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Equilibrium Modeling of a MOX-Iron Corrosion System

A Simulation of Chaos, but Controlled, in a Digital Environment

Master's thesis in Physics

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Abstract

Anoxic iron corrosion is expected to play a key role in limiting radionuclide release from spent nuclear fuel following a canister breach, making it important to understand and model the interaction between nuclear fuel and water with increased iron levels. This thesis develops an equilibrium model of the nuclear fuel-water system as a step towards a more predictive model of MOX fuel corrosion under repository conditions. The experimental system is defined by two main processes: the corrosion of iron and the addition of the MOX pellet containing UO_2 , PuO_2 and trace amounts of AmO_2 . The developed model, based on this system, focuses on iron corrosion, controlling uranium solubility and potential precipitation of secondary phases. To decide the optimal iron corrosion configuration, equilibration with an unconstrained or a constrained amount of available metallic iron was studied. The MOX pellet was modeled as a solid solution. Different phases containing uranium and americium were equilibrated with the solution to bring their dissolved molalities down to physically reasonable levels; uraninite and $\text{Am}(\text{OH})_3(\text{am})$ were found to work best. Precipitation of secondary phases was tested by placing them in equilibrium with the solution, first one by one, and then in pairs of two. The simulation showed that the constrained iron model matched the experiment more closely than the unconstrained model, based on pH, pE, and the molalities of $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$. Addition of the MOX pellet further increased the reducing conditions of the system. As the secondary phases were tested, all were thermodynamically possible, but no clear correlations were found to decide whether they were present or not. The lack of kinetic parameters limited the model, as it was developed as an equilibrium model and thus shows the system's conditions at a specific point in time rather than its continuous development. The results of the simulation showed reasonable agreement with the experimental system it was based on, though the model's consistently more reducing conditions suggest that further development would be needed for closer replication or the experimental results.

Keywords: PHREEQC, geochemical modeling, leaching, uranium, plutonium, americium, secondary phases

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Contents

List of Tables	xi
1 Introduction	1
2 Theory	3
2.1 Nuclear- and MOX fuel	3
2.2 Leaching and dissolution	4
2.3 Geochemical modeling using PHREEQC	4
2.3.1 Speciation	5
2.3.2 Chemical equilibrium	5
2.3.3 Solid solutions	6
2.3.4 Activity Coefficients	7
3 Methods	9
3.1 Software	9
3.2 Experimental basis	9
3.3 PHREEQC setup	10
3.4 Modeling approach	10
3.4.1 Stage 1	10
3.4.1.1 Fe constraint	11
3.4.2 Stage 2	11
3.4.2.1 MOX solid solution	11
3.4.2.2 Uranium control	11
3.4.2.3 Americium control	12
3.4.3 Stage 3	12
3.4.3.1 Secondary phases	12
3.5 Modeling assumptions	13
4 Results	15
4.1 Stage 1	15
4.1.1 Unconstrained Iron	15
4.1.2 Constrained Iron	15
4.1.3 Comparison	16
4.2 Stage 2	17
4.2.1 MOX pellet	17
4.2.2 MOX addition	17
4.2.3 Phase investigation	18

4.2.4	Uranium control	19
4.2.4.1	Coffinite	19
4.2.4.2	UO _{2.25}	20
4.2.4.3	Uraninite	21
4.2.4.4	Comparison Uranium	21
4.2.5	Americium control	22
4.2.5.1	Am(OH) ₃ (am)	22
4.2.5.2	Comparison Americium	23
4.3	Stage 3	24
4.3.1	Secondary phases identified from the literature	24
4.3.2	Saturation index evaluation	25
4.3.3	Combining phases	25
5	Discussion	29
5.1	Uranium control and phase selection	29
5.2	Americium control	30
5.3	Carbonate chemistry and secondary phases	30
5.4	Comparison with experimental observations	31
5.5	Model limitations	32
6	Conclusion	35
	Bibliography	37
A	Input files	I
B	Database modifications	XXXI

List of Tables

3.1	Secondary phases added to the input files via PHASES, including values of $\log K$, ΔH in kJ/mol, and V_m in cm^3/mol	13
4.1	pH and pe for the unconstrained dissolved iron in the unconstrained model.	15
4.2	Total molality, in mol/l, for each oxidation state of dissolved iron in the unconstrained model.	15
4.3	Most abundant species of each oxidation state of dissolved iron in the unconstrained model.	15
4.4	pH and pe for the constrained dissolved iron	16
4.5	Total molality, in mol/l, for each oxidation state of dissolved iron for the constrained iron model.	16
4.6	Most abundant species of each oxidation state of dissolved iron in the constrained iron model.	16
4.7	Values for pH and pe, for the unconstrained model and the constrained model	16
4.8	Total molality, in mol/l, for each oxidation state of dissolved iron for the unconstrained and the constrained iron model.	16
4.9	Most abundant species for each of the Fe oxidation state, for the unconstrained and the constrained iron model.	17
4.10	Values for the MOX pellet moles calculation including the weight percentage, mass (m_i), molar mass (M_i) and calculated amount of moles (n_i) for each element.	17
4.11	pH and pe values after adding MOX pellet, without additional phases.	17
4.12	Total molality, in mol/l, for the dissolved species of each oxidation state of U, when adding MOX with no additional phases.	18
4.13	Total molality, in mol/l, for the dissolved species of each oxidation state of Pu, when adding MOX with no additional phases.	18
4.14	Total molality, in mol/l, for the dissolved species of each oxidation state of Am, when adding MOX with no additional phases.	18
4.15	The most abundant species for each oxidation state of U, when adding MOX with no additional phases.	18
4.16	The most abundant species for each oxidation state of Am, when adding MOX with no additional phases.	18
4.17	Supersaturated uranium phases and their SI-values, when adding MOX with no additional phases, where SI is $\log_{10}(\text{IAP}/K_s)$	19

4.18	Supersaturated americium phases and their SI-values, when adding MOX with no additional phases, where SI is $\log_{10}(\text{IAP}/K_s)$	19
4.19	Values for pH and pe when in equilibrium with coffinite	19
4.20	Total molalities, in mol/l, of dissolved species of each oxidation state of U when in equilibrium with coffinite.	19
4.21	The most abundant species of each oxidation state of U, when in equilibrium with coffinite.	20
4.22	Values for pH and pe when in equilibrium with $\text{UO}_{2.25}$	20
4.23	Total molalities, in mol/l, of dissolved species of each oxidation state of U when in equilibrium with $\text{UO}_{2.25}$	20
4.24	The most abundant species of each oxidation state of U, when in equilibrium with $\text{UO}_{2.25}$	20
4.25	Values for pH and pe when in equilibrium with uraninite.	21
4.26	Total molalities, in mol/l, of dissolved species of each oxidation state of U when in equilibrium with uraninite.	21
4.27	The most abundant species of each oxidation state of U, when in equilibrium with uraninite.	21
4.28	pH and pe values for equilibration with Fe only, Coffinite, $\text{UO}_{2.25}$, and uraninite.	21
4.29	Total molalities, in mol/l, for dissolved species of each oxidation state of U, when equilibrating with Fe only, Coffinite, $\text{UO}_{2.25}$, and uraninite.	22
4.30	Most abundant species for each oxidation state of U when equilibrated with Fe only, Coffinite, $\text{UO}_{2.25}$, and uraninite.	22
4.31	Values for pH and pe when in equilibrium with $\text{Am}(\text{OH})_3(\text{am})$	22
4.32	Total molalities, in mol/l, of dissolved species of each oxidation state of Am when in equilibrium with $\text{Am}(\text{OH})_3(\text{am})$	23
4.33	Most abundant species for each oxidation state of Am when equilibrated with $\text{Am}(\text{OH})_3(\text{am})$	23
4.34	pH and pe values for equilibration with Fe only and $\text{Am}(\text{OH})_3(\text{am})$	23
4.35	Total molalities, in mol/l, for dissolved species of each oxidation state of U, when equilibrating with Fe only and $\text{Am}(\text{OH})_3(\text{am})$	23
4.36	Most abundant species for each oxidation state of Am when equilibrated with Fe only and $\text{Am}(\text{OH})_3(\text{am})$	24
4.37	Total molalities, in mol/l, of the dissolved species of the oxidation states of Fe and U when equilibrated with no phase, ankerite, calcite, chukanovite, cronstedtite and siderite.	24
4.38	Values for pH, pe and SI, for all tested phases, where $\text{SI} = \log_{10}(\text{IAP}/K_s)$. pH and pe are measured for each separate run simulation, while SI is measured in ‘No phase’'s simulation.	25
4.39	Total molalities, in mol/l, of the dissolved species of the oxidation states of Fe and U when simulating a combination of phases.	26
4.40	Values for pH and pe for secondary phases tested in combination.	27

1

Introduction

Being able to produce carbon-neutral energy is an important step to limit global warming [1]. Currently, the burning of fossil fuels accounts for approximately 80% of the total global energy supply as a combination of oil, coal and natural gas [2]. To stop fossil fuel dependence, renewable and low-carbon energy sources such as nuclear power, hydropower, and wind power are essential [3, 4]. With about 440 nuclear reactors worldwide, nuclear power makes up $\sim 9\%$ of global electricity generation as of 2024 [5]. Sweden has three nuclear sites with a total of six active reactors. The Oskarshamn plant has one active reactor and Clab, which is a central interim storage facility for spent nuclear fuel [6]. Ringhals has two active reactors, while Forsmark has three [7, 8]. A closer look at the Forsmark power plant shows it currently has a repository for low and medium waste, compared to Oskarshamn and Ringhals only having repositories for low-activity waste. In 2022, the Swedish government granted Forsmark permission to build a final repository for nuclear fuel; this repository is currently being planned [9].

A nuclear reactor produces energy by fission. When U^{235} absorbs a neutron, it forms a highly excited, unstable U^{236} nucleus, which splits almost immediately into two lighter fission fragments, releasing several neutrons and a large amount of energy. The energy released by fission is used to boil the water in the reactor. From the boiling water, steam that rises powers the turbines, which in turn generate electricity [10]. As nuclear fuel used in thermal reactors contains a majority of U^{238} , U^{239} will frequently be created by U^{238} absorbing a neutron, which decays to Pu^{239} via β^- -decay [11].



Pu^{239} , when capturing a neutron, forms Pu^{240} [5]. Pu^{240} can then capture another neutron, resulting in Pu^{241} , that via β^- -decay ends up with Am^{241} [5].



The reaction pathway, starting with U^{238} and ending with Am^{241} , shows that the spent nuclear fuel may contain isotopes of U, Pu and Am.

Fission products will be stored in a final repository, whose environment will determine the conditions under which any future canister breach would occur. By analyzing and predicting the fission products and their behavior, an understanding can be reached and preventative measures can be taken to decrease the severity of an accident. In Sweden, low- and medium-level waste is deposited in the Final Repository for Short-lived Radioactive Waste, or SFR, which is located at the Forsmark nuclear facility [12]. It was the first of its kind in the world when operation started in 1988 [12]. The SFR comprises four 160-meter rock vaults and a chamber in the bedrock with a 50-meter-high concrete silo for the most radioactive waste, all of which are situated 60 meters below the bottom of the Baltic Sea [12]. In addition to the SFR, the planned repository for nuclear fuel will be located at Forsmark and will store spent fuel [9]. The spent fuel stored in the repository is placed inside canisters made of or including a significant amount of iron [13]. Outside the iron layer is a layer of copper that prevents corrosion of the iron in the first place [14], but if that layer is compromised, water will come into contact with the iron and corrode it. In a groundwater contact scenario, the canister's iron content is the first step of protection if the radioactive contents begin to leak out. Since the canisters are stored at a depth of several hundred meters, in anoxic groundwater conditions, corrosion from spent nuclear fuel is expected to occur simultaneously with anoxic iron corrosion. To further predict and prepare for a canister failure scenario leading to groundwater contact, the ability to model the corrosion and its effects is crucial. Studying how leaching from spent fuel is affected by simultaneous anoxic corrosion will further understanding of its environmental impact.

This thesis uses the experimental system described by Saleh et al. as the basis for equilibrium geochemical modeling in PHREEQC, focusing on the iron corrosion, uranium solubility control, and carbonate secondary phases within that system [13]. The aim of this thesis is to study the effects of anoxic groundwater on fuel in a compromised iron canister and explore if it is possible to create a model in PHREEQC that resembles the experimental setup used. Using the developed model, the thesis will also explore the results in relation to those of Saleh et al. [13]. While most things from the experimental study are possible to recreate using PHREEQC, some things will need to be modified to achieve a result. For example, PHREEQC uses batch reactions or one-dimensional models to build simulations on, resulting in an equilibrium model instead of a continuous one [15]. The kinetic component will also not be considered due to a lack of available kinetic information.

2

Theory

This section will lay the theoretical groundwork for the study of data from M. Saleh's paper [13].

2.1 Nuclear- and MOX fuel

MOX fuel, or mixed-oxide fuel, is a type of nuclear fuel made of a mixture of more than one oxide, most commonly uranium dioxide (UO_2) and plutonium dioxide (PuO_2) [16]. It usually appears in the form of a pellet [17]. This fuel was initially developed for use in, amongst others, Light Water Reactors (LWRs), in an attempt to recycle and reprocess used fuel [17]. Uranium dioxide content in MOX depends on the application, but may consist of either natural, enriched, or depleted uranium [16]. MOX fuel generally contains 3-5% plutonium dioxide blended with depleted or natural uranium dioxide [18]. Unlike conventional UO_2 fuel, where U-235 provides the fissile content, in MOX fuel PuO_2 supplies the fissile material via Pu-239 [17]. Due to the use of plutonium in MOX fuel in the EU, 605 tonnes of natural uranium were saved in 2024 [19]. The isotopic composition of plutonium in a MOX pellet is dependent on the type of reactor it is formed in, as well as the initial enrichment of uranium, the discharge burnup, and the time of intermediate storage of the reprocessed fuel [20].

MOX fuel is characterized by a heterogeneous, spatially dependent plutonium concentration, featuring high-concentration plutonium agglomerates inside a depleted or natural oxide matrix [17]. While the masterblend used in the MIMAS process for modern MOX fuel contains 20-30% PuO_2 on average, local concentrations can range from almost zero to 100% PuO_2 in certain instances. Specific plutonium-rich zones, or agglomerates, within a uranium-rich zone, or matrix, will affect the behavior of oxygen in the fuel [17]. There exists a variety of fabrication processes for LWR MOX fuel, with the most relevant being MIMAS, as this is the type of pellet used in the study by M. Saleh [17, 13]. Originally developed by Belgonucleaire in the 1980s, the MIMAS MOX process, where MIMAS stands for micronized master blend, is an adaptation of a previous commercial process [17]. The fabrication process includes micronizing, or mechanical blending and milling, of PuO_2 and UO_2 powders that form a masterblend with a plutonium content in the range of 20-30% [17]. The resulting powder is then pressed into a pellet.

2.2 Leaching and dissolution

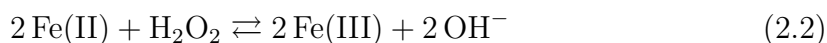
When discussing MOX fuels and nuclear fuels in general, important concepts to consider are dissolution and leaching. Dissolution refers to the process where a solute in solid, liquid, or gaseous phase is dissolved in a solvent to create a solution [21]. How well a solute is dissolved depends on the solubility, which dictates the maximum concentration of a solute that can be dissolved in a solvent at a given temperature [22]. Leaching describes the process of extracting a soluble material from an insoluble solid via dissolution in a solvent [23].

A MOX pellet placed in synthetic groundwater will undergo leaching and affect the surrounding solution and environment. The synthetic groundwater used mimics the reducing conditions expected in a real deep repository [24]. Under these reducing conditions, $\text{UO}_2(\text{s})$ has a low solubility, which ensures the stability of the fuel matrix containing the radionuclides [13, 25]. Due to exposure to ionizing radiation from the active MOX pellet, the redox conditions will be altered near the pellet's surface, leading to oxidizing and reducing species being produced [13]. Oxidizing species, such as $\text{OH}\cdot$, $\text{HO}_2\cdot$, H_2O_2 and O_2 , will oxidize the $\text{U}(\text{IV})$ in the fuel matrix to create the more soluble $\text{U}(\text{VI})$ and in turn increase the rate of oxidative dissolution [13, 25]. Oxidation occurs in two steps: first, $\text{U}(\text{IV})$ at the pellet surface releases an electron, forming $\text{U}(\text{V})$ as an intermediate species. Then the $\text{U}(\text{V})$ species either further oxidizes to $\text{U}(\text{VI})$ or gets involved in catalytic decomposition of oxidizing species [25].

When the metallic iron reacts with the groundwater according to



it corrodes, and causes more reducing conditions due to the higher concentration of H_2 and $\text{Fe}(\text{II})$ [13]. As the concentration of $\text{Fe}(\text{II})$ increases, reactions with $\text{Fe}(\text{II})$ also increase, including



where $\text{Fe}(\text{II})$ oxidizes to $\text{Fe}(\text{III})$ by reacting with radiolytic oxidants such as H_2O_2 [13]. The dissolved $\text{Fe}(\text{II})$ also plays a significant role in decreasing the dissolution of the MOX fuel, as $\text{Fe}(\text{II})$ reacts with the radiolytic oxidizing species that exist at the interface between the MOX pellet and the water [13, 25]. The reducing species caused by ionization include $\text{e}^-(\text{aq})$, $\text{H}\cdot$ and H_2 , and will lead to locally oxidizing conditions near the pellet surface due to their lower reactivity [13].

2.3 Geochemical modeling using PHREEQC

Theoretical models and simulations of chemical processes allow for predictive extrapolation of properties. Following these predictions, further hypotheses can be explored without needing to perform additional experiments. Modeling also allows for visualization of structures and processes, where experiments may fall short. When combined with experimental data, modeling techniques can be utilized to expand knowledge and increase understanding of the experimental results. The drawback

with modeling comes when assumptions and simplifications are necessary to perform the required calculations. In this study, the main principles of modeling and simulation include speciation, equilibrium, solid solutions and activity coefficients.

2.3.1 Speciation

A chemical species refers to a specific form of an element, exemplified by an isotopic composition, oxidation or electronic state, or a complex or molecular structure [26]. Measuring the quantities of one or more species or analyzing a sample analytically is part of the process of speciation analysis. Studying the composition of a solution, and specifically the distribution of an element's species, is referred to as speciation of an element. In chemical modeling, speciation is used to define the original solution of the experiment as well as to decide the continuous and final composition of solutions. Each element can occur in several oxidation states, which impacts the way it interacts. The oxidation state is decided based on electronegativity properties and measures the degree of oxidation of an atom in a compound [27]. A free uncombined element has an oxidation number of zero, while a monatomic ion has an oxidation number equal to its charge. When included in a compound, an atom can take on different oxidation numbers based on the combination of elements included [27]. For example, nitrogen can take on two different oxidation states, where for ammonium, or NH_4^+ , the nitrogen shows up as N(-3) and for nitrate, or NO_3^- , it shows up as N(5) [28]. This is useful to distinguish between the oxidation states when calculating the speciation, opposed to studying nitrogen without specifying the oxidation states and leaving out important detail. Oxidation states also aids when calculating the redox conditions, which are based on the movement of the electrons impacting the oxidation numbers [29]. When more than one oxidation state of an element is known in the same reaction, such as the nitrogen pair of N(-3)/N(5), the value of pe can be concluded if the reaction is in equilibrium [28]. Here, pe is defined as the negative logarithm of the activity of an electron and is used to measure the redox potential [28]. A lower value of pe indicates a more reducing environment, as the electron movement increases, where a higher value of pe indicates an oxidizing environment with low electron availability [29]. Using PHREEQC, the existence of an element pair means the redox conditions are calculated based on that interaction, instead of an externally decided value [28]. As mentioned, the distinction between the oxidation states is important for speciation. This is also showcased through the different species of uranium, for example. In PHREEQC, both the total concentration of an element can be calculated, which includes all species including uranium, as well as the concentration of a species [30]. A concentration of U could thus be distributed among species such as UO_2 , $\text{U}(\text{OH})_4$ or UO_2CO_3 without knowing the species concentrations [30]. The specific species concentrations could likewise be calculated without knowing the total amount [30].

2.3.2 Chemical equilibrium

Chemical equilibrium is reached when the rate of a forward reaction is equal to the rate of the backwards reaction [22]. In this state, concentrations of reactants and

products remain constant over time. When modeling in PHREEQC, phases and amounts will be defined [31]. Following the definition, phases are allowed to react until equilibrium, or a specified gas partial pressure or saturation index, is reached. Another way to set up the experiment is to allow an alternative reaction to occur to the necessary extent that equilibrium, or the specified gas partial pressure or saturation index, is reached with the specific pure phase. This is used to predict final composition, maximum theoretical yield, and stability of a chemical system at specific temperatures, pressures, or compositions. In PHREEQC, a phase can purposely be set to either dissolve or precipitate based on the intended outcome. Chemistry is not checked in these instances, and PHREEQC will calculate the input whether it is chemically correct or not.

2.3.3 Solid solutions

By dissolving a solute in a solvent, a solution is acquired. A solute is the substance being dissolved, and the solvent is the substance in which it is dissolved. This creates a homogeneous solution in the sense that it generally is a single-phase substance with uniform chemical, physical and mechanical properties [32]. Solute and solvent can be in either solid, liquid or gas phase independently of the other, where the solution assumes the same phase as the solvent. In general, the solubility limit in a liquid state is higher than that of the solid state. Looking at solid solutions, their properties are largely based on their composition [32]. Additionally, the bulk performance, or material behavior, of the solid solution is influenced by the type of components and their morphology to a significant degree [32].

The types of solid solutions mentioned above are assumed to be binary, meaning they are made of two components. That would result in a formula

$$A_xB_{(1-x)} \quad (2.3)$$

where A and B are two arbitrary compounds and x is the mole fraction of A, that together with the $(1 - x)$ mole fraction of B sum to one. However, this thesis will look mainly at ternary systems, meaning the solid solution is composed of three components. This looks like

$$A_\alpha B_\beta C_\gamma \quad (2.4)$$

where A, B and C are arbitrary compounds, and α , β & γ are the mole fractions, of A, B and C respectively, whose sum totals 1. For the MOX pellet modeled in this thesis, A, B, and C correspond to $UO_2(am)$, PuO_2 , and AmO_2 respectively.

When using PHREEQC to study a MOX pellet, it can be considered a solid solution. PHREEQC creates solid solutions by allowing the definition of each component and the amount. When studying a ternary solid solution all components are assumed to be ideal, since calculation with three activity coefficients would entail further manual expansion of the program. In the ideal case, the activity is assumed to be equal to the mole fraction,

$$a_i = \gamma_i x_i \quad (2.5)$$

where γ_i is the activity coefficient and x_i is the mole fraction, making the activity a_i equal to x_i [33]. This leads to, for example, the mole fractions of Equation

2.4 summing to one and thus the activity of the same equation also summing to one. Therefore, in PHREEQC, ternary solid solutions are treated as ideal [34]. In a binary, non-ideal solid solution, the two components are defined along with e.g. activity coefficients, which are converted to nondimensional Guggenheim parameters that are used for calculation [34]. When performing a calculation including a solid solution in PHREEQC, it's assumed all solid solutions dissolve entirely to then reprecipitate in equilibrium with the solution [34].

2.3.4 Activity Coefficients

In real solutions, including solid solutions, the final thermodynamic activity of an endmember differs from the initial mole fraction [33]. Equation 2.5 shows how the activity coefficient affects the relation between the activity and the mole fraction. x_i can, in addition to mole fraction, be used as a description of molar concentration, molality or partial pressure. The activity coefficient γ_i is used to correct and adjust for non-ideal behavior of a solute [35]. As mentioned with Equation 2.5, if γ_i is equal to one, the solution is ideal. The ideality of a solid solution is dependent on the mixing properties, which describe the difference in thermodynamic properties between the solid solution and a mechanical mixture of its endmembers [35].

PHREEQC executes thermodynamic calculations based on the activity of a species and not purely its concentration. For an aqueous species, the relation between activity, a_i , and molal concentration, m_i , uses the activity coefficient, γ_i , according to: $a_i = \gamma_i \cdot m_i$ [36]. At infinite dilution, when the solute is surrounded by solvent molecules, γ_i approaches 1, meaning activity approaches concentration [37]. As ionic strength, I , increases, electrostatic interactions between dissolved ions cause deviations from the ideal behavior, causing γ_i to compensate [38]. PHREEQC calculates γ_i using the Debye-Hückel expression

$$\log(\gamma_i) = -\frac{A_\gamma z_i^2 \sqrt{I}}{1 + \tilde{a}_i B_\gamma \sqrt{I}} + \dot{B}I \quad (2.6)$$

from [39], where A_γ and B_γ are the Debye-Hückel A and B parameter respectively, $\dot{B}$ is the Debye-Hückel B -dot parameter, $\tilde{a}_i$ is the hard-core diameter specific to each aqueous species, and z_i is the charge of species i . The database used for these simulations, *llnl.dat*, defines $\tilde{a}_i$ with the parameter `-llnl_gamma` [39]. PHREEQC then uses the `-llnl_gamma` parameter to calculate the actual γ_i based on the ionic strength, as `-llnl_gamma` only defines the hard-core diameter [39]. The same principle applies to solid solution endmembers, where γ_i instead corrects for non-ideal mixing between components rather than electrostatic interactions in the solution [35]. When calculating a non-ideal solid solution, PHREEQC converts the activity factors to Guggenheim parameters and uses those alongside the input of temperature and number of moles [34]. However, as all solid solutions covered in this thesis are treated as ideal, this is irrelevant for this case.

3

Methods

To answer the question “What happens to the fuel in a compromised iron canister in anoxic groundwater and is it possible to model it in equilibrium using PHREEQC?”, some experiments are needed. The following chapter details the methods and software used for this study to reach a conclusion, as well as methods of previously conducted and relevant studies.

3.1 Software

To investigate, and specifically model, these circumstances, PHREEQC Interactive version 3.8.6-17100 was used. Here, the experimental model was developed and refined with the use of a modified version of the *lnl.dat* database that contains phases and parameters to support the Lawrence Livermore National Laboratory aqueous model [39]. *lnl.dat* is included in the PHREEQC download package [15]. For further development, PHREEQC was used in combination with Python, version 3.14.3, via the IPhreeqcCOM 3.8.6-17100 COM-system allowing Python to run PHREEQC input files when using Windows. The combined use of Python and PHREEQC allowed program development that was planned to help continuous testing while adjusting parameters. Due to the constraints of the project, this was a secondary focus that didn’t come to fruition in the planned way.

3.2 Experimental basis

Data for the initial solution of the simulation is based on a study done by Saleh in the paper “Dissolution of unirradiated MOX fuel in the presence of metallic iron” [13]. Originally, the experiment was conducted in an airtight autoclave, with an Ar atmosphere with a small fraction of CO₂ to emulate the anoxic environment. Using synthetic Forsmark groundwater, iron powder was introduced into the solution together with two iron strips that underwent corrosion. After 101 days of undisturbed corrosion, a MOX pellet was added to the solution, and its leaching effects were studied. Initial values of the pH and the speciation of the Forsmark groundwater were noted and replicated for the following study in this report. Final concentrations of species from Saleh’s experiment were used to make comparisons to the results of the following study in this report.

3.3 PHREEQC setup

The program was set up in stages using PHREEQC to model the most effective way to perform the simulation. The exact steps taken and which parameters were studied will be explained in Section 3.4. A few blocks were used to create the model. SOLUTION was defined following the study of Saleh’s paper [13], using the described speciation of synthetic Forsmark groundwater, together with the original temperature and pH of the solution [30]. GAS_PHASE was used to establish the gas phase surrounding the solution, including pressure, volume, temperature and makeup of the gas. The definition of the parameters followed from the experimental setup where the autoclave was flushed with CO₂ and subsequently filled with argon gas [40]. The EQUILIBRIUM_PHASES block was used to equilibrate the solution with the available metallic iron and the potential secondary phases that precipitated [31]. Finally, the SOLID_SOLUTIONS block was used to mimic the addition of the MOX pellet into the solution, and the temperature as well as the elements and fractions were defined according to Saleh’s study [13, 34].

alt:

3.4 Modeling approach

Studying this system, the equilibrium model was the closest approach possible based on the available parameters and values. A kinetic model would have required extensive additional calculations, as rates are largely unknown for a ternary system like a MOX pellet. Due to the nature of a ternary solid solution, the rate becomes a complex calculation. When constructing the model, the environment of the simulation was set up using the original solution and the surrounding gas phase. Both were decided using data from Saleh’s study [13]. To further increase understanding of each part of the model, the implementation was done in stages. Stage 1 included the establishment of the model environment which allowed the experimentation of the iron constraint. Stage 2 included the addition of the MOX pellet and the following study of the molalities of the interesting phases. Stage 3 included the study of the secondary phases of interest, and how they affected the outcome.

3.4.1 Stage 1

This stage established the environment in which the simulation takes place. To ensure an anoxic environment, like the setup by Saleh [13], the simulated atmosphere needed to be void of oxygen. This was achieved by using a nonreactive gas, in this case argon, to occupy the atmosphere in a mix with a small amount of CO₂. The volume of the gas was originally fixed due to the physical constraints of the autoclave, meaning the gas amount needed to be finite in the model and the ratio between Ar and CO₂ needed to be fixed as well. Using the ratio, a partial pressure for each species could be established. Together with the volume and pressure being fixed, the temperature of the environment was also specified, in line with the initial solution.

3.4.1.1 Fe constraint

To be able to observe the effect of the metallic iron placed in the solution, two cases were studied to decide the optimal setup for the Fe addition. The first case included an unconstrained addition of metallic iron, where 10 moles of Fe(s) were placed in equilibrium with the groundwater solution. This was supposed to represent there being more iron available than what the solution could dissolve, causing the solution to be supersaturated with iron. The second case studied was a constrained addition of metallic iron, using the calculated amount of metallic iron available before the addition of the MOX pellet, using Saleh's results [13]. This calculation was based on subtracting the concentration of Fe(II) in the initial step of the experiment from the concentration of Fe(II) in the step where the MOX pellet was added, which was recalculated to metallic iron via the molar mass. After calculation, $4.479\text{e-}4$ moles of metallic iron was added to equilibrate with the groundwater solution.

3.4.2 Stage 2

This stage studied the addition of the MOX pellet as well as the subsequent phase effect. Of extra interest were the phases that were added together with the MOX pellet, containing uranium, plutonium and americium.

3.4.2.1 MOX solid solution

Based on the molecular structure of a MOX pellet, it was assumed to be compatible with a solid solution structure, thus making it the preferred way to introduce the pellet to synthetic groundwater. After calculating the amount of moles of each component, using the weight percentages from the work by Saleh [13], the component and the number of moles were added to the file together with the temperature. Due to the solid solution being ternary with the three components, UO_2 , PuO_2 and AmO_2 , PHREEQC restricted it to being ideal [34]. Had it been made up of two components, for example if the americium were left out due to it being of lower quantity, it would have been possible to look at different interaction parameters between the elements. Due to the increase of elements in the solid solution, the number of interaction parameters rises from one binary to three binary parameters and one ternary [33], making it impossible for PHREEQC to calculate [34]. The only additional parameter considered was the temperature, in accordance with the original temperature. By studying the resulting output file, the supersaturated phases containing uranium and americium were noted and further investigated.

3.4.2.2 Uranium control

After the MOX solid solution had been added and the results had been noted, those uranium containing species were tested. The criterion was being a supersaturated uranium phase, meaning a positive SI-value. Three of these phases were found and studied further, namely Coffinite, $\text{UO}_{2.25}$ and Uraninite. To achieve a reasonable amount of uranium in the final solution, each of the supersaturated species was tested separately by equilibrating it with the new solution including the MOX pellet.

When a phase was found to reduce the dissolved uranium significantly, it was kept moving forward. How each phase affected the solution can be seen in Section 4.2.4.

3.4.2.3 Americium control

Following the same procedure as for the uranium-containing phases, positive SI values were identified, and the supersaturated phases containing americium were studied further. Four phases were found, including $\text{Am}(\text{OH})_3$, AmOHCO_3 , $\text{Am}(\text{OH})_3(\text{am})$ and $\text{Am}_2(\text{CO}_3)_3$. Each phase was equilibrated together with the solution containing the MOX pellet and uraninite, as it was chosen to move forward with. How the phases affected the solution can be seen in Section 4.2.5.2

3.4.3 Stage 3

This stage studied the effects the secondary phases had on the solution. The phases were equilibrated with the MOX pellet solution.

3.4.3.1 Secondary phases

In Saleh's paper [13], a few secondary phases, or precipitates, are mentioned. Observed precipitates primarily consisted of compounds containing Fe, which formed at the interface between fuel and water through oxidation from Fe(II) to Fe(III). Previous studies carried out on alpha-doped UO_2 pellets have shown precipitates on the surface of MOX pellets, such as iron oxyhydroxides like akaganeite ($\beta\text{-FeOOH}$). EDX analysis concluded the presence of Fe and O as the main elements formed, as well as trace amounts of Si, C, Ca, Na, S, Cl, and Mn, but no U. Studying the deposit on the MOX pellet's surface with X-ray diffraction revealed some amorphous phases with no distinct peaks. Comparing the amorphous peaks against the ICDD database, matches were found for a variety of Fe(III)oxides such as lepidocrocite, goethite, akaganeite, hematite and maghemite. Cross-referencing of the Raman spectra shows a probability of precipitates including akaganeite and lepidocrocite due to characteristic peaks matching the sample. Since this thesis is not focused on the effects of alpha doping on pellets, some phases were ruled out of the study. Akaganeite, goethite, hematite and lepidocrocite were all formed because of alpha radiolysis, and will not be covered here [13]. Magnetite was mentioned but ruled out by Saleh [13]. To investigate which of the secondary phases affected the results, the phases were equilibrated with the solution to precipitate, one by one. Some phases, with available thermodynamic information, were added to the input files via PHASES [41]. Out of the relevant phases, calcite, cronstedtite, and siderite existed in the database, while ankerite and chukanovite were added to the relevant input files via PHASES, as seen in Appendix A [41]. Table 3.1 shows the values for the input, and additions to PHASES can be seen in full in Appendix B. The result of each phase was saved and compared.

Table 3.1: Secondary phases added to the input files via PHASES, including values of $\log K$, ΔH in kJ/mol, and V_m in cm^3/mol .

Phase	$\log K$	ΔH	V_m
Ankerite	-20.873 [42]	-	66.06 [42]
Chukanovite	16.216 [43]	294.6 [43]	-

3.5 Modeling assumptions

PHREEQC is a geochemical modeling program that focuses mainly on aqueous models, and it does well with calculating one-dimensional transport problems and batch reactions [15]. The developed equilibrium model is based on a batch reaction, as the equilibration happens in one step and is assumed to be well mixed. This was something that needed to be considered when adapting the different parameters to fit the model. The method of equilibrating the iron was one of those, as different approaches were tested. At first, placing the undissolved metallic iron directly into the solution was tested without success as PHREEQC only handles dissolved ions in SOLUTION [30]. Then, the amount of metallic iron was recalculated to dissolved Fe(II) and kept in the initial solution, which is described in Section 3.4.1.1. Finally, the metallic iron amount was equilibrated with the solution using the EQUILIBRIUM_PHASES block as discussed in Section 3.4.1.1, which gave the closest result to the experimental result of Saleh [31, 13]. The forced equilibrium of the dissolved iron resulted in a different final molality than the experimental result based on the same values, as the experimentally measured dissolved amount was calculated and used at face value. Total dissolution was not originally the goal, as the experimental case showed the iron strips in the final solution [13]. When studying the secondary phases, as discussed in Section 3.4.3.1, all phases were assumed to appear with the same likelihood, as no differentiation was made in the model. No difference was made in the model whether a phase was more likely to appear in combination with another phase, as all phases and combinations were treated the same. This may lead to discrepancies, since when described by Saleh, some phases were assumed to be more likely than others [13]. For example, calcite and ankerite were described as most likely observed while cronstedtite and chukanovite were described as couldn't be ruled out. As ankerite and chukanovite were added manually, the results produced should be observed with caution.

4

Results

This chapter covers the results from the simulations. It follows the development of the final program through the buildup of stages 1, 2 and 3.

4.1 Stage 1

Stage 1 includes the creation of the simulation environment. This section looks at how the constraint on the dissolved iron affects the conditions.

4.1.1 Unconstrained Iron

The unconstrained iron model equilibrates an unlimited amount of available metallic iron with the groundwater solution.

Table 4.1: pH and pe for the unconstrained dissolved iron in the unconstrained model.

pH	10.9
pe	-9.95

Table 4.2: Total molality, in mol/l, for each oxidation state of dissolved iron in the unconstrained model.

Oxidation state	Fe(II)	Fe(III)
Molality	3.03e-2	3.11e-5

Table 4.3: Most abundant species of each oxidation state of dissolved iron in the unconstrained model.

Oxidation state	Fe(II)	Fe(III)
Species	Fe(OH)_3^-	Fe(OH)_4^-

4.1.2 Constrained Iron

The constrained iron model equilibrates an amount of available metallic iron equivalent to the iron powder and the iron strips with the groundwater solution.

Table 4.4: pH and pe for the constrained dissolved iron

pH	9.04
pe	-5.81

Table 4.5: Total molality, in mol/l, for each oxidation state of dissolved iron for the constrained iron model.

Oxidation state	Fe(II)	Fe(III)
Molality	6.00e-4	2.19e-8

Table 4.6: Most abundant species of each oxidation state of dissolved iron in the constrained iron model.

Oxidation state	Fe(II)	Fe(III)
Species	Fe^{2+} , FeCO_3	$\text{Fe}(\text{OH})_3$

4.1.3 Comparison

Here, the unconstrained and the constrained iron models are compared.

Table 4.7: Values for pH and pe, for the unconstrained model and the constrained model

Model	pH	pe
Unconstrained	10.9	-9.95
Constrained	9.04	-5.81

Table 4.7 shows the values of pH and pe for the unconstrained and the constrained model, respectively. The constrained model is closer to a neutral pH and is less reducing, while the unconstrained model is more basic and more reducing.

Table 4.8: Total molality, in mol/l, for each oxidation state of dissolved iron for the unconstrained and the constrained iron model.

Model	Fe(II)	Fe(III)
Unconstrained	3.03e-2	3.11e-5
Constrained	6.00e-4	2.19e-8

Table 4.8 shows the total molality, in mol/l, for all species in each oxidation stage. The unconstrained model shows a higher molality with two and three orders of magnitude, for Fe(II) and Fe(III) respectively.

Table 4.9: Most abundant species for each of the Fe oxidation state, for the unconstrained and the constrained iron model.

Model	Fe(II)	Fe(III)
Unconstrained	$\text{Fe}(\text{OH})_3^-$	$\text{Fe}(\text{OH})_4^-$
Constrained	Fe^{2+} , FeCO_3	$\text{Fe}(\text{OH})_3$

Table 4.9 shows the species that contribute to the molality with an amount of the same order of magnitude as the total molality. For both oxidation states, the two models show different species of highest abundance. The unconstrained model shows $\text{Fe}(\text{OH})_3^-$ and $\text{Fe}(\text{OH})_4^-$ as most abundant for Fe(II) and Fe(III) respectively, while the constrained model shows Fe^{2+} and FeCO_3 for Fe(II), and $\text{Fe}(\text{OH})_3$ for Fe(III).

4.2 Stage 2

Stage 2 includes the addition of the MOX pellet, as well as controlling the necessary U- and Am-species.

4.2.1 MOX pellet

When adding the MOX pellet into the PHREEQC file, which can be seen in Appendix A under Stage 2 - No Control.pqi, the moles of each element were calculated using the values in Table 4.10.

Table 4.10: Values for the MOX pellet moles calculation including the weight percentage, mass (m_i), molar mass (M_i) and calculated amount of moles (n_i) for each element.

Species (i)	Weight %	m_i [g]	M_i [g/mol]	n_i [mol]
UO_2	89.2	1.49	270	5.50e-3
PuO_2	10.2	0.169	276	6.14e-4
AmO_2	0.63	0.0105	275	3.82e-5

4.2.2 MOX addition

Continuing with the constrained Fe model, this section covers the addition of the MOX pellet without any additional phases.

Table 4.11: pH and pe values after adding MOX pellet, without additional phases.

pH	9.75
pe	-6.65

Table 4.11 shows the pH and pe of the solution after adding the MOX pellet to the constrained Fe model. Comparing to the values in Table 4.1, the pH increases and the pe decreases, making the solution more basic and more reducing.

Table 4.12: Total molality, in mol/l, for the dissolved species of each oxidation state of U, when adding MOX with no additional phases.

Species	U(III)	U(IV)	U(V)	U(VI)
Molality	0e0	2.16e-5	5.09e-15	1.67e-9

Table 4.12 shows the total molalities of the dissolved U-species of each oxidation state in the final solution. The molality of U(IV) was higher than expected, making it necessary to investigate the cause.

Table 4.13: Total molality, in mol/l, for the dissolved species of each oxidation state of Pu, when adding MOX with no additional phases.

Species	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
Molality	5.40e-22	1.04e-18	3.01e-34	0e0

Table 4.13 shows the total molalities of the dissolved Pu-species for each oxidation state in the final solution.

Table 4.14: Total molality, in mol/l, for the dissolved species of each oxidation state of Am, when adding MOX with no additional phases.

Species	Am(II)	Am(III)	Am(IV)	Am(V)	Am(VI)
Molality	0e0	4.77e-5	2.21e-38	0e0	0e0

Table 4.14 shows the total molality for the dissolved species of each oxidation state of Am.

4.2.3 Phase investigation

U and Am shows unnaturally high concentrations, in Tables 4.12 and 4.14 respectively, meaning a further investigation is needed of those two. Especially of concern are the molalities of U(IV) and Am(III). The most abundant species of U for each oxidation state is shown in Table 4.15, with the most abundant meaning all species that contribute to the molality to the same order of magnitude as the total molality. The most abundant species of Am for each oxidation state is shown in Table 4.16.

Table 4.15: The most abundant species for each oxidation state of U, when adding MOX with no additional phases.

Most abundant species	U(III)	U(IV)	U(V)	U(VI)
Constrained	U^{3+}	$U(OH)_4$	UO_2^+	$Ca_2UO_2(CO_3)_3$

Table 4.16: The most abundant species for each oxidation state of Am, when adding MOX with no additional phases.

Most abundant species	Am(II)	Am(III)	Am(IV)	Am(V)	Am(VI)
Constrained	Am^{2+}	$Am(OH)_2^+$	$Am(CO_3)_5^{6-}$	AmO_2^+	AmO_2^{2+}

When studying the phases containing uranium, there are three that are supersaturated ones. These are uraninite, coffinite and $\text{UO}_{2.25}$, and their saturation indices can be found in Table 4.17.

Table 4.17: Supersaturated uranium phases and their SI-values, when adding MOX with no additional phases, where SI is $\log_{10}(\text{IAP}/K_s)$.

Phase	SI
Uraninite	4.71
Coffinite	4.19
$\text{UO}_{2.25}$	2.5

Studying the Am-containing phases in the same predicament, four phases are found to be supersaturated. These include $\text{Am}(\text{OH})_3$, AmOHCO_3 , $\text{Am}(\text{OH})_3(\text{am})$ and $\text{Am}_2(\text{CO}_3)_3$, and their saturation indices can be found in Table 4.18.

Table 4.18: Supersaturated americium phases and their SI-values, when adding MOX with no additional phases, where SI is $\log_{10}(\text{IAP}/K_s)$.

Phase	SI
$\text{Am}(\text{OH})_3$	4.14
AmOHCO_3	2.89
$\text{Am}(\text{OH})_3(\text{am})$	2.34
$\text{Am}_2(\text{CO}_3)_3$	1.14

4.2.4 Uranium control

To be able to control the amount of dissolved U(IV)-phases, the three supersaturated phases were studied to conclude if they could control the amount. Equilibration with $\text{U}(\text{OH})_4$ was also studied but showed no significant effect on the output.

4.2.4.1 Coffinite

This subsection shows the values for when the solution with MOX-addition is equilibrated with coffinite.

Table 4.19: Values for pH and pe when in equilibrium with coffinite

pH	9.86
pe	-6.77

Table 4.19 shows the pH and pe after the equilibration with coffinite. Compared to Table 4.11, it shows a small increase in the basic and reducing environment.

Table 4.20: Total molalities, in mol/l, of dissolved species of each oxidation state of U when in equilibrium with coffinite.

Species	U(III)	U(IV)	U(V)	U(VI)
Molality	0e0	2.15e-5	3.85e-15	1.16e-9

Table 4.20 shows the total molalities of each oxidation state of U when in equilibrium with coffinite. The U(IV) molality barely decreases compared to Table 4.12.

Table 4.21: The most abundant species of each oxidation state of U, when in equilibrium with coffinite.

Most abundant species	U(III)	U(IV)	U(V)	U(VI)
Constrained	U^{3+}	$\text{U}(\text{OH})_4$	UO_2^+	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$

Table 4.21 shows the most abundant species for each oxidation state. U(IV) has the largest gap, with 14 orders of magnitude differing between $\text{U}(\text{OH})_4$ and the next largest one. U(V) and U(VI) have a gap of two orders of magnitude each. Comparing the species to Table 4.15, they remain the same.

4.2.4.2 $\text{UO}_{2.25}$

This subsection shows the values for when the solution with MOX-addition is equilibrated with $\text{UO}_{2.25}$.

Table 4.22: Values for pH and pe when in equilibrium with $\text{UO}_{2.25}$.

pH	10.01
pe	-7.00

Table 4.22 shows the pH and pe after the equilibration with $\text{UO}_{2.25}$. Compared to Table 4.11, it shows an increase in the basic and reducing environment.

Table 4.23: Total molalities, in mol/l, of dissolved species of each oxidation state of U when in equilibrium with $\text{UO}_{2.25}$.

Species	U(III)	U(IV)	U(V)	U(VI)
Molality	0e0	8.78e-8	9.37e-18	2.13e-12

Table 4.23 shows the total molalities of each oxidation state of U when in equilibrium with $\text{UO}_{2.25}$. The U(IV) molality decreases with three orders of magnitude compared to Table 4.12.

Table 4.24: The most abundant species of each oxidation state of U, when in equilibrium with $\text{UO}_{2.25}$.

Most abundant species	U(III)	U(IV)	U(V)	U(VI)
Constrained	U^{3+}	$\text{U}(\text{OH})_4$	UO_2^+	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$

Table 4.24 shows the most abundant species for each oxidation state. U(IV) has the largest gap, with 14 orders of magnitude differing between $\text{U}(\text{OH})_4$ and the next largest one. U(V) and U(VI) have a gap of one and two orders of magnitude, respectively. Comparing the species to Table 4.15, they remain the same.

4.2.4.3 Uraninite

This subsection shows the values for when the solution with MOX-addition is equilibrated with uraninite.

Table 4.25: Values for pH and pe when in equilibrium with uraninite.

pH	9.75
pe	-6.65

Table 4.25 shows the pH and pe after the equilibration with coffinite. Compared to Table 4.11, it shows approximately the same environment.

Table 4.26: Total molalities, in mol/l, of dissolved species of each oxidation state of U when in equilibrium with uraninite.

Species	U(III)	U(IV)	U(V)	U(VI)
Molality	0e0	4.20e-10	9.92e-20	3.25e-14

Table 4.26 shows the total molalities of each oxidation state of U when in equilibrium with coffinite. The U(IV) molality decreases with five orders of magnitude compared to Table 4.12, meaning two orders of magnitude more than Table 4.23.

Table 4.27: The most abundant species of each oxidation state of U, when in equilibrium with uraninite.

Most abundant species	U(III)	U(IV)	U(V)	U(VI)
Constrained	U^{3+}	$U(OH)_4$	UO_2^+	$Ca_2UO_2(CO_3)_3$

Table 4.27 shows the most abundant species for each oxidation state. U(IV) has the largest gap, with 13 orders of magnitude differing between $U(OH)_4$ and the next largest one. U(V) and U(VI) have a gap of one order of magnitude each. Comparing the species to Table 4.15, they remain the same.

4.2.4.4 Comparison Uranium

This section compares the effects of equilibrating with either coffinite, $UO_{2.25}$, or uraninite. The reference state is equilibrated with Fe only, as can be seen in Appendix A, under Stage 2 - No Control.pqi. $U(OH)_4$ was also tested, but all values remained the same as ‘Fe only’, making it redundant.

Table 4.28: pH and pe values for equilibration with Fe only, Coffinite, $UO_{2.25}$, and uraninite.

Phase	pH	pe
Fe only	9.75	-6.65
Coffinite	9.86	-6.77
$UO_{2.25}$	10.0	-7.00
Uraninite	9.75	-6.65

As can be seen in Table 4.28, that shows the pH and pe values for each phase, uraninite is the only phase of the three that doesn't change the pH and pe values. Both coffinite and $\text{UO}_{2.25}$ decrease pe and increase pH.

Table 4.29: Total molalities, in mol/l, for dissolved species of each oxidation state of U, when equilibrating with Fe only, Coffinite, $\text{UO}_{2.25}$, and uraninite.

Phases	U(III)	U(IV)	U(V)	U(VI)
Fe only	0e0	2.16e-5	5.09e-15	1.67e-9
Coffinite	0e0	2.15e-5	3.85e-15	1.16e-9
$\text{UO}_{2.25}$	0e0	8.78e-8	9.37e-18	2.13e-12
Uraninite	0e0	4.20e-10	9.92e-20	3.25e-14

Table 4.29 shows how coffinite barely changes the molalities for each oxidation state, whereas $\text{UO}_{2.25}$ and uraninite changes the molalities with three and five orders of magnitudes for U(IV) and U(V), and four and six orders for U(VI), respectively.

Table 4.30: Most abundant species for each oxidation state of U when equilibrated with Fe only, Coffinite, $\text{UO}_{2.25}$, and uraninite.

Most abundant species	U(III)	U(IV)	U(V)	U(VI)
Fe only	U^{3+}	$\text{U}(\text{OH})_4$	UO_2^+	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$
Coffinite	U^{3+}	$\text{U}(\text{OH})_4$	UO_2^+	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$
$\text{UO}_{2.25}$	U^{3+}	$\text{U}(\text{OH})_4$	UO_2^+	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$
Uraninite	U^{3+}	$\text{U}(\text{OH})_4$	UO_2^+	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$

In Table 4.30, all phases have the same most abundant species for each oxidation state.

4.2.5 Americium control

All supersaturated phases from Table 4.18 were tested one by one to see if they were able to control the dissolved americium in the equilibrium phase. As uraninite was concluded first, the phases were equilibrated in combination with that. $\text{Am}(\text{OH})_3(\text{am})$ was the only phase where the simulation converged.

4.2.5.1 $\text{Am}(\text{OH})_3(\text{am})$

Table 4.31: Values for pH and pe when in equilibrium with $\text{Am}(\text{OH})_3(\text{am})$.

pH	9.72
pe	-6.61

Table 4.31 shows the pH and pe after the equilibration with $\text{Am}(\text{OH})_3(\text{am})$. It shows a reducing and basic environment.

Table 4.32: Total molalities, in mol/l, of dissolved species of each oxidation state of Am when in equilibrium with Am(OH)₃(am).

Species	Am(II)	Am(III)	Am(IV)	Am(V)	Am(VI)
Molality	0e0	2.40e-7	1.27e-40	0e0	0e0

Table 4.32 shows the total molalities of each oxidation state of Am when in equilibrium with Am(OH)₃(am).

Table 4.33: Most abundant species for each oxidation state of Am when equilibrated with Am(OH)₃(am).

Most abundant species	Am(II)	Am(III)	Am(IV)	Am(V)	Am(VI)
Constrained	Am ²⁺	Am(OH) ₂ ⁺	Am(CO) ₅ ⁶⁻	AmO ₂ ⁺	AmO ₂ ²⁺

Table 4.33 shows the most abundant species for each oxidation state, where the most abundant species are the ones with a molality of the same magnitude as the total molality of an oxidation state.

4.2.5.2 Comparison Americium

Am(OH)₃(am) was the only phase that converged in simulation, and here it is compared to the equilibration of only Fe. As uraninite was decided in the previous step, Am(OH)₃(am) is equilibrated together with uraninite. The state with only uraninite equilibration will not be compared here, as the Am molalities don't change from Fe only.

Table 4.34: pH and pe values for equilibration with Fe only and Am(OH)₃(am).

Phase	pH	pe
Fe only	9.75	-6.65
Am(OH) ₃ (am)	9.72	-6.61

Table 4.34 shows the pH and pe values for Am(OH)₃(am) and Fe only. The pH decreases and the pe increases with the addition of Am(OH)₃(am).

Table 4.35: Total molalities, in mol/l, for dissolved species of each oxidation state of U, when equilibrating with Fe only and Am(OH)₃(am).

Phase	Am(II)	Am(III)	Am(IV)	Am(V)	Am(VI)
Fe only	0e0	4.77e-5	2.21e-38	0e0	0e0
Am(OH) ₃ (am)	0e0	2.40e-7	1.27e-40	0e0	0e0

Table 4.35 shows the total molalities of each oxidation state of Am. With the addition of Am(OH)₃(am), Am(III) decreases with two orders of magnitude. Am(IV) shows molalities of physical insignificance at 2.21e-38 and 1.27e-40 for Fe only and Am(OH)₃(am), respectively.

Table 4.36: Most abundant species for each oxidation state of Am when equilibrated with Fe only and Am(OH)₃(am).

Most abundant species	Am(II)	Am(III)	Am(IV)	Am(V)	Am(VI)
Fe only	Am ²⁺	Am(OH) ₂ ⁺	Am(CO) ₅ ⁶⁻	AmO ₂ ⁺	AmO ₂ ²⁺
Am(OH) ₃ (am)	Am ²⁺	Am(OH) ₂ ⁺	Am(CO) ₅ ⁶⁻	AmO ₂ ⁺	AmO ₂ ²⁺

Am(OH)₃(am) Table 4.36 shows the most abundant species of each oxidation state of Am, meaning the species that contributes to the molality with the same order of magnitude as the total molality. They remain the same in both cases.

4.3 Stage 3

Stage 3 includes studying the secondary phases and their effects on iron and uranium concentrations. The reference state mentioned, also called ‘No Phase’, is Stage 2 with which uraninite and Am(OH)₃(am) is equilibrated.

4.3.1 Secondary phases identified from the literature

After reviewing the literature, ankerite, calcite, chukanovite, cronstedtite and siderite were chosen for further studies. As reference, the state where no extra phase was equilibrated was used. Each input file can be found in Appendix A, where they will be named Stage 3 [phase].pqi.

Table 4.37: Total molalities, in mol/l, of the dissolved species of the oxidation states of Fe and U when equilibrated with no phase, ankerite, calcite, chukanovite, cronstedtite and siderite.

Phase	Fe(II)	Fe(III)	U(III)	U(IV)	U(V)	U(VI)
No phase	1.13e-3	9.57e-7	0e0	4.20e-10	1.08e-19	3.66e-14
Ankerite	1.54e-5	1.71e-10	0e0	4.20e-10	1.57e-18	3.28e-18
Calcite	1.13e-3	7.83e-9	0e0	4.20e-10	2.06e-18	9.12e-18
Chukanovite	2.73e-4	1.70e-8	0e0	4.20e-10	4.47e-19	1.25e-13
Cronstedtite	2.47e-4	2.16e-9	0e0	4.20e-10	1.32e-18	3.03e-13
Siderite	6.53e-6	1.25e-8	0e0	4.20e-10	7.62e-20	5.84e-15

In Table 4.37, siderite has the biggest impact on decreasing Fe(II), while ankerite has the most impact on decreasing Fe(III). Calcite increases, albeit barely, Fe(II). It also shows that none of the phases have any impact on either U(III) or U(IV). However, siderite is the only phase that decreases U(V), while the other causes an increase. Chukanovite and cronstedtite increases U(VI) by less than an order of magnitude, while siderite decreases it by less than an order of magnitude. Both ankerite and calcite decrease U(VI) with four orders of magnitude.

Table 4.38: Values for pH, pe and SI, for all tested phases, where $SI = \log_{10}(IAP/K_s)$. pH and pe are measured for each separate run simulation, while SI is measured in ‘No phase’'s simulation.

Phase	pH	pe	SI
No phase	9.72	-6.61	-
Ankerite	8.68	-5.44	6.32
Calcite	8.57	-5.32	2.12
Chukanovite	9.16	-5.99	2.24
Cronstedtite	8.73	-5.51	21.1
Siderite	9.85	-6.75	2.39

4.3.2 Saturation index evaluation

With the equilibration of every phase, the pH, pe and saturation index change. When the model isn't equilibrated with an additional secondary phase, the saturation indices are collected for each phase studied. Looking at Table 4.38, it can be observed that all phases decrease the pH except for siderite. Regarding pe, the phases follow the same trend but in reverse. The values for SI show that all phases are supersaturated, since they are positive.

4.3.3 Combining phases

To find out whether it is thermodynamically favorable to combine phases, all phases were tested together in pairs of two.

In Table 4.39, all molalities for the Fe and U oxidation states can be seen for the combinations of secondary phases. Ankerite+cronstedtite can be seen to reduce the iron species the most. All combinations except for calcite+chukanovite decreases Fe(II). Calcite+cronstedtite is the only pair that has a measurable amount of U(III). All combinations retain the same molality for U(IV). Chukanovite+siderite is the only combination of phases to decrease U(V), and it also results in the highest molality of U(VI). All ankerite combinations, except cronstedtite, have the least amount of U(VI).

Table 4.39: Total molalities, in mol/l, of the dissolved species of the oxidation states of Fe and U when simulating a combination of phases.

Phases	Fe(II)	Fe(III)	U(III)	U(IV)	U(V)	U(VI)
No phase	1.13e-3	9.57e-7	0e0	4.20e-10	1.08e-19	3.66e-14
Ankerite, Calcite	1.54e-5	1.71e-10	0e0	4.20e-10	1.57e-18	3.28e-18
Ankerite, Chukanovite	1.54e-5	1.71e-10	0e0	4.20e-10	1.57e-18	3.28e-18
Ankerite, Cronstedtite	6.95e-7	1.84e-12	0e0	4.20e-10	3.55e-18	2.00e-16
Ankerite, Siderite	1.54e-5	1.71e-10	0e0	4.20e-10	1.57e-18	3.28e-18
Calcite, Chukanovite	1.13e-3	7.83e-9	0e0	4.20e-10	2.06e-18	9.12e-18
Calcite, Cronstedtite	2.81e-4	5.14e-12	6.80e-39	4.20e-10	7.36e-17	7.58e-15
Calcite, Siderite	2.21e-4	2.93e-9	0e0	4.20e-10	1.41e-18	5.80e-18
Chukanovite, Cronstedtite	2.47e-4	2.16e-9	0e0	4.20e-10	1.32e-18	3.03e-13
Chukanovite, Siderite	6.53e-6	1.25e-8	0e0	4.20e-10	7.62e-20	5.84e-13
Cronstedtite, Siderite	9.63e-6	4.37e-11	0e0	4.20e-10	2.02e-18	2.32e-13

Table 4.40: Values for pH and pe for secondary phases tested in combination.

Phases	pH	pe
No phase	9.72	-6.61
Ankerite, Calcite	8.68	-5.44
Ankerite, Chukanovite	8.68	-5.44
Ankerite, Cronstedtite	8.36	-5.08
Ankerite, Siderite	8.68	-5.44
Calcite, Chukanovite	8.57	-5.32
Calcite, Cronstedtite	7.20	-3.77
Calcite, Siderite	8.72	-5.48
Chukanovite, Cronstedtite	8.73	-5.51
Chukanovite, Siderite	9.85	-6.75
Cronstedtite, Siderite	8.57	-5.33

Table 4.40 shows the pH values for the combinations of two secondary phases at a time. Ankerite retains its pH in all combinations except with cronstedtite, which affects the pH, making it lower than both phases separately, as seen in Table 4.38. Cronstedtite decreases the pH below both separate values in each combination, compared to Table 4.38, except for chukanovite that takes on the pH of cronstedtite directly. Chukanovite adopts the pH of the other phase in each combination, as seen in Table 4.38. Calcite and siderite decrease their pH in combination with cronstedtite, while retaining their pH in relation to chukanovite. In combination, calcite and siderite show a pH between the values for each phase separately, as shown in Table 4.38. The values sticking out are calcite+cronstedtite having $\text{pH} < 8$ and chukanovite+siderite having $\text{pH} > 9$, while the rest of the values remain between 8.55 ± 0.19 .

Table 4.40 also shows the pe values for the combinations of two secondary phases at a time. The same trends that are observed for pH, show in reverse for pe. This includes ankerite retaining its pe in all combinations except the one with cronstedtite. It also includes cronstedtite increasing the pe of all combinations above each phase specific value for Table 4.38, and chukanovite taking on the pe of the other phase in each combination. Calcite and siderite decreases their pe in combination with cronstedtite, while the calcite+siderite combination results in a pe between the two separate pe's. The values sticking out are calcite+cronstedtite being $\text{pe} > -4$, and chukanovite+siderite being $\text{pe} < -6$, while the other combinations remain within -5.30 ± 0.22 .

5

Discussion

5.1 Uranium control and phase selection

When studying the molalities of the oxidation states after addition of the MOX pellet in Section 4.2.1, Table 4.12 shows proportionally higher molalities of U(IV), U(V) and U(VI) compared to Pu(III), Pu(IV) and Pu(V) in Table 4.13. As shown in Table 4.10, the initial difference between UO_2 and PuO_2 is about an order of magnitude difference, where the final amount differs about 13 orders of magnitude between U(IV) and Pu(IV), as seen in Tables 4.12 and 4.13. This shows the unexpectedly high molality of the U(IV) oxidation state, which should be closer to the level of Pu(IV). Because of the discrepancy, the phases were investigated further to find a more reasonable molality. By equilibrating the solution including the iron corroded during the MOX pellet's leaching and the MOX pellet, with the supersaturated uranium phases in Table 4.17 one by one, new molalities as well as pH and pe values were achieved. When comparing all of the uranium phases, Table 4.28 shows the values for pH and pe, where coffinite and $\text{UO}_{2.25}$ caused an increase in pH and decrease in pe. This means these phases caused the solution to be more basic, and more reducing, with $\text{UO}_{2.25}$ causing the most effect. Equilibrating with uraninite, on the other hand, caused almost no change in pH and no change in pe. Looking further, at Table 4.29, and comparing the molalities of each oxidation state, the opposite trend can be seen. Despite increasing and decreasing pH and pe the most, respectively, $\text{UO}_{2.25}$ is not the best at reducing the molality, even if it's better than coffinite. Coffinite decreases the molality of U(IV) with less than one order of magnitude and $\text{UO}_{2.25}$ causes a decrease of three orders of magnitude. Uraninite causes a decrease of five orders of magnitude to U(IV), without changing the pH and pe. Looking at Table 4.30, none of the phases cause a change in the most abundant species.

The specific high molality to investigate is the one for $\text{U}(\text{OH})_4$. In the original solution with no extra added phase, the next highest molality is $4.492\text{e-}17$, making it an outlier. Therefore, if control can be established over $\text{U}(\text{OH})_4$, the solubility of U(IV) is also under control. According to Saleh [13], traces of U(VI) are reduced and precipitate as $\text{UO}_2(\text{s})$ on the surface of corroding metallic iron, making uraninite a good choice to equilibrate with. By choosing to move on with the uraninite phase, there's still a gap down the next phase, but the total amount is lower. Thus, it is concluded that the equilibration with uraninite helps with the dissolution of uranium species. Since all phases show the same most abundant species for each oxidation state, as seen in Table 4.30, the effect from the equilibration should be equal on all

phases relative to the species.

5.2 Americium control

When observing the molalities of the oxidation states of americium in Table 4.14 the difference in magnitude between Am(III) and Am(IV) is apparent. The AmO_2 in the solid solution releases Am as Am(IV), which reduces to Am(III) in the basic and reducing conditions [44]. With nothing to cap its solubility, almost all the MOX pellet's Am inventory dissolves, which is not physically plausible. To find a way to model without the Am(IV) runaway, the supersaturated phases containing americium were equilibrated with the MOX solution as well as uraninite. All phases can be seen in Table 4.18, together with their saturation indices. Out of the available phases, only $\text{Am}(\text{OH})_3(\text{am})$ was able to run the full simulation. Since uraninite was confirmed before the Am phases were run, it might be the cause of the non-converged simulations of the other three tested phases. When comparing the values of pH and pe to before the equilibration with uraninite to after the equilibration with $\text{Am}(\text{OH})_3(\text{am})$, as in Table 4.34, the pH decreases, making the solution less basic. The pe, on the other hand, increases, making the solution less reducing. Molalities for before and after equilibration can be seen in Table 4.35, and for both Am(III) and Am(IV) the molality decreases with two orders of magnitude making it more reasonable. As shown in Table 4.36, the most abundant species remain the same before and after the equilibration.

Pu has no supersaturated phases in this state, and was therefore not investigated, combined with the fact that its molality was at a reasonable level from the start, as seen in Table 4.13, and compared to Saleh's results [13].

5.3 Carbonate chemistry and secondary phases

In his paper [13], Saleh mentions finding ankerite, calcite, chukanovite, goethite, lepidocrocite and akaganeite among the precipitated phases. Other potential phases, established from studying the peaks of the acquired Raman spectra in combination with the EDX elemental component analysis, include hematite, maghemite, and cronstedtite. Magnetite was mentioned as a possible precipitate but not detected in the experiment and ruled out. Siderite was also mentioned as a possible phase in equilibrium, although it was described as being of low concentration. As goethite, akaganeite, lepidocrocite and hematite are radiolytic oxidants, formed because of alpha radiolysis, they were not studied since their conditions are incompatible with the constructed model [13]. Thus, the phases studied were ankerite, calcite, chukanovite, cronstedtite and siderite, which were tested for precipitation to determine whether they're likely to occur.

In Table 4.37, all secondary phases studied, when studied one by one, are shown together with their respective molalities for the Fe and U oxidation states. Ankerite causes a two-order decrease in the molality of Fe(II), which is the second largest drop, as well as an almost four-order decrease in molality of Fe(III), which is the lowest value. For U(V), ankerite increases the molality by one order of magnitude

and it decreases U(VI) by four orders of magnitude, being the lowest molality. Calcite has close to no effect on Fe(II), but decreases the molality of Fe(III) with two orders of magnitude. Like ankerite, it increases the molality of U(V) by one order of magnitude and decreases the molality of U(VI) with almost four orders of magnitude. Chukanovite decreases the molality of Fe(II) with about half an order and Fe(III) with close to two orders of magnitude, while increasing the molality of U(V) and U(VI) with about half an order of magnitude each. Cronstedtite decreases the molalities of Fe(II) and Fe(III) with almost one and a little less than three orders of magnitude respectively, while increasing both U(V) and U(VI) one order of magnitude each. Siderite is the only phase that decreases all oxidation states, except for U(III) and U(IV). It causes a decrease of about two orders of magnitude for the molality of Fe(II) and Fe(III), less than half an order of magnitude for U(V) and almost an order of magnitude of the molality of U(VI). None of the phases affect either U(III), as the value is zero for all of them, or U(IV), as the value remains $4.202\text{e-}10$ mol/l.

When looking at Table 4.38, it can be concluded that all phases are supersaturated, and therefore possible to precipitate. It doesn't mean they have to, but it's possible. Regarding the pH, all phases except siderite cause a decrease, meaning the solution becomes less basic. For pe, all phases cause a decrease, except siderite, which leads to a more reducing environment. The SI values seem to have no correlation with either Table 4.37 or 4.38.

When studying the combination of two phases as once, looking at Table 4.39, pH and pe have been observed. In combination with ankerite, only cronstedtite affected the values of pH and pe, and it decreased the pH and increased pe. Across all combinations, when combined with cronstedtite, a phase will achieve a lower pH and a higher pe than it did when equilibrated alone. Even if cronstedtite on its own, as in Table 4.38, has a higher pH than ankerite and calcite, they both experience a decrease in the combination. The SI of cronstedtite is higher than all other phases; see Table 4.38, which may be a factor.

Ankerite consistently overrides the phase it's paired with, producing identical results regardless of partner phase, excluding cronstedtite. This may be because the thermodynamic data is sourced from a different database than the `llnl.dat` one containing calcite, cronstedtite and siderite, which raises an uncertainty of the values produced. A logK not calibrated against the same framework as the rest of the model could produce an artificially dominant equilibrium rather than reflect realistic ankerite behavior. The same uncertainty can be applied to the chukanovite combinations, as the chukanovite data also was collected from a source outside `llnl.dat`. Thus, these combinations may also not reflect realistic behavior of chukanovite.

5.4 Comparison with experimental observations

Comparing the results of this thesis with those of Saleh et al. [13], there are some similarities and some differences. Starting with comparing the pH values, Saleh measured pH in the range of 6.9 ± 0.1 to 7.2 ± 0.1 [13]. One instance can be found from the results of the model that lies in this span, which is calcite+cronstedtite

at pH = 7.20. The rest of the pH values from the model are higher, and the next lowest one is ankerite+cronstedtite with 8.36. Looking at the pe values, there are no such values mentioned by Saleh [13], but he details values of the redox potential Eh that can be recalculated to pe. Using this formula, $pe = Eh \cdot (F / (R \cdot T \cdot \ln(10)))$ [45], where F is the Faraday constant, T is temperature and R is the gas constant, Eh = [-30,-40] becomes pe = [-0.51,-0.69]. This calculation uses the values F = 96485.33 C/mol [46], T = 294.15 K and R = 8.314 J/(mol·K) [46]. When referencing the pe values in Tables 4.38 and 4.40, all values are approximately an order of magnitude wrong. Had the Eh values been ten times larger, the pe values would have all been in the range, except for ankerite+cronstedtite and calcite+cronstedtite. Unfortunately for the model, Saleh mentions that the redox potential is likely to be higher than his measured value due to the amount of hydrogen being active on the Pt electrode but not in the bulk solution [13]. Saleh also mentions the U concentration being approximately e-8.5, which is equal to 3.16e-9 mol/l, and somewhat close to the 4.202e-10 mol/l observed in Table 4.37 while also showing that Pu rapidly lowers in molality [13]. He describes a low initial concentration of U that suggests that a potential pre-oxidized surface layer was minimized, as the start concentration possibly should have been higher otherwise [13]. This is not something the model has taken into consideration, but it operates as if there is no oxidized layer on the pellet, which could lead to a higher concentration of U. When discussing iron corrosion, Saleh also mentions the expectation that it releases redox reactive species such as Fe(II) and H₂, which in turn causes reducing conditions [13]. He continues talking about how the creation of these species plays a significant role in suppressing oxidative dissolution of MOX and its components [13]. When studying Table 4.37, this trend is not observed, as the Fe(II) molalities show no universal correlation with either U(V) or U(VI).

5.5 Model limitations

Throughout the creation of the model, a few different paths were tested and parameters were evaluated. Only one setup was tested for the gas configuration in the model as it was close to the experimental setup, and no further data has been collected to evaluate against. As the surrounding gas supply is limited due to the autoclave, the gas needed to be limited, which was solved using the GAS_PHASE block in PHREEQC since it allows limiting the volume of the gas.

Two different approaches were tested to decide how the metallic iron corrosion should be represented in the model. The first approach included letting the metallic iron equilibrate with the groundwater solution without a limit, as seen in Section 4.1.1 for results and Appendix A for input file. The second approach entailed a calculation of the amount of iron dissolved before MOX-pellet addition, and equilibrating that amount with the groundwater solution, as seen in Section 4.1.2 for results and Appendix A for the input file. Comparing the results of pH and pe, in Table 4.7, the constrained Fe-model resulted in values closer to the experimental ones by Saleh [13].

The addition of the MOX pellet was treated as an ideal solid solution, as this is

how PHREEQC treats ternary solid solutions. Preferably, the rate constants would have been found, and a kinetic model would have been used to get as close to experimental procedure as possible. The acquisition of rate constants would have required some experiments that would have required time outside of the time frame of the project. This probably leads to some discrepancies in the final concentrations and ratios between the involved elements compared to the experimental results [13]. As the model is an equilibrium model that is based on an average of iron corroded over time, it is difficult to compare. The observed effect on the elements of the solid solution, after MOX pellet addition, shows a significantly higher molality of U and Am than of Pu. This can be seen in Tables 4.12, 4.13 and 4.14, where both U and Am show a total molality of the magnitude of $e-5$, while Pu shows a molality of the magnitude of $e-18$. To curb those effects, phases were tested in equilibrium with the existing solution to decide whether it affected the molality. For U, three phases were tested, as can be seen in Table 4.17. The results showed uraninite as decreasing the molality the most, while keeping the pH and pe values stable. Uraninite was kept in the model and was equilibrated when studying the Am phases. As for the studied Am phases, shown in Table 4.18, the phases were equilibrated one by one together with uraninite. Only one phase, $\text{Am}(\text{OH})_3(\text{am})$, managed to converge the simulation. This was probably due to the involvement of uraninite, which affected the creation of the solution. The equilibration of $\text{Am}(\text{OH})_3(\text{am})$ caused a decrease of two orders of magnitude, as shown in Table 4.35. This shows a result closer to Saleh's [13], which meant carrying the $\text{Am}(\text{OH})_3(\text{am})$ forward together with uraninite.

Five phases were chosen for further study, after examination of Saleh's paper [13], including ankerite, calcite, chukanovite, cronstedtite and siderite. These phases were tested one by one to decide what effect they had on the solution. The phases and the resulting molalities are shown in Table 4.37, and it showed that only siderite decreased all Fe and U molalities. U(III) and U(IV) were unchanged for all equilibrations, at 0 and $4.20e-10$ mol/l respectively. No further studies were conducted to decide the cause of the U(IV) stagnation in molality. Siderite was also the only phase to decrease both U phases, while ankerite and calcite also decreased U(VI). Comparing to Saleh's results for the Fe(II) concentration at $9.16e-4$ mol/l [13], the closest simulated value was 'no phase' and calcite at $1.132e-3$ and $1.133e-3$ mol/l, followed by chukanovite and cronstedtite at $2.73e-4$ and $2.47e-4$ mol/l. Saleh's value for U molality in the experimental data is $1.39e-9$, causing all the phases to be equally far away due to their highest molality being U(IV) [13].

When the phases had been tested separately, they were then equilibrated in pairs of two. This resulted in ten combinations, where each phase appears four times. The molalities measured are shown in Table 4.39. U(IV) remains unchanged at $4.20e-10$ mol/l for all combinations, and U(III) is increased to $6.80e-39$ mol/l for the combination of calcite and cronstedtite. Studying U oxidation states, none of the combinations managed to reduce both U(V) and U(VI). Chukanovite+siderite was the only combination able to reduce U(V), and it decreased by one order of magnitude, while all other combinations except calcite+cronstedtite increased the molality by one order of magnitude instead of the two from calcite+cronstedtite. For U(VI), all ankerite and calcite combinations managed to reduce the molality with one to four orders of magnitude. Chukanovite+cronstedtite, chukanovite+siderite

and cronstedtite+siderite increase the molality of U(VI) one order of magnitude. When studying the Fe oxidation states, it showed that ankerite+cronstedtite decreases both Fe(II) and Fe(III) more than all other combinations. Some trends could be seen as well for both Fe and U, where all combinations including ankerite, except for ankerite+cronstedtite, showed the same molality. Calcite, cronstedtite and siderite showed the next most impact, where their molalities showed through the combination with chukanovite. Any combination with chukanovite showed the value of the molality for the other phase. Even if cronstedtite only managed to influence the combination chukanovite+cronstedtite to take on its value, it impacted all other phases to reduce their molality below the value of the other phase in the combination. Comparing the combinations to the values from Saleh's paper [13], the U molality is still the same as for the one-by-one phases. For Fe(II), the value of 9.16×10^{-4} mol/l [13] is closest to the 'no phase' solution, and the calcite+chukanovite combination, with the same values as for 'no phase' and calcite previously discussed. The next in proximity are calcite+cronstedtite with 2.81×10^{-4} mol/l, chukanovite+cronstedtite with 2.47×10^{-4} mol/l and calcite+siderite with 2.21×10^{-4} mol/l.

When looking at the model in its entirety, it can be concluded that it is structured somewhat similarly to the experimental setup, but with a few deviations that cause discrepancies in the results. The environment consisting of the gas and the Forsmark groundwater is assumed to be a good replica of the experiment [13]. Fe placement was chosen to achieve the closest replication of the experimental setup but may result in a higher concentration of iron in the solution. MOX pellet addition was treated as ideal, which could have led to a higher concentration of the elements included as well as a different final ratio between the elements.

6

Conclusion

The purpose of this thesis is to reflect on what happens to a system while leaching metallic iron and a MOX pellet and to build a model to simulate the environment and outcome of those conditions. Corrosion of iron and leaching of a MOX pellet have been studied both via experimental results and simulation results. The corrosion of metallic iron was tested in two different ways in the process of creating the model, where the first way included an unconstrained amount of dissolved iron and the second way included the equivalent amount of metallic iron dissolved as the solution had before the MOX pellet addition. Equilibrating the calculated amount of metallic iron with the groundwater was the best of the tested methods, but the model still systematically over-predicts reducing conditions at every stage. The experimental environment was set up using a non-reactive gas phase, allowing the system to remain anoxic. In the model, this was implemented using the same parameters, meaning the results should be unaffected. The original solution of the model is taken directly from the experiment, and thus speciation should be identical. Leaching of the MOX pellet was likened to a solid solution and assumed to be ideal due to limitations of PHREEQC. Compared to the experimental conditions, some actinide components behaved unexpectedly, causing molalities to be both higher and lower. High molalities of iron were observed from the simulated results, making the model more reducing than the experiment. To control the actinide molalities, a few phases were tested in equilibrium with the solution including MOX. For the uranium phases, uraninite showed a clear difference while not affecting the starting conditions. Regarding americium phases, as they were tested together with uraninite already equilibrated, only $\text{Am}(\text{OH})_3(\text{am})$ managed to complete the simulation. This resulted in a reduction of americium in the final solution, as well as less reducing and basic conditions. All the secondary phases were tested in equilibrium with the solution, first separately and then in pairs, and for most cases the conditions were more basic and a lot more reducing than the experiment. Only the calcite+cronstedtite simulation was in bounds for the pH. The results of the simulations followed the expected trends of the solution becoming less basic and reducing when equilibrated, but the resulting values didn't reach the expected levels. Thus, none of the simulations with the secondary phases, either alone or paired up, closely match the results from the experiment. Saleh proposes that the true redox state is more reducing than he presents [13], which aligns with the results of the simulation.

To summarize, the model is an equilibrium model, causing it to only show a snapshot of a simplified version of the intended system. The environment works well, as nothing else can be decided. Iron corrosion is closer to reality than the other tested

options. MOX pellet leaching is idealized, most probably causing some discrepancies. The molalities of some uranium and americium oxidation states exceed realistic limits, which necessitates controlling equilibrations with specific phases. Equilibration with secondary phases shows no clear indication of whether they are present or not, as all phases are thermodynamically possible per our model.

To further develop the model, a kinetic model should be considered, as it would more accurately show the course of the experiment. Developing the current model, a new approach to the solid solution could be helpful as the current one disregards all imperfections of the pellet. It would also require experimental studies to decide the activity factors between the elements in the solid solution. If the activity factors are required, the model could be reworked into a kinetic model. To assist the model, a program shell could be constructed to allow the user to run simulations consecutively while studying the effect of different parameters that can be changed between simulations.

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A

Input files

This appendix contains the full input file for each step of the process of finding the final model. Table 2 referred to in the code is Table 2 in Saleh's paper [13]. Stage 1 contains the setup of the environment, stage 2 includes the addition of the MOX pellet, and stage 3 tests equilibration with secondary phases.

Stage 1.pqi

Setting up the experimental environment with argon gas and the synthetic groundwater.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp      21
5      pH        7.19
6      pe        4
7      units     mmol/L
8      density   1.002
9      Na        96.57
10     K          0.93
11     Ca         22.21
12     Mg         10.04
13     Alkalinity 2.07
14     Cl         148.9
15     S(6)       5.28 as S04
16     Si         0.22
17     Br         0.3
18     Fe(2)      0.04
19     Sr         0.1
20     -water     0.8
21
22  EQUILIBRIUM_PHASES 1
23     Fe 0.0 4.479e-4
24
25  GAS_PHASE 1
26     -fixed_pressure
27     -pressure   9.86923267
28     -volume     0.2
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g)  0.9996
32

```

A. Input files

```
33 SELECTED_OUTPUT
34     -reset false
35     -high_precision true
36     -pH true
37     -pe true
38     -totals Fe C(4) S(6) Ca Mg
39     -equilibrium_phases Fe
40     -saturation_indices Calcite Siderite Magnetite
41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
```

Stage1 - Fe Unconstrained.pqi

Unconstrained Fe model. Includes available metallic Fe from iron corrosion, that was recalculated to Fe(II), and added to SOLUTION.

```
1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2  # Fe Unconstrained - "unlimited" amount of Fe added to SOLUTION
3
4  SOLUTION 1 Forsmark_groundwater
5      temp      21
6      pH        7.19
7      pe        4
8      units     mmol/L
9      density   1.002
10     Na        96.57
11     K          0.93
12     Ca        22.21
13     Mg        10.04
14     Alkalinity 2.07
15     Cl        148.9
16     S(6)      5.28 as S04
17     Si        0.22
18     Br        0.3
19     Fe(2)     0.04
20     Sr        0.1
21     -water    0.8
22
23 EQUILIBRIUM_PHASES 1
24     Fe 0.0 10
25
26 GAS_PHASE 1
27     -fixed_pressure
28     -pressure   9.86923267
29     -volume     0.2
30     -temperature 21.0
31     CO2(g) 0.0004
32     Ar(g)  0.9996
33
34 SELECTED_OUTPUT
```

```

35     -reset false
36     -high_precision true
37     -pH true
38     -pe true
39     -totals Fe C(4) S(6) Ca Mg
40     -equilibrium_phases Fe
41     -saturation_indices Calcite Siderite Magnetite
42
43 SAVE solution 1
44 SAVE equilibrium_phases 1
45 SAVE gas_phase 1
46
47 END

```

Stage 1 - Fe Constrained.pqi

Constrained Fe model. Includes available metallic Fe from iron corrosion, which was added to EQUILIBRIUM_PHASES.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2  # Fe constrained - Fe added to EQUILIBRIUM_PHASES
3
4  SOLUTION 1 Forsmark_groundwater
5      temp      21
6      pH        7.19
7      pe        4
8      units     mmol/L
9      density    1.002
10     Na        96.57
11     K         0.93
12     Ca        22.21
13     Mg        10.04
14     Alkalinity 2.07
15     Cl        148.9
16     S(6)      5.28 as S04
17     Si        0.22
18     Br        0.3
19     Fe(2)     0.04
20     Sr        0.1
21     -water    0.8
22
23 EQUILIBRIUM_PHASES 1
24     Fe 0.0 4.479e-4
25
26 GAS_PHASE 1
27     -fixed_pressure
28     -pressure   9.86923267
29     -volume     0.2
30     -temperature 21.0
31     CO2(g) 0.0004
32     Ar(g)  0.9996
33
34 SELECTED_OUTPUT
35     -reset false

```

A. Input files

```
36     -high_precision true
37     -pH true
38     -pe true
39     -totals Fe C(4) S(6) Ca Mg
40     -equilibrium_phases Fe
41     -saturation_indices Calcite Siderite Magnetite
42
43 SAVE solution 1
44 SAVE equilibrium_phases 1
45 SAVE gas_phase 1
46
47 END
```

Stage 2.pqi

Addition of MOX pellet. This is the final version of Stage 2, with the MOX pellet addition and the chosen equilibrated phases.

```
1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp      21
5      pH        7.19
6      pe        4
7      units     mmol/L
8      density   1.002
9      Na        96.57
10     K         0.93
11     Ca        22.21
12     Mg        10.04
13     Alkalinity 2.07
14     Cl        148.9
15     S(6)      5.28 as S04
16     Si        0.22
17     Br        0.3
18     Fe(2)     0.04
19     Sr        0.1
20     -water    0.8
21
22 EQUILIBRIUM_PHASES 1
23     Fe 0.0 4.479e-4
24
25 GAS_PHASE 1
26     -fixed_pressure
27     -pressure   9.86923267
28     -volume     0.2
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g)  0.9996
32
33 SELECTED_OUTPUT
34     -reset false
35     -high_precision true
36     -pH true
```

```

37     -pe true
38     -totals Fe C(4) S(6) Ca Mg
39     -equilibrium_phases Fe
40     -saturation_indices Calcite Siderite Magnetite
41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
47
48 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
      Uraninite (U control), Am(OH)3(am) (Am control), plus the post
      -MOX Fe increment (4.263e-4 mol)
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55     -comp UO2(am) 0.00550240863910409
56     -comp PuO2    0.000613778686802078
57     -comp AmO2    0.0000381599502541837
58     -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
61     Fe          0.0 4.263e-4
62     Uraninite   0.0 0.0
63     Am(OH)3(am) 0.0 0.0
64
65 SELECTED_OUTPUT
66     -reset false
67     -high_precision true
68     -pH true
69     -pe true
70     -totals Fe U Pu Am C(4) S(6) Ca Mg
71     -equilibrium_phases Fe Uraninite Am(OH)3(am)
72     -solid_solutions MOX
73     -saturation_indices Calcite Siderite Magnetite UO2(am)
74
75 SAVE solution 1
76 SAVE equilibrium_phases 1
77 SAVE gas_phase 1
78 SAVE solid_solutions 1
79
80 END

```

Stage 2 - No Control.pqi

Addition of MOX pellet. MOX pellet addition with no extra equilibrated control phase, only Fe.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
2     corrosion (pre-MOX, 101-day phase)

```

A. Input files

```
3 SOLUTION 1 Forsmark_groundwater
4   temp      21
5   pH        7.19
6   pe        4
7   units     mmol/L
8   density   1.002
9   Na        96.57
10  K         0.93
11  Ca        22.21
12  Mg        10.04
13  Alkalinity 2.07
14  Cl        148.9
15  S(6)      5.28 as S04
16  Si        0.22
17  Br        0.3
18  Fe(2)     0.04
19  Sr        0.1
20  -water    0.8
21
22 EQUILIBRIUM_PHASES 1
23   Fe 0.0 4.479e-4
24
25 GAS_PHASE 1
26   -fixed_pressure
27   -pressure    9.86923267
28   -volume      0.2
29   -temperature 21.0
30   CO2(g) 0.0004
31   Ar(g)  0.9996
32
33 SELECTED_OUTPUT
34   -reset false
35   -high_precision true
36   -pH true
37   -pe true
38   -totals Fe C(4) S(6) Ca Mg
39   -equilibrium_phases Fe
40   -saturation_indices Calcite Siderite Magnetite
41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
47
48 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
    Uraninite (U control), Am(OH)3(am) (Am control), plus the post
    -MOX Fe increment (4.263e-4 mol)
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55   -comp UO2(am) 0.00550240863910409
56   -comp PuO2    0.000613778686802078
```

```

57 -comp AmO2      0.0000381599502541837
58 -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
61   Fe              0.0 4.263e-4
62
63 SELECTED_OUTPUT
64   -reset false
65   -high_precision true
66   -pH true
67   -pe true
68   -totals Fe U Pu Am C(4) S(6) Ca Mg
69   -equilibrium_phases Fe Uraninite Am(OH)3(am)
70   -solid_solutions MOX
71   -saturation_indices Calcite Siderite Magnetite UO2(am)
72
73 SAVE solution 1
74 SAVE equilibrium_phases 1
75 SAVE gas_phase 1
76 SAVE solid_solutions 1
77
78 END

```

Stage 2 + Coffinite.pqi

Addition of MOX pellet. MOX pellet addition including equilibration with coffinite as a potential control phase.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4    temp      21
5    pH        7.19
6    pe        4
7    units     mmol/L
8    density   1.002
9    Na        96.57
10   K         0.93
11   Ca        22.21
12   Mg        10.04
13   Alkalinity 2.07
14   Cl        148.9
15   S(6)      5.28 as S04
16   Si        0.22
17   Br        0.3
18   Fe(2)     0.04
19   Sr        0.1
20   -water    0.8
21
22 EQUILIBRIUM_PHASES 1
23   Fe 0.0 4.479e-4
24
25 GAS_PHASE 1
26   -fixed_pressure

```

A. Input files

```
27 -pressure      9.86923267
28 -volume        0.2
29 -temperature   21.0
30 CO2(g) 0.0004
31 Ar(g)  0.9996
32
33 SELECTED_OUTPUT
34 -reset false
35 -high_precision true
36 -pH true
37 -pe true
38 -totals Fe C(4) S(6) Ca Mg
39 -equilibrium_phases Fe
40 -saturation_indices Calcite Siderite Magnetite
41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
47
48 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
    Uraninite (U control), Am(OH)3(am) (Am control), plus the post
    -MOX Fe increment (4.263e-4 mol)
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55 -comp UO2(am) 0.00550240863910409
56 -comp PuO2 0.000613778686802078
57 -comp AmO2 0.0000381599502541837
58 -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
61 Fe 0.0 4.263e-4
62 Coffinite 0.0 0.0
63
64 SELECTED_OUTPUT
65 -reset false
66 -high_precision true
67 -pH true
68 -pe true
69 -totals Fe U Pu Am C(4) S(6) Ca Mg
70 -equilibrium_phases Fe Uraninite Am(OH)3(am)
71 -solid_solutions MOX
72 -saturation_indices Calcite Siderite Magnetite UO2(am)
73
74 SAVE solution 1
75 SAVE equilibrium_phases 1
76 SAVE gas_phase 1
77 SAVE solid_solutions 1
78
79 END
```

Stage 2 + UO₂.25.pqi

Addition of MOX pellet. MOX pellet addition including equilibration with UO_{2.25} as a potential control phase.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp      21
5      pH        7.19
6      pe        4
7      units     mmol/L
8      density   1.002
9      Na        96.57
10     K         0.93
11     Ca        22.21
12     Mg        10.04
13     Alkalinity 2.07
14     Cl        148.9
15     S(6)      5.28 as S04
16     Si        0.22
17     Br        0.3
18     Fe(2)     0.04
19     Sr        0.1
20     -water    0.8
21
22  EQUILIBRIUM_PHASES 1
23     Fe 0.0 4.479e-4
24
25  GAS_PHASE 1
26     -fixed_pressure
27     -pressure   9.86923267
28     -volume     0.2
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g)  0.9996
32
33  SELECTED_OUTPUT
34     -reset false
35     -high_precision true
36     -pH true
37     -pe true
38     -totals Fe C(4) S(6) Ca Mg
39     -equilibrium_phases Fe
40     -saturation_indices Calcite Siderite Magnetite
41
42  SAVE solution 1
43  SAVE equilibrium_phases 1
44  SAVE gas_phase 1
45
46  END
47
48  TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
   Uraninite (U control), Am(OH)3(am) (Am control), plus the post
   -MOX Fe increment (4.263e-4 mol)

```

A. Input files

```
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55     -comp UO2(am) 0.00550240863910409
56     -comp PuO2    0.000613778686802078
57     -comp AmO2    0.0000381599502541837
58     -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
61     Fe          0.0 4.263e-4
62     UO2.25      0.0 0.0
63
64 SELECTED_OUTPUT
65     -reset false
66     -high_precision true
67     -pH true
68     -pe true
69     -totals Fe U Pu Am C(4) S(6) Ca Mg
70     -equilibrium_phases Fe Uraninite Am(OH)3(am)
71     -solid_solutions MOX
72     -saturation_indices Calcite Siderite Magnetite UO2(am)
73
74 SAVE solution 1
75 SAVE equilibrium_phases 1
76 SAVE gas_phase 1
77 SAVE solid_solutions 1
78
79 END
```

Stage 2 + Uraninite.pqi

Addition of MOX pellet. MOX pellet addition including equilibration with uraninite as a potential control phase.

```
1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp      21
5      pH        7.19
6      pe        4
7      units     mmol/L
8      density   1.002
9      Na        96.57
10     K          0.93
11     Ca         22.21
12     Mg         10.04
13     Alkalinity 2.07
14     Cl         148.9
15     S(6)       5.28 as S04
16     Si         0.22
17     Br         0.3
```

```

18      Fe(2)      0.04
19      Sr         0.1
20      -water     0.8
21
22  EQUILIBRIUM_PHASES 1
23      Fe 0.0 4.479e-4
24
25  GAS_PHASE 1
26      -fixed_pressure
27      -pressure   9.86923267
28      -volume     0.2
29      -temperature 21.0
30      CO2(g) 0.0004
31      Ar(g)  0.9996
32
33  SELECTED_OUTPUT
34      -reset false
35      -high_precision true
36      -pH true
37      -pe true
38      -totals Fe C(4) S(6) Ca Mg
39      -equilibrium_phases Fe
40      -saturation_indices Calcite Siderite Magnetite
41
42  SAVE solution 1
43  SAVE equilibrium_phases 1
44  SAVE gas_phase 1
45
46  END
47
48  TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
      Uraninite (U control), Am(OH)3(am) (Am control), plus the post
      -MOX Fe increment (4.263e-4 mol)
49
50  USE solution 1
51  USE gas_phase 1
52
53  SOLID_SOLUTIONS 1
54  MOX
55      -comp UO2(am) 0.00550240863910409
56      -comp PuO2   0.000613778686802078
57      -comp AmO2    0.0000381599502541837
58      -tempK 294.15
59
60  EQUILIBRIUM_PHASES 1
61      Fe          0.0 4.263e-4
62      Uraninite    0.0 0.0
63
64  SELECTED_OUTPUT
65      -reset false
66      -high_precision true
67      -pH true
68      -pe true
69      -totals Fe U Pu Am C(4) S(6) Ca Mg
70      -equilibrium_phases Fe Uraninite Am(OH)3(am)
71      -solid_solutions MOX

```

A. Input files

```
72 -saturation_indices Calcite Siderite Magnetite UO2(am)
73
74 SAVE solution 1
75 SAVE equilibrium_phases 1
76 SAVE gas_phase 1
77 SAVE solid_solutions 1
78
79 END
```

Stage 2 + Am(OH)₃(am).pqi

Addition of MOX pellet. MOX pellet addition including equilibration with Am(OH)₃(am) as a potential control phase in combination with uraninite.

```
1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4    temp      21
5    pH        7.19
6    pe        4
7    units     mmol/L
8    density   1.002
9    Na        96.57
10   K         0.93
11   Ca        22.21
12   Mg        10.04
13   Alkalinity 2.07
14   Cl        148.9
15   S(6)      5.28 as S04
16   Si        0.22
17   Br        0.3
18   Fe(2)     0.04
19   Sr        0.1
20   -water    0.8
21
22  EQUILIBRIUM_PHASES 1
23    Fe 0.0 4.479e-4
24
25  GAS_PHASE 1
26    -fixed_pressure
27    -pressure  9.86923267
28    -volume    0.2
29    -temperature 21.0
30    CO2(g) 0.0004
31    Ar(g)  0.9996
32
33  SELECTED_OUTPUT
34    -reset false
35    -high_precision true
36    -pH true
37    -pe true
38    -totals Fe C(4) S(6) Ca Mg
39    -equilibrium_phases Fe
40    -saturation_indices Calcite Siderite Magnetite
```

```

41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
47
48 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
    Uraninite (U control), Am(OH)3(am) (Am control), plus the post
    -MOX Fe increment (4.263e-4 mol)
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55     -comp UO2(am) 0.00550240863910409
56     -comp PuO2    0.000613778686802078
57     -comp AmO2    0.0000381599502541837
58     -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
61     Fe          0.0 4.263e-4
62     Uraninite   0.0 0.0
63     Am(OH)3(am) 0.0 0.0
64
65 SELECTED_OUTPUT
66     -reset false
67     -high_precision true
68     -pH true
69     -pe true
70     -totals Fe U Pu Am C(4) S(6) Ca Mg
71     -equilibrium_phases Fe Uraninite Am(OH)3(am)
72     -solid_solutions MOX
73     -saturation_indices Calcite Siderite Magnetite UO2(am)
74
75 SAVE solution 1
76 SAVE equilibrium_phases 1
77 SAVE gas_phase 1
78 SAVE solid_solutions 1
79
80 END

```

Stage 3 - No Phase.pqi

Equilibration with secondary phases. Equilibrating with no additional phase other than the uraninite and Am(OH)₃(am) control phases.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp      21
5      pH        7.19
6      pe        4

```

A. Input files

```
7      units      mmol/L
8      density    1.002
9      Na         96.57
10     K          0.93
11     Ca         22.21
12     Mg         10.04
13     Alkalinity  2.07
14     Cl         148.9
15     S(6)       5.28 as S04
16     Si         0.22
17     Br         0.3
18     Fe(2)      0.04
19     Sr         0.1
20     -water     0.8
21
22 EQUILIBRIUM_PHASES 1
23     Fe 0.0 4.479e-4
24
25 GAS_PHASE 1
26     -fixed_pressure
27     -pressure   9.86923267
28     -volume     0.2
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g)  0.9996
32
33 SELECTED_OUTPUT
34     -reset false
35     -high_precision true
36     -pH true
37     -pe true
38     -totals Fe C(4) S(6) Ca Mg
39     -equilibrium_phases Fe
40     -saturation_indices Calcite Siderite Magnetite
41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
47
48 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
      Uraninite (U control), Am(OH)3(am) (Am control), plus the post
      -MOX Fe increment (4.263e-4 mol)
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55     -comp UO2(am) 0.00550240863910409
56     -comp PuO2   0.000613778686802078
57     -comp AmO2   0.0000381599502541837
58     -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
```

```

61      Fe          0.0 4.263e-4
62      Uraninite   0.0 0.0
63      Am(OH)3(am) 0.0 0.0
64
65  SELECTED_OUTPUT
66      -reset false
67      -high_precision true
68      -pH true
69      -pe true
70      -totals Fe U Pu Am C(4) S(6) Ca Mg
71      -equilibrium_phases Fe Uraninite Am(OH)3(am)
72      -solid_solutions MOX
73      -saturation_indices Calcite Siderite Magnetite UO2(am)
74
75  SAVE solution 1
76  SAVE equilibrium_phases 1
77  SAVE gas_phase 1
78  SAVE solid_solutions 1
79
80  END
81
82  TITLE Stage 3 - add Phase, carrying forward the ACTUAL remaining
      Fe/Uraninite/Am(OH)3(am) from Stage 2
83
84  USE solution 1
85  USE gas_phase 1
86  USE solid_solutions 1
87
88  PHASES
89  Ankerite
90      CaFe(CO3)2 = Ca+2 + Fe+2 + 2 CO3-2
91      log_k      -20.8732
92      -analytic  6743.140988642074 2.3089611210263445
      -252723.63251182728 -2681.493160205648 9.661065201605685e6
      -0.0008807525923414785 # HP11 + CHNOSZ/OBIGT/SUPCRTBL -
      D08,Z+16
93      -Vm 66.060
94  Chukanovite
95      Fe2(OH)2CO3 + 3.0000 H+ = 2.0000 Fe++ + 1.0000 HCO3- + 2.0000
      H2O
96      log_k      16.216
97      -delta_H 294.6 kJ/mol # Calculated enthalpy of reaction
98
99  EQUILIBRIUM_PHASES 1
100      Fe          0.0 0.0
101      Uraninite   0.0 0.005502397539696082
102      Am(OH)3(am) 0.0 0.00003796812705808989
103
104
105  SELECTED_OUTPUT
106      -reset false
107      -high_precision true
108      -pH true
109      -pe true
110      -totals Fe U Pu Am C(4) S(6) S(-2) Ca Mg
111      -molalities Fe+2 Fe+3 FeCO3 FeSO4 FeHCO3+ FeOH+ Fe(OH)2 FeCl+

```

A. Input files

```
112      H2 U+4 UO2+2 U(OH)4
      -equilibrium_phases Fe Uraninite Am(OH)3(am) Ankerite Calcite
      Chukanovite Cronstedtite-7A Siderite
113      -solid_solutions MOX
114      -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
      -7A Siderite Fe(OH)2 UO2(am)
115
116 END
```

Stage 3 + Ankerite.pqi

Equilibration with secondary phases. Equilibrating with ankerite in addition to the uraninite and $\text{Am}(\text{OH})_3(\text{am})$ control phases.

```
1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp      21
5      pH        7.19
6      pe        4
7      units     mmol/L
8      density   1.002
9      Na        96.57
10     K         0.93
11     Ca        22.21
12     Mg        10.04
13     Alkalinity 2.07
14     Cl        148.9
15     S(6)      5.28 as S04
16     Si        0.22
17     Br        0.3
18     Fe(2)     0.04
19     Sr        0.1
20     -water    0.8
21
22  EQUILIBRIUM_PHASES 1
23     Fe 0.0 4.479e-4
24
25  GAS_PHASE 1
26     -fixed_pressure
27     -pressure   9.86923267
28     -volume    0.2
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g)  0.9996
32
33  SELECTED_OUTPUT
34     -reset false
35     -high_precision true
36     -pH true
37     -pe true
38     -totals Fe C(4) S(6) Ca Mg
39     -equilibrium_phases Fe
40     -saturation_indices Calcite Siderite Magnetite
```

```

41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
47
48 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
    Uraninite (U control), Am(OH)3(am) (Am control), plus the post
    -MOX Fe increment (4.263e-4 mol)
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55     -comp UO2(am) 0.00550240863910409
56     -comp PuO2    0.000613778686802078
57     -comp AmO2    0.0000381599502541837
58     -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
61     Fe          0.0 4.263e-4
62     Uraninite   0.0 0.0
63     Am(OH)3(am) 0.0 0.0
64
65 SELECTED_OUTPUT
66     -reset false
67     -high_precision true
68     -pH true
69     -pe true
70     -totals Fe U Pu Am C(4) S(6) Ca Mg
71     -equilibrium_phases Fe Uraninite Am(OH)3(am)
72     -solid_solutions MOX
73     -saturation_indices Calcite Siderite Magnetite UO2(am)
74
75 SAVE solution 1
76 SAVE equilibrium_phases 1
77 SAVE gas_phase 1
78 SAVE solid_solutions 1
79
80 END
81
82 TITLE Stage 3 - add Ankerite, carrying forward the ACTUAL
    remaining Fe/Uraninite/Am(OH)3(am) from Stage 2
83
84 USE solution 1
85 USE gas_phase 1
86 USE solid_solutions 1
87
88 PHASES
89 Ankerite
90     CaFe(CO3)2 = Ca+2 + Fe+2 + 2 CO3-2
91     log_k      -20.8732
92     -analytic  6743.140988642074 2.3089611210263445
    -252723.63251182728 -2681.493160205648 9.661065201605685e6

```

A. Input files

```
          -0.0008807525923414785 # HP11 + CHNOSZ/OBIGT/SUPCRTBL -
          D08,Z+16
93      -Vm 66.060
94      Chukanovite
95      Fe2(OH)2CO3 + 3.0000 H+ = 2.0000 Fe++ + 1.0000 HCO3- + 2.0000
          H2O
96      log_k 16.216
97      -delta_H 294.6 kJ/mol # Calculated enthalpy of reaction
98
99      EQUILIBRIUM_PHASES 1
100      Fe 0.0 0.0
101      Uraninite 0.0 0.005502397539696082
102      Am(OH)3(am) 0.0 0.00003796812705808989
103      Ankerite 0.0 0.0
104
105
106      SELECTED_OUTPUT
107      -reset false
108      -high_precision true
109      -pH true
110      -pe true
111      -totals Fe U Pu Am C(4) S(6) S(-2) Ca Mg
112      -molalities Fe+2 Fe+3 FeCO3 FeSO4 FeHCO3+ FeOH+ Fe(OH)2 FeCl+
          H2 U+4 UO2+2 U(OH)4
113      -equilibrium_phases Fe Uraninite Am(OH)3(am) Ankerite Calcite
          Chukanovite Cronstedtite-7A Siderite
114      -solid_solutions MOX
115      -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
          -7A Siderite Fe(OH)2 UO2(am)
116
117      END
```

Stage 3 Calcite.pqi

Equilibration with secondary phases. Equilibrating with calcite in addition to the uraninite and Am(OH)₃(am) control phases.

```
1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp 21
5      pH 7.19
6      pe 4
7      units mmol/L
8      density 1.002
9      Na 96.57
10     K 0.93
11     Ca 22.21
12     Mg 10.04
13     Alkalinity 2.07
14     Cl 148.9
15     S(6) 5.28 as S04
16     Si 0.22
17     Br 0.3
```

```

18      Fe(2)      0.04
19      Sr         0.1
20      -water     0.8
21
22 EQUILIBRIUM_PHASES 1
23      Fe 0.0 4.479e-4
24
25 GAS_PHASE 1
26      -fixed_pressure
27      -pressure   9.86923267
28      -volume     0.2
29      -temperature 21.0
30      CO2(g) 0.0004
31      Ar(g)  0.9996
32
33 SELECTED_OUTPUT
34      -reset false
35      -high_precision true
36      -pH true
37      -pe true
38      -totals Fe C(4) S(6) Ca Mg
39      -equilibrium_phases Fe
40      -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
41      -7A Siderite Fe(OH)2 UO2(am)
42
43 SAVE solution 1
44 SAVE equilibrium_phases 1
45 SAVE gas_phase 1
46
47 END
48
49 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
50      Uraninite (U control), Am(OH)3(am) (Am control), plus the post
51      -MOX Fe increment (4.263e-4 mol)
52
53 USE solution 1
54 USE gas_phase 1
55
56 SOLID_SOLUTIONS 1
57 MOX
58      -comp UO2(am) 0.00550240863910409
59      -comp PuO2    0.000613778686802078
60      -comp AmO2    0.0000381599502541837
61      -tempK 294.15
62
63 EQUILIBRIUM_PHASES 1
64      Fe          0.0 4.263e-4
65      Uraninite    0.0 0.0
66      Am(OH)3(am) 0.0 0.0
67
68 SELECTED_OUTPUT
69      -reset false
70      -high_precision true
71      -pH true
72      -pe true
73      -totals Fe U Pu Am C(4) S(6) Ca Mg

```

A. Input files

```
71 -equilibrium_phases Fe Uraninite Am(OH)3(am)
72 -solid_solutions MOX
73 -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
    -7A Siderite Fe(OH)2 UO2(am)
74
75 SAVE solution 1
76 SAVE equilibrium_phases 1
77 SAVE gas_phase 1
78 SAVE solid_solutions 1
79
80 END
81
82 TITLE Stage 3 - add Calcite, carrying forward the ACTUAL remaining
    Fe/Uraninite/Am(OH)3(am) from Stage 2
83
84 USE solution 1
85 USE gas_phase 1
86 USE solid_solutions 1
87
88 PHASES
89 Ankerite
90 CaFe(CO3)2 = Ca+2 + Fe+2 + 2 CO3-2
91 log_k -20.8732
92 -analytic 6743.140988642074 2.3089611210263445
    -252723.63251182728 -2681.493160205648 9.661065201605685e6
    -0.0008807525923414785 # HP11 + CHNOSZ/OBIGT/SUPCRTBL -
    D08,Z+16
93 -Vm 66.060
94 Chukanovite
95 Fe2(OH)2CO3 + 3.0000 H+ = 2.0000 Fe++ + 1.0000 HCO3- + 2.0000
    H2O
96 log_k 16.216
97 -delta_H 294.6 kJ/mol # Calculated enthalpy of reaction
98
99 EQUILIBRIUM_PHASES 1
100 Fe 0.0 0.0
101 Uraninite 0.0 0.005502397539696082
102 Am(OH)3(am) 0.0 0.00003796812705808989
103 Calcite 0.0 0.0
104
105 SELECTED_OUTPUT
106 -reset false
107 -high_precision true
108 -pH true
109 -pe true
110 -totals Fe U Pu Am C(4) S(6) S(-2) Ca Mg
111 -molalities Fe+2 Fe+3 FeCO3 FeSO4 FeHCO3+ FeOH+ Fe(OH)2 FeCl+
    H2 U+4 UO2+2 U(OH)4
112 -equilibrium_phases Fe Uraninite Am(OH)3(am) Ankerite Calcite
    Chukanovite Cronstedtite-7A Siderite
113 -solid_solutions MOX
114 -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
    -7A Siderite Fe(OH)2 UO2(am)
115
116 END
```

Stage 3 + Chukanovite.pqi

Equilibration with secondary phases. Equilibrating with chukanovite in addition to the uraninite and Am(OH)₃(am) control phases.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp      21
5      pH        7.19
6      pe        4
7      units     mmol/L
8      density   1.002
9      Na        96.57
10     K          0.93
11     Ca        22.21
12     Mg        10.04
13     Alkalinity 2.07
14     Cl        148.9
15     S(6)      5.28 as S04
16     Si        0.22
17     Br        0.3
18     Fe(2)     0.04
19     Sr        0.1
20     -water    0.8
21
22  EQUILIBRIUM_PHASES 1
23     Fe 0.0 4.479e-4
24
25  GAS_PHASE 1
26     -fixed_pressure
27     -pressure   9.86923267
28     -volume     0.2
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g)  0.9996
32
33  SELECTED_OUTPUT
34     -reset false
35     -high_precision true
36     -pH true
37     -pe true
38     -totals Fe C(4) S(6) Ca Mg
39     -equilibrium_phases Fe
40     -saturation_indices Calcite Siderite Magnetite
41
42  SAVE solution 1
43  SAVE equilibrium_phases 1
44  SAVE gas_phase 1
45
46  END
47
48  TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
   Uraninite (U control), Am(OH)3(am) (Am control), plus the post
   -MOX Fe increment (4.263e-4 mol)

```

A. Input files

```
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55     -comp UO2(am) 0.00550240863910409
56     -comp PuO2    0.000613778686802078
57     -comp AmO2    0.0000381599502541837
58     -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
61     Fe          0.0 4.263e-4
62     Uraninite   0.0 0.0
63     Am(OH)3(am) 0.0 0.0
64
65 SELECTED_OUTPUT
66     -reset false
67     -high_precision true
68     -pH true
69     -pe true
70     -totals Fe U Pu Am C(4) S(6) Ca Mg
71     -equilibrium_phases Fe Uraninite Am(OH)3(am)
72     -solid_solutions MOX
73     -saturation_indices Calcite Siderite Magnetite UO2(am)
74
75 SAVE solution 1
76 SAVE equilibrium_phases 1
77 SAVE gas_phase 1
78 SAVE solid_solutions 1
79
80 END
81
82 TITLE Stage 3 - add Chukanovite, carrying forward the ACTUAL
      remaining Fe/Uraninite/Am(OH)3(am) from Stage 2
83
84 USE solution 1
85 USE gas_phase 1
86 USE solid_solutions 1
87
88 PHASES
89 Ankerite
90     CaFe(CO3)2 = Ca+2 + Fe+2 + 2 CO3-2
91     log_k      -20.8732
92     -analytic  6743.140988642074 2.3089611210263445
      -252723.63251182728 -2681.493160205648 9.661065201605685e6
      -0.0008807525923414785 # HP11 + CHNOSZ/OBIGT/SUPCRTBL -
      D08,Z+16
93     -Vm 66.060
94 Chukanovite
95     Fe2(OH)2CO3 + 3.0000 H+ = 2.0000 Fe++ + 1.0000 HCO3- + 2.0000
      H2O
96     log_k      16.216
97     -delta_H 294.6 kJ/mol # Calculated enthalpy of reaction
98
99 EQUILIBRIUM_PHASES 1
```

```

100      Fe          0.0 0.0
101      Uraninite   0.0 0.005502397539696082
102      Am(OH)3(am) 0.0 0.00003796812705808989
103      Chukanovite 0.0 0.0
104
105      SELECTED_OUTPUT
106      -reset false
107      -high_precision true
108      -pH true
109      -pe true
110      -totals Fe U Pu Am C(4) S(6) S(-2) Ca Mg
111      -molalities Fe+2 Fe+3 FeCO3 FeSO4 FeHCO3+ FeOH+ Fe(OH)2 FeCl+
112      H2 U+4 UO2+2 U(OH)4
113      -equilibrium_phases Fe Uraninite Am(OH)3(am) Ankerite Calcite
114      Chukanovite Cronstedtite-7A Siderite
115      -solid_solutions MOX
116      -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
117      -7A Siderite Fe(OH)2 UO2(am)
118
119      END

```

Stage 3 + Cronstedtite.pqi

Equilibration with secondary phases. Equilibrating with cronstedtite in addition to the uraninite and Am(OH)₃(am) control phases.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
2      corrosion (pre-MOX, 101-day phase)
3
4  SOLUTION 1 Forsmark_groundwater
5      temp      21
6      pH        7.19
7      pe        4
8      units     mmol/L
9      density   1.002
10     Na        96.57
11     K         0.93
12     Ca        22.21
13     Mg        10.04
14     Alkalinity 2.07
15     Cl        148.9
16     S(6)      5.28 as SO4
17     Si        0.22
18     Br        0.3
19     Fe(2)     0.04
20     Sr        0.1
21     -water    0.8
22
23  EQUILIBRIUM_PHASES 1
24     Fe 0.0 4.479e-4
25
26  GAS_PHASE 1
27     -fixed_pressure
28     -pressure    9.86923267
29     -volume      0.2

```

A. Input files

```
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g) 0.9996
32
33     SELECTED_OUTPUT
34         -reset false
35         -high_precision true
36         -pH true
37         -pe true
38         -totals Fe C(4) S(6) Ca Mg
39         -equilibrium_phases Fe
40         -saturation_indices Calcite Siderite Magnetite
41
42     SAVE solution 1
43     SAVE equilibrium_phases 1
44     SAVE gas_phase 1
45
46     END
47
48     TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
49         Uraninite (U control), Am(OH)3(am) (Am control), plus the post
50         -MOX Fe increment (4.263e-4 mol)
51
52     USE solution 1
53     USE gas_phase 1
54
55     SOLID_SOLUTIONS 1
56     MOX
57         -comp UO2(am) 0.00550240863910409
58         -comp PuO2 0.000613778686802078
59         -comp AmO2 0.0000381599502541837
60         -tempK 294.15
61
62     EQUILIBRIUM_PHASES 1
63         Fe 0.0 4.263e-4
64         Uraninite 0.0 0.0
65         Am(OH)3(am) 0.0 0.0
66
67     SELECTED_OUTPUT
68         -reset false
69         -high_precision true
70         -pH true
71         -pe true
72         -totals Fe U Pu Am C(4) S(6) Ca Mg
73         -equilibrium_phases Fe Uraninite Am(OH)3(am)
74         -solid_solutions MOX
75         -saturation_indices Calcite Siderite Magnetite UO2(am)
76
77     SAVE solution 1
78     SAVE equilibrium_phases 1
79     SAVE gas_phase 1
80     SAVE solid_solutions 1
81
82     END
83
84     TITLE Stage 3 - add Cronstedtite, carrying forward the ACTUAL
```

```

83     remaining Fe/Uraninite/Am(OH)3(am) from Stage 2
84 USE solution 1
85 USE gas_phase 1
86 USE solid_solutions 1
87
88 PHASES
89 Ankerite
90   CaFe(CO3)2 = Ca+2 + Fe+2 + 2 CO3-2
91   log_k      -20.8732
92   -analytic  6743.140988642074 2.3089611210263445
93             -252723.63251182728 -2681.493160205648 9.661065201605685e6
94             -0.0008807525923414785 # HP11 + CHNOSZ/OBIGT/SUPCRTBL -
95             D08,Z+16
96   -Vm 66.060
97 Chukanovite
98   Fe2(OH)2CO3 + 3.0000 H+ = 2.0000 Fe++ + 1.0000 HCO3- + 2.0000
99   H2O
100  log_k      16.216
101  -delta_H 294.6 kJ/mol # Calculated enthalpy of reaction
102
103 EQUILIBRIUM_PHASES 1
104   Fe          0.0 0.0
105   Uraninite   0.0 0.005502397539696082
106   Am(OH)3(am) 0.0 0.00003796812705808989
107   Cronstedtite-7A 0.0 0.0
108
109 SELECTED_OUTPUT
110   -reset false
111   -high_precision true
112   -pH true
113   -pe true
114   -totals Fe U Pu Am C(4) S(6) S(-2) Ca Mg
115   -molalities Fe+2 Fe+3 FeCO3 FeSO4 FeHCO3+ FeOH+ Fe(OH)2 FeCl+
116   H2 U+4 UO2+2 U(OH)4
117   -equilibrium_phases Fe Uraninite Am(OH)3(am) Ankerite Calcite
118   Chukanovite Cronstedtite-7A Siderite
119   -solid_solutions MOX
120   -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
121   -7A Siderite Fe(OH)2 UO2(am)
122
123 END

```

Stage 3 + Siderite.pqi

Equilibration with secondary phases. Equilibrating with siderite in addition to the uraninite and Am(OH)₃(am) control phases.

```

1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
2    corrosion (pre-MOX, 101-day phase)
3
4  SOLUTION 1 Forsmark_groundwater
5    temp      21
6    pH        7.19
7    pe        4

```

A. Input files

```
7      units      mmol/L
8      density    1.002
9      Na         96.57
10     K          0.93
11     Ca         22.21
12     Mg         10.04
13     Alkalinity  2.07
14     Cl         148.9
15     S(6)       5.28 as S04
16     Si         0.22
17     Br         0.3
18     Fe(2)      0.04
19     Sr         0.1
20     -water     0.8
21
22 EQUILIBRIUM_PHASES 1
23     Fe 0.0 4.479e-4
24
25 GAS_PHASE 1
26     -fixed_pressure
27     -pressure   9.86923267
28     -volume     0.2
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g)  0.9996
32
33 SELECTED_OUTPUT
34     -reset false
35     -high_precision true
36     -pH true
37     -pe true
38     -totals Fe C(4) S(6) Ca Mg
39     -equilibrium_phases Fe
40     -saturation_indices Calcite Siderite Magnetite
41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
47
48 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
      Uraninite (U control), Am(OH)3(am) (Am control), plus the post
      -MOX Fe increment (4.263e-4 mol)
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55     -comp UO2(am) 0.00550240863910409
56     -comp PuO2   0.000613778686802078
57     -comp AmO2   0.0000381599502541837
58     -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
```

```

61      Fe          0.0 4.263e-4
62      Uraninite   0.0 0.0
63      Am(OH)3(am) 0.0 0.0
64
65  SELECTED_OUTPUT
66      -reset false
67      -high_precision true
68      -pH true
69      -pe true
70      -totals Fe U Pu Am C(4) S(6) Ca Mg
71      -equilibrium_phases Fe Uraninite Am(OH)3(am)
72      -solid_solutions MOX
73      -saturation_indices Calcite Siderite Magnetite UO2(am)
74
75  SAVE solution 1
76  SAVE equilibrium_phases 1
77  SAVE gas_phase 1
78  SAVE solid_solutions 1
79
80  END
81
82  TITLE Stage 3 - add Siderite, carrying forward the ACTUAL
      remaining Fe/Uraninite/Am(OH)3(am) from Stage 2
83
84  USE solution 1
85  USE gas_phase 1
86  USE solid_solutions 1
87
88  PHASES
89  Ankerite
90      CaFe(CO3)2 = Ca+2 + Fe+2 + 2 CO3-2
91      log_k      -20.8732
92      -analytic  6743.140988642074 2.3089611210263445
      -252723.63251182728 -2681.493160205648 9.661065201605685e6
      -0.0008807525923414785 # HP11 + CHNOSZ/OBIGT/SUPCRTBL -
      D08,Z+16
93      -Vm 66.060
94  Chukanovite
95      Fe2(OH)2CO3 + 3.0000 H+ = 2.0000 Fe++ + 1.0000 HCO3- + 2.0000
      H2O
96      log_k      16.216
97      -delta_H 294.6 kJ/mol # Calculated enthalpy of reaction
98
99  EQUILIBRIUM_PHASES 1
100      Fe          0.0 0.0
101      Uraninite   0.0 0.005502397539696082
102      Am(OH)3(am) 0.0 0.00003796812705808989
103      Siderite    0.0 0.0
104
105  SELECTED_OUTPUT
106      -reset false
107      -high_precision true
108      -pH true
109      -pe true
110      -totals Fe U Pu Am C(4) S(6) S(-2) Ca Mg
111      -molalities Fe+2 Fe+3 FeCO3 FeSO4 FeHCO3+ FeOH+ Fe(OH)2 FeCl+

```

A. Input files

```
112      H2 U+4 UO2+2 U(OH)4
      -equilibrium_phases Fe Uraninite Am(OH)3(am) Ankerite Calcite
      Chukanovite Cronstedtite-7A Siderite
113      -solid_solutions MOX
114      -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
      -7A Siderite Fe(OH)2 UO2(am)
115
116 END
```

Stage 3 + Phase1+Phase2.pqi

Equilibration with secondary phases combined. Equilibrating with Phase 1 and Phase 2 in addition to the uraninite and Am(OH)₃(am) control phases. Phase 1 and Phase 2 can be any phases used above.

```
1  TITLE Stage 1 - Groundwater (with Table 2 baseline Fe(II)) + Fe
   corrosion (pre-MOX, 101-day phase)
2
3  SOLUTION 1 Forsmark_groundwater
4      temp      21
5      pH        7.19
6      pe        4
7      units     mmol/L
8      density   1.002
9      Na        96.57
10     K         0.93
11     Ca        22.21
12     Mg        10.04
13     Alkalinity 2.07
14     Cl        148.9
15     S(6)      5.28 as S04
16     Si        0.22
17     Br        0.3
18     Fe(2)     0.04
19     Sr        0.1
20     -water    0.8
21
22  EQUILIBRIUM_PHASES 1
23     Fe 0.0 4.479e-4
24
25  GAS_PHASE 1
26     -fixed_pressure
27     -pressure   9.86923267
28     -volume     0.2
29     -temperature 21.0
30     CO2(g) 0.0004
31     Ar(g)  0.9996
32
33  SELECTED_OUTPUT
34     -reset false
35     -high_precision true
36     -pH true
37     -pe true
38     -totals Fe C(4) S(6) Ca Mg
```

```

39     -equilibrium_phases Fe
40     -saturation_indices Calcite Siderite Magnetite
41
42 SAVE solution 1
43 SAVE equilibrium_phases 1
44 SAVE gas_phase 1
45
46 END
47
48 TITLE Stage 2 - MOX pellet introduced: add MOX solid solution,
      Uraninite (U control), Am(OH)3(am) (Am control), plus the post
      -MOX Fe increment (4.263e-4 mol)
49
50 USE solution 1
51 USE gas_phase 1
52
53 SOLID_SOLUTIONS 1
54 MOX
55     -comp UO2(am) 0.00550240863910409
56     -comp PuO2    0.000613778686802078
57     -comp AmO2    0.0000381599502541837
58     -tempK 294.15
59
60 EQUILIBRIUM_PHASES 1
61     Fe          0.0 4.263e-4
62     Uraninite   0.0 0.0
63     Am(OH)3(am) 0.0 0.0
64
65 SELECTED_OUTPUT
66     -reset false
67     -high_precision true
68     -pH true
69     -pe true
70     -totals Fe U Pu Am C(4) S(6) Ca Mg
71     -equilibrium_phases Fe Uraninite Am(OH)3(am)
72     -solid_solutions MOX
73     -saturation_indices Calcite Siderite Magnetite UO2(am)
74
75 SAVE solution 1
76 SAVE equilibrium_phases 1
77 SAVE gas_phase 1
78 SAVE solid_solutions 1
79
80 END
81
82 TITLE Stage 3 - add Phase 1 and Phase 2, carrying forward the
      ACTUAL remaining Fe/Uraninite/Am(OH)3(am) from Stage 2
83
84 USE solution 1
85 USE gas_phase 1
86 USE solid_solutions 1
87
88 PHASES
89 Ankerite
90     CaFe(CO3)2 = Ca+2 + Fe+2 + 2 CO3-2
91     log_k      -20.8732

```

A. Input files

```
92      -analytic 6743.140988642074 2.3089611210263445
          -252723.63251182728 -2681.493160205648 9.661065201605685e6
          -0.0008807525923414785 # HP11 + CHNOSZ/OBIGT/SUPCRTBL -
          D08,Z+16
93      -Vm 66.060
94      Chukanovite
95      Fe2(OH)2CO3 + 3.0000 H+ = 2.0000 Fe++ + 1.0000 HCO3- + 2.0000
          H2O
96      log_k 16.216
97      -delta_H 294.6 kJ/mol # Calculated enthalpy of reaction
98
99      EQUILIBRIUM_PHASES 1
100      Fe 0.0 0.0
101      Uraninite 0.0 0.005502397539696082
102      Am(OH)3(am) 0.0 0.00003796812705808989
103      Phase 1 0.0 0.0
104      Phase 2 0.0 0.0
105
106      SELECTED_OUTPUT
107      -reset false
108      -high_precision true
109      -pH true
110      -pe true
111      -totals Fe U Pu Am C(4) S(6) S(-2) Ca Mg
112      -molalities Fe+2 Fe+3 FeCO3 FeSO4 FeHCO3+ FeOH+ Fe(OH)2 FeCl+
          H2 U+4 UO2+2 U(OH)4
113      -equilibrium_phases Fe Uraninite Am(OH)3(am) Ankerite Calcite
          Chukanovite Cronstedtite-7A Siderite
114      -solid_solutions MOX
115      -saturation_indices Ankerite Calcite Chukanovite Cronstedtite
          -7A Siderite Fe(OH)2 UO2(am)
116
117      END
```

B

Database modifications

For chukanovite ΔH was calculated for the dissolution reaction included, and for ankerite the file was found in full. ΔH_f values for H_2O , H^+ , Ca^{2+} , Fe^{2+} and CO_3^{2-} came from [47].

Ankerite

For ankerite, the input file was found in full [42].

```
1 Ankerite
2   CaFe(CO3)2 = +1.0000 Ca++ + 1.0000 Fe++ + 2.0000 CO3--
3   log_k   -20.8732 # HP11 + CHNOSZ/OBIGT/SUPCRTBL - D08,Z+16
4   -analytic 6743.140988642074 2.3089611210263445
        -252723.63251182728 -2681.493160205648 9.661065201605685
        e6 -0.0008807525923414785 # HP11 + CHNOSZ/OBIGT/SUPCRTBL
        - D08,Z+16
5   -Vm      66.060 # HP11
```

Chukanovite

For chukanovite, log K and ΔH_f were found in [43].

```
1 Chukanovite
2   Fe2(OH)2CO3 + 3.0000 H+ = 2.0000 Fe++ + 1.0000 HCO3- + 2.0000
        H2O
3   log_k   16.216
4   -delta_H 294.6   kJ/mol # Calculated enthalpy of reaction
5   # Enthalpy of formation: -1149.8 kJ/mol
```

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