposal agencies, such as, the International Atomic Energy Agency (IAEA), spent considerable effort to develop and apply safety assessment methodologies for both high level radioactive waste and low and itermediate level radioactive waste (LILW).

To improve the confidence in safety assessment approach IAEA launched a Coordinated Research Project (CRP) titled Near-Surface Radioactive Waste Disposal Safety Assessment Reliability Study (NSARS). This project was focused on developing confidence in modelling of physical processes related to safety of waste disposal facilities. This bore considerable benefit as it identified needed improvement to the overall safety assessment process and was later developed into the Improvement of Safety Assessment Methodologies for Near Surface Disposal Facilities (ISAM) [24]. The ISAM project was used to develop safety assessment methodology recomendations.

The methodology developed was for long term safety assessment for near surface radioactive waste disposal facilities. The waste associated is of low and intermediate level that could be generated through the operation of nuclear power plants, research, industrial processes, medical and any other radioactive material applications. As this work is about near-surface low and intermediate level waste, we will use the ISAM methodology guidance. The methodology uses step-wise approiach with the key components as follows [24][25]:

- The specification of the assessment context;

- The description of the disposal system;

- The development and justification of scenarios;

- The formulation and implementation of models;

- The calculation and derivation of illustrative activity limits.

Following this approach, a framework for the assessment is defined and the disposal system is specified. Then radionuclide migration scenario is formulated and transformed into conceptual and mathematical model/ Then, the models are implemented into computer tools, calculations are performed and results are analysed.

2.2.1. Assessment context

The main purpose of this work is to assess decalcification of concrete due to leaching with different water types and to analyze its impact on radionuclide release from the repository to surrounding environment.

The main object of the assessment is a potential near surface disposal facility constructed in the region of Ignalina nuclear power plant. Only post-closure period of the repository is considered.

The assessment is limited to radionuclide transfer through the concrete bottom slab along the path of water flow at the specified water infiltration rate. Concrete degradation of this barrier is assessed.

Three water types are specified for the investigations based on the local environment conditions.

The assessment of radionuclide migration or dose assessment is usually performed for the time period that allows to demonstrate that the peak flux or peak dose has been reached [25]. The typical assessment time-frame for near surface repositories are about 1E+5 years [24]. Therefore, for this work the model will be run to simulate 100000 years of concrete degradation and radionuclide leaching, to determine the impact of different water types.

As output of the assessment, radionuclide fractional flux (estimated radionuclide flux to the environment divided by the initial activity of the radionuclide in the repository) is considered.

2.3. System description and tasks of the work

The system is described as a near-sruface radioactive waste repository and the general image is provided in **Fig 5**. The repository is a system of cemented radioactive materials with a technological concrete barrier, that prevents radionuclide leaching out of the waste zone.

The main task of this Master's thesis is to analyse, how radionuclide transfer out of the waste matrix changes when due to water flow through the concrete barriers, it slowly degrades and radionuclide sorption slowly changes.

The analysed system is a near-surface radioactive waste repository, in which, low and intermediate level waste is disposed of by cementing it in concrete barrier systems and then stored. The scheme is provided below in **Fig 5**.
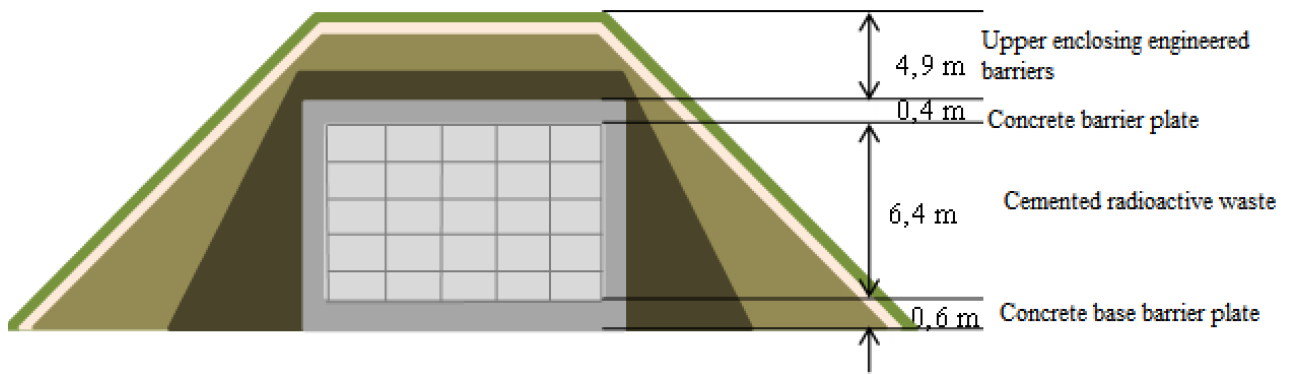
Fig. 6 Examined near-surface radioactive waste repository schematic.

The radionuclides present in the waste matrix, for which the influence of concrete degradation will be evaluated are: C-14, Cl-36, Cs-137, I-129, Pu-239. All of these radionuclides are to be evaluated as having the activity of 1TBq (1E+12 Bq).

Water flow through the waste repository (Darcy velocity, v_D) after evaluating the influence of engineered barriers reducing water flow is provided in a graph below.
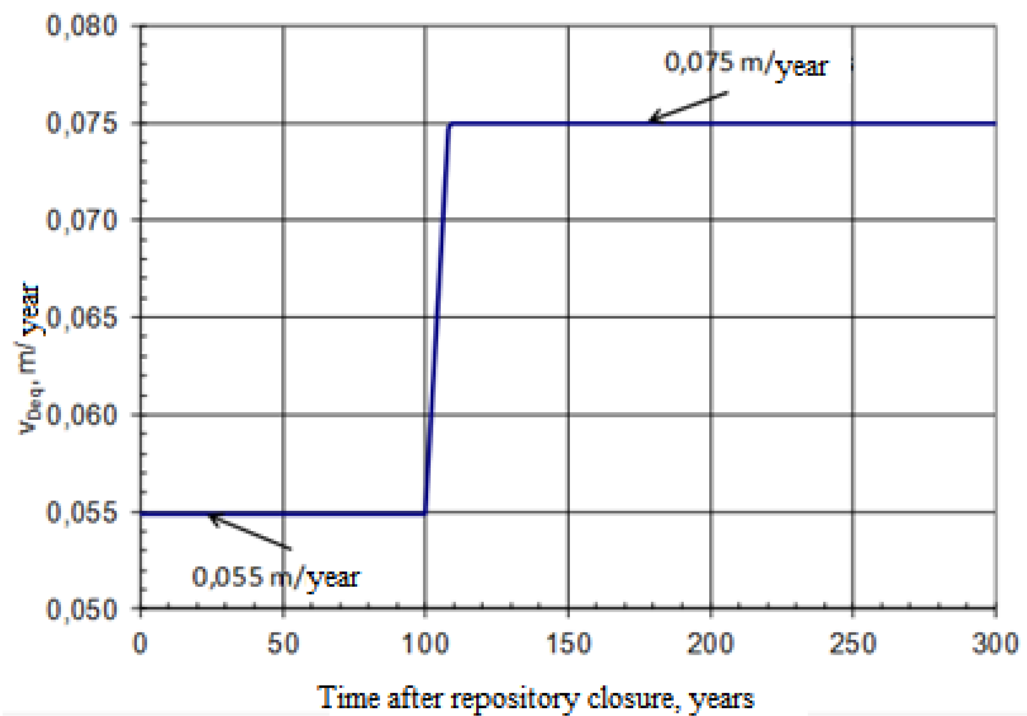
Fig. 7 Speed of water filtration through the waste repository.

As can be seen in **Fig. 6**, the Darcy speed, at which water flows through the waste repository is 0,055m/year. The speed at which water flows through the repository largely depends on the state of the top engineered barrier (see **Fig. 5**). As time goes on, this barrier slowly degrades, and, after a 100 years after the repository was entombed, the water flow speed slowly increases. At around 110 years, the barrier is degraded enough, that water flow reaches natural water infiltration speed (which is 0,075 m/year).

To determine radionuclide leaching out of the waste, we will have to model the chemical degradation of conrete for the bottom barrier, as such, the minerological composition of the base concrete barrier (**Fig. 5**) is provided in the table below.

Table 3. Initial concrete barrier minerological composition.

Mineral	mol/dm^3
CSH-jeniteD *(angl. CSH-jenniteD)*	0.657611
CSH-jeniteH *(angl. CSH-jenniteH)*	0.420682
CSH-tobermoriteD *(angl. CSH-tobermoriteD)*	0.494318
CSH-tobermoriteH *(angl. CSH-tobermoriteH)*	0.020808
KSiOH	0.143761
NaSiOH	0.024625
Etringite *(angl. ettringite)*	0.05304
Monokarbonate *(angl. monocarbonate)*	0.091911
Calcite *(angl. calcite)*	1.975944
C3FS0.84H4.32	0.064141
Portlandite *(angl. portlandite)*	1.65189
Hidrotalcite *(angl. hydrotalcite)*	0.036091

To properly evaluate the chemical degradation of concrete, it is also important to evaluate the initial pore water of the concrete barrier which is provided in the table below.

Table 4. Initial pore water composition of the concrete barrier.

Component	Concentration(mol/l)
Al	8.20E-05
C(4)	2.06E-04
Ca	9.59E-04
Cl	5.51E-07
Fe	1.23E-07
K	4.11E-01
Mg	1.33E-09
Na	7.53E-03
S(6)	5.08E-03
Si	7.56E-05
pH	13.45
pe	5.362

The physical properties, that could influence water flow through the concrete barriers are provided below.

Table 5. Concrete barrier and waste zone physical properties.

Material	Density (kg/m^3)	Porosity (-)	Effective diffusion coefficient (m^2/s)
Concrete barrier	2300	0,15 / 0,25 / 0,25*	1E-11 / 1E-10 / 5E-10*
Waste zone	2000	0,25	5E-10

*First measure represents the undegraded concrete, second and third represent second and third degradation states respectavely.

For this work 3 tasks are given to assess the impact of different environmental conditions on radionuclide leaching from near surface radioactive waste repositories:

1) To model concrete barrier chemical degradation after repository closure due to leaching with water of different chemical composition, to represent different environmental conditions:

   a. Rainwater,

   b. Rainwater with an increased partial pressure of CO_2, to represent microbiological processes in the ground above the waste repository,

   c. Groundwater.

2) To link the change in radionuclide sorption coefficient, with concrete degradation stages, and obtain sorption coefficient in concrete dependancy on time.

3) To evaluate, how radionuclide flux out of the waste zone changes depending on the evaluated sorption coefficient in concrete change. Compare it with the case when local conditions for concrete degradation are not taken into account.

2.4. Radionuclide migration scenario

After the repository closure, potential water infiltration would be through the top of the structure as rainfall, with potential for increased acidity due to microbiological processes in the top soil layer covering the repository. It is assumed that radionuclides are leached from the waste with infiltrated water are transferred down through the repository bottom slab into the environment.

2.5. Conceptual and mathematical models

2.5.1. Conceptual model

In the case of radionuclide migration modelling, the primary radionuclide release route into the environment is leaching of waste due to rainwater infiltration and flow through the waste. Infiltrating into the soil over the repository water also causes chemical degradation of concrete. The scheme of the conceptual model is provided in **Fig. 8**.
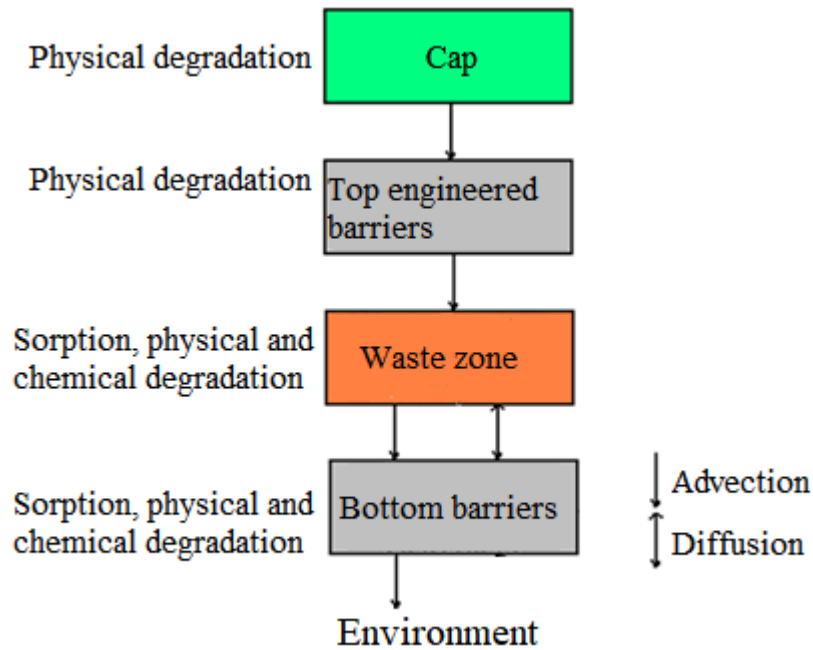
Fig. 8 Conceptual model of radionuclides leaching out of the waste repository.

The radionuclides washed out from the waste zone would then go down into the concrete barrier (bottom slab). The main processes considered in the assessment include: advection, diffusion, chemical degradation (decalcification), physical degradation (taking into account in water infiltration rate presented under the system description), sorption, radioactive decay.

In this assessment it is assumed, that the waste zone is a homogenous area filled with radionuclides evenly and does not consist of multiple containers. Also, it is assumed that the system is already saturated with water. These additional effects would be difficult to account for and could potentially increase the computational cost for modelling [26]. This would be a conservative estimate, as water flow is greatly reduced due to various capilary flow effects, if the system is not saturated with water[26][27].

2.5.2. Mathematical model

The mathematical model consists of a finite source of radionuclides (the activity of which is 1TBq, these radionuclides are also reducing due to radioactive decay) being the waste zone, the concrete barrier preventing nuclide leaching into the environment and a constant water flow, as described earlier and depicted in **Fig. 6** and concpetual model as depiced in **Fig. 8**.

The chemical reactions occuring in the concrete barrier during chemical degradation for each chemical reaction can be described through the mass action law[28]:

$$aA + bB \leftrightarrow cC + dD \tag{1}$$

$$K = \frac{\{C^c\}\{D^d\}}{\{A^a\}\{B^b\}} \tag{2}$$

Each chemical reaction has a specific constant K that determined the thermodynamic equilibrium of the reaction [28][29]. This can be used in large thermodynamic databases to determine the order of

chemical reactions (what reagents react first), the amount of reaction products and remaining reagents, as not all chemical compounds are used up in chemical reactions. This is used by the computer software PHREEQC used in this work.

Water flow through porous medium is described by Darcy's law [27][30]:

$$Q = \frac{-kA(h_b - h_a)}{\mu L} \qquad (3)$$

Where:

k – porosity,

A – area of water flow,

$(hb-ha)$ – total pressure drop,

L – the lenght over which the pressure drop takes place

μ – the viscosity of the liquid.

This is the general formula, that is used by PHAST program, to determine water flow through porous medium. The negative sign is necessary as it determines that, the fluid flows from high pressure to low pressure [30]. This determined the rate, at which water flows through the concrete barrier in the case of this work.

For radionuclide leaching scenario, after the near-surface waste storage facility closure, radionuclide transport through the waste disposal system is modelled as a diffusive-advective transfer, that takes into account hydrodynamic dispersion and radioactive decay [24]:

$$\frac{\partial}{\partial t}(R\theta C) = \frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x}\right) - \frac{\partial}{\partial x}(qC) - \lambda RC_{,d} \qquad (4)$$

Where:

C – activity concentration of a radionuclide in pore water, Bq/m^3;

θ – effective porosity;

D – diffusion-dispersion coefficient, m^2/s;

λ_d – decay constant, $year^{-1}$;

R – retardation (delay) coefficient, -;

q – rate of water flow, m/s;

t – time, s;

x – distance in the direction of water flow, m.

Retardation coefficient determined how much slower a contaminant moves through porous medium, that water does and is expressed [31]:

$$R = 1 + \frac{\rho_b k_d}{\theta} \tag{5}$$

Where:

K_d – sorption coefficient of the porous medium,

ρ_b – bulk density of porous medium,

θ – porosity.

2.6. Programs used in the analysis

A multitude of programs was used to properly evaluate both concrete degradation during water flow and radionuclide leaching and sorption in the concrete barrier.

2.6.1. Radionuclide transport through the components of the disposal system

2.6.2. PHREEQC

PHREEQC is a geochemical calculation program based on C and C++ programming languages, which uses text input to determine the various variables that can be used to describe water solutions, concrete mineralogical composition, cement composition. This is done using PHREEQC programs user interface, an example is provided below:

Fig. 10 PHREEQC user interface.

PHREEQC uses thermodynamic databases such as WATEQ4F (The default database for PHREEQC is Phreeqc.dat but is quite limited and better alternatives are used) or some more specialised databases written specifically for the task of accurately describing chemical reactions, that occur in concrete during chemical degradation, such as CEMDATA18. In this work CEMDATA18 is used as it can accurately determine potassium and sodium silica hidrates as well as other cement phases.

These databases are based on the mass action law, that determines that the rate of any chemical reaction is proportional to the product masses of the reacting substances, with each mass raised to a power equal to the coefficient that occurs in the chemical equation. Generally, these databases have

the coefficient written down, and only require input from the user, on the initial chemical reagents, that could react [32, 33]. The chemical reactions eventually reaches equilibrium, that can be described with a unitless constant, these constants are what databases cosist of. PHREEQC uses these coefficients to describe the expected chemical composition, after the reactions occur.

2.6.3. PHAST

PHAST is a geochemical water solute transport and reaction simulation program, that can be used to simulate water flow, and solution transportation and chemical reactions in porous medium, such as concrete. This is done by assigning a spatial area with physical properties [34].
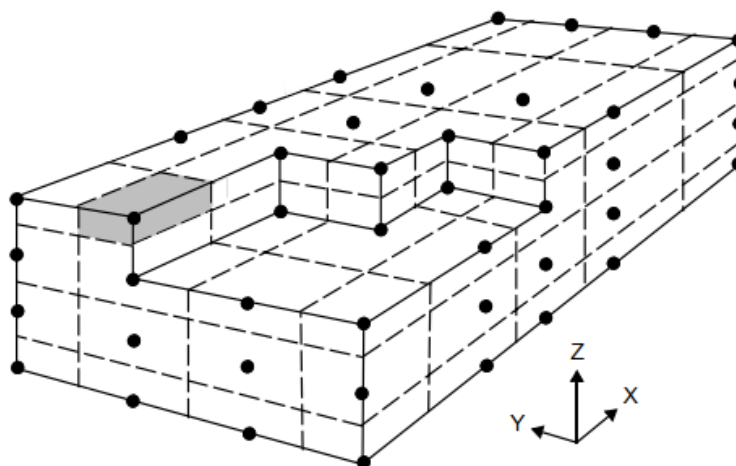

Fig. 11 PHAST spatial area grid (solid lines), with boundary nodes (dots) and cell boundaries (dashed lines) [34].

After the physical properties are assigned to each node of the grid, water flow is simulated in accordance to the physical properties of each cell. After which, a call to the thermodynamic databases is made (these databases and descriptions of solutions, and chemical compositions of flowing water, pore water, and the material through which the water flows are done in PHREEQC), after which, PHAST reads the input chemical data and performs calculations in accordance to the thermodynamic database [34].

For each step in time transport data and chemical reaction data is simulated and is internally recorded (an externally if specified by the user) for the next steps, this is repeated, until the end of the simulation.

2.6.4. AMBER

The computer tool AMBER was used to perform calculations in the case of radionuclide leaching out of the waste zone into the concrete barrier. This computer tool is listed in computer codes that are applied for radionuclide migration analysis by the IAEA [35] and has been verified in a number of cases and reports for it's use.

AMBER is a flexible software tool that allows users to build their own dynamic compartmental models, to represent the migration and fate of contaminants in a system. Using this tool it is assumed, that the contaminants (the object of interest in this tool) are uniformly mixed in a series of compartments, between which advective-diffusive transfer takes place and each transfer depends

directly on the amount of material present in the compartment, through which the material is moving. The rate, at which the compartment inventory changes with time is [36]:

$$\frac{dN_i}{dt} = \left(\sum_{j \neq i} \lambda_{ji} N_j + \lambda_M M_i + S_i(t)\right) - \left(\sum_{j \neq i} \lambda_{ij} N_i + \lambda_N N_i\right) \tag{8}$$

where

i and j - compartments the transfer of radionuclides between which is taking place;

N and M - activity (Bq) of radionuclides N and M in a compartment (M is the precursor of N in a decay chain);

S(t) - time dependent external source of radionuclide N, Bq/year;

λ_{ji} and λ_{ij} - transfer coefficients (1/year) representing the gain and loss of radionuclide N from compartments i and j;

λ_N and λ_M - the decay constants for radionuclide N and M (1/year).

2.7. Rainwater and groundwater

Rainwater and groundwater chemical composition descriptions are necessary to account for the potential chemical reactions, that are likely to be induced in the concrete barrier.

2.7.1. Rainwater and rainwater with increased CO_2 partial pressure

Rainwater description is provided in the table below:

Table 6. Rainwater chemical composition, total average data of 10 years [37].

Chemical element		Units	Total average over 10 years
sulfate	S	mg/l	0.733
nitrate	N	mg/l	0.71115
amonium	N	mg/l	1.17365
chloride	Cl	mg/l	0.723
sodium	Na	mg/l	0.6895
potassium	K	mg/l	0.3745
calcium	Ca	mg/l	0.876
magnesium	Mg	mg/l	0.197
pH	pH	pH	5.4405

The data used was obtained from localised air pollution data station [37], 10 years of data were selected to calculate an average. As this water is interacting with the atmosphere, potentialy carbon dioxide could end up solving in this water. To account for this, additionally in water description steps, we will add carbon dioxide partial pressure into the water. This is done in accordance to the partial pressure of CO_2 in atmosphere, this CO_2 can be solved in rainwater and infiltrate into the concrete barrier [21]. Partial pressure of CO_2 in the atmosphere is $10^{-3.5}$ atm.

Due to various microbiological processes partial pressure of CO_2 in the soil can be much higher than in atmosphere. This is described in the same manner as in the case before, but the partial pressure value is higher: $10^{-2.3}$ atm [38].

2.7.2. Groundwater

Groundwater chemical composition was taken from an analysis of groundwater well near the near-surface radioactive waste disposal site [39], the chemical composition is provided below:

Table 7. Chemical composition of groundwater [39]

Well number	Cl	SO₄	HCO₃	NO₃	Na	K	Ca	Mg	NH₄	pH	SiO₂
6k	77.5	51.4	788	0.05	31	5.5	207	62.5	0.385	6.84	18.53
7k	9.6	11.9	459	0.248	18.5	2.9	101	32	0.084	7.24	13.48
8k	3.6	14	215	39.1	3.7	1.6	71.2	17.7	0.202	7.5	5.55
average	30.23	25.76	487.33	13.13	17.73	3.33	126.4	37.4	0.22	7.19	12.52

2.8. Radionuclide sorption values for each concrete degradation stage

As was discussed before, concrete slowly degrades in a set of 4 stages, [21, 22] with sodium and potassium being washed out in phase 1, Portlandite being leached out in stage 2, in stage 3 C-S-H gets washed out, and in the final stage only filler materials and the basic cement skeleton remaining.

In all these stages these substances impact the capability of concrete to absorb and retain radionuclides in itself. These sorption values for each radionuclide are different [21, 22, 24, 40] and are provided in the table below

Table 8. Radionuclide sorption values per concrete degradation stage compiled from multiple sources [21, 22, 24, 40].

Radionuclide	Stage 1	Unit	Stage 2	Unit	Stage 3	Unit	Stage 4	Unit
C-14	2	m³kg⁻¹	5	m³kg⁻¹	2	m³kg⁻¹	1.00E-04	m³kg⁻¹
Cl-36	5.00E-03	m³kg⁻¹	5.00E-03	m³kg⁻¹	5.00E-04	m³kg⁻¹	0.00E+00	m³kg⁻¹
Cs-137	2.00E-03	m³kg⁻¹	2.00E-02	m³kg⁻¹	2.00E-02	m³kg⁻¹	0.00E+00	m³kg⁻¹
I-129	1.00E-02	m³kg⁻¹	1.00E-02	m³kg⁻¹	1.00E-03	m³kg⁻¹	1.50E-04	m³kg⁻¹
Pu-239	5	m³kg⁻¹	5	m³kg⁻¹	1	m³kg⁻¹	1.75E-01	m³kg⁻¹

In past works reactive transport modelling was quite limited and sorption values from literature surveys were selected. In this case, local geochemical conditions were not taken into account. To compare how radionuclide flux into the environment out of the waste repository changes when geochemical conditions are evaluated and not, additional calculations were done. For this purpose the K_d values for degraded and non-degraded concrete were selected from the literature survey (see Table 8).

Table 9. Radionuclide sorption for degraded and undegraded concrete [21, 22, 24, 40].

Radionuclide	Undegraded concrete sorption	Unit	Degraded concrete sorption	Unit
C-14	2	m^3kg^{-1}	1.00E-04	m^3kg^{-1}
Cl-36	5.00E-04	m^3kg^{-1}	0	m^3kg^{-1}
Cs-137	2.00E-03	m^3kg^{-1}	0	m^3kg^{-1}
I-129	1.00E-03	m^3kg^{-1}	1.50E-04	m^3kg^{-1}
Pu-239	1	m^3kg^{-1}	1.75E-01	m^3kg^{-1}

It is assumed that sorption vallues lineraly degrade over 1000 years from the first value undegraded concrete value to the degraded concrete value.

2.9. Model implementation for the task

The model done for this task is implemented by first modelling the chemical degradation of the concrete barrier, first using PHREEQC to describe the chemical composition of each part of the model, and then running it, to quickly determine the composition changes in the concrete.

For a more accurate representation of the processes, for each case of: rainwater, rainwater with increased CO_2 and groundwater, the described solutions in PHREEQC will be run in a PHAST model. It is important to note, that only the bottom concrete barrier will be modelled, as radionuclides move downwards and bottom slab is one of the most important barriers to prevent or reduce radionuclide leaching into the environment.

1D model was constructed in this case, we only care about the vertical component of radionuclide leaching and as such, to reduce the computation time, the model is done only for vertical transfer. The model is provided below (**Fig. 12**). Two boundary conditions were set for this model. At the top, infiltrating water flux as shown in **Fig. 7**. The infiltrating water is of the chemical composition of the 3 water types. The bottom boundary condition is of the same water flux, that would infiltrate into the barrier, but of different composition after the chemical reactions that occured in the cement.
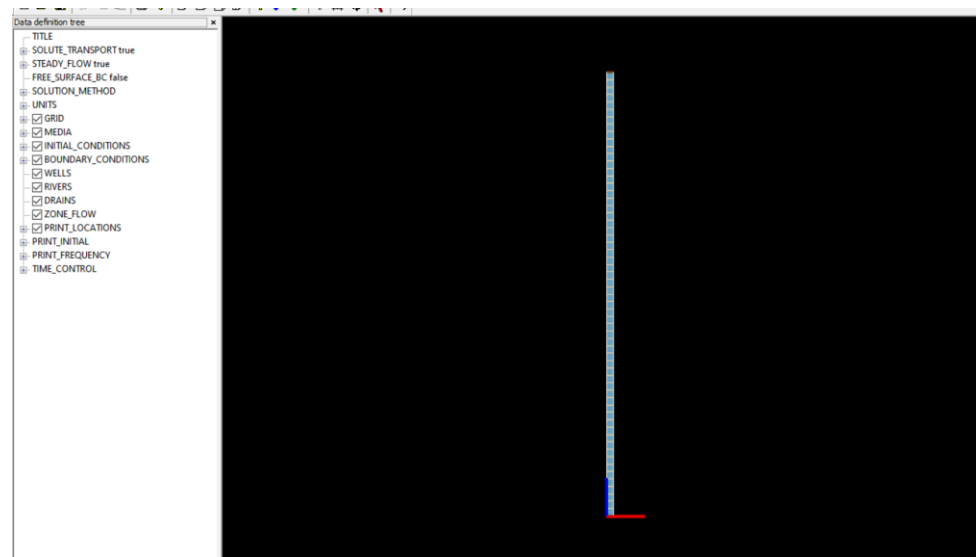

Fig. 12 Model of the vertical part of the concrete barrier (lenght 0,6 m), 1D model.

This will provide the required data about the chemical condition of the concrete, to determine the stage of degradation at which the barrier is at. This allows us to establish the change on sorption coefficient in time for further use in AMBER.

In AMBER the radionuclides in the waste zone are assumed to be homogenously spread in 10 compartments to simulate internal advective and diffusive transfer of radionuclides as well as the initial radionuclide activity (1TBq) divided equally in those compartments. The bottom slab is divided into 6 compartements. Advective and diffusive transfers between compartments are defined. An example of an AMBER model is provided below in **Fig. 13**.
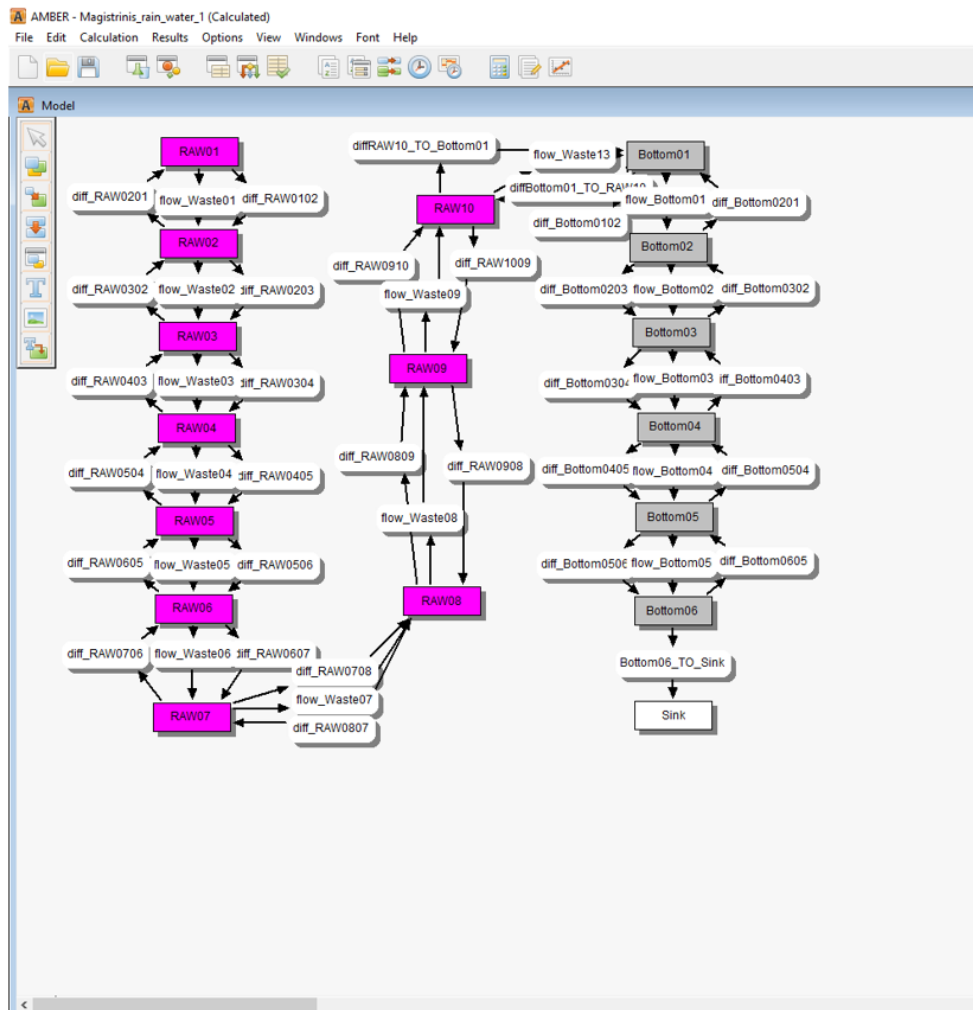

Fig. 13 AMBER model of radionuclide leaching from waste repository into the environment.

3. Results and result analysis

Radionuclide release from a near surface radioactive waste repository was modelled for three different infiltrating water compositions and in the case when local geochemical conditions are not taken into account. The modelling results will be presented in this section in the following sequence:

1) First, concrete degradation will be presented for the three different water types, rainwater, rainwater with increased CO_2 partial pressure and groundwater.

2) Having the data on the stages of concrete degradation, the change in sorption coefficient according to literature data is presented.

3) Finally, the results of radionuclide leaching out of the concrete barrier are discussed.

3.1. Concrete degradation

First, all 3 models are run, to check the pH change in the concrete barrier over time, as to make a rough estimate about concrete degradation stages, as compared to those shown in **Fig. 3**. The results are provided below:
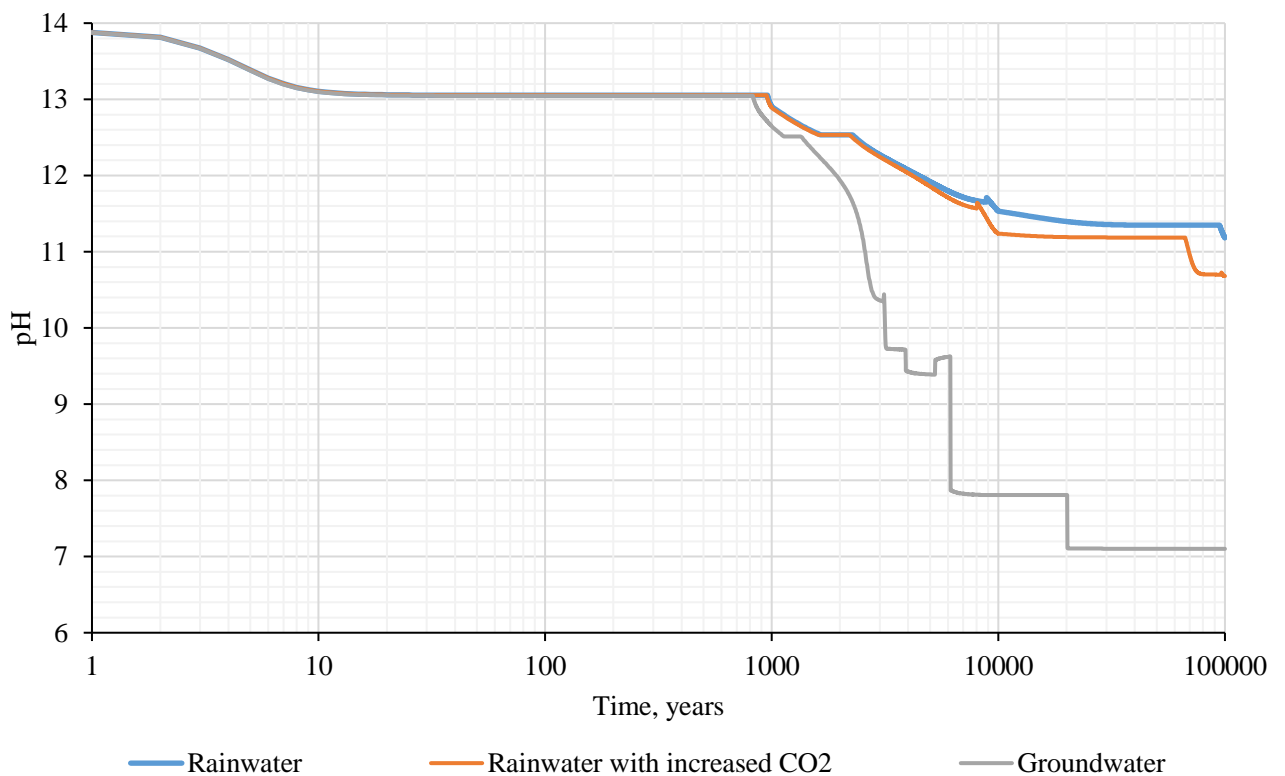

Fig. 14 Change of pH value in concrete barrier depending on infiltrated water chemical composition.

As can be seen the obtained results followed the general pattern presented in **Fig. 3** and described in literature [21].

Rainwater and rainwater with increased CO_2 pressure bear vast similarities. This indicates that the increased carbon dioxide partial pressure did not seem to have a large impact on how the concrete chemical evolution progresses.

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In the case of groundwater, it is quite clear, that the concrete undergoes a much more rapid form of evolution.

According to D. Jacques [21] and methodological guidelines of IAEA concrete degradation occurs in 4 stages.

In stage 1, it is stated that potasium and sodium are washed out first due to the high activity of these materials.

In stage 2, Portlandite ($Ca(OH)_2$) is washed out, as by this point, it is the material with the highest chemical activity in the concrete matrix. It is worth noting, that Portlandite is the main material in concrete accounting to effective radionuclide sorption [24].

In stage 3, C-S-H minerals are washed out, first, Jenite, a mineral with a high calcium content, then by the end of stage 3 Tobemorite, which has a higher content of silica. The end of stage 3 is marked with complete washing out of any of C-S-H minerals out of the concrete matrix.

In stage 4, only the skeletal porous structure of the concrete mineral remains, without any sorbents remaining. These stages can potentially be linked to the change in the pH value of the concrete pore water, but to accurately determine concrete degradation stages it is necessary to determine when each material is washed out.

3.1.1. Rainwater

The mineralogical compostion of concrete for degradation under the effects of rainwater (chemical composition provided in **table 5**) is provided below.
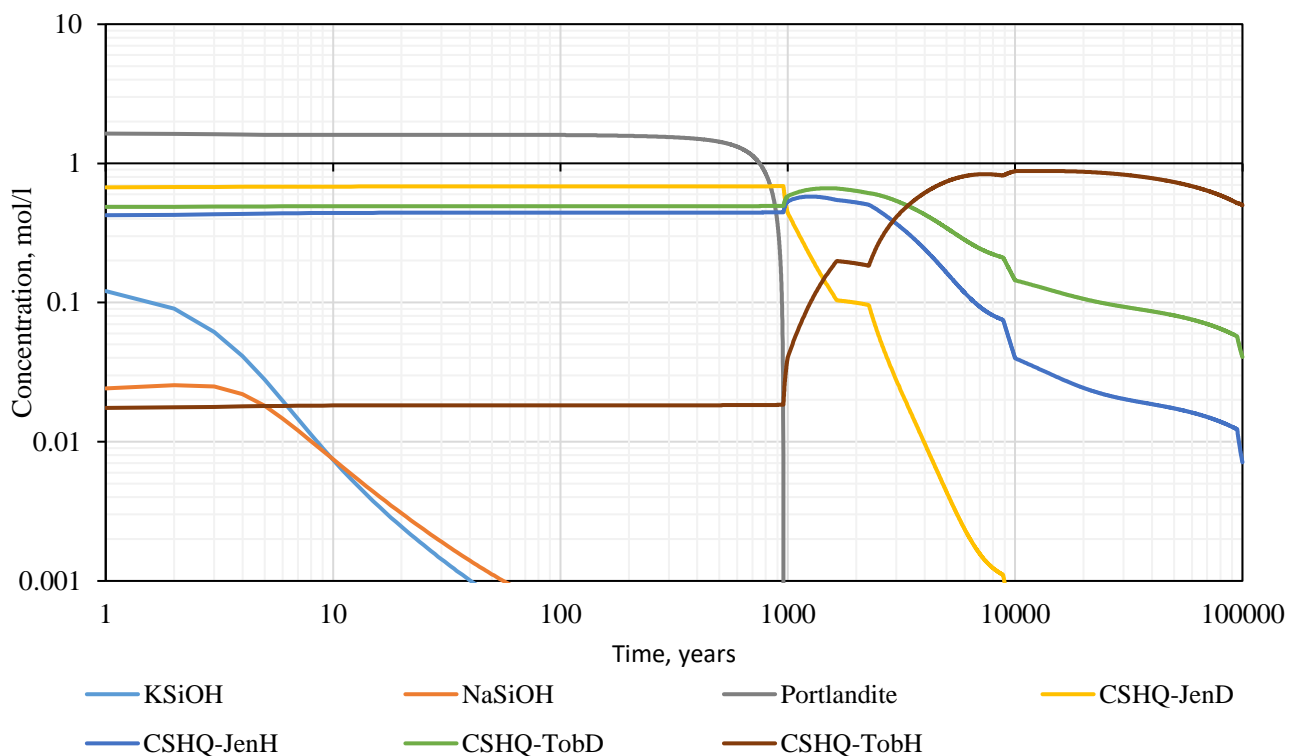

Fig. 16 Mineralogical composition of concrete during degradation due to leaching with rainwater.

From the presented graph we can see that the potassium and sodium concentrations start reducing in concentration at around 5 years, with being nearly completely washed out after around 10 years,

further their concentration is nearly negligible. The first stage ends at around this point and seems to have happened by the time of 5 years repository closure.

Stage 2, as according to literature ends when most of the Portlandite has been washed out, in our case, the reduction in Portlandite concentration starts at around 500 years, and is completely washed out after about 1000 years. This is where stage 3 begins.

In our case, during stage 3 most of Jenite is washed out, and only Tobemorite remains. However, it is not completely washed out, and thus, we can say, that, after 100 thousand years after the repository closure, the state 3 was still not finished.

3.1.2. Rainwater with increased CO_2 partial pressure

To account for potentially differing conditions, for example, microbiological processes, in the cover soil, that could end up producing additional carbon dioxide, we added additional carbon dioxide partial pressure in the chemical description of the rainwater using PHREEQC, with the rest rainwater composition remaining the same.

This could potentially lead to a faster concrete evolution rate, as carbon dioxide reacting with water can produce hydrocarbon acid, that can react with the minerals in concrete. The results are provided below:
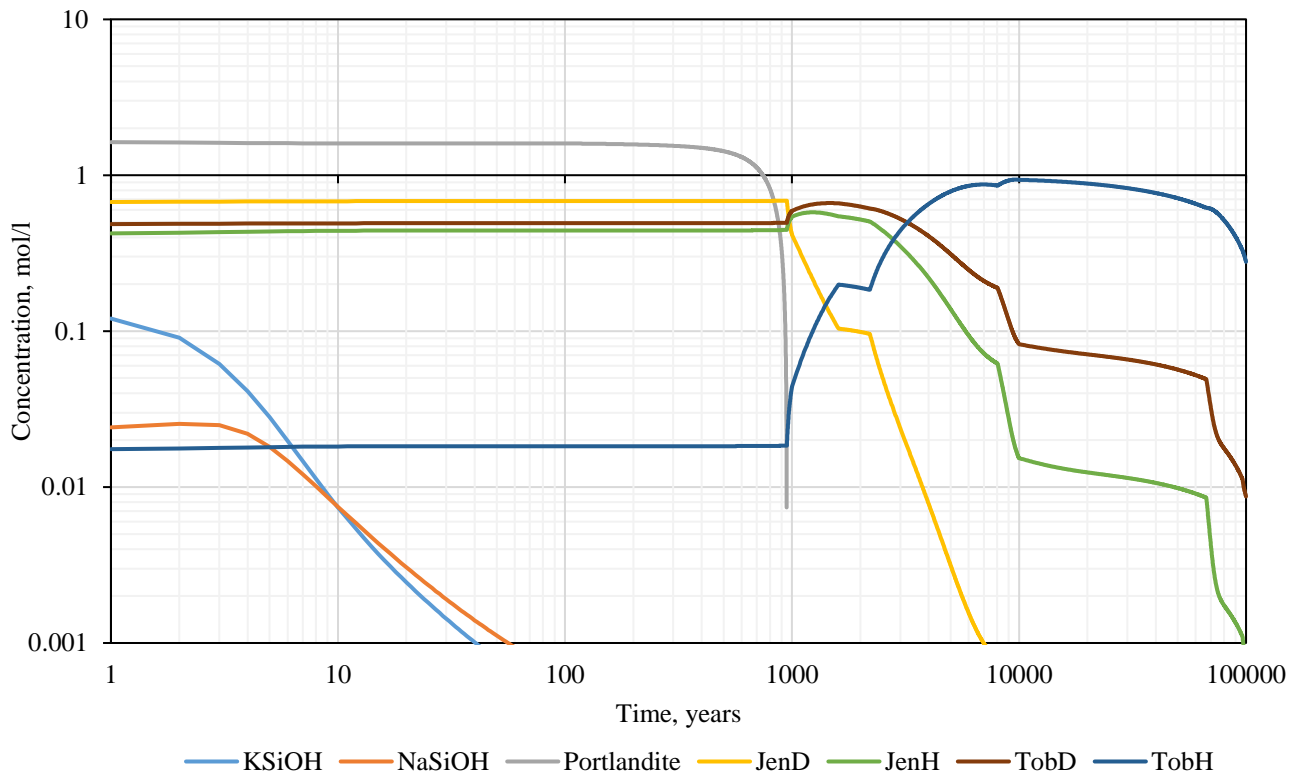

Fig. 17 Mineralogical composition of concrete during degradation due to rainwater with increased carbon dioxide partial pressure.

Similar to the case with regular rainwater, potassium and sodium are being washed out at a similar rate, with them being completely washed out after 10 years and beginning to be washed out at around 5. As such Stage 1 ends after 5 years.

In a similar manner to before, portlandite begins being washed out after 500 years, and it's concentration significantly drops after about 1000 years, marking the end of stage2.

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However, differently to the regular rainwater case, we can see that both Jenite and Tobemorite are significantly washed out after 100 thousand years, and while the concentration of Tobemorite is still significant, we can determine, that it's concentration is due to drop significantly soon, marking the end of stage 3.

3.1.3. Groundwater

Finally, we evaluate the effects of groundwater on concrete degradation. It's chemical composition is provided in **table 6**. One thing of note, groundwater has a high concentration of carbonic acid, which means it is quite chemically agressive and we can expect concrete degradation to occur much more rapidly, which was in agreement with the pH value graph (**Fig. 11**).

Modelling of groundwater impact is important to determine what could happen, should groundwater come into contact with radioactive waste storage facility, and the necessity to prevent such occurances, as most of the time, groundwater is going to have a high fraction of various chemical materials as they are washed out of various mineral deposits, through which groundwater flows.

The graphs of groundwater impact on the mineralogical composition of concrete are provided below:
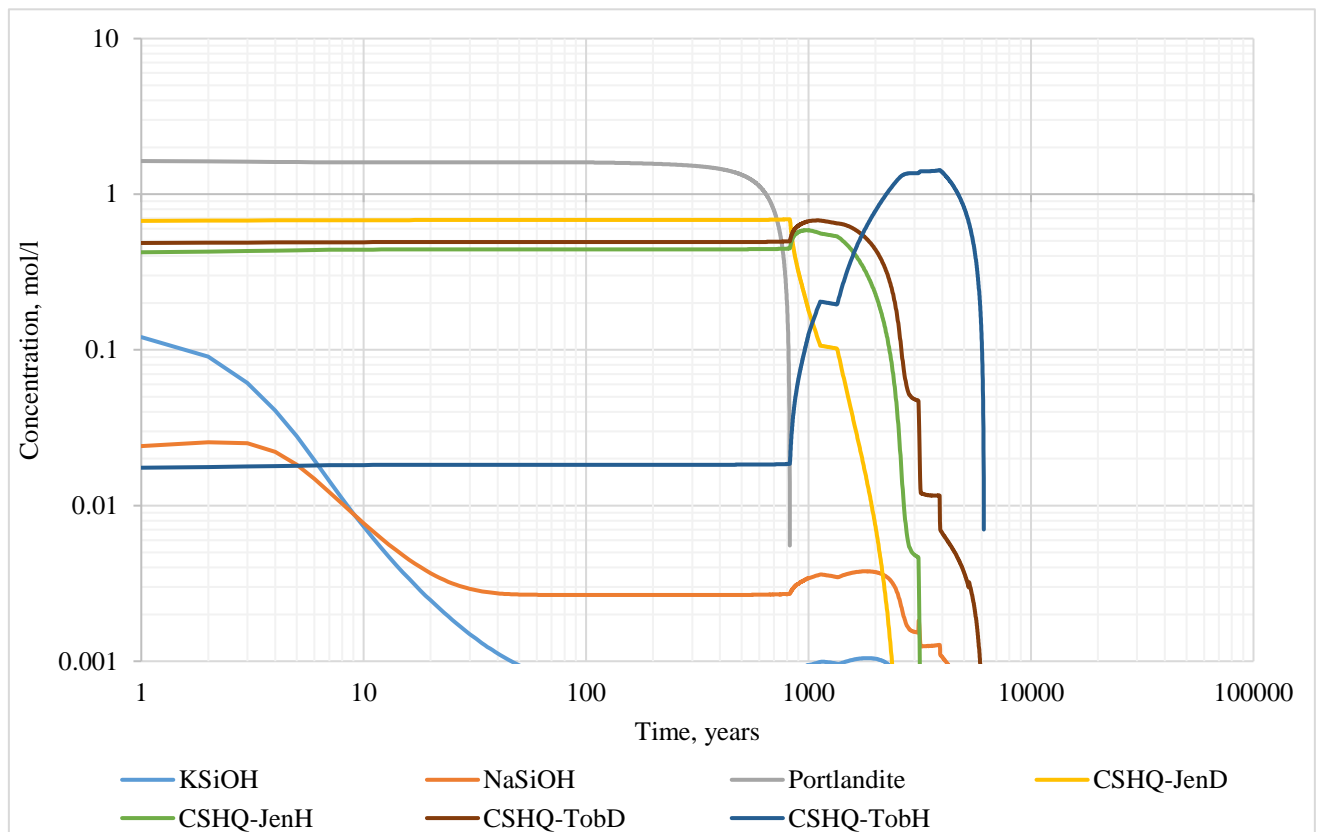

Fig. 18 Mineralogical composition of concrete during degradation due to groundwater flow.

As it was expected, the chemical evolution of concrete appears to be happening at an increased rate as compared to the previous two cases.

Stage 1 again ends at around 5 years after repository closure, however it can be seen, that the concentration of both potassium and sodium does not completely drop, even as it is being washed out. This is happening, because the groundwater chemical composition has a significant presence of both of these minerals solved, leading to relatively constant concentration of both of these minerals, furthermore, other minerals being washed out leads to both potassium and sodium containing

minerals constantly reprecipitate, and finally being fully washed out during stage 3. But, the bulk of the material is already washed out again after around 5 years, similarly to previous cases.

The largest difference to rainwater can be seen in stage 2 and 3. In stage 2, we can see, that the concentration of Portlandite begins dropping after 300 years, and sharply drops at around 800 years, marking the end of stage 2. In stage 3 we can see, that C-S-H minerals, Jenite and Tobemorite are completely washed out after 6000 years. Marking the end of stage 3.

3.1.4. Summary of concrete degradation stages

To summarise the results on concrete degradation, we have determined, that:

When only rainwater is present, concrete degrades quite slowly, and does not reach stage 4 of evolution, meaning, that radionuclide sorption remains quite high in this case. Stage 1 ends after 5 years, stage 2 ends after 1000 years and stage 3 does not end even after 100000 years.

When the rainwater gains additional carbon dioxide solved in it, the change in concrete degradation is quite insignificant, as again stage 1 ends after 5 years, stage 2 after 1000 and stage 3 ends at around 100000 years, for a conservative estimate.

Groundwater because of it's high content of hydrocarbon acid has a much quicker evolution cycle, with stage 1 ending after 5 years, stage 2 ending after 800 years and stage 3 after 6000, leading to a high probability of radionuclide leaching.

3.2. Radionuclide sorption change in time

To properly account for radionuclide leaching, we have to link the radionuclide sorption values, obtained from various literature sources, to the concrete degradation stages, that we have described in the previous part. This will be done for each type of water seperately.

In accordance to radionuclide sorption values determined in literature and concrete degradation stages determined in the previous part, for each type of water, radionuclide sorption (K_d) values are provided in the 3 figures below (**Fig. 19, Fig. 20, Fig. 21**)
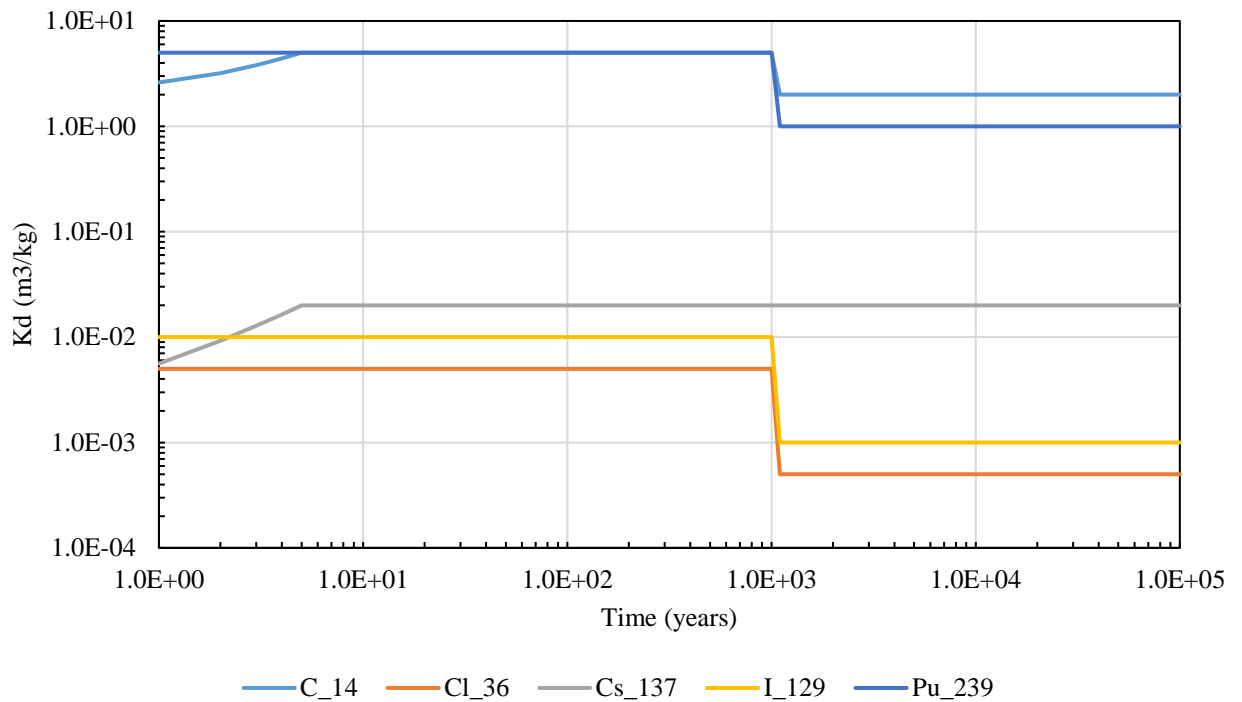

Fig. 19 Radionuclide sorption change over time when concrete degrades, due to rainwater flow.

In the case with rainwater (**Fig. 19**) sorption change is largely linked to the stages described in the previous section. It can be seen, that Portlandite is an excellent sorbent [24] leading to an increased radionuclide sorption across the entirety of stage 2 of concrete degradation.

In the case of rainwater with increased CO_2 partial pressure, the distribution coefficient values follow a similar pattern to the previous case, however it can be seen that towards the end, they slowly reach a much lower value, due to all sorbents being washed out of the concrete matrix, and the only remaining being various filler materials. The graphs for sorption change during rainwater with increased CO_2 partial pressure flow are provided in the **Fig. 20** below.

As with previous cases, during groundwater flow, sorption coefficient depends on the stage of concrete evolution. However, as the water flowing through the concrete is much more chemically aggressive these stage will advance quite rapidly, leading to a decreased sorption rate, seen at the end of the previous case, much faster, that could lead to a higher fraction of radionuclide leaching into the environment.
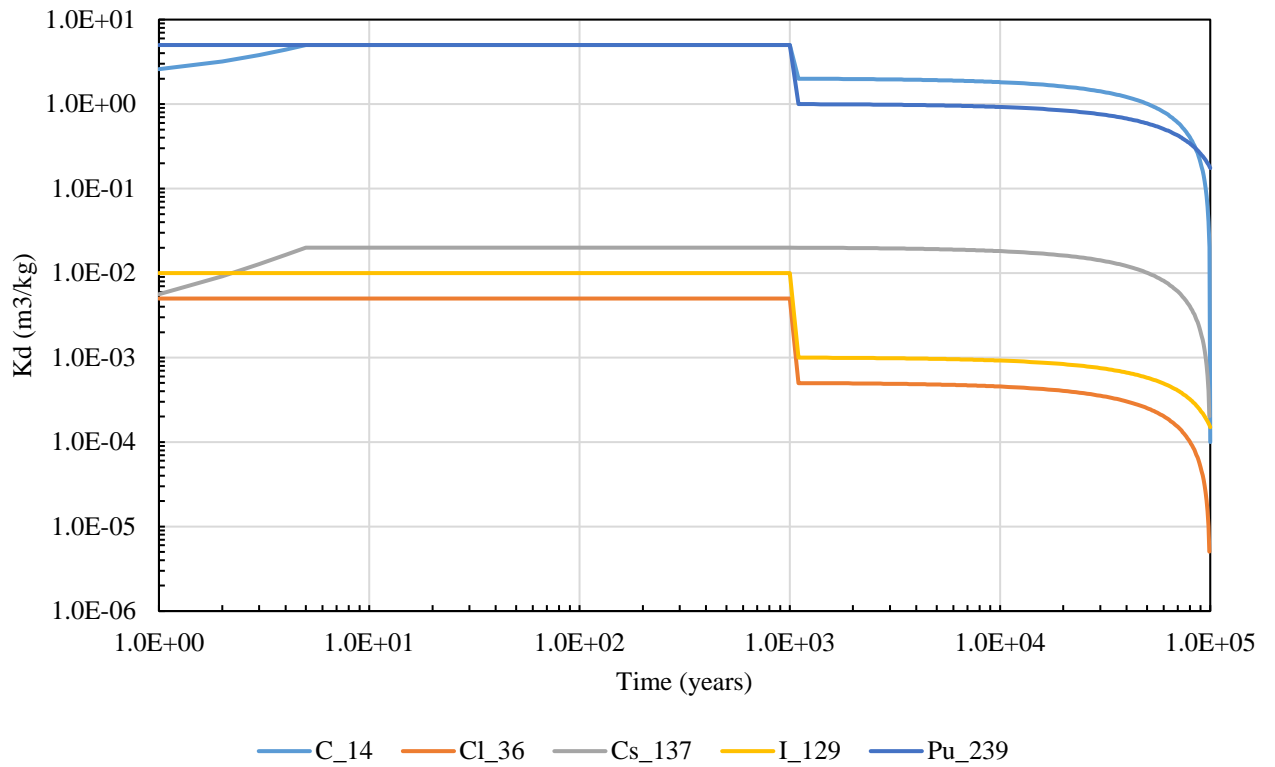
Fig. 20 Radionuclide sorption change over time when concrete degrades, due to rainwater with increased carbon dioxide partial pressure flow.

The graph for sorption change due to groundwater flow is provided in **Fig. 21**.

What can be seen is that as predicted, sorption values decrease quite rapidly once stage 3 reaches it's end, and remains at the level, eqvuivalent to low sorption of filling materials.
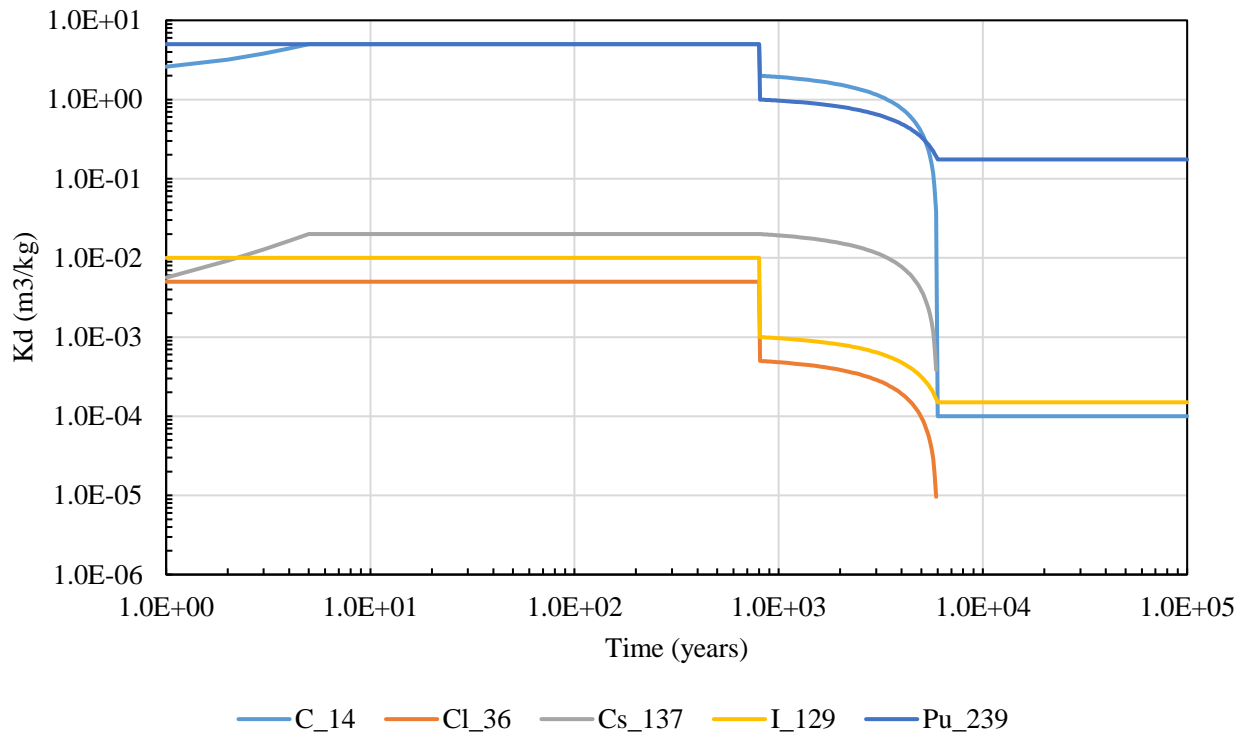

Fig. 21 Radionuclide sorption change over time when concrete degrades, due to groundwater flow.

3.3. Radionuclide leaching from the concrete barrier evaluation.

The previous part of this work was necessary to allow for a proper evaluation of potential hazards of concrete degradation in near-surface waste repositories. As concrete degrades, the potential for radionuclides to leach out of the waste matrix to the concrete barrier and then finally to the environment increases. As was already established, the sorption coefficient decreases as time goes on, meaning, that an increased flux of radionuclides is probable and dangerous contamination is possible.

The resulpts of radionuclide migration modelling are presented for each radionuclide in the following subchapters

3.3.1. Carbon 14 (C-14)

The graphs of carbon leaching out of the bottom of the concrete barrier under rainwater, rainwater with increased CO_2 partial pressure and groundwater as well as the case when local geochemical conditions were not considered are provided below:
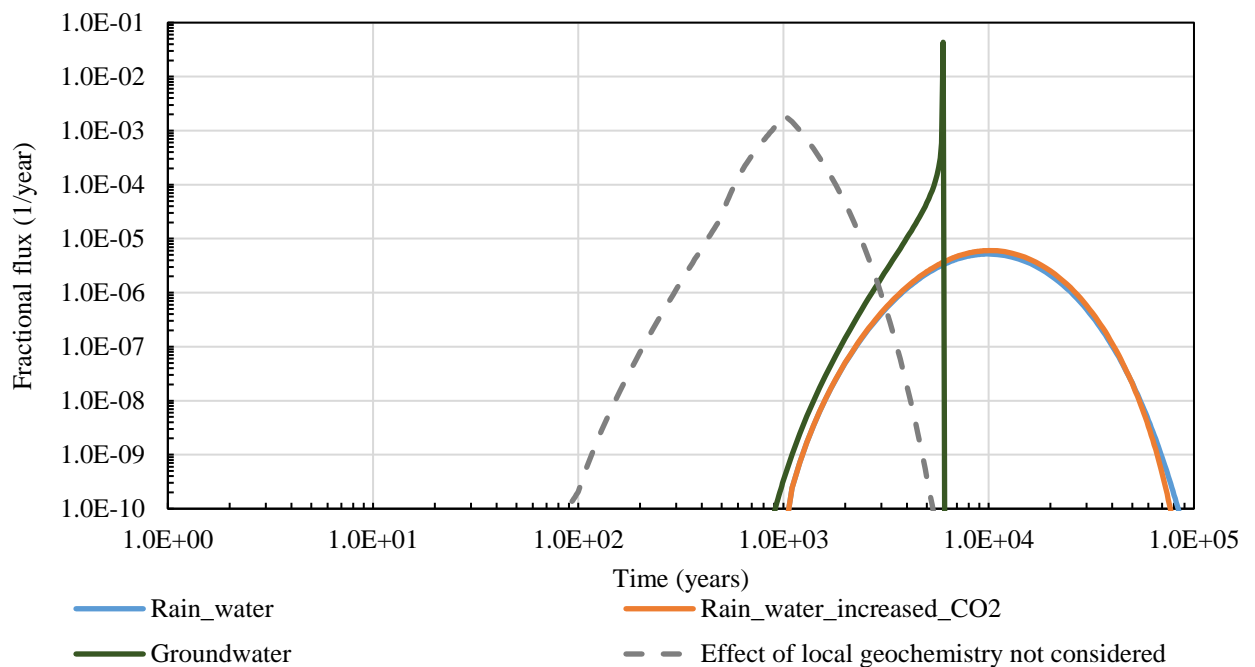

Fig. 22 C – 14 flux out of the bottom of the concrete barrier under the effects of different types of water.

It can be seen, that, the flux of radioactive carbon, out of the bottom of the barrier, only slightly differs for leaching with rain water and rainwater with increased CO_2 partial pressure, but, when concrete degrades due to leaching with groundwater, the C-14 flux increases quite rapidly. As there is no sorption of C-14 in the concrete during stage IV, in the case of groundwater a sharp increase and then drop of fractional flux is observed, indicating very fast C-14 migration with all C-14 radionuclides being completely leached out of the concrete barrier.

In the case where geochemical conditions are not evaluated, it can be seen that the radionuclides begin leaching out of the bottom of the barrier at the 90 years after repository closure, and predates the increase of water flux (see **Fig. 7**, water flux begins increasing at the 100 year mark). As well as, the peak of radionuclide flux when compared to the case in rainwater is two orders of magnitude higher.

3.3.2. Chlorine-36 (Cl-36)

The graph for chlorine – 36 flux out of the bottom of the barrier is provided below:
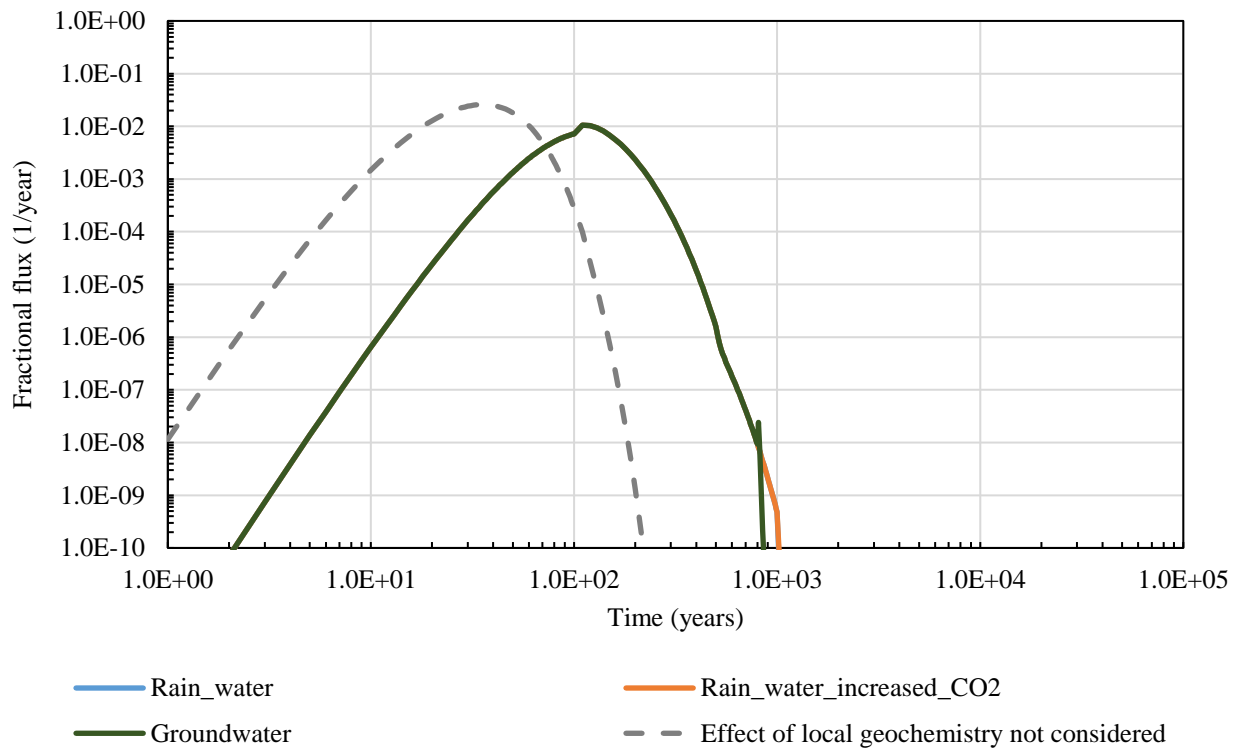

Fig. 23 Cl – 36 flux out of the bottom of the concrete barrier under leaching with different types of water.

Chlorine -36 has a low sorption value, regardless of the state of the concrete barrier. Thus the flux of leached chlorine – 36 constantly increases over time, reaching a peak at around 100 years after repository closure. It should be pointed out that fractional flux of Cl-36 in case of leaching with rainwater and in case of leaching with rainwater with increased CO_2 is the same (overlaps in **Fig. 23**).

By the time of stage III of concrete degradation (in the case of rainwater and rainwater with increased carbon dioxide partial pressure) all of Cl-36 has already been leached out due to low soprtion values, regardless of the state of the concrete. In the case of groundwater, a secondary peak in radionuclide flux out of the barrier is observed at the time of concrete entering stage III degradation, when sorption value falls by one order of magnitude (see **table 7**). This means, that the remainder of the radionuclides leach out at a faster rate, however at that point, most of the radionuclides have been leached out.

In all 3 of these cases, it can be seen, that the increase in water flow through the concrete barrier had a marginal impact on radionuclide leaching.

When local geochemical conditions are not evaluated, it can be seen, that radionuclide leaching begins immediately after repository closure and reaches a peak at around 40 years. And, like in the other 3 cases, Cl-36 radionuclides get leached out of the barrier quite quickly.

3.3.3. Cesium – 137 (Cs-137)

Cesium 137, is a dangerous radionuclide, with a high probability of it entering the food chain, because of its capability to be absorbed by plants, instead of potassium and sodium.

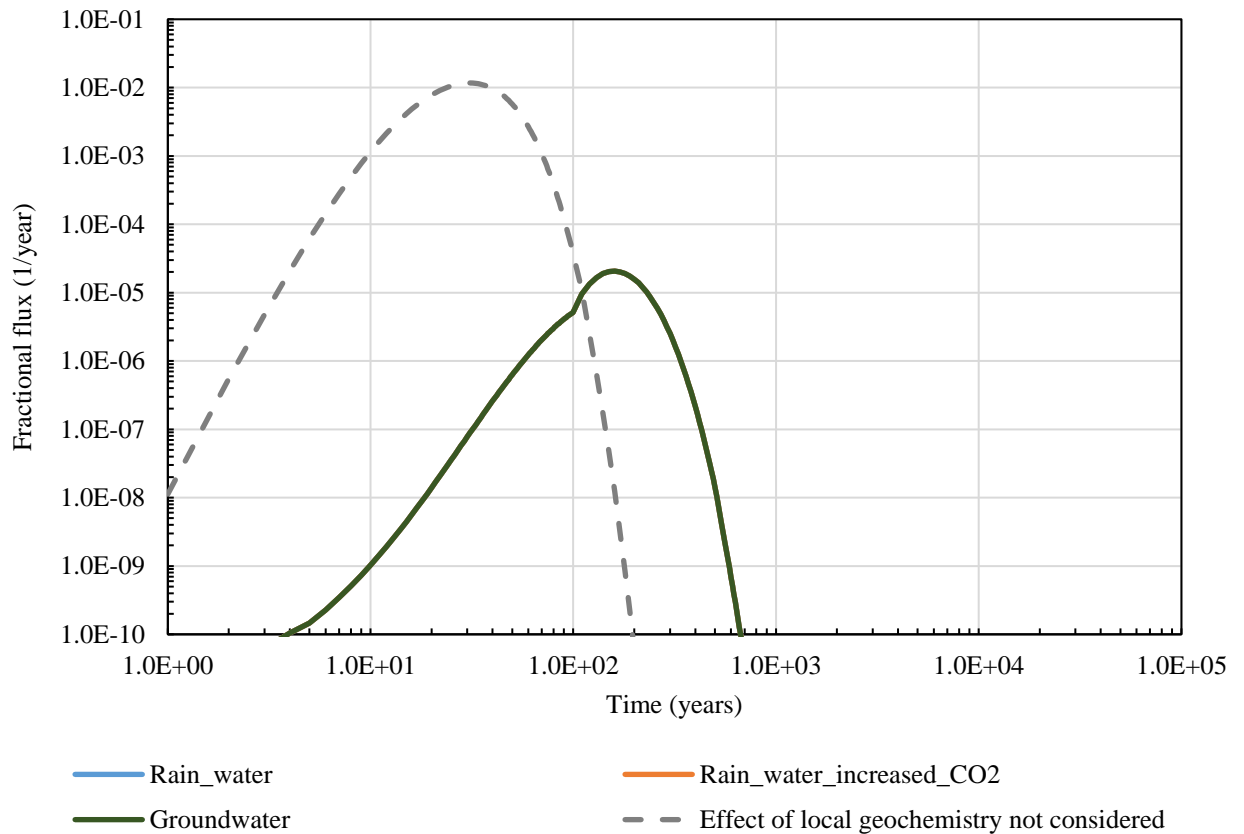Leaching of cesium 137 is provided in the graph below:

Fig. 24 Cs – 137 flux out of the bottom of the concrete barrier under leaching with different types of water.

It can be seen from the **Fig. 24** that in all cases when local geochemical conditions are modelled the flux of Cs-137 into the environment is the same (rainwater, rainwater with increased CO_2 and groundwater lines overlap) This is because Cs-137 has a relatively short half-life of around 30 years and it significantly decays before the effect of concrete degradation takes place..

From the graph, we can also see the flux of Cs-137 at around 100 years increased more rapidly and reaches a peak at around 200 years after repository closureThis is related to the increased water flux through the repository (as can be seen in **Fig. 7**).

In the case, when local geochemical conditions are not evaluated, radionuclide leaching begins immediately and readionuclide flux is more than 2 orders of magnitude higher than in the previous 3 cases. This is due to poor sorption of Cs-137. In the previous 3 cases, the better sorption coefficient in undegraded concrete decreased the rate at which radionuclides leached out, to the point where the short half-life of Cs-137 began to take effect and the radionuclides began to decay, further reducing the radionuclide flux. In the case where geochemical conditions are not evaluated, most of the radionuclide leaches out over the period of around 200 years.

3.3.4. Iodine – 129 (I-129)

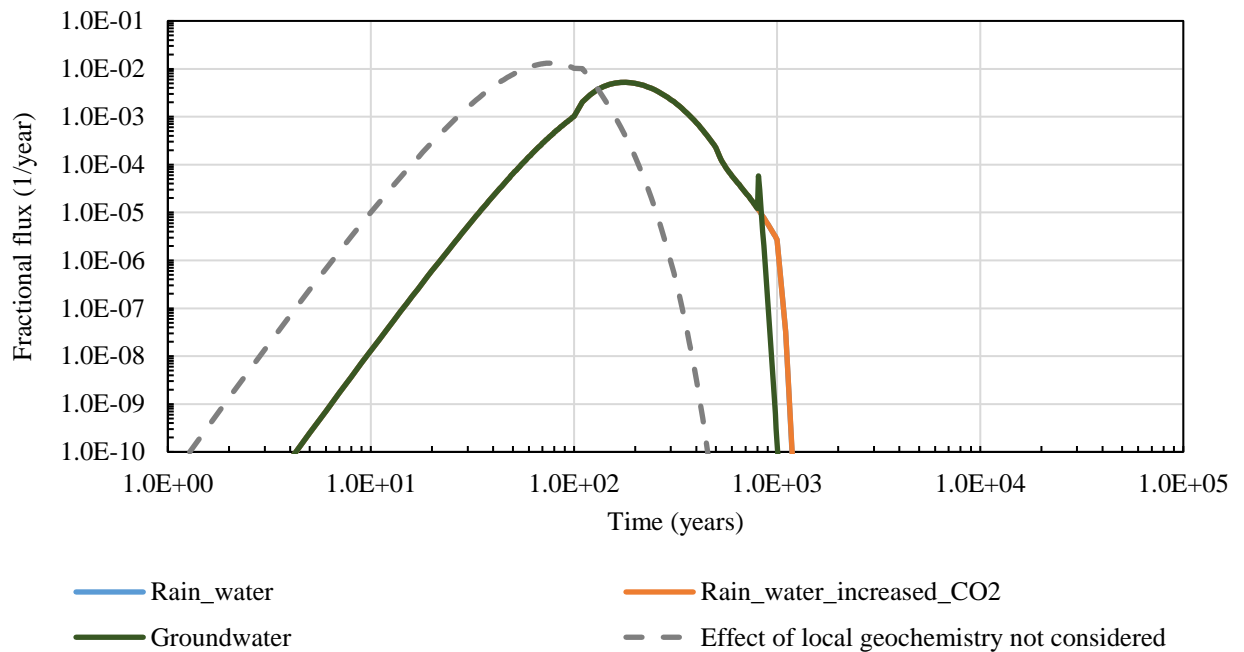The graph of iodine – 129 flux is provided below:

Fig. 25 I – 129 flux out of the bottom of the concrete barrier under leaching with different types of water.

Similar to previous graphs, in stage 2 of concrete degradation, and an increase in water flow through the waste zone and, the flux out of the bottom of the concrete barrier increases at about 100 years after repository closure due to increase of water flux. In addition, in case of leaching with groundwater, one more sharp peak is observed. It is related to beginning of concrete degradation stage III, when I-129 soprtion coefficient value decreases about one order of magnitude and thus I-129 is more rapidly released into environment.

In the case, where local geochemical conditions are not evaluated, radionuclide flux begins much sooner, but due to long half-life of I-129 and low sorption values in concrete the radionuclide flux remains the same as in previous 3 cases.

3.3.5. Plutonium -239 (Pu-239)

Plutonium – 239 is a radionuclide with a good sorption value in concrete, even when that concrete is in stage III of degradation.

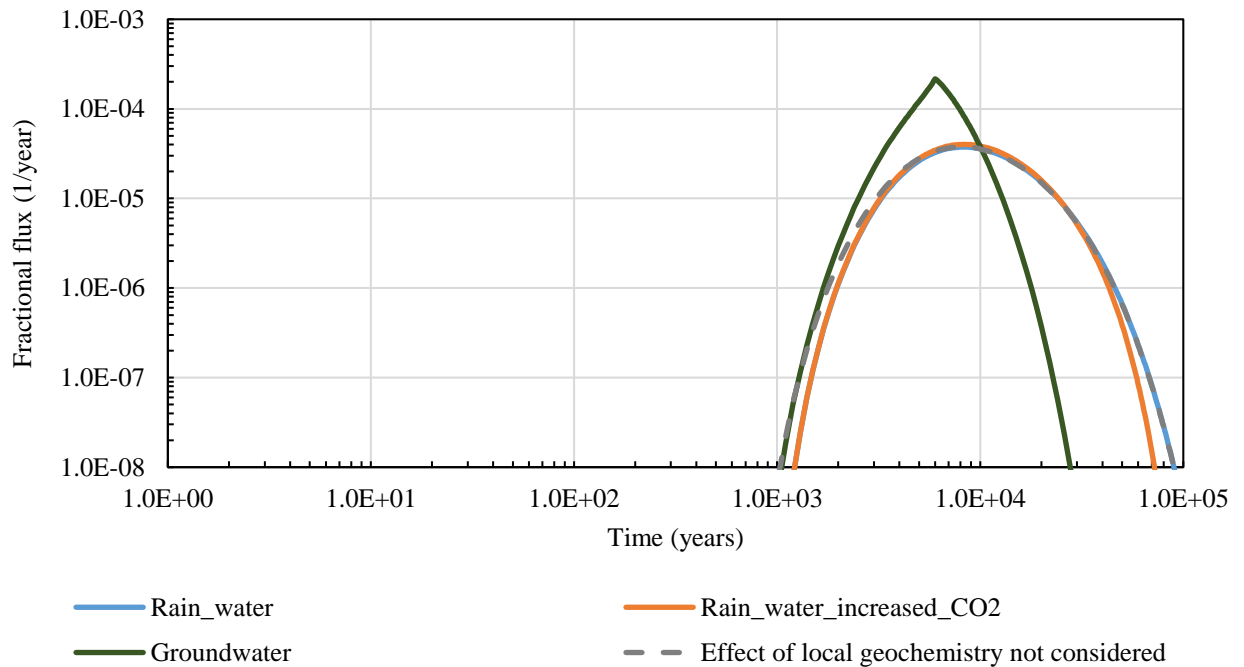The graph of plutonium flux out of the bottom of the concrete barrier is provided below:

Fig. 26 Pu – 239 flux out of the bottom of the concrete barrier under leaching with different types of water.

In **Fig. 26**, we can see, that like for most other radionuclides, plutonium flux increases with time until the peak in about 6000 years is reached. What can also be seen, is that groundwater increases the rate, at which Pu-239 is leached out of the concrete barrier. This can be linked to the rapid chemical evolution of concrete, as when groundwater flows through concrete it reaches stage IV evolution in around 6000 years after which the peak in radionuclide flux can be observed.

Due to good sorption values of Pu-239, the flux can be observed to appear only when around 1000 years after repository closure (800 in groundwater case), when geochemical conditions are evaluated. As Pu-239 sorption value decreases due to concrete going into stage III of degradation, the flux can be observed to increase, until all radionuclides are leached out.

In the case, when local geochemical conditions are not considered, the radionuclide flux begins sooner similar to the case with groundwater but does not go above the values observed when modelling rainwater and rainwater with increased carbon dioxide partial pressure.

4. Conclusions

Investigation on concrete leaching with different water types and its impact on radionuclide sorption and consequently release from the repository, leads to the following conclusions:

The effects of concrete degradation due to water flow, largely depend on the ammount of chemically agressive material (such as hydrocarbon acids) present in the water solution that flows through the concrete. This can leads to a quickened pace of concrete degradation. This can be seen in the results of task 1 where:

- Rainwater caused degradation was slow, and stages advances quite slowly, with stage 2 ending after 1000 years and stage 3 not even approaching the very end. This means that concrete retains it's capability to absorb radionuclides.

- If the water flowing through the initial barriers is enriched with more carbon dioxide due to various microbiological processes, the acidity of the water solution increases, although not quite so much, that the concrete evolution would be quickened to an extreme degree. This, however, is still undesireable, as it can lead to a reduction in concrete capability to retain radionuclides.

- Should groundwater, heavily filled with various solved compounds come into contact with concrete, due to quite high levels of both acids and other materials, concrete degradation is quickened heavily, with it ending stage 2 at around 800 years (200 years sooner than other cases) and with stage 3 lasting up to 6000 years leading to a low sorption in stage 4 with increased potential of radionuclide leaching, in contrast to concrete not degradint to stage 4 in previous cases.

With this accounted for, sorption values have been assigned to each stage of the degradation process and a model was made to account for leaching of radionuclides out of the concrete barrier.

The highest fractional flux from the repository is for mobile long-lived radionuclides Cl-36 and I-129, while C-14 and Pu-239 fluxes remained lower, mostly due to much higher sorption values in concrete.

Radionuclide release from the repository in case of concrete leaching with rainwater and rainwater with increase carbon dioxide partial pressure are very similar. For radionuclides Cl-36, I-129 and Cs-137 the fractional flux to the environment in both cases is the same, while for radionuclides C-14 and Pu-239 the difference between maxima fractional fluxes makes less than around 16% for C-14 and less than around 6% for Pu-239.

Concrete leaching with groundwater caused significantly increased concrete degradation, leading to increased radionuclide leaching out of the concrete barrier. The exception is only radionuclide Cs-137 as due to its short half-life it decays significantly before the effect of concrete degradation takes place.

Radionuclide flux from the repository in case when local geochemical conditions are not taken into account causes earlier radionuclide release and higher maximal fractional flux that in case when leaching with rainwater is considered. This means that the assumptions regarding selection of K_d values when local geochemistry is not considered were conservative. The highest difference between

maximal fractional flux is for radionuclides C-14 and Cs-137 and is more than 2 orders of magnitude.This indicates that modelling of local geochemical conditions can significantly reduce the conservatism in the radionuclide migration assessment.

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