Co-funded by the







DISCO

Grant Agreement: 755443

DELIVERABLE D5.7

Modeling of U_{0.73}Pu_{0.27}O₂ radiolytic dissolution as a simulant of the alteration of MOX fuel matrices in an underground disposal cell

Laurent DE WINDT & Patrick GOBLET (ARMINES, MINES ParisTech), Valentin KERLEGUER (CEA, MINES ParisTech) & Christophe JEGOU (CEA)

Date of issue of this report: 30/07/2021

Report number of pages: 71

Start date of project: 01/06/2017

Duration: 48 Months

Project co-funded by the European Commission under the Euratom Research and Training Programme on Nuclear Energy within the Horizon 2020 Framework Programme					
Dissemination Level					
PU	Public	Х			
PP	Restricted to other programme participants (including the Commission Services)				
RE	Restricted to a group specified by the partners of the Disco project				
CO	Confidential, only for partners of the Disco project				

Table of content

<u>SUN</u>	IMARY	5
<u>1</u>	CONTEXT AND OBJECTIVES	7
1.1	MOX vs. UOX LONG-TERM CORROSION IN THE DISPOSAL ENVIRONMENT	7
1.2	CHEMICAL AND REACTIVE TRANSPORT MODELING OF UOX AND MOX ALTERATION	8
1.3	OBJECTIVES AND CONTENT OF THIS FINAL REPORT	9
<u>2</u>	MAIN EQUATIONS OF THE CHESS/HYTEC CODES AND THERMODYNAMIC DATA	13
2.1	MAIN CHEMICAL EQUATIONS	13
2.2	REACTIVE TRANSPORT EQUATION	14
2.3	CHEMICAL THERMODYNAMIC DATA	14
<u>3</u>	MODELING OF U _{0.73} PU _{0.27} O ₂ ALTERATION UNDER SELF α -RADIOLYSIS	17
3.1	MATERIAL AND LEACHING EXPERIMENT	17
3.1.1	L U _{0.73} PU _{0.27} O ₂ PELLET	17
3.1.2	2 BATCH EXPERIMENT	18
3.2	MODELING OF KINETIC PROCESSES	18
3.2.1	H ₂ O ₂ as the predominant alpha radiolytic species	18
3.2.2	2 RADIOLYTIC PRODUCTION OF H ₂ O ₂	19
3.2.3	RADIOLYTIC OXIDATION OF $U_{0.73}PU_{0.27}O_2$ by H_2O_2	19
3.2.4	H_2O_2 DISPROPORTIONATION ONTO THE $U_{0.73}PU_{0.27}O_2$ SURFACE	21
3.3	MODELING OF GEOCHEMICAL EVOLUTION AND U/PU RELEASE	22
3.3.1	Model A with a constant disproportionation rate of H_2O_2	22
3.3.2	Model B with an increasing disproportionation rate of H_2O_2 with PU enrichment	25
3.4	MODELING OF THE FEEDBACK EFFECT OF PU(OH) ₄ FORMATION ON KINETICS	26
<u>4</u> [MODELING OF U0.73PU0.27O2 ALTERATION IN SYNTHETIC CLAYSTONE WATER AND THE P	RESENCE
<u>OF N</u>	/IETALLIC IRON	29
4.1	MATERIALS AND EXPERIMENTAL SET-UP	29
4.1.1	L U _{0.73} PU _{0.27} O ₂ Pellet, COX synthetic water and iron foil	29
4.1.2	2 LEACHING CELL SET-UP	29
4.2	MODELING GRID, BOUNDARY CONDITIONS AND DIFFUSION COEFFICIENT	30
4.3	MODELING OF KINETIC PROCESSES	31
4.3.1	Prerequisite on the kinetics of $Fe(II)/H_2O_2$ reaction in solution	31
4.3.2	MODELING OF H_2O_2 production and disproportionation by the $U_{0.73}PU_{0.27}O_2$ surface	33
4.3.3	RADIOLYTIC OXIDATION OF $U_{0.73}PU_{0.27}O_2$ by H_2O_2	34
4.3.4	DISSOLUTION OF $U_{0.73}PU_{0.27}O_2$ UNDER REDUCING CONDITIONS	34
4.3.5	ANOXIC CORROSION OF METALLIC IRON	34
4.3.6	S SECONDARY SOLID PHASES	35
4.4	MODELING OF THE SOLUTION CHEMISTRY	35

4.5	MODELING OF IRON CORROSION	36
4.5.1	IRON CORROSION PRODUCTS	36
4.5.2	IRON DISSOLVED CONCENTRATION	38
4.6	SCAVENGING EFFECT OF FE(II) VERSUS THE H ₂ O ₂ PLUME	39
4.6.1	BASE CASE MODELING	39
4.6.2	Sensitivity analysis vs. The intensity of the H_2O_2 radiolytic effective production	41
4.7	MODELING URANIUM AND PLUTONIUM RELEASES	43
4.7.1	URANIUM DISSOLVED CONCENTRATION AND SOLUBILITY-CONTROLLING PHASE	43
4.7.2	PLUTONIUM DISSOLVED CONCENTRATION AND SOLUBILITY-CONTROLLING PHASE	46
4.8	SUMMARY OF THE FULLY COUPLED MECHANISMS	49
E 11		E1
<u>5 U</u>	P-SCALING OF THE MODEL TO A GENERIC DISPOSAL CELL OF SPENT MOX FUELS	
5.1	GENERIC DISPOSAL CELL OF SPENT MOX FUELS	51
5.1.1	CONFIGURATION OF THE DISPOSAL CELL	51
5.1.2	PROPERTIES OF THE DISPOSAL CELL COMPONENTS	53
5.2	MODELING APPROACH AND SCENARIOS	54
5.2.1	KINETICS OF THE MAIN PROCESSES AND SIMULATION GRID	54
5.2.2	Modeling scenarios vs. The intensity of the $lpha$ -radiolysis and corrosion products	55
5.3	MODELING RESULTS AND DISCUSSION	57
5.3.1	Modeling of the redox front and H_2O_2 scavenging by Fe(II) without MOX dissolution	57
5.3.2	MODELING OF THE MOX DISSOLUTION	60
<u>6</u> <u>C</u>	ONCLUSION AND PERSPECTIVES	63
<u>ACKN</u>	IOWLEDGEMENT	65
REFE	RENCES	67

Summary

The present study brought insights into two main objectives of the DISCO project. The first goal was to assess whether novel types of fuel (MOX in the present study) behave like the conventional UOX ones. The second objective was to better understand the dissolution of spent fuel matrix under conditions representative of failed containers (carbon steel in the present study) under reducing repository environments. The present study assumed that the host rock consisted of the Callovo-Oxfordian (COx) claystone.

Chemical and reactive transport models were been developed and validated from leaching experiments of a non-irradiated homogenous MOX pellet ($U_{0.73}Pu_{0.27}O_2$). The Pu content and isotopy generates an alpha activity equivalent to 50-year old spent fuel MOX at a burn-up of 47.5 GWd.t⁻¹. The first experiment was performed in carbonated water to get the intrinsic kinetics of dissolution, and the second one in synthetic COx claystone groundwater representative of the French disposal site in the presence of an iron foil simulating the steel container. The latter experiment was performed by CEA in the WP4 of DISCO. The models took into account the kinetics of hydrogen peroxide (H₂O₂) radiolytic production and disproportionation at the MOX pellet surface, the kinetics of the oxidative dissolution of the MOX matrix by H₂O₂, the kinetics of reducing dissolution of the MOX matrix, and the kinetics of anoxic corrosion of the iron foil. A large set of reactions at thermodynamic equilibrium were considered by using the ThermoChimie database, in particular the redox of iron, plutonium and uranium species.

The incongruent release of uranium and plutonium controlled by the precipitation of an amorphous $Pu(OH)_4$ altered layer, and the high disproportionation of H_2O_2 by the $U_{0.73}Pu_{0.27}O_2$ surface were correctly modeled. The model helped to interpret the key geochemical and mineralogical processes, as well as the U and Pu chemistry. Both experimental and modeling results shown that the release of uranium in groundwater in the presence of metallic iron became very significantly lowered compared to carbonated water conditions. The Fe(II) released in solution by the iron foil anoxic corrosion consumed H_2O_2 produced by alpha-radiolysis of water. This redox reaction occurred where radiolytic H_2O_2 was produced, i.e. on the surface of the MOX pellets. The redox product Fe(III) precipitated immediately onto the MOX pellets as magnetite. The oxidative dissolution was strongly inhibited despite a high alpha activity due to plutonium. The release of uranium and plutonium were controlled by $UO_2.2H_2O$ and $Pu(OH)_4$, respectively. Chukanovite and aragonite precipitated on the iron foil during the anoxic corrosion.

The reactive transport model that had been validated on lab experiments was then up-scaled to a disposal cell of spent MOX fuel assemblies. The generic configuration was derived from the present French waste concept for vitrified high-level waste. One single MOX assembly is inserted in carbon steel overpack. The overpack is directly placed in a carbon steel liner within the COx host rock. The full mass of metallic iron Fe(0) were assumed to be corroded into either chukanovite or siderite, respectively corresponding to high or low dissolved Fe(II)concentrations. The purpose of this modeling was to perform mass-balance simulations at the scale of a disposal cell between the diffusive flux of radiolytic H_2O_2 and the diffusive flux of the reducing scavenger Fe(II). Two equivalent durations of alpha decay and radiolytic productions were studied, the present 50-year case and a 1000-year equivalent of decay. In the 50-y case, the diffusive flux of dissolved Fe(II) is not sufficiently high. The redox front occurred at the very boundary of the assembly whereby the steel corrosion products represented a large mineral stock of reducing Fe(II) in mass for a very long duration. The redox potential was clearly oxidizing in the assembly zone and reducing in the corroded steel and claystone. For the equivalent 2000-year α -activity, there was a complete exhaustion of H₂O₂ everywhere in the near-field of the disposal cell. The processes were similar to what had been modeled in the leaching cell experiments. Eventually, it is worth mentioning that the Fe(II) reactivity has to be seen as a complementary beneficial action to the well-known H₂ scavenging effect that would probably be the dominant process.

In comparison with the experimental results of Odorowski et al. (2016) on α -doped UO₂, the plutonium content made the solid solution U_{0.73}Pu_{0.27}O₂ more resistant than UO₂ towards leaching. Despite a higher alpha activity due to the higher plutonium content, the release of uranium was lower and the consumption of H₂O₂ was higher. The experiments and modeling of the more complete system with the synthetic claystone water and the iron foil did not show any significance differences between the α -doped UO₂ and U_{0.73}Pu_{0.27}O₂ MOX pellets.

1 Context and objectives

1.1 MOX vs. UOX long-term corrosion in the disposal environment

MOX (mixed plutonium and uranium oxide) fuels have become more frequent in the past years and are now commonly used in several European nuclear reactors. The direct disposal of irradiated MOX fuels in deep geological repositories is, therefore, a major societal issue. This option requires a thorough knowledge of the processes which may lead to any releases of radionuclides into the biosphere. The geologic disposal of spent MOX fuels is still an open option in France (vs. reprocessing). The French National Radioactive Waste Management Agency (Andra) has selected a Callovo-Oxfordian (COx) claystone formation for the deep repository of radioactive waste. The claystone reducing environment is interesting due to the low solubility of uranium dioxide (UO₂) under such conditions (around 10⁻⁹ mol.L⁻¹) due to a thermodynamic control of the alteration by the formation of UO₂:2H₂O(am) without any changes in the oxidation state of uranium.

However, when assessing the long-term behavior of spent nuclear fuels (irradiated MOx fuels or irradiated UO₂ fuels), one needs to consider both alpha irradiation (predominant on the long term) and beta/gamma irradiation of long-lived actinides, activation and fission products. Radiolysis of water in the near field is accompanied by the formation of equimolar amounts of oxidizing and reducing species. Due to the relatively high reactivity of oxidizing radiolysis products, in particular H₂O₂, compared to the reactivity of the main reducing radiolysis product H₂, essentially an oxidative environment is expected to result from the radiolysis in the close vicinity of spent nuclear fuels (Shoesmith, 2000; Ewing, 2015). Provided that the alpha radiolysis is above a threshold of activity (Poinssot et al., 2005), the transformation rate of the essentially insoluble U(IV) in the fuel matrix to the much more soluble oxidized U(VI) compounds is a critical issue because actinides and fission products are entrapped in the U₁. _xPu_xO₂ matrix. It will be responsible for the long-term radionuclide releases beyond the instant release fraction (IRF). This sequence of mechanisms is known as the radiolytic dissolution (Shoesmith, 2000; Ewing, 2015).

In the hypothesis of direct disposal of spent fuel, whether the knowledge acquired for UOX fuels (Ewing, 2015) can be transferred to MOX fuels is still a debated issue. The activity of the MOX is higher but the resistance of Pu-enriched agglomerates specifically found in MOX fuels is expected to play a beneficial role. Typically, the result of Odorowski et al. (2016) indicated a very fast dissolution of UO₂ grains, likely due to the high alpha-activity induced by the surrounding plutonium agglomerates. On the contrary, the plutonium-enriched agglomerates were not altered over the leaching. It is consistent with the stabilizing effect of the plutonium on the oxidation of the fluorite matrix (Jégou et al., 2010). Bauhn et al. (2018) also concluded that plutonium led to a higher stability in high-Pu content heterogeneous MOX (24%). From a scientific perspective, the understanding of the properties of Pu-enriched agglomerates can be addressed by studying simpler homogeneous MOX materials.

In recent years, there has been an increasing focus on ensuring that data and models are capable of supporting the long-term performance assessment of geological repositories (De Windt and Spycher, 2019). This means that spent nuclear fuel experiments must be done under repository-like conditions and using materials representative of those expected in the repository. As a main issue there is a need to understand the behavior of the fuel in truly reducing conditions imposed by the corrosion of the metallic iron containers encapsulating the waste. In this context, it is well known that the presence of redox active species like hydrogen in the environmental water may scavenge the radiolytic dissolution od spent-fuel (e.g. Spahiu et al., 2004; Ewing, 2015). Whether iron may also counteract the water radiolysis effects has been studied more recently (Amme et al., 2012; Liu et al., 2016; Odorowski et al., 2017). In particular, there is a need to understand the behavior of the fuel in truly reducing conditions imposed by the corrosion of the metallic iron containers encapsulating the waste. In this context, recent laboratory experiments (Odorowski et al., 2017) investigate the effect of ferrous iron (Fe²⁺), a reducing aqueous species coming from the corrosion of the steel canisters, on the oxidative dissolution of UO₂. The studies showed that the consumption of H₂O₂ by Fe(II) at the uranium fuel pellet's surface prevented UO₂ dissolution by H₂O₂ and leading to Fe(III)-(oxy)hydroxide precipitation on the UO₂ surface.

1.2 Chemical and reactive transport modeling of UOX and MOX alteration

Reactive transport models, by definition, can simulate the transport and chemical reactions of multiple solutes (and gases) and their chemical interaction with rocks over various time and spatial scales. Reactive transport models have, therefore, become an invaluable component in supporting lab experiments as well as in assessing the potential performance of a repository, which requires understanding how the various barriers evolve through space and time (Bildstein et al., 2019; De Windt and Spycher, 2019). Reactive transport modeling is also capable of great generality and flexibility and can be applied to a wide range of natural processes, as well as to engineering issues such as metal corrosion or bentonite alteration. Although the use of reactive transport modeling for deterministic predictive simulations is limited, these models can help constrain future repository behavior with sensitivity analyses and scenario modeling of the various disposal subsystems.

The reactive transport code HYTEC has already been extensively used for modeling the interactions and evolution of the components of radioactive waste geologic disposals, such as for instance the dissolution of nuclear glass (Debure et al., 2013), the oxidative transient phase (De Windt et al., 2014), the cement/clay interactions (De Windt et al., 2004). With respect to the present study, the oxidative dissolution of spent UOX fuel in a disposal cell have been investigated with HYTEC (De Windt et al., 2003 & 2005). De Windt et al. (2005) included in their model corroded C-steel canisters, bentonite backfills and a clayey host-rock. The UOX evolution took into account radiolytic-enhanced corrosion and long-term solubility-controlled dissolution. The calculations show that spent-fuel dissolution has no significant alteration effect on the near-field components except an oxidizing plume in the vicinity of the waste packages. The dissolved uranyl species, partly precipitate as schoepite on the fuel pellets, and partly diffuse in the near-field where magnetite and pyrite reduce U(VI) to yield uraninite precipitation.

The modeling of processes of the dissolution of UO_2 -based materials under waste disposal conditions have already been undertaken by several other reactive transport codes. Wu et al. (2014) have tackled with the influence of the alpha water radiolysis using a full radiolytic reaction kinetic set using the code COMSOL Multiphysics at 1 mm spatial scale around the UO2 pellet. Their model demonstrated that H₂O₂ is the dominant oxidant and the decrease of H₂O₂ by reaction with Fe²⁺ can significantly reduce UO₂ corrosion rate. They also showed that UO₂ dissolution was very sensitive to the concentrations of the competing dissolved species Fe^{2+} and H_2 brought into the solution by the metallic iron anoxic corrosion. Liu et al. (2017) applied an improved version of the model to predict the corrosion rate of α -doped UO₂ in a failed nuclear waste container in C-steel. The authors demonstrated that the UO₂ dissolution rate is dependent on the oxidant H₂O₂. Their calculations also showed that the radiolytically produced H₂ had the most effective influence in decreasing the rate of UOX fuel corrosion to negligible level on the long term. The H₂O₂ decomposition ratio, the intensity of the dose rate, and the surface coverage of ε particles had only a short-term effect. Very recently, Liu et al. (2020) performed pore-scale reactive transport simulations of the UO₂ corrosion process at the spatial scale of a defective fuel rod with their own code. The essential processes of fluid flow and solute transport were considered in addition to diffusion implemented in the previous modeling. They demonstrated that the most detrimental effect on the corrosion rate occurred when the angle between the clad crack and the groundwater flow direction reaches 180°. Within the framework of the WP5 of DISCO, Riba et al. (2020) implemented a 1D reactive transport model in the iCP code to assess the corrosion of the nonconventional UOX fuels doped with Pd. Their model also took into account a complete radiolysis set of kinetic reactions for the alpha radiolysis of water, as well as kinetics oxidative dissolution reactions coupled to the subsequent reduction of oxidized fuel due to H₂ activation by Pd. Their model was the used to derive global UO₂ dissolution rates that can be used in safety assessments.

Data gathered from experiments (DISCO and others) were considered in this study and used to develop thermodynamic and kinetic chemical models, as well as reactive transport model, which will provide the basis for understanding the behavior of spent nuclear MOX fuel in the presence of components of the near field of the disposal cell. A reactive transport model has already been applied to the set of laboratory experiments of Odorowski et al. (2017) on Pudoped UO₂. Modeling accurately reproduced the mineralogy of the system under study and predicted the nature of the phases under observation, as well as the location of their precipitation. Inverse modeling also quantified the reaction kinetics and diffusion fluxes between the different oxidizing and reducing species. Modeling showed that a lower reaction rate would displace the Fe^{2+}/H_2O_2 redox front farther away from the pellet's surface, coinciding with the release of uranium and the formation of FeOOH colloids. However, this alternative model result disagreed with the experimental data.

1.3 Objectives and content of this final report

The work package WP5 of the DISCO project focused on the development and application of chemical and reactive transport models describing the solid and aqueous phases of different

types of spent fuels. A tight collaboration between the experimental contribution from CEA (WP4) and the modeling work of Armines/MINES ParisTech (WP5) was developed in DISCO for the leaching of homogeneous unirradiated MOx pellets (24 wt.% Pu, $U_{0.73}Pu_{0.27}O_2$). Its alpha-activity is sufficient to induce radiolytically enhanced dissolution. This material was considered to better investigate the effect of plutonium (content and repartition) on the dissolution resistance and mechanisms.

Indeed, to the best of our knowledge, no data were found in the literature on the kinetics of dissolution of homogeneous $U_{1-x}Pu_xO_2$ with high plutonium content under environmental conditions (neutral pH...). This is a key point required for the safety assessment of future disposals of any kinds of MOx fuels. More generally, data is also needed for a better understanding of the chemistry of Pu-U oxide solid solutions in contact with water.

With this respect, all the objectives initially scheduled in the DISCO – WP 5 were fully achieved:

- 1. To develop a geochemical model of the homogeneous MOX leaching in carbonated water;
- 2. To develop a reactive Transport model of homogeneous MOX leaching in clay groundwater in presence of metallic iron;
- 3. To up-scale the reactive transport model to a simplified and generic MOX fuel disposal cell.

The main processes considered in the CHESS code (chemical modeling) and HYTEC code (reactive transport modeling) are provide in Chapter 2, as well as the selected thermodynamic data.

Modeling was first applied (in Chapter 3) to the experiments of Kerleguer et al. (2020) that were conducted in carbonated water to quantify the dissolution rates of the homogeneous MOX matrix, with an emphasis on the strong disproportionation of H_2O_2 at the surface of the Pu-enriched oxide. The experimental data had not been acquired in the framework of the DISCO Project. However, further modeling of these experiments was done in the DISCO Project for the sake of developing a full reactive transport model. Chapter 3 has been published in peer-reviewed journal in collaboration with the CEA contributors of WP4 (Kerleguer et al., 2020).

In a second step (Chapter 4), the reactive transport modeling dealt with leaching experiments that were carried out in order to determine the effect of the near-field repository environment; that is to say synthetic COx clay water with a coupon (foil) of metallic iron. A second peer-reviewed paper based on Chapter 4 is in preparation.

As mentioned, emphasis was given on the development of a model useful for performance analysis of representative configuration of spent MOX fuel package in a disposal cell. Chapter 5 transposed the full model of Chapters 3 and 4 to a generic configuration of an underground disposal cell in a clayey geologic formation. Finally, Chapter 6 draws the main conclusions

acquired in the present WP5 subtask and gives some perspectives for further modeling of MOX fuel corrosion under disposal environmental conditions.

2 Main equations of the CHESS/HYTEC codes and thermodynamic data

2.1 Main chemical equations

CHESS is the geochemical module of HYTEC (van der Lee et al., 2002 & 2003) that simulates the chemical equilibrium state of complex aqueous systems, including minerals, organics, colloids and gases. Aqueous speciation and reaction, precipitation/dissolution of solid phases, sorption (surface complexation, ion exchange) and reaction path simulations can be done with CHESS/HYTEC. The aqueous chemistry includes acid/base reactions, oxidation and reduction (redox) processes and aqueous complexation by organic and inorganic ligands. The thermodynamic equilibrium state of the chemical system is calculated according to the usual mass action equation

$$n_A A + n_B B \leftrightarrow n_C C + n_D D \tag{2-1a}$$

$$K(T) = \frac{(C)^{n_C}(D)^{n_D}}{(A)^{n_A}(B)^{n_B}} = exp\left(\frac{-\Delta_R G^0}{RT}\right)$$
(2-1b)

where the parenthesis () stands for the activity of the species, n_i is the stoichiometric coefficient, K is the thermodynamic equilibrium constant of formation, G_0 is the Gibbs free energy of the reaction, R is the perfect gas constant and T is the absolute temperature. CHESS/HYTEC uses equilibrium constants, not Gibbs free energy data.

The species activity is calculated as the product of the species concentration by the activity coefficient. Several mathematical relations have been developed for aqueous solutions of increasing ionic strengths I. The empirical formula of the truncated Davies model derived from the Debye-Huckel model of activity corrections of dissolved ions, and applicable at low to moderate ionic strengths (I \leq 0.5 mol/kg), was used for the present calculations. In this formulation, the activity coefficient γ_i is calculated by

$$\ln \gamma_i = -Az_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - bI \right]$$
(2-2)

with

- z_i the electrical charge of the species *i*;
- I the ionic strength;
- A and b empirical constants.

The explicit modelling of kinetic control is required in key reactions such as iron corrosion or the dissolution of the MOX matrix. The rate of dissolution or precipitation of a mineral M_i is modelled by the following rate law in CHESS/HYTEC:

$$\frac{d[M_i]}{dt} = k_i A_{\nu,i} \prod_i (E)^{p_i} \left(\left(\frac{Q_i}{K_i^{-1}} \right)^m - 1 \right)^n$$
(2-3)

The variation of the mineral concentration is proportional to the intrinsic kinetic constant of the reaction, k_i (mol.m⁻².s⁻¹) and to the mineral surface area per unit volume, A_v (m².L⁻¹). The term $\left(\left(\frac{Q_i}{K_i^{-1}}\right)^m - 1\right)^n$ is dependent on the deviation from thermodynamic equilibrium and related to the concept of the saturation index (Q_i stands for the ion activity product, K_i is the thermodynamic formation constant that is the inverse of the solubility product K_s). Precipitation (oversaturation state) takes place if $Q > K_s$. The dissolution (undersaturation state) of the present mineral can occur if $Q < K_s$. The term *m* and *n* are empirical exponents. The product term Π_i describes the dependence of the reaction rate with respect to the chemistry of solution. The term (E_i) is the concentration of a dissolved species (e.g. the hydrogen peroxide H₂O₂) and p_i is a power-constant, mechanistically-based or fitted to experimental data. The species act as catalysts if the exponent p_i is positive, or as inhibitors if the exponent is negative.

A summation of several kinetics laws similar to Equation 2-3 is frequent for a same mineral, typically to take into account specific pH-dependencies for acidic, neutral or alkaline conditions, as well as redox-dependency with specific laws under oxic and reducing conditions.

2.2 Reactive transport equation

The diffusive transport of a reactive species i is coupled to chemistry in HYTEC (van der Lee et al., 2002 and 2003) according to the following equation:

$$\frac{\partial \omega C_i}{\partial t} = \nabla \cdot (D_e \nabla C_i) - \frac{\partial \omega \overline{C}_i}{\partial t}$$
(2-4)

The term D_e is the effective diffusion coefficient, ω is the porosity, c_i and $\overline{c_i}$ are the mobile and immobile concentrations of a basis component *i* per unit volume of solution, respectively. The sorbed or solid phase concentration (immobile) is evaluated by the chemical calculations, whereas the aqueous concentration (mobile) is a function of the transport processes only. HYTEC uses a single diffusion coefficient common to all dissolved species. Chemistry and transport are coupled through a sequential iterative algorithm.

The transport module is based on the representative elementary volume (REV) approach with finite volume calculation. HYTEC handles 1D - 3D grids in Cartesian coordinates as well as 1D (pseudo 2D) in radial and 2D (pseudo 3D) in cylindrical (axis symmetric) coordinates.

2.3 Chemical thermodynamic data

The thermodynamic database "ThermoChimie" (Giffaut et al., 2014) was used for all the simulations. This thermodynamic database is developed by ANDRA, ONDRAF and RWM for the performance assessment of the geologic disposal of radioactive waste (Giffaut et al., 2014, https://www.thermochimie-tdb.com). ThermoChimie provides formation constants for a wide range of radionuclides and the mineral of multi-barrier components, including host-rock solid phases, bentonites, cements, steel, and their evolving secondary phases. The database is

formatted for several reactive transport models including HYTEC. In particular, the database is up-to-date with respect to the NEA compilation on the thermodynamics of fission products and actinides (Guillaumont et al., 2003). The version 9 of Thermochimie was used for the present modeling, including the strong ternary aqueous complexes $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3$.

With respect to the redox species, three kinetic constrains were set in the modeling. First, molecular hydrogen H₂ produced by the anoxic corrosion of iron was fully decoupled (kinetic inhibition) from the redox reactions in the modeling, e.g. it could not reduce H₂O₂, Pu(VI) or U(VI) in solution. Secondly, the disproportionation of H₂O₂ was under kinetic control only. For the sake of simplicity, the chemical reactivity of O₂ produced by H₂O₂ disproportionation was not considered in the present modeling since the kinetic of oxidative dissolution by O₂ is much slower than the oxidative dissolution by H₂O₂. Thirdly, sulfates reduction into sulfides was also inhibited (decoupled) in the modeling since this reaction did not occur under the experimental conditions of the WP 4 experiments. That is to say a low temperature of 20°C and no identified microbial activities by sulfur reducing bacteria SRB such as iron sulfide formation or consumption of dissolved SO₄.

The solid phase $U_{0.73}Pu_{0.27}O_2$ was included in the database, but its dissolution was calculated under kinetic control only. With respect to the basis components, it writes

$$0.73 U^{4+} + 0.27 Pu^{4+} + 2 H_2O \le (U_{0.73}Pu_{0.27})O_2 + 4 H^+$$
(2-5)

Based on the literature review (Haschke and Oversby, 2002; Altmaier et al., 2013), a subset of uranium and plutonium solids that could precipitate as secondary phases was selected from the ThermoChimie database:

- U(IV), UO₂:2H₂O(am);
- U(VI), schoepite, soddyite and uranophane;
- Pu(III), PuCO₃OH(s);
- Pu(IV), PuO₂(coll-hyd), Pu(OH)₄(am);
- Pu(V), PuO₂(OH)(s);
- Pu(VI), PuO₂(OH)₂:H₂O(s), PuO₂(CO₃)(s).

The selection of the secondary minerals could vary according to the experiments.

The well-crystallized UO₂, PuO₂ and Pu(OH)₃ were discarded since they were not expected to precipitate in the present experimental conditions. The thermodynamic constant of the amorphous phase UO₂:2H₂O was slightly adjusted to better fit the experimental results, by taking into account the lower limit of solubility reported in the literature (see Odorowski et al., 2017). That is to say

$$1 U^{4+} + 4 H_2O \iff UO_2 \bullet 2H_2O(am) + 4 H^+; \log K_f = -1.50 \implies -0.60$$
(2-6)

The anoxic corrosion of metallic iron Fe(0) was under kinetic control only but the precipitation of the corrosion products was calculated at thermodynamic equilibrium. Based on the experimental results and the literature, one considered the Fe(II)-carbonates $FeCO_3$

(siderite) and $Fe_2(OH)_2CO_3$ (chukanovite), as well as the Fe(III)-hydroxide FeOOH (goethite) and the mixed Fe(II)-Fe(III) oxide Fe_3O_4 (magnetite). The thermodynamic constant of chukanovite formation:

$$2 \operatorname{Fe}^{2+} + 1 \operatorname{CO}_{3^{2-}} + 2 \operatorname{H}_{2}\operatorname{O} \stackrel{<}{=} \operatorname{Fe}_{2}(\operatorname{OH})_{2}\operatorname{CO}_{3} + 2 \operatorname{H}^{+}; \log K_{\mathrm{f}} = -2.1$$
(2-7)

was taken from the experimental study of Azoulay et al. (2012) since it is not included in ThermoChime.

3 Modeling of $U_{0.73}Pu_{0.27}O_2$ alteration under self α -radiolysis

3.1 Material and leaching experiment

3.1.1 U_{0.73}Pu_{0.27}O₂ pellet

The reference material $U_{0.73}Pu_{0.27}O_2$ was the same as the one considered in the CEA contributions to WP 4 of DISCO.

The unirradiated $U_{0.73}Pu_{0.27}O_2$ pellets were fabricated at CEA Cadarache (COCA Process) and stored under air in a hot-cell. After 30 years of storage period, the pellets were cut, polished and then annealed under Ar/H₂ 4% atmosphere to recover the radiation damage and to restore the stoichiometry of the sample (O/M = 2.00). The dimensions of the pellets were about 2 mm thick and 5.4 mm in diameter, their density about 10.4 kg.dm⁻³ and their specific surface without roughness factor about 2.87×10⁻⁴ m².g⁻¹ (Kerleguer et al., 2020). Figure 3-1 shows the surface of the homogeneous MOX after leaching.

The α -activity of a pellet was 2.2×10^9 Bq.g⁻¹, which corresponds to an α -dose rate received by the solution of 9730 Gy.h⁻¹. The α dose rate was, therefore, 5 to 6 orders of magnitude higher than the β/γ dose rates, and the deposited α energy into the solution was estimated to be two orders of magnitude higher than the β/γ energies (Kerleguer et al., 2020). Therefore, only α irradiation was assumed to be the main source of H₂O₂ production. It is worth pointing out that this model material has a major α activity that will be well predominant for the spent fuel under geological disposal conditions.



Figure 3-1. Surface of the homogeneous $U_{0.73}Pu_{0.27}O_2$ MOX after leaching (Kerkeguer et al., 2020).

3.1.2 Batch experiment

After annealing, the pellets were transferred to an anoxic alpha-glovebox (argon atmosphere, $[O_2] < 2$ vppm) for the leaching experiment. The two MOx pellets were submitted to 10 preleaching cycles in carbonated water ([NaHCO₃] = 10^{-3} mol.L⁻¹) in order to remove the potential oxidized layer that could have been formed on the surface. The two pellets were then inserted in a titanium dioxide sample holder and leached in 155 mL of carbonated water ([NaHCO₃] = 10^{-2} mol.L⁻¹). All the parts of the leaching reactor in direct contact with solution were in titanium dioxide, which is relatively chemically inert towards radiolytical species.

The leaching test lasted 342 days and were regularly sampled with time. The last sample was filtered at 0.45 μ m and ultra-filtered at 20 nm to determine the presence of any colloids. Successive acid rinses of the reactor permitted the total quantification of colloids and species sorbed or precipitated on the walls of the titanium oxide reactor (Kerleguer et al., 2020).

At the end of the experiment, pellets were dried and stored under Ar atmosphere until surface characterization. The initial and corroded states of the pellet surface was characterized by Scanning Electron Microscopy (SEM). The electron probe micro-analyzer (EPMA) technique was used to determine the distribution of Pu. Raman spectra were also acquired on the leached samples.

3.2 Modeling of kinetic processes

3.2.1 H₂O₂ as the predominant alpha radiolytic species

Modeling of the batch experiments of chapter 3 were fully performed with the geochemical code CHESS without considering any reactive transport modeling with HYTEC, since there was only one type of material (the pellets, with no iron foils).

 H_2O_2 is generally considered as the most important species regarding UO₂ dissolution under alpha irradiation (Ekeroth et al., 2006; Lousada et al., 2013; Liu et al., 2016). The modeling study of Wu et al. (2014) applied to α -doped UO₂ radiolytic corrosion in the presence of iron canister led to the same conclusion. Furthermore, the main oxidative species in terms of concentrations produced by the alpha radiolysis of water is H_2O_2 according to CHEMSIMUL calculation (Odorowski, 2016). But it is not sure whether CHEMSIMUL has the full set of kinetic rate constants for all the radicals induced by radiolysis in the complex chemistry of the COx water at neutral pH. All these reactions are very sensitive to the chemistry and taking a semi-empirical calibration versus experiments where H_2O_2 is measured seems a reasonable approach within DISCO. Along the same lines, many experimentalists have calibrated the corrosion of UO₂ versus the aqueous concentration of H_2O_2 (e.g. Merino et al., 2005).

Therefore, the hydrogen peroxide concentration in solution was controlled by one production term due to water radiolysis and two consumption terms related to H_2O_2 disproportionation and MOX oxidation by H_2O_2 . The first step in the model development was, therefore, to take into account the kinetics of the following simultaneous processes:

- H₂O₂ production by water radiolysis;
- H_2O_2 disproportionation onto the surface of the $U_{0.73}Pu_{0.27}O_2$ pellet;
- H_2O_2 consumption by the radiolytic dissolution of the $U_{0.73}Pu_{0.27}O_2$ matrix.

Two additional possible mechanisms of consumption had been discarded by Kerleguer et al (2020). A blank experiment of hydrogen peroxide disproportionation in pure water inside the TiO_2 cell used for the experiments had shown that this process was very slow (< 1 % per day). Raman spectroscopy did not indicate any precipitation of peroxide compounds at the surface of the pellets.

3.2.2 Radiolytic production of H₂O₂

As mentioned above, the $\alpha\beta\gamma$ activities of the MOX fuel were recalculated at the date of the leaching experiment and the alpha, beta and gamma dose rates determined at the surface of a pellet and in the homogeneous aqueous solution. These calculations indicated that the α irradiation field was the main source of H₂O₂ radiolytic production.

The hydrogen peroxide production rate law by alpha water radiolysis at the vicinity of the MOX pellet was:

$$\frac{d[H_2O_2(aq)]}{dt} = \left(k^{prod}\right)A_v \tag{3-1}$$

where A_v is the volumetric surface area of the pellet in $m^2 L^{-1}$ (i.e. the specific surface A_s in $m^2 .g^{-1}$ times the concentration in $g.L^{-1}$).

The constant k^{prod} normalized to the surface pellet was calculated to be 1.10×10^{-8} mol.m⁻².s⁻¹ (i.e. 9.5×10^{-4} mol.m⁻².d⁻¹) considering:

- the alpha dose rate of 9730 Gy.h⁻¹;
- an alpha primary yield of 0.98 molecule/100eV for H₂O₂;
- an average α particle range of 40 μ m in water;
- the geometric surface of the pellets.

The hydrogen peroxide production rate was assumed to be constant during all the experiment, i.e. neglecting any effects of the chemical evolution with time of the surface of the pellets. With such a production rate, the concentration of H_2O_2 would increase by 8×10^{-7} mol.L⁻¹.d⁻¹, and thus be above the limit of quantification already in the very first hours, provided there was no consumption by disproportionation and uranium oxidation.

3.2.3 Radiolytic oxidation of $U_{0.73}Pu_{0.27}O_2$ by H_2O_2

In carbonated water, strong uranyl carbonate complexes prevent the precipitation of secondary species and uranium can be used as a tracer of the alteration (De Pablo et al., 2001; Stroes-Gascoyne et al., 2005). The dissolution rate of U(VI) from the UO₂ surface is also enhanced by such carbonate complexes (Casas et al., 2009). Therefore, the radiolytic

dissolution mechanism is mostly controlled by the oxidation by H_2O_2 and the uranium concentration can be used to determine the intrinsic kinetic rate constant of oxidation/dissolution. This kinetic has already been extensively studied for simple UO_2 matrix, but there is still a lack of information about the behavior of MOX ($U_{1-x}Pu_xO_2$) fuels.

Furthermore, one mole of uranyl in solution corresponds to one mole of H_2O_2 consumption, thus the kinetic of uranium dissolution is equal to the H_2O_2 consumption. The oxidative dissolution rate law of the $U_{0.73}Pu_{0.27}O_2$ matrix was set as a first order on H_2O_2 concentration:

$$\frac{d[U_{0.73}Pu_{0.27}O_2]}{dt} = \left(-k_{MOX}^{oxid}[H_2O_2]\right)A_{\nu}$$
(3-2)

where k_{MOX}^{oxid} is the intrinsic rate constant in L.m⁻².s⁻¹, A_v is again the volumetric surface area of the MOX pellet in m².L⁻¹. This equation is similar to the dissolution law given by Merino et al. (2005) for the radiolytic dissolution of UO₂ powder.

Due to the stoichiometry of the MOX, the rate constant k_{MOX}^{oxid} is linked to k_U^{oxid} fitted onto the release uranium by the relationship

$$k_{MOx}^{ox} = k_U^{ox} \times \frac{1}{0.73}$$
(3-3)

For the initial dissolution, the uranium oxidation rate $(k_U^{oxid}[H_2O_2])$ was fitted as 1.4×10^{-9} mol.m⁻².s⁻¹ (i.e. 1.2×10^{-4} mol.m⁻².d⁻¹). This indicates that 12.5% of the radiolytically-produced H₂O₂ was consumed by oxidation of the MOx pellet during the initial dissolution step. The long-term dissolution rate was fitted as 8.8×10^{-11} mol.m⁻².s⁻¹ (i.e. 7.6×10^{-6} mol.m⁻².d⁻¹), indicating that less than 1% of the H₂O₂ was consumed by the oxidation of the MOx pellet during the long-term dissolution. Considering a constant H₂O₂ concentration of 1×10^{-7} mol.L⁻¹ (i.e. the limit of quantification), two kinetic rate constants for the uranium dissolution k_U^{oxid} were calculated: an initial kinetic rate constant of 1.4×10^{-2} L.m⁻².s⁻¹ and a long term kinetic rate constant of 8.8×10^{-4} L.m⁻².s⁻¹ (approximately 16 times lower). Table 3-1 gives the full set of rate constants k_U^{oxid} used in the modeling.

Table 3-1.Kinetic rate constants used in the geochemical modelperformed with CHESS.

* *		
	Model A	Model B
	Constant H ₂ O ₂ disproportionation	Increasing H ₂ O ₂ disproportionation
k^{prod} (mol.m ⁻² .s ⁻¹)	1.1>	<10 ⁻⁸
k^{oxid}_U (L.m ⁻² .s ⁻¹)	8.8×10 ⁻⁴	1.4×10 ⁻²
k^{oxid}_{MOx} (L.m ⁻² .s ⁻¹)	1.2×10 ⁻³	1.9×10 ⁻²
$k^{disprop}$ (L.m ⁻² .s ⁻¹)	1.1×10^{-1}	17×10 ⁻¹

The decrease in the rates with time was probably linked to the formation of a Pu-enriched layer at the surface of the pellets. SEM-EDX analysis of Kerleguer et al. indicated a plutonium enrichment of the surface, with a homogeneous plutonium content (Pu/(U+Pu)) of 39 wt.% (against 27 wt.%, initially). The present chemical model considered a congruent dissolution with a surface reprecipitation/enrichment of amorphous Pu(OH)₄ layer, as discussed below. This dual scheme globally simulated an incongruent dissolution. Such a passivating layer is quite consistent with the observation made on other actinides, such as thorium, uranium and neptunium (Neck and Kim, 2001). The model was only able to simulate the dissolved plutonium concentration and the formation of Pu(OH)₄ if the reaction of H₂O₂ with U(IV) was thermodynamically favored with respect to the reaction with Pu(IV).

3.2.4 H_2O_2 disproportionation onto the $U_{0.73}Pu_{0.27}O_2$ surface

The disproportionation reaction

$$H_2 O_2 \to H_2 O + 0.5 O_2$$
 (3-4)

was also modeled according to a kinetic law of first-order on H2O2 concentration as

$$\frac{d[H_2O_2]}{dt} = \left(-k^{disprop} \left[H_2O_2\right]\right) A_v \tag{3-5}$$

where A_v is again the volumetric surface area of the MOX pellet in m².L⁻¹.

The disproportionation rate constant was estimated assuming a stationary state on H_2O_2 concentration, considered as constant at the limit of quantification (LQ) of 1×10^{-7} mol.L⁻¹. That is to say:

$$\frac{d[H_2O_2]}{dt} = \left(k^{prod} - k^{disprop} \left[H_2O_2\right] - k_U^{oxid} \left[H_2O_2\right]\right) A_v = 0$$
(3-6)

As mentioned, for the initial phase of the dissolution, 12.5 % of the radiolytically-produced H_2O_2 was consumed by oxidation of the MOX pellet during the initial dissolution step. The remaining 87.5 % of radiolytically-produced H_2O_2 was consistent with the disproportionation already measured on UO₂ pellets (Nilsson et al., 2011; Pehrman et al., 2012). Considering the catalytic disproportionation of H_2O_2 as the main mechanism, a disproportionation rate $(k^{disprop} [H_2O_2])$ of 9.6×10⁻⁹ mol.m⁻².s⁻¹ was estimated, and hence a rate constant $k^{disprop}$ of 9.6×10⁻² L.m⁻².s⁻¹ could be calculated.

On the long-term, the H_2O_2 concentration was under the limit of quantification, meaning that 99 % of the radiolytically-produced H_2O_2 was consumed by the catalytic disproportionation on the MOX pellet surface (against 86 % for UO₂ pellets). Such a high consumption is consistent with the values that have been experimentally determined for Pu-doped UO₂ and SIMFUEL pellets (Nilsson et al., 2011; Pehrman et al., 2012). Considering the catalytic disproportionation of H_2O_2 as the main mechanism, a disproportionation rate $k^{disprop}$ of

 1.1×10^{-8} mol.m⁻².s⁻¹ was estimated, and hence a rate constant $k^{disprop}$ of 1.1×10^{-1} L.m⁻².s⁻¹ could be calculated.

The evolution of the catalytic properties $k^{disprop}$ of the MOX surface can be induced by the Pu enrichment. Different disproportionation mechanisms involving different oxidation state of plutonium can be considered.

The evolution of the catalytic properties $k^{disprop}$ of the MOX surface can be induced by the Pu enrichment. Different disproportionation mechanisms involving different oxidation state of plutonium can be considered. Korzhavyi et al. (2004) described a possible surface-catalyzed decomposition of H₂O₂ on the PuO₂ surface by the mean of the reactions 4 and 5:

$$4 PuO_2 + H_2O_2 \to Pu_4O_9 + H_2O \tag{3-7}$$

$$Pu_4 O_9 + H_2 O_2 \to 4 Pu O_2 + H_2 O + O_2$$
(3-8)

However, this mechanism is not likely to occur as no evidence of plutonium oxidation was actually confirmed in the solid. Another possible mechanism could be the reduction of Pu(IV) to Pu(III), followed by the oxidation of the latter (Maillard and Adnet, 2001):

$$2 P u^{4+} + H_2 O_2 \to 2 P u^{3+} + O_2 + 2 H^+$$
(3-9)

$$2Pu^{3+} + H_2O_2 + 2H^+ \to 2Pu^{4+} + 2H_2O$$
(3-10)

In the absence of data on plutonium speciation at the surface it is difficult to conclude, nevertheless these processes cannot be discarded at this stage.

Eventually, it is worth mentioning that the oxidative dissolution by dissolved molecular oxygen generated by disproportionation of hydrogen peroxide was not taken into account in the modeling for the sake of simplicity, since the kinetics of the reaction of UO_2 with O_2 is known to be slower than the reaction with H_2O_2 .

3.3 Modeling of geochemical evolution and U/Pu release

In both the experiment and the modeling, the pH of the solution was slightly alkaline and constantly buffered at 9.3 by HCO_3^- anions. The redox potential was around +0.350 V/SHE, which corresponds to mildly oxidizing conditions at this pH.

3.3.1 Model A with a constant disproportionation rate of H_2O_2

The overall consistency of the kinetic rate constants (Table 3-1) obtained for the long-term leaching is very well illustrated in Figure 3-2 that shows a complete model/experiment agreement with respect to the evolution with time of U, Pu and H_2O_2 concentrations. The model should be, therefore, relatively robust for up-scaling.

The model A was performed by introducing the constants determined for H_2O_2 production and disproportionation and MOX oxidation. In the model, the amorphous $Pu(OH)_4$ phase was allowed to precipitate and the uranium concentration measured after 30 days was added to the calculated ones.

Kerleguer et al. (2020) observed that the colloidal fraction was low (<1 wt.%) and almost no U precipitated or sorbed (around 4 wt.%) onto the TiO₂ surface. The released uranium concentration was consistent with the uranium solubility diagram of Figure 3-2, where uranium is stabilized in solution as the strong U(VI) complex UO₂(CO₃)₃⁴⁻, in the range 10⁻⁶ – 10⁻⁴ mol/L, well below the solubility limit of schoepite. Although mathematically correct, Figure 3a overestimates the solubility of schoepite. Figure 3-3b took into a better account that the activity of the species CO₃²⁻ is significantly lower than the total concentration of CO₃²⁻ (about 8×10⁻⁴ instead of 10⁻²), due to the high solubility of schoepite (increasing the concentration of UO₂²⁺ in solution), the strong binding of CO₃²⁻ with UO₂²⁺, and the stoichiometry of 4 CO₃²⁻ for 1 UO₂²⁺. However, the diagram of Figure 3-3b is itself not fully representative of the true speciation (that was calculated with CHESS) since the main species at equilibrium with schoepite is UO₂(CO₃)₃⁴⁻ and not (UO₂)₂CO₃(OH)₃⁻. Whatsoever, in both diagrams, the experimental condition could not lead to the precipitation of schoepite due to the high total concentration in carbonates.



Figure 3-2. CHESS modelling of the long-term kinetic leaching of the homogeneous MOX pellet in carbonated water ($[NaHCO_3] = 10^2$ mol/L) under anoxic conditions (argon atmosphere, $[O_2] < 2$ vppm). The model A considered a fixed rate constant of H_2O_2 disproportionation and the long-term rate constant of the MOX oxidation.



Figure 3-3. CHESS solubility diagrams of uranium as a function of redox potential (V/SHE). The diagrams were plotted at a temperature of 25 °C, a pH of 9, an activity of HCO_3^- of 10^{-2} (a) and 8×10^{-4} (b). The red dots represent the experimental concentrations for the present homogeneous MOX (Kerleguer et al.), and the blue squares for a heterogeneous MOX (Odorowski et al., 2016).



Figure 3-4. CHESS solubility diagrams of plutonium as a function of redox potential (V/SHE). The diagrams were plotted at a temperature of 25 °C, a pH of 9, an activity of HCO_3^- of 10^{-2} . The red dots represent the experimental concentrations for the present homogeneous MOX (Kerleguer et al.), and the blue squares a heterogeneous MOX (Odorowski et al., 2016).

Contrary to the uranium, the soluble plutonium fraction (2 wt.%) was negligible, few colloids were detected (<1 wt% with a cut-off at 20 nm). The majority of the released plutonium was precipitated (or maybe partially sorbed) on the walls of the reactor (97 wt.%, Kerleguer et al., 2020). The plutonium concentration in solution was almost constant, around 10^{-9} mol/L (Figure 3-2) over the duration of the leaching test. The solubility diagram of plutonium (Figure 3-4) shows that the predominant species in solution is the carbonate complex Pu(CO₃)₂(OH)₂²⁻ at pH 9 and Eh around 0.35 – 0.40 V. Under such chemical conditions, the plutonium concentration is compatible with a thermodynamic control by the amorphous phase Pu(OH)₄ (Lemire and Garisto, 1989). The amorphous phase PuO₂:2H₂O (Neck and Kim, 2001) has the same stoichiometry as Pu(OH)₄(am), but clearly it does not match with the present experimental data. However, the system could be in a metastable condition with respect to this phase. Eventually, the hydrated colloidal phase PuO₂ equilibrium is not far from the experimental data, but slightly too soluble.

3.3.2 Model B with an increasing disproportionation rate of H_2O_2 with Pu enrichment

Another hypothesis (model B) could be that the initial rate constant k_U^{oxid} is applicable for the long-term dissolution, but that the disproportionation of H₂O₂ increases over time due to the Pu-enrichment of the surface. Therefore, the H₂O₂ concentration would decrease all along



Figure 3-5. Modelling of the long-term kinetic leaching of the homogeneous MOX pellet in carbonated water ($[NaHCO_3] = 10^{-2} \text{ mol/L}$) under anoxic conditions (argon atmosphere, $[O_2] < 2$ vppm). The model B considered the initial rate constant of the MOX oxidation with an enhanced long-term rate constant of disproportionation.

the experiment. As shown in Figure 3-5, the long-term steady-state concentration of H_2O_2 would be around 6×10^{-9} mol.L⁻¹ in order to fit the long-term concentration of uranium in solution. The corresponding disproportionation rate constant $k^{disprop}$ would be about one order of magnitude higher, as detailed in Table 3-1. An accurate measurement of low H_2O_2 concentrations would be necessary to discriminate among these two processes. The mechanism occurring is likely in between the two hypotheses, with both an increased disproportionation and a decreased reactivity of the surface against oxidation.

3.4 Modeling of the feedback effect of Pu(OH)₄ formation on kinetics

Kerleguer et al. (2020) measured a Pu enrichment of the surface, with a homogeneous Pu content (Pu/(U+Pu)) of 39 wt.% against 27 wt.%, initially. Such a behavior was already observed by Stroes-Gascoyne et al. (2005) on UO₂ pellets doped with 0.6 Pu wt.%. They concluded that the uranium release was very fast compared to the plutonium one, leading to a Pu enrichment of the pellet surface. The observed Pu-enrichment can have different origins, such as a uranium depletion of the fluorite structure, the precipitation of secondary phases like peroxides or either the formation of an amorphous Pu(OH)₄ layer as suggested by the solubility diagram of plutonium (Figure 3-4). This last hypothesis was considered in the present modeling.

Figure 3-6 shows a previous attempt to model the results over the full duration of the experiment with a transition from the preliminary step to the long-term regime (De Windt et al., 2019). The model took into account a negative feedback (partial passivation) of the formation of the $Pu(OH)_4$ layer on the kinetics of the oxidative dissolution of $U_{0.73}Pu_{0.27}O_2$. The passivation was modeled with a phenomenological (empirical) law

$$\frac{d[U_{0.73}Pu_{0.27}O_2]}{dt} = \left(-k^{oxid,pass} \left(\frac{1}{\kappa^n + [Pu(OH)_4]^n}\right)[H_2O_2(aq)]\right)A_\nu$$
(3-11)

inversely dependent on the layer thickness, as expected, κ is a thickness threshold around which the kinetics decreases (similar to the half-life of the Monod equation) and n stands for the roughness of the transition (the higher n is, the faster the transition is).

The agreement with the experimental results is very good over time, with the capability to simulate the smooth transition between the two regimes of uranium release. However, this model is still strictly empirical and cannot estimate a priori the thickness threshold. Only the long-term model developed in Section 3.2, which considers the formation of Pu(OH)₄ but without any feedback effect, can be realistically used in the current state of understanding of the leaching experiment.



Figure 3-6. (a) CHESS modeling of the kinetic leaching of the homogeneous MOX pellet in carbonated water (10^2 mol/L) during the full experiment, from the initial state towards the long-term steady state. (b). The model took into account a negative feedback of the formation of the $Pu(OH)_4$ layer on the oxidative dissolution of $U_{0.73}Pu_{0.27}O_2$.

4 Modeling of U_{0.73}Pu_{0.27}O₂ alteration in synthetic claystone water and the presence of metallic iron

4.1 Materials and experimental set-up

4.1.1 $U_{0.73}Pu_{0.27}O_2$ pellet, COX synthetic water and iron foil

The reference homogeneous MOX pellets $U_{0.73}Pu_{0.27}O_2$ were exactly the same as the ones considered in Chapter 3 and the CEA contributions to WP 4 of DISCO, and followed a similar sequence of annealing, polishing and pre-leaching treatments.

The leaching solution was a synthetic groundwater representative of Callovo-Oxfordian (COx) claystone groundwater. The synthetic COx water was put under Ar/CO_2 3000 ppm atmosphere pressurized at 3.5 bars at room temperature. The composition of the synthetic water under such an atmosphere is given in Table 4-1. During the experiments, the pH was around 8.0 and the measured carbonate content about 10 - 20 mg/L.

A rolled 99.99 % pure iron foil was used. Its size was 2.5 cm by 2.5 cm for a thickness of 125 μ m and a weight of around 0.64 g per foil.

4.1.2 Leaching cell set-up

All leaching tests were performed under static conditions without stirring in a TiO_2 reactor cell at room temperature. In a preliminary step, the iron foils were first pre-corroded in 180 mL of synthetic COx water for around 80-90 days in the absence of the MOX pellets. This first step was intended to ensure the presence of corrosion products on the iron foil surface, to obtain a solution chemistry containing Fe^{2+} ions not initially present in the synthetic COx water, and to have reducing conditions when the MOX pellets were introduced at a later date. After the iron pre-corrosion phase, the reactor was opened to add two MOX pellets, which were placed on a support above the iron foil. The reactor was then closed again, purged with a mixture of Ar/CO_2 3000 ppm for 30 min, and returned to a pressure of 3.5 bars. Figure 4-1 gives a schematic representation of the cylindrical leaching cell of the homogeneous MOX pellets.

Samples of the leaching solution were regularly collected over time. The last sample was filtered at 0.45 μ m and ultra-filtered at 20 nm to determine the presence of any colloids. Successive acid rinses of the reactor permitted the total quantification of colloids and species sorbed or precipitated on the walls of the titanium oxide reactor. After surface characterization, the iron foils were rinsed for 30 min in 10 mL of HNO₃ 0.5 M to quantify the uranium and plutonium adsorbed or precipitated onto the foil.

		-						
	[Na ⁺]	$[K^+]$	[Ca ²⁺]	$[Mg^{2+}]$	$[\mathrm{Sr}^{2+}]$	[Cl ⁻]	[SO4 ²⁻]	[Si]
mg.L ⁻¹	993	39.1	341	131	17.5	1454	1412	5.62
mol.L ⁻¹	0.0432	0.0010	0.0085	0.0054	0.0002	0.0410	0.0147	0.0002

Table 4-1. Composition of the initial synthetic Callovian-Oxfordian groundwater at 20°C used for the pre-corrosion step.



Figure 4-1. Schematic representation of the cylindrical leaching cell of the homogeneous MOX pellets in synthetic COx groundwater in presence of a pre-corroded iron foil.

At the end of the experiment, pellets were dried and stored under Ar atmosphere until surface characterization. The initial and corroded states of the pellet surface was characterized by Scanning Electron Microscopy (SEM). The electron probe micro-analyzer (EPMA) technique was used to determine the distribution of Pu. Raman spectra were also acquired on the leached samples.

4.2 Modeling grid, boundary conditions and diffusion coefficient

HYTEC modeling was applied to the leaching experiments in presence of the iron foil, instead of a simple geochemical CHESS model. Indeed, only time-related results could be calculated with CHESS in batch mode, whereas the geometric configuration of the experimental set-up could be modeled with HYTEC. In this experimental set-up without stirring, the transport of species was driven by diffusion within the solution, especially between the MOX pellets and the iron foil separated by just a few centimeters. This spatial modeling helped to better understand the mechanisms and the location of the front between the oxidizing zone induced by the α -activity of the MOX pellets and the reducing zone generated by the iron foil.



Figure 4-2. Simulation grid of the leaching cell used for the HYTEC calculations in 2D (pseudo 3D) cylindrical (axis symmetric) geometry.

Figure 4-2 shows the simulation grid of the cylindrical leaching cell used for the HYTEC calculations in 2D (pseudo 3D) cylindrical (axis symmetric) geometry. The amount of metallic iron was renormalized to take into account the correct mass present in the experiment (contrarily to the pellets, the foil was rectangular, not cylindrical as assumed in the axis symmetry). The upper limit of the grid simulated the constraint on the dissolved CO₂ content set by the partial pressure in gaseous CO₂ above the solution in the experiment (i.e. 3 bars gas mixture of Ar/CO₂ at 3000 ppm). The grid mesh size was fixed to 5×10^{-4} m by 5×10^{-4} m (i.e. 0.5 mm by 0.5 mm). A common diffusion coefficient of 2×10^{-9} m².s⁻¹ in water was considered for all the dissolved species in the calculations.

4.3 Modeling of kinetic processes

4.3.1 Prerequisite on the kinetics of $Fe(II)/H_2O_2$ reaction in solution

The experimental and modeling study of the effect of metallic iron on the oxidative dissolution of UO_2 doped with a radioactive alpha emitter (Odorowski et al., 2017) demonstrated that the redox reaction between dissolved ferrous iron (produced by iron corrosion) and hydrogen peroxide (produced by water radiolysis and enhancing UO_2 dissolution)

$$2Fe^{2+} + H_2O_2 \to 2Fe^{3+} + 2OH^- \tag{4-1}$$

was a key reaction in the present system. The authors considered an instantaneous thermodynamic equilibrium for this homogeneous chemical reaction in solution, by lack of data but also because the experimental results were correctly modeled with this hypothesis.

To further validate this assumption a kinetic control was introduced on Equation 4-1 in the model based on a literature review. Many studies dealt with the Fenton reaction under acidic to slightly acidic conditions. But only few papers relevant for Equation 4-1 under geological conditions at neutral pH could be found.

The combination of two first-order reactions is commonly encountered in the literature

$$R(mol. L^{-1}. s^{-1}) = \frac{d[H_2 O_2]}{dt} = \frac{1}{2} \frac{d[Fe^{2+}]}{dt} = -k \ [Fe^{2+}] \ [H_2 O_2]$$
(4-2)

The value of the rate constant k varies over several orders of magnitude:

- from 5×10¹ L.mol⁻¹.s⁻¹ in acidic pure water (CHEMSIMUL data: from Hardwick, 1956; Christensen and Bjergbakke, 1986);
- to more than 10⁴ L.mol⁻¹.s⁻¹ in moderately saline and alkaline water, likewise the COx groundwater (Millero and Sotolongo, 1989);
- Wu et al. (2014) selected a constant of 10⁶ L.mol⁻¹.s⁻¹.

Figure 4-3 shows the value of the rate constant k of Equation 4-2 with respect to the pH and the ionic strength in seawater at 25°C (Millero and Sotolongo, 1989). The strong effect of pH is due to the higher reactivity of Fe(OH)⁺ hydroxyl complex (whose proportion increases with pH) compared to pure Fe²⁺ ions. The effect of the ionic strength is much more moderate. Still in Millero and Sotolongo (1989), a rate constant value of about 10⁵ mol/L/s is reported in pure 10⁻² M NaHCO₃ solution at 25°C; that is to say fully representative of the present leaching conditions.

Furthermore, the mass transport over space plays an important role. The hydrogen peroxide generated within the alpha-track is initially very close to the fuel surface (tens of μ m), while the ferrous iron generated through corrosion of metallic iron lies usually much longer from the fuel surface (cm scale). The sensitivity analysis of these coupled processes was, therefore, performed with HYTEC. Figure 4-4 shows that the kinetics of



Figure 4-3. The effect of pH (a) and the ionic strength (b) on the rate constant of the oxidation of Fe(II) with H_2O_2 in seawater at different temperatures (Millero and Sotolongo, 1989).



Figure 4-4. HYTEC modeling of Pu-doped UO_2 pellets in synthetic COx groundwater in presence of a pristine iron foil: sensitivity of the calculated concentrations of dissolved uranium (a) and iron (b) with respect to the kinetic rate constant, Equation 4-2.

the homogeneous reaction between Fe(II) and H_2O_2 is fast with respect to the oxidation of the oxide matrix. Therefore, this reaction can be modeled at thermodynamic equilibrium for the sake of reducing the computational CPU time.

4.3.2 Modeling of H_2O_2 production and disproportionation by the $U_{0.73}Pu_{0.27}O_2$ surface

Preliminary HYTEC calculations were performed with Equation 3-1 (radiolytic production of H_2O_2) and Equation 3-2 (disproportionation of H_2O_2) with the long-term kinetic rate constants. The timestep imposed by the coupling was rather low and led to long CPU time. It was found that similar results could be obtained in a numerically more fast and robust way by decreasing the production rate to model the effect of disproportionation as followed

$$\frac{d[H_2O_2(aq)]}{dt} = \left(k^{prod}\right)A_v \tag{4-3}$$

The decreased rate constants of $k^{prod} = 1.10 \times 10^{-8} / 100 = 1.10 \times 10^{-11} \text{ mol.m}^{-2}.\text{s}^{-1}$ (99 % disproportionation, as obtained in the MOX pellet in carbonated water) and 1.10×10^{-9} mol.m⁻².s⁻¹ (90 % disproportionation) were both tested. As discussed below, the agreement with the experimental results (in particular the mass of magnetite that precipitated on the pellet surface) was better with 1.10×10^{-9} mol.m⁻².s⁻¹. It means that H₂O₂ disproportionation was not fully achieved and competed with the reaction between H₂O₂ and dissolved iron.

4.3.3 Radiolytic oxidation of $U_{0.73}Pu_{0.27}O_2$ by H_2O_2

Equation 3-3 and the long-term rate constant of k_{MOx}^{oxid} 1.2×10⁻³ L.m⁻².s⁻¹ were considered in the modeling of the kinetics of radiolytic dissolution of the U_{0.73}Pu_{0.27}O₂ matrix.

4.3.4 Dissolution of $U_{0.73}Pu_{0.27}O_2$ under reducing conditions

 $U_{0.73}Pu_{0.27}O_2$ is also expected to dissolve under the reducing conditions without any radiolytic oxidants. To the best of our knowledge, there is no information in the literature about the corresponding rate constant k_{MOx}^{red} . The kinetics of the MOX pellet dissolution were modeled by the following law:

$$\frac{d[U_{0.73}Pu_{0.27}O_2]}{dt} = \left(-k \frac{red}{MOx}\right) A_v \tag{4-4}$$

It is worth noting that no thermodynamic equilibrium dependency, i.e. no $\left(\frac{IAP}{K_{UO_2}}-1\right)$ term, were considered due to the lack of data on the formation constant of the solid solution U_{0.73}Pu_{0.27}O₂.

In a first step, a rate constant value of 2×10^{-12} mol.m⁻².s⁻¹ was taken from the literature on UO₂ as in Odorowski et al. (2017). Bruno et al. (1991) gave a dissolution rate of UO₂ under reducing conditions of 1.9×10^{-12} mol.m⁻².s⁻¹ for $7 \le \text{pH} \le 11$, and Ulrich and al. (2008) gave a similar value of 2×10^{-12} mol.m⁻².s⁻¹ for $3 \le \text{pH} \le 8$. Both studies were carried out in pH ranges representative of the pH measured in our leaching experiments (pH ~ 7). This kinetics under reducing conditions is clearly slower than the oxidative dissolution one. The mass balance on the release of uranium (in solution, colloidal and sorbed) at the end of the WP4 experiment provided some insights into the actual value of k^{red} . In a second step detailed below, the rate constant was slightly adjusted on the experimental data to a value of 9×10^{-13} mol.m⁻².s⁻¹., i.e. almost no effect of the plutonium content on the kinetics compared to a pure UO₂ phase.

4.3.5 Anoxic corrosion of metallic iron

The aqueous corrosion of the metallic iron Fe(0) foil in anoxic media can be written as:

$$Fe(0) + 2 H_2 O \rightarrow Fe^{2+} + 2 OH^- + H_2$$
 (4-5)

A kinetic constraint was imposed on this corrosion process using the following law:

$$\frac{d[Fe(0)]}{dt} = -k^{corr} A_v \tag{4-6}$$

where k^{corr} is the intrinsic kinetic rate constant of iron corrosion under anoxic conditions (mol.m⁻².s⁻¹), A_v is the volumetric surface area of the metallic iron foil (m².L⁻¹). The kinetic rate constant k_{anox} was fixed to about 5 ×10⁻⁹ mol.m⁻².s⁻¹, which corresponds to a mean value of 1 µm.y⁻¹ commonly found in the literature for anoxic corrosion at neutral pH and claystone water (De Combarieu et al., 2007; Féron et al., 2009).

4.3.6 Secondary solid phases

For the sake of simplicity, all the secondary solid phases were modeled at thermodynamic equilibrium without kinetics. That is to say the corrosion products (e.g. goethite, siderite), as well as the solid phase $Pu(OH)_4(am)$ and $UO_2:2H_2O(am)$, precipitated at thermodynamic equilibrium.

To be in agreement with the experimental results, an inhibiting kinetic effect was assumed on calcite to allow the formation of the metastable polymorph aragonite, as well as on siderite to permit the precipitation of the metastable phase chukanovite. It is worth noting that the aragonite/chukanovite paragenesis was only considered in the reference case, whereas the calcite/siderite paragenesis was used in the complementary modeling cases.

4.4 Modeling of the solution chemistry

HYTEC modeling gave a redox potential Eh of -450 mV (SHE) at pH 8 (Figure 4-5a), that is to say reducing but not strongly reducing since dissolved H₂ produced by iron corrosion was decoupled from the redox state. The redox potential was mostly controlled by the dissolved aqueous release of ferrous iron Fe(II) by the corrosion of the iron foil. The measured ex-situ experimental Eh value was higher, around -100 mV (SHE). The in-situ Eh measurements would have been more representative. Under similar conditions, the redox potential measured directly in-situ potential was -200 mV below the ex-situ one (Odorowski et al., 2017). The present measured Eh was, therefore, semi quantitative only but proved that the experimental system was mildly reducing, neither oxidizing, nor strongly reducing.

Most of main COx water constituents (K, Na, Mg, Cl⁻, SO₄²⁻) did not show any significant variation in concentration during the leaching of the MOX pellet after the pre-corrosion stage, both in the experiment and the model. It was essentially due to the high solution to solid ratio of the experiments. The main evolution was found for Ca whose concentration decreased by about 30 mg.L⁻¹ in the experiment and by about 10 mg.L⁻¹ in the model, probably due to CaCO₃ (aragonite) precipitation.

4.5 Modeling of iron corrosion

4.5.1 Iron corrosion products

The corrosion of the iron foil (Equation 4-5) released ferrous iron ions into the synthetic COx solution (Figure 4-5a). A fraction of them precipitates as the carbonated corrosion product chukanovite both in the experiment (Figure 4-6) and the modeling (Figure 4-5c), the remaining fraction diffused from the foil throughout the cell solution.

Figure 4-5b also shows that the pH profile was not fully homogeneous within the aqueous solution. The model predicted a slight increase in pH locally around the iron foil because the anoxic corrosion liberates hydroxide ions (Equation 4-5). This local increase in pH shifted the bicarbonate equilibriums towards carbonates (Equation 4-7a) and favored the precipitation of the carbonated minerals chukanovite Fe₂(OH)₂CO₃ (Equation 4-7b, Figure 4-5c) and aragonite CaCO₃ (Equation, 4-7c, Figure 4-5d) according to the following set of reactions:

$$HCO_3^- + OH^- \to CO_3^{2-} + H_2O$$
 (4-7a)

$$2 Fe^{2+} + 2 OH^{-} + CO_3^{2-} \to Fe_2(OH)_2CO_3$$
(4-7b)

$$Ca^{2+} + CO_3^{2-} \to CaCO_3 \tag{4-7c}$$

The synthetic COx groundwater was the source of calcium and bicarbonates. Precipitation occurred onto the surface of the iron foil in both the experiment and the modeling.

It will be noted that the mineral chukanovite contains Fe^{2+} cations clearly indicating reducing conditions at the level of the iron foil. Aragonite is a by-product of the reaction but not, strictly speaking, a corrosion product. The literature reports that aragonite may be favored to calcite in the presence of high concentrations of Mg²⁺ (De Choudens-Sanchez and Gonzalez, 2009; Niedermayr et al., 2013; Boyd et al., 2014), which was the case in the synthetic COx water.



Figure 4-5. HYTEC modeling of ferrous iron concentration (a) and pH (b) in the solution, as well as the precipitation of chukanovite and calcite (d) on the iron foil, after 400 days of leaching of the homogeneous MOX pellets in synthetic COx groundwater in presence of a pre-corroded iron foil.



Figure 4-6. Raman spectra of the carbonated secondary phases that formed on the iron foil during the experiments (Kerleguer, 2020; Deliverable WP4).

4.5.2 Iron dissolved concentration

The pre-corroded state of the iron foil was taken into account in the modeling by considering since the beginning of the calculations a dissolved total concentration of iron of about 20 mg.L⁻¹ (3.6×10^{-4} mol.L⁻¹) as well as the initial presence of some chukanovite onto the foil surface.

Figure 4-7 shows that the modeled dissolved iron concentration was within the range of the experimental data, i.e. a mean dissolved iron concentration of 15.6 mg.L⁻¹ (2.8×10^{-4} mol.L⁻¹). Dissolved iron was under the Fe(II) redox state in the calculations with the following main aqueous species Fe²⁺ > FeCO₃ > FeSO₄. The modeling underestimated the iron concentration by a factor 3, probably because chukanovite was probably not at equilibrium with the solution in reality. Introducing a kinetic on precipitation should improve the modeling but also increased the number of parameters to take into account in the model. Furthermore, modeling gave a constant concentration over time and failed to simulate the transition from 20 mg.L⁻¹ (3.6×10^{-4} mol.L⁻¹) in the pre-corrosion to 50 mg.L⁻¹ (8.9×10^{-4} mol.L⁻¹) after 150 days, to eventually come back to a concentration of 40 mg.L⁻¹ (7.1×10^{-4} mol.L⁻¹) after 400 days.

Chukanovite is generally not stable over time and may evolve into siderite. A complementary modeling performed with siderite as the main corrosion product instead of chukanovite clearly underestimated the experimental data, with a mean dissolved iron concentration of 2 mg.L⁻¹ (3.5×10^{-5} mol.L⁻¹), by a factor 30, as shown in Figure 4-7.



Figure 4-7. Experimental and HYTEC modeling results of ferrous iron concentration in the solution controlled by the precipitation of chukanovite or siderite during the leaching of homogeneous MOX pellet in synthetic COx groundwater in presence of a pre-corroded iron foil.

4.6 Scavenging effect of Fe(II) versus the H₂O₂ plume

4.6.1 Base case modeling

The complete consumption of hydrogen peroxide H_2O_2 by aqueous ferrous iron (mostly Fe²⁺, but also FeCO₃... in the COx water) can be schematized by the following mass balance equation

$$\frac{1}{2}H_2O_2 + Fe^{2+} \to Fe^{3+} + OH^-$$
(4-8)

The fact this reaction prevents any oxidative dissolution of $U_{0.73}Pu_{0.27}O_2$ in the modeling is supported by three modeling results:

- the lack of H₂O₂ in solution (Figure 4-8a) that could raise the potential towards more oxidizing values, globally the conditions were significantly reducing as indicated by the calculated redox potential (Figure 4-8b);
- the (slight) decrease of Fe(II) concentration in the solution in contact with the MOX pellets (Figure 4-8c);
- the precipitation of the Fe(III)-phase magnetite Fe(II)Fe₂(III)O₄ on the pellet surface (Figure 4-8d) from the Fe(III) species produced according to the Equation 4.8.

Indeed, Fe³⁺ was very insoluble at pH 8 and precipitated immediately as magnetite:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$
 (4-9)

The lack of H_2O_2 in the solution (i.e. below the quantification limit of 10^{-7} mol.L⁻¹) and magnetite formation on the pellet surface is in full agreement with the WP4 experiment (Figure 4-9). Considering the surface of the pellets, the calculated concentration of magnetite after 400 days with a 90 % disproportionation corresponds to an

average thickness of 2 um assuming that magnetite precipitates as a dense layer over the full surface. SEM



Figure 4-8. HYTEC modeling of the redox potential (a), hydrogen peroxide (b) and ferrous iron (c) concentrations in the solution, as well as the precipitation of magnetite (d) on the MOX pellet, after 400 days of leaching of homogeneous MOX pellet in synthetic COx groundwater in presence of a pre-corroded iron foil.

DisCo



Figure 4-9. Raman spectra of the magnetite that formed onto the MOX pellets during the experiments (Kerleguer, 2020; Deliverable WP4).



Figure 4-10. Pourbaix diagram calculated with the ThermoChimie database for the COx porewater: corrosion products of iron vs pH.

observation showed a non-dense layer of magnetite with a dozen of um thickness in average. Although the model agreement is reasonably good, it would mean that the proportion of H_2O_2 that had reacted with Fe(II) could be higher than assumed in Section 4-3-2.

The precipitation of akaganeite Fe(III)OOH on α -doped UO₂ pellets was observed under similar experimental conditions (Odoroswki et al., 2017). Akagenite is not in included in the ThermoChimie database was reasonably well simulated by its polymorph goethite in the HYTEC calculations. Figure 4-10 indicates the shift from akageneite/goethite towards magnetite was probably due to the fact that the pH of the leaching solution was slightly more alkaline in the present experiments with MOX (pH 8 instead of pH 7).

4.6.2 Sensitivity analysis vs. the intensity of the H_2O_2 radiolytic effective production

Figure 4-11 gives the sensitivity analysis by HYTEC modeling on the ferrous iron and hydrogen peroxide concentrations in the solution as a function of the disproportionation efficiency with siderite as corrosion product. The smaller the disproportionation is, the higher the H_2O_2 global stock available for corrosion is, the more iron flux is required to kill the

oxidant plume. Globally, the sensitivity analysis demonstrated the relevance and flexibility with the experimental conditions of the present reactive transport model.

Only the worst unrealistic case of no disproportionation (a ten-fold increase) is able to keep a bubble of H_2O_2 and to attack the MOX pellet. However, this result should be requalified while considering chukanovite instead of siderite, since the simulated iron concentration in solution is underestimated by more than a factor 10 with siderite. The no-disproportionation case would displace the Fe²⁺/H₂O₂ redox front farther away from the MOX pellet's surface, coinciding with the formation of FeOOH colloids (Figure 4-11c). This was in disagreement with the present experimental results but FeOOH colloids were observed in the case of irradiated MOX leaching with γ -induced radiolysis throughout the cell solution (Odorowski, 2015).



Figure 4-11. Sensitivity analysis on the ferrous iron and hydrogen peroxide concentrations in the solution versus the disproportionation efficiency considering siderite as the main corrosion product.

4.7 Modeling uranium and plutonium releases

4.7.1 Uranium dissolved concentration and solubility-controlling phase

The uranium dissolved concentration in the COx water/iron system became lowered by four orders of magnitude compared to carbonated water, approximately from 5×10^{-6} mol.L⁻¹ (Figure 3-2) to 5×10^{-10} mol.L⁻¹ (Figure 4-12). The experimental and modeled concentrations are very close and related to the thermodynamic equilibrium with the amorphous U(IV) phase

 $UO_2:2H_2O$. The speciation diagram of uranium of Figure 4-13 was drawn with the present database and the synthetic COx water chemistry. The modeling results of the uranium dissolved concentration, the secondary phase $UO_2:2H_2O$ solubility limit and the reducing potential Eh below -400 mV are fully consistent with each other. The diagram also indicates that the measured ex-situ value of Eh is probably too high since at -100 mV the strong complexe $Ca_2UO_2(CO_3)_3$ should raise the uranium concentration in solution well above 10^{-9} mol.L⁻¹. Based on a reactive transport modeling with HYTEC, Figure 4-14a shows that the dissolved of uranium is homogenously diluted into the synthetic COx solution to reach the concentrations shown in Figure 4-12. Figure 4-14b also indicates that the formation of $UO_2:2H_2O(am)$ takes place right on the MOX pellet surface and not inside the solution in the model.

The H₂O₂ consumed by Fe²⁺ and the subsequent precipitation of Fe³⁺ as magnetite means that no oxidant was still available for the oxidative dissolution of the MOX. That is to say the oxidative dissolution could be stopped in the presence of metallic iron. No quantity of U was indeed experimentally found on the iron foil. Most of the released U was sorbed or precipitated onto TiO₂, but also represents a low quantity (0.8 µg, Table 4-2). This means that the oxidative dissolution of U_{0.73}Pu_{0.27}O₂ by H₂O₂ followed by the further reduction of U(VI) by Fe(II) did not occur either. Direct U(IV)-sorption onto TiO₂ could be the mechanism explaining the presence of U on the reactor walls (Odorowski et al., 2017). This dramatic effect of the environment on the uranium release is very similar to what had been obtained for α -doped UO₂ with an alpha activity corresponding to a spent UOX of 50 years old (Odorowski et al., 2017).

A mass balance calculation on uranium was also carried out using the HYTEC simulations. Table 4-2 reports the quantities of uranium released and retrapped in a solid form as amorphous UO₂.2H₂O, which helped to fit the intrinsic rate constant k_{MOx}^{red} of Equation 4-4. The new fitted rate constant is only twice lower than the value used for the UO₂ pellet without any indications of a significant stabilizing effect of plutonium. However, this result was inferred from a strongly coupled system. It should be confirmed by a dedicated and more simple experiment on the dissolution kinetics of the homogeneous MOX under reducing conditions.

	Solid phase	U in solution
Experiment	0.8 μg	0.023 µg
HYTEC modeling		
$k_{MOx}^{red} = 2 \times 10^{-12} \text{ mol.m}^{-2} \text{.s}^{-1}$	4.2 µg	0.019 µg
$k_{MOx}^{red} = 9 \times 10^{-13} \text{ mol.m}^{-2} \text{.s}^{-1}$	0.8 µg	0.019 µg

Table 4-2. Mass balance of the released uranium after 400 days of leaching.



Figure 4-12. Experimental and HYTEC modeling results of uranium dissolved concentration for the homogeneous MOX pellet in carbonated water and in synthetic COx groundwater in presence of a pre-corroded iron foil.



Figure 4-13. CHESS solubility diagrams of uranium as a function of redox potential Eh (V/SHE). The diagram was plotted at a temperature of 25 °C, a pH of 8.1, an activity of $Ca^{2+}of 2.5 \times 10^{-3}$, HCO_3^{-} of 4×10^{-4} and H_4SiO_4 of 2×10^{-4} . The blue circle stands for the modeled Eh and U concentration; the blue triangle for the measured exsitu Eh and U concentration.



Figure 4-14. HYTEC modeling of the aqueous concentrations of uranium (a) and the precipitation of $UO_2:2H_2O$ (b) after 400 days of leaching of homogeneous MOX pellet in synthetic COx groundwater in presence of a pre-corroded iron foil.

4.7.2 Plutonium dissolved concentration and solubility-controlling phase

Figure 4-15 shows that the release of plutonium in the COx water/iron system is within the same order of magnitude compared to carbonated water (Figure 3-2). The Pu concentration is close to the thermodynamic equilibrium with the amorphous Pu(IV)-phase $Pu(OH)_4(am)$ under both experimental conditions (as already discussed in Chapter 3). Similarly to uranium, Figure 4-16a shows that the dissolved plutonium is homogenously diluted into the synthetic COx solution to reach the steady concentration of Figure 4-16b indicates that the formation of $Pu(OH)_4(am)$ takes place right on the MOX pellet surface and not in the solution in the model, similarly to $UO_2:2H_2O$.

The release of plutonium in the iron foil was well captured by the model provided that Pu(III) was decoupled from the redox reactions, but the model diverged from the experimental data when the whole redox states of the plutonium were taken into account. The Pu aqueous concentration increased constantly in time to reach levels above the experimental measured concentrations. In the full redox model, the Pu(III) species predominated in solution over the Pu(IV) species since the redox conditions were sufficiently reducing due to the presence of Fe(II) in solution, to allow the reduction of Pu(IV) into Pu(III).

The global mechanism that takes place in the experiment is, therefore, not well understood for the moment. A first explanation would be that the reduction of Pu(IV) to Pu(III) by Fe(II) could be hindered within the altered layer. The precipitation of amorphous Pu(OH)₃ controlling the dissolved Pu concentration could be another possibility. A sensitivity analysis was done on the solubility product of Pu(OH)₃ whose solubility product varies over one order of magnitude in the literature. Recently, it was shown that the formation constant of Pu(OH)₃ could be re-evaluated from 15.8 to 14.7 (Tasi et al., 2018). But the calculated aqueous concentration and the location of the Pu precipitates were never in agreement with the experimental observations with Pu(OH)₃ (Table 4-3).

The speciation diagram of Figure 4-17 summarizes the different scenario of the Pu solubility control in the COx water / metal iron system. The rather high amount of dissolved iron in equilibrium with the soluble chukanovite imposes reducing conditions (< -400 mV at pH 8.1) that could favor the more soluble Pu(III) redox species over the Pu(IV) ones. If the reduction is inhibited, Pu(OH)₄ remains stable even at -400 mV and limits Pu dissolved concentrations below 5×10^{-10} mol.L⁻¹. The measured ex-situ Eh potential of -100 mV is consistent with the predominance of the Pu(IV) state, but has been found to be inconsistent with respect to the uranium concentration and the presence of metallic iron (Section 4.7.1).

LogK _f Pu(OH) ₃	Pu dissolved total concentr. after 400 days (mol.L ⁻¹)	Location of Pu solid phase precipitation
-15.8	4×10 ⁻⁸	No secondary phase
-14.7	4×10 ⁻⁸	No secondary phase
Pu(III) decoupled	5×10 ⁻¹⁰	Pu(OH) ₄ on the MOX pellets

Table 4-3. HYTEC sensitivity analysis vs. the formation constant of the amorphous $Pu(OH)_3$ solid phase.



Figure 4-15. Experimental and HYTEC modeling results of plutonium dissolved concentration for the homogeneous MOX pellet in carbonated water and in synthetic COx groundwater in presence of a pre-corroded iron foil.

DisCo



Figure 4-16. HYTEC modeling of the aqueous concentrations of plutonium (a) and the precipitation of $Pu(OH)_4$ (b), after 400 days of leaching of homogeneous MOX pellet in synthetic COx groundwater in presence of a pre-corroded iron foil.



Figure 4-17. CHESS solubility diagrams of plutonium as a function of redox potential Eh (V/SHE). The diagram was plotted at a temperature of 25 °C, a pH of 8.1, an activity of HCO_3^- of 4×10^{-4} , SO_4^{-2-} of 10^{-2} (the sulfates were decoupled from the redox). The blue circle stands for the modeled Eh and U concentration; the blue triangle for the measured ex-situ Eh and U concentration; the dotted line corresponds to the $Pu(OH)_4$ solubility when the Pu(III) redox state is discarded.

4.8 Summary of the fully coupled mechanisms

The present reactive transport model fully coupled the interconnected key geochemical reactions, schematically represented in Figure 4-18. The model simulated reasonably well – over more than 1 year – the experimental evolution of the aqueous chemistry, the degree of alteration of the homogeneous MOX matrix, the corrosion of the iron, the location of the redox front and the subsequent precipitation of magnetite.

There was no oxidative dissolution of $U_{0.73}Pu_{0.27}O_2$ releasing U(VI) in solution followed by a reduction to U(IV) by Fe(II). Fe(II) released in solution by the iron foil anoxic corrosion consumed H₂O₂ produced by alpha-radiolysis of water. This redox reaction occurred where radiolytic H₂O₂ was produced, i.e. on the surface of the UO₂ pellets. The resulting Fe(III) precipitated immediately onto the UO₂ pellets as magnetite. The redox front was located right at the surface pellet in the present study due to the fast homogeneous H₂O₂/Fe(II) reaction and significant diffusion and concentration of Fe(II) around the MOX pellets compared to the H₂O₂ production. A potential contribution from the rather small amount of H₂ produced by the water radiolysis and the anoxic corrosion of the iron foil cannot be excluded. However, it is worth noting that an experiment carried out as part of the Kerleguer's PhD thesis (2020) showed that the oxidative dissolution of a heterogeneous MOX was not impacted by hydrogen under 3 bars at 30 % H₂. Globally, it is clear that iron played a major role in the oxidizing dissolution inhibition process for the system presently investigated (localized alpha radiolysis).

There was a weak dissolution of $U_{0.73}Pu_{0.27}O_2$ under reducing conditions and the dissolved uranium concentration was in equilibrium with $UO_2 \cdot xH_2O(am)$. The dissolved concentration of plutonium remained also low in the solution and controlled by the solubility of $Pu(OH)_4$ solid phase.

A local increase in pH around the iron foil due to its anoxic corrosion enabled the precipitation of carbonated secondary phases (aragonite, chukanovite) on its surface.

The coupled geochemical scheme, the mineralogical secondary products, the kinetics, as well as the actinide concentrations, were very close to the results already obtained for alpha-doped UO₂ which is a relevant proxy for the UOX fuel matrix.



Figure 4-18. Coupled reactions taken into account in the reactive transport modeling of the homogeneous MOX alteration in synthetic COx porewater in the presence of metallic iron.

5 Up-scaling of the model to a generic disposal cell of spent MOX fuels

5.1 Generic disposal cell of spent MOX fuels

5.1.1 Configuration of the disposal cell

The knowledge gained from the reactive transport modeling developed in Chapter 4 on the experimental set obtained at the laboratory scale served as a basis for a generic and very simplified configuration of a disposal cell of spent MOX fuels for the up-scaled modeling. The direct disposal of spent MOX fuel is still an open question in France and there were no well-defined disposal concepts that were available at the time of the DISCO project. It could be possible that the configuration partly relied upon the present concept developed for the underground disposal of vitrified high-level waste (HLW) in the Callovo-Oxfordian claystone formation. The concept consists of low-carbon steel overpack of 6 cm thickness encapsulates a single waste canister that contains the radioactive waste. A 2.5 cm thick liner (sleeve) made of low-carbon steel is emplaced along the cell in the indurated clay formation. A technical gap (void) of 1.5 cm can be present between the overpack and the liner. This configuration was clearly simplified and adapted to the spent MOX fuel to lead to the schematic cross-section of Figure 5-1.

The purpose of such calculations was to perform mass-balance simulations at the scale of a disposal cell of spent MOX fuel between the diffusive flux of radiolytic H_2O_2 from the one hand and the diffusive flux of the iron reducing scavenger from the one hand. The location of this front will, generally speaking, depend on the nature of the irradiation fields, their intensity, and the flux of matter between oxidizing and reducing species coming from the fuel and from the environment. It would be interesting to estimate whether the scavenging effect of iron observed and modeled in the leaching cell of Chapter 4 would still hold in the case of a disposal cell.

The characteristic spatial scale was roughly similar in both cases, from a few centimeters in the cell to a dozen of centimeters in the near-field of the spent-fuel assembly. On the other side, there were several differences among the two configurations. Firstly, the flux of dissolved iron took place all around the pellets in 3D in the experiment whereas flux will only occur at the boundary between the fuel assembly and the steel overpack in a 2D-radial geometry (Figure 5-2). The core of the assembly will not be in direct contact with the solution containing iron. Secondly, the water/liquid on solid L/S ratio in the experiment was much higher than expected in the disposal cell (with almost no void and low inner porosities of the disposal components filled by water). The absolute values of the masses were on the contrary much greater in the disposal cell than in the leaching cell. Eventually, the characteristic duration is completely different: in the range of one year in the experiment, for 100 000 years in the geologic disposal (Ewing, 2015; De Windt and Spycher, 2019). Furthermore, the radioactive decay of the alpha emitters of the MOX will progressively decrease the production rate of the radiolytic species.



Figure 5-1. Cross-section of the simplified and generic configuration of the MOX fuel disposal cell in a claystone formation considered in the reactive transport modeling.



Figure 5-2. Illustration of the main differences in terms of diffusive flux geometry and water on solid ratio between the lab test (a) and the disposal cell (b).

5.1.2 Properties of the disposal cell components

MOX assembly and pellets

The homogeneous $U_{0.73}Pu_{0.27}O_2$ MOX stood as a proxy for the matrix of the MOX pellets of the single spent fuel assembly. The assembly zone was seen as a homogenized elementary representative volume at the scale of the grid size. The volume fraction of the MOX pellets inside the assembly zone was fixed to 0.40 according to the schematic cross-section of a MOX assembly given in Figure 5-3. No diffusive barrier function was given to the cladding for the sake of simplicity. This latter hypothesis would be a strongly penalizing assumption for a true performance assessment of a MOX cell disposal.

The full surface of the MOX $U_{0.73}Pu_{0.27}O_2$ pellet is assumed to be in contact with the solution and to generate the radiolytic H₂O₂. This could also be a penalizing hypothesis since the surface of contact could be only the lateral one, not the basal plane of the pellets, depending on the stacking of the pellets. On the other hand, the reactive surface may become greater than the geometric one inside the rim or in case of grain boundary dissolution on the long term. Again, the objective was to scale-up the cell leaching configuration, not a performance assessment.

The pore diffusion coefficient in the assembly zone was set to 10^{-9} m².s⁻¹ as in the leaching cell test (Table 5-1), i.e. without any tortuosity effect.

	MOX assembly	Corroded C-steel	COx claystone
Porosity	0.30	0.20	0.18
D_p	$10^{-9} \text{ m}^2.\text{s}^{-1}$	$10^{-9} \text{ m}^2.\text{s}^{-1}$	$1.7 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$
D_{eff}	$3 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$	$2 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$	$3 \times 10^{-11} \text{ m}^2.\text{s}^{-1}$

 Table 5-1. Porosity and diffusion parameters considered in the HYTEC modeling.



(b)



Figure 5-3. (a) The modeling assumed a volumic fraction of the MOX pellets around 0.40 in the assembly (https://www.laradioactivite.com) and (b) a reactivity of the full geometric surface of the pellet.

The C-steel overpack and liner/sleeve

The overpack and liner (sleeves) in C-steel were assumed to be fully corroded and not watertight, the expansive corrosion products having filled all gaps. The full mass of the metallic iron was supposed to be transformed into the two types of iron corrosion products found in the lab experiments in α -doped UO₂ and MOX pellet, i.e. siderite at pH 7 and chukanovite at pH 8, respectively. Chukanovite was used instead of siderite in the claystone mineralogy when chukanovite was the main corrosion product. It is worth noting that chukanovite would probably change into the more stable Fe-carbonate siderite on the long disposal term. However, one considered the two types of corrosion products for the sake of a sensitivity analysis on the dissolved iron content in equilibrium with these corrosion products (at least 10 times higher for chukanovite than siderite). Other corrosion products such as magnetite, iron-silicates as greenalite, should be investigated in a further step.

The same pore diffusion coefficient as for the MOX assembly was set in the modeling (Table 5-1). This was an overestimated and pessimistic value since the corrosion products should have some inner tortuosity but this diffusion coefficient was directly comparable to the conditions of the leaching cell.

Claystone

The geochemical and diffusion properties of the Callovo-Oxfordian claystone were taken from the benchmark of Marty et al. (2015). For the sake of simplicity, the mineralogy consisted of calcite, siderite and quartz. The clay fraction was not taken into account in the present modeling that focused on the MOX/steel interaction. The water chemistry was identical to the synthetic porewater used in Chapter 4 (Table 4-1), that is to say moderately mineralized, pH of 8, sodium as the predominant cation, chlorides and sulfates as the predominant anions. The porosity and the diffusion coefficient given by Marty et al. (2015) are reported in Table 5-1.

5.2 Modeling approach and scenarios

5.2.1 Kinetics of the main processes and simulation grid

The thermodynamic data, the kinetic laws and the kinetic parameters were exactly the same as the ones used for the modeling of the MOX leaching test in synthetic COx water in presence of a partially corroded metallic iron in Chapter 4, that is to say:

- Modeling of H_2O_2 production implicitly reduced by disproportionation on the $U_{0.73}Pu_{0.27}O_2$ surface (Section 4-3-2, Equation 4-3);
- Radiolytic oxidation of U_{0.73}Pu_{0.27}O₂ by H₂O₂ (Section 4-3-3, Equation 3-3);
- Dissolution of $U_{0.73}Pu_{0.27}O_2$ under reducing conditions (Section 4-3-4, Equation 4-4).



Figure 5-4. HYTEC modeling grid in 1-D radial geometry of the generic cell configuration with the assembly in red, the fully corroded steel in gray and the COx claystone in blue.

There were, nevertheless, three differences:

- The reduction of the H₂O₂ production was fixed to 99% as in the MOX experiment in carbonated water since the modeling results demonstrated that a substantial part of the MOX pellet was not in direct contact with dissolved iron at the highest α-activity;
- The anoxic corrosion of metallic iron (Section 4-3-5) was not simulated since the steel was fully assumed to be corroded when the MOX fuel was put in contact with the environment;
- The pH was fixed (set constant) in the modeling, either at pH 7 with siderite as corrosion product, or at pH 8 with chukanovite as corrosion product.

The pH values were fixed to be as close as possible to the leaching cell conditions. A second reason to set pH constant was that a precise modeling of the pH evolution would have required a full geochemical model taking into account pH buffers as the clay minerals...; which was beyond the scope of this study.

Figure 5-4 shows the HYTEC modeling grid in 1-D radial geometry (pseudo 2D) of the generic cell configuration with the assembly, the fully corroded steel and the COx claystone. The grid node size was 5×10^{-3} m in the reactive zone composed of the assembly/overpack/liner system.

5.2.2 Modeling scenarios vs. the intensity of the α -radiolysis and corrosion products

With respect to the modeling scenario, a constant temperature of 25°C and water resaturated conditions were set in the modeling for the sake of a direct up-scaling of the leaching cell model. This is not fully representative of the disposal conditions. The temperature should be in the range of 50 – 70 °C for several dozens of years and the release of hydrogen by anoxic iron corrosion should partly desaturate the near-field of the disposal cell for at least a dozen of years. Figure 5-5 gives the decrease with time of the α -activity of irradiated MOX at a burn-up of 47.5 GWd.t⁻¹. Two time periods were studied in the present modeling: *period I* with an α -activity equivalent to 50 years of decay (the studied U_{0.73}Pu_{0.27}O₂ in Chapters 3 and 4), and then *period II* of 2000 years equivalent to a ten-fold decay of the α -activity.

Table 5-2 details the different cases investigated by the reactive transport modeling with respect to the equivalent α -activity and the nature of the corrosion products. The consumption of H₂O₂ by the MOX was discarded in a first step to better emphasize the scavenging effect of

dissolved Fe(II) alone. The calculations were relaunched in a second stage while considering the full reactivity of the MOX versus the hydrogen peroxide.

A duration of 100 years of interaction between the different components of the near field was set for each calculation. This duration was large enough to reach a steady state in the aqueous concentrations and to emphasize the main geochemical evolution of the solid phases.



Figure 5-5. Decrease with time of the α -activity of irradiated MOX at a burn-up of 47.5 GWd.t⁻¹; the red dots correspond to the model considered MOX pellets with an α -activity equivalent to 50 years of decay (the studied $U_{0.73}Pu_{0.27}O_2$ in Chapters 3 and 4, period I in Chapter 5) and to 2000 years of decay (period II in Chapter 5, ten time lower).

Table	<i>5-2</i> .	Matrix	of	the	different	scenarios	investigated	by	the	reactive
transp	ort m	odeling	with	resp	pect to the	e equivalen	t α -activity of	^c irra	adiat	ed MOX
at a bi	ırn-up	o of 47.5	GW	$d.t^{-1}$	and the n	ature of th	e corrosion p	rodu	ects;	in a first
step th	ne co	nsumptio	on oj	$f H_2$	O_2 by the	e MOX wa	s discarded i	to en	mpha	size the
scaven	ging	effect of	disse	olve	d Fe(II) a	lone.			_	

MOX oxidative dissolution	Period I (50 y of alpha decay)	Period I (2000 y of alpha decay)
No	chukanovite siderite	chukanovite
Yes	chukanovite	chukanovite

5.3 Modeling results and discussion

5.3.1 Modeling of the redox front and H_2O_2 scavenging by Fe(II) without MOX dissolution

This first set of calculations did not include the modeling of the MOX oxidative dissolution by H_2O_2 in order to better illustrate the modeling of the redox front and H_2O_2 scavenging by Fe(II). Figure 5-6a shows the concentration profile of H_2O_2 throughout the near-field barrier system. A steady-state of H_2O_2 is quickly reached in less than 1 year.

For the equivalent 50-y α -activity, the concentration of H₂O₂ remains rather high in the most of the MOX assembly volume because the diffusive flux of dissolved Fe(II) in equilibrium with chukanovite is not sufficiently high to kill the α -radiolytic H₂O₂. Figure 5-7 indicates that the redox potential is clearly oxidizing in this zone and reducing in the corroded steel and claystone. The Fe(II) concentration in solution (Figure 5-6a) is controlled by the dissolution of chukanovite (Figure 5-8a) whose solubility ultimately limits the magnitude of the diffusive flux of reducing Fe(II) species towards the MOX assembly. The scavenging and redox front only occurs at the very boundary of the assembly whereby the steel corrosion products represents a large mineral stock of reducing Fe(II) in mass for a very long duration. Magnetite precipitates at the redox front and maintains a remaining concentration of dissolved iron into the assembly, as shown in Figure 5-8b. Fe(II) species on the left hand side. The unusual Fe(III) concentration in solution of Figure-6b is linked to the formation of the Fe(III)CO₃OH complex in solution due to the large amount of carbonates (5×10⁻² mol.L⁻¹) gradually brought by the dissolution of chukanovite.

For the equivalent 2000-y α -activity, there is a complete exhaustion of H₂O₂ everywhere in the near-field. As indicated by Figure 5-6a, the diffusive flux of dissolved Fe(II) is sufficiently high with respect to the rate of H₂O₂ production to be able to propagate into the full MOX assembly zone. All the system in now under reducing conditions, as shown by Figure 5-7. In the assembly, the Eh potential varies from -300 mV (at pH 8) at the inner zone to -400 mV at the boundary with the corrosion products. The dissolution of chukanovite is less important compared to the 50-y case (Figure 5-8a) and the amount of magnetite is also consequently lower (Figure 5-8b). The most significant difference with this respect is that magnetite now precipitates uniformly over the full assembly zone (as magnetite does over the full pellet surface in the leaching test).

The less soluble siderite was also considered as the main corrosion product instead of chukanovite. For the equivalent 50-y α -activity, the concentration and diffusive flux of dissolved iron becomes lower as expected from the lower solubility. Accordingly, the profile of H₂O₂ becomes slightly more intense with an extension up to the very limit of the corroded steel (Figure 5-9). For the equivalent 2000-y α -activity, the H₂O₂ concentration is decreased by a factor 10 but the dissolved iron content is not able to fully scavenge the H2O2 production. One has to go to a alpha decay of about 10 0000 years to reach depletion.



Figure 5-6. HYTEC modeling of the steady-state concentration of the dissolved total concentration in H_2O_2 (a) and Fe(II) (b) in the disposal cell as a function of the α -activity; with chukanovite as the corrosion product of the C-steel, a H_2O_2 disproportionation of 99 %, and no MOX oxidative dissolution by H_2O_2 .



Figure 5-7. HYTEC modeling of the steady-state redox potential Eh at pH 8 in the disposal cell as a function of the α -activity; with chukanovite as the corrosion product of the C-steel, a H_2O_2 disproportionation of 99 %, and no MOX oxidative dissolution by H_2O_2 .



Figure 5-8. HYTEC modeling of the dissolution of chukanovite (a) and the precipitation of magnetite (b) as a function of the α -activity after 100 years of evolution; with a H_2O_2 disproportionation of 99 %, and no MOX oxidative dissolution by H_2O_2 .



Figure 5-9. HYTEC modeling of the steady-state concentration of the dissolved total concentration in H_2O_2 (a) and Fe(II) (b) in the disposal cell as a function of the nature of the corrosion product of the C-steel (chukanovite vs. siderite); with a H_2O_2 disproportionation of 99 %, and no MOX oxidative dissolution by H_2O_2 .

5.3.2 Modeling of the MOX dissolution

Introducing the MOX oxidative dissolution in the model significantly depletes the H_2O_2 concentration in the assembly zone in the case of the equivalent 50-years of alpha activity. The mean value decreases by three orders of magnitude, from 5×10^{-4} mol.L⁻¹ (Figure 5-6a) to 2×10^{-7} mol.L⁻¹ (Figure 5-10). It is worth pointing out that the concentration obtained with the combination of an implicit H_2O_2 disproportionation of 99 % and a kinetics of MOX oxidative dissolution leads to a steady-state value (1.8×10^{-7} mol.L⁻¹), which is very close to the value found in the modeling of the MOX pellet in carbonated water with an explicit kinetic modeling of the disproportionation (1.0×10^{-7} mol.L⁻¹, Figure 3-2). The agreement demonstrates the robustness and versatility of the reactive transport model.

The amount of magnetite is only slightly decreased in intensity (Figure 5-11) indicating that the diffusive flux of the radiolytic H_2O_2 towards the corroded overpack is faster than the rate of consumption by the additional MOX dissolution.

The main effect of introducing the dissolution of $U_{0.73}Pu_{0.27}O_2$ in the model is the release of oxidized U(VI) species in the case of the 50-year α -activity, as shown in Figure 5-12a. The dissolved uranium concentration rises to a steady-state concentration of about 5×10^{-4} mol.L⁻¹. Uranophane cannot precipitate in the assembly zone despite the concomitant presence of dissolved U(VI), Ca and H₄SiO₄ due to high stability of the ternary Ca–U(VI)–CO₃ complexes.

The steady-state results from the combination of a source-term by MOX dissolution, the diffusion of U(VI) in the direction of the corroded steel and a sink-term induced by the reduction into U(IV) due to the homogeneous reaction with dissolved Fe(II). The latter reaction occurs at thermodynamic equilibrium in the model, and leads to the precipitation of $UO_2:2H_2O$ right at the redox front (Figure 5-12b). Cui and Spahiu (2003) pointed out the experimental possibility of the reduction of U(VI) on corroded iron under anoxic conditions. In the present modeling, this mechanism dramatically limits the migration of U(IV) within the host-rock due to the low solubility of $UO_2:2H_2O$. However, the dissolution of an irradiated MOX matrix would liberate fission products that would not necessarily be reduced at the redox front and would migrate through the claystone host rock.

Eventually, there is no modification in the 1000-year α -activity case since H₂O₂ has already been fully depleted by the Fe(II) flux before the introduction of the MOX oxidative dissolution, in a similar scheme as observed in the lab leaching test of Chapter 4. The formation of UO₂:2H₂O is here due to the slow dissolution of U_{0.73}Pu_{0.27}O₂ under reducing conditions according to Equation 4-4.



Figure 5-10. HYTEC modeling of the steady-state concentration of the dissolved total concentration in H_2O_2 in the disposal cell as a function of the α -activity; with chukanovite as the corrosion product of the C-steel, a H_2O_2 disproportionation of 99 %, as well as MOX oxidative dissolution by H_2O_2 .



Figure 5-11. HYTEC modeling of the precipitation of magnetite as a function of the α -activity after 100 years of evolution; with chukanovite as the corrosion product of the C-steel, a H_2O_2 disproportionation of 99 %, as well as MOX oxidative dissolution by H_2O_2 .



Figure 5-12. HYTEC modeling of the dissolved total concentration in uranium (a) and of the precipitation of UO_2 : $2H_2O$ (b) as a function of the α -activity after 100 years of evolution; with chukanovite as the corrosion product of the C-steel, a H_2O_2 disproportionation of 99 %, as well as MOX oxidative dissolution by H_2O_2 .

(a)

6 Conclusion and perspectives

Recall of the main objectives

The present study brought insights into two main objectives of the DISCO project. The first goal was to assess whether novel types of fuel (MOX in the present study) behave like the conventional UOX ones. The second objective was to better understand the dissolution of spent fuel matrix under conditions representative of failed containers (carbon steel in the present study) under reducing repository environments. The present study assumed that the host rock consisted of the Callovo-Oxfordian (COx) claystone.

Modeling approaches and results

Chemical and reactive transport models were been developed and validated from leaching experiments of a non-irradiated homogenous MOX pellet ($U_{0.73}Pu_{0.27}O_2$). The Pu content and isotopy generates an alpha activity equivalent to 50-year old spent fuel MOX at a burn-up of 47.5 GWd.t⁻¹. The first experiment was performed in carbonated water to get the intrinsic kinetics of dissolution, and the second one in synthetic COx claystone groundwater representative of the French disposal site in the presence of an iron foil simulating the steel container. The latter experiment was performed by CEA in the WP4 of DISCO. The models took into account the kinetics of hydrogen peroxide (H₂O₂) radiolytic production and disproportionation at the MOX pellet surface, the kinetics of the oxidative dissolution of the MOX matrix by H₂O₂, the kinetics of reducing dissolution of the MOX matrix, and the kinetics of anoxic corrosion of the iron foil. A large set of reactions at thermodynamic equilibrium were considered by using the ThermoChimie database, in particular the redox of iron, plutonium and uranium species.

The incongruent release of uranium and plutonium controlled by the precipitation of an amorphous $Pu(OH)_4$ altered layer, and the high disproportionation of H_2O_2 by the $U_{0.73}Pu_{0.27}O_2$ surface were correctly modeled. The model helped to interpret the key geochemical and mineralogical processes, as well as the U and Pu chemistry. Both experimental and modeling results shown that the release of uranium in groundwater in the presence of metallic iron became very significantly lowered compared to carbonated water conditions. The Fe(II) released in solution by the iron foil anoxic corrosion consumed H_2O_2 produced by alpha-radiolysis of water. This redox reaction occurred where radiolytic H_2O_2 was produced, i.e. on the surface of the MOX pellets. The redox product Fe(III) precipitated immediately onto the MOX pellets as magnetite. The oxidative dissolution was strongly inhibited despite a high alpha activity due to plutonium. The release of uranium and plutonium were controlled by $UO_2.2H_2O$ and $Pu(OH)_4$, respectively. Chukanovite and aragonite precipitated on the iron foil during the anoxic corrosion in full agreement with the experimental analysis and observations.

The present reactive transport model also presented some weak points. First, it did not include any detailed mechanistic processes of the radiolytic chemistry and the numerous radical species beside the production of the predominant oxidant H_2O_2 . This level of accuracy has been reached by Wu et al. (2014) or Riba et al. (2020). But the present model was, on the contrary, easily compatible with reactive transport models of cement leaching, bentonite/iron interaction, etc. at higher spatial scales (from the mm to the dozen of meters) than it can usually be handled with the detailed radiolytic models. Along the same lines, a second weakness of the model is that H_2O_2 disproportionation onto the MOX pellet that was simulated as an empirical first order law without explicitly simulated the detailed reaction (e.g. the modification of the redox state of Pu, as briefly explained in Section 3-2-4).

Up-scaling to a disposal cell

The reactive transport model that had been validated on lab experiments was then up-scaled to a disposal cell of spent MOX fuel assemblies. The generic configuration was derived from the present French waste concept for vitrified high-level waste. One single MOX assembly is inserted in carbon steel overpack. The overpack is directly placed in a carbon steel liner within the COx host rock. The full mass of metallic iron Fe(0) were assumed to be corroded into either chukanovite or siderite, respectively corresponding to high or low dissolved Fe(II) concentrations. The U_{0.73}Pu_{0.27}O₂ matrix served as a simplified proxy for the complex irradiated spent fuel. The purpose of this modeling was to perform mass-balance simulations at the scale of a disposal cell between the diffusive flux of radiolytic H₂O₂ and the diffusive flux of the reducing scavenger Fe(II). Two equivalent durations of alpha decay and radiolytic productions were studied, the present 50-year case and a 1000-year equivalent of decay. In the 50-y case, the diffusive flux of dissolved Fe(II) is not sufficiently high. The redox front occurred at the very boundary of the assembly whereby the steel corrosion products represented a large mineral stock of reducing Fe(II) in mass for a very long duration. The redox potential was clearly oxidizing in the assembly zone and reducing in the corroded steel and claystone. There was a dissolution of the MOX matrix with a release of U(VI) in solution, followed by the reduction and precipitation of U(IV) as UO₂:2H₂O. For the equivalent 2000year α -activity, there was a complete exhaustion of H₂O₂ everywhere in the near-field of the disposal cell. The processes were similar to what had been modeled in the leaching cell experiments. Eventually, it is worth mentioning that the Fe(II) reactivity has to be seen as a complementary beneficial action to the well-known H₂ scavenging effect that would probably be the dominant process.

Comparison with UOX type fuel

In comparison with the experimental results of Odorowski et al. (2016) on α -doped UO₂, the plutonium content made the solid solution U_{0.73}Pu_{0.27}O₂ more resistant than UO₂ towards leaching. Despite a higher alpha activity due to the higher plutonium content, the release of uranium was lower and the consumption of H₂O₂ was higher. The experiments and modeling of the more complete system with the synthetic claystone water and the iron foil did not show any significance differences between the α -doped UO₂ and U_{0.73}Pu_{0.27}O₂ MOX pellets.

Some perspectives

Perspectives in the straight lines of this study would to develop a more detailed mechanisms of Pu(IV) surface enrichment of the MOX along with a solid solution model of $U_{0.73}Pu_{0.27}O_2$ matrix. A complementary investigation on the inhibition role of the chemistry of the COx

claystone groundwater on uranium and plutonium releases in solution can also developed in a further modeling provided that dedicated experiments would be available. The redox chemistry of the plutonium should also be better understood and modeled, in particular the apparent stability of the Pu(IV) redox state over Pu(III) in reducing conditions. The two HYTEC models validated for the UO₂ pure structure and the $U_{0.73}Pu_{0.27}O_2$ mixed oxide should also be combined for a better description of heterogeneous microstructural MOX fuels (with Pu-enriched agglomerates within a UO₂ matrix) currently in use in the nuclear power plants.

Acknowledgement

Dr. Christelle Martin (Andra) and Dr. Florent Tocino (EdF) are gratefully acknowledged for their regular scientific discussions on the modeling results and their suggestions about the disposal concepts all along the DISCO project. Several relevant comments of Dr Enzo Curti (PSI) on Chapters 3 and 4 that helped to improve the quality and correctness of the report is also gratefully acknowledged.



The research leading to these results has received funding from the European Commission Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2016-2017-1) under grant agreement n° 755443 (DisCo project).

References

- Altmaier, M., Gaona, X., Fanghänel, T. (2013). Recent Advances in Aqueous Actinide Chemistry and Thermodynamics. Chem Rev 113, 901–943.
- Amme, M., Pehrman, R., Deutsch, R., Roth, O., Jonsson, M. (2012). Combined effects of Fe(II) and oxidizing radiolysis products on UO₂ and PuO₂ dissolution in a system containing solid UO₂ and PuO₂. J Nucl Mater 430, 1–5.
- Azoulay, I., Rémazeilles, C., Refait, P. (2012). Determination of standard Gibbs free energy of formation of chukanovite and Pourbaix diagrams of iron in carbonated media. Corros. Sci. 58, 229–236.
- Bauhn, L., Hansson, N., Ekberg, C., Fors, P., Delville, R., Spahiu, K. (2018). The interaction of molecular hydrogen with α-radiolytic oxidants on a (U,Pu)O₂ surface. J Nucl Mater 505, 54–61.
- Bildstein, O., Claret, F., Frugier, P. (2019). RTM for Waste Repositories. Reviews in Mineralogy and Geochemistry 85, 419–457.
- Boyd V., Yoon H., Zhang C., Oostrom M., Hess N., Fouke B., Valocchi A.J., Werth, C.J. (2014). Influence of Mg²⁺ on CaCO₃ precipitation during subsurface reactive transport in a homogeneous silicon-etched pore network. Geochim. Cosmochim. Acta 135, 321–335.
- Bruno, J., Casas, I., Puigdomenech, I. (1991). The kinetics of dissolution of UO_2 under reducing conditions and the influence of an oxidized surface-layer (UO_{2+x}) Application of a continuous flow-through reactor. Geochim Cosmochim Acta 55, 647–658.
- Casas, I., De Pablo, J., Clarens, F., Giménez, J., Merino, J., Bruno, J., Martínez-Esparza, A. (2009). Combined effect of H₂O₂ and HCO₃⁻ on UO₂(s) dissolution rates under anoxic conditions. Radiochim. Acta. 97, 485–490
- Christensen, H., Bjergbakke, E. (1986). Application of CHEMSIMUL for groundwater radiolysis. Nucl Chem Waste Manag 6, 265–270.
- Cui, D.Q., Spahiu K. (2002). The reduction of U(VI) on corroded iron under anoxic conditions. Radiochim. Acta 90, 623–628.
- Debure, M., De Windt, L., Frugier, P., Gin, S. (2013). HLWglass dissolution in the presence of magnesium carbonate : Diffusion cell experiment and coupled modeling of diffusion and geochemical interactions. Journal of Nuclear Materials 443, 507–521.
- De Choudens-Sanchez V., Gonzalez, L.A. (2009). Calcite and aragonite precipitation under controlled instantaneous supersaturation: Elucidating the role of CaCO₃ saturation state and Mg/Ca ratio on calcium carbonate polymorphism. J. Sed. Res. 79, 363–376.

- De Combarieu, G., Barboux, P., Minet, Y. (2007). Iron corrosion in Callovian-Oxfordian argilite: From experiments to thermodynamic/kinetic modelling. Phys. Chem. Earth 32, 346–358.
- De Pablo, J., Clarens, F., El Aamrani, F., Rovira, M. (2001). The Effect of Hydrogen Peroxide Concentration on the Oxidative Dissolution of Unirradiated Uranium Dioxide. Mat. Res. Soc. Symp. Proc. 663, 409–416.
- De Windt, L., Burnol, A., Montarnal, P., van der Lee, J. (2003). Intercomparison of reactive transport models applied to UO₂ oxidative dissolution and uranium migration. Journal of Contaminant Hydrology 61, 303–312.
- De Windt, L., Pellegrini, D., van der Lee, J. (2004). Coupled modeling of cement/ claystone interactions and radionuclides migration, Journal of Contaminant Hydrology 68, 165–182.
- De Windt, L., Schneider, H., Ferry, C., Catalette, H., Lagneau, V., Poinssot, C., Poulesquen, A., Jégou, C. (2006). Modeling radionuclide source-terms and release in a spent nuclear fuel disposal. Radiochimica Acta 94, 787–794.
- De Windt, L., Marsal, F., Corvisier, J., Pellegrini, D. (2014). Modeling of oxygen gas diffusion and consumption during the oxic transient in a disposal cell of radioactive waste. Applied Geochemistry 41, 115–127.
- De Windt, L., Spycher, N. (2019). Reactive Transport Modeling: A Key Performance Assessment Tool for the Geologic Disposal of Nuclear Waste. Elements 15, 99–102.
- De Windt, L., Goblet, P., Kerleguer, V., Jégou, C. (2019). Progress on the modeling of the homogeneous U0.73Pu0.27O2 alteration as a simulant of MOX fuel matrices in an underground disposal cell. DISCO Grant Agreement: 755443, DELIVERABLE D5.3.
- Ekeroth, E., Roth, O., Jonsson M. (2006). The relative impact of radiolysis products in radiation induced oxidative dissolution of UO₂. J. Nucl. Mater. 355, 38–46.
- Ewing, R. C. (2015). Long-term storage of spent nuclear fuel. Nat Mater 14, 252–257.
- Féron, D., Crusset, D., Gras, J.M. (2009). Corrosion Issues in the French High-Level Nuclear Waste Program. Corrosion 65, 213–223.
- Giffaut, E., Grive, M., Blanc, P., Vieillard, P., Colas, E., Gailhanou, H., Gaboreau, S., Marty, N., Made, B., Duro, L. (2014). Andra thermodynamic database for performance assessment: ThermoChimie. Appl Geochem 49, 225–236.
- Guillaumont, R., Fanghanel, T., Neck, V., Fuger, J., Palmer, D. A., Grenthe, I., Rand, M. H. (2003). Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium. Elsevier, Amsterdam, The Netherlands.
- Hardwick, T.J. (1957). The rate constant of the reaction between ferrous ions and hydrogen peroxide in acid solution. Canad J Chem 35, 428–436.

- Haschke, J.M., Oversby, V.M. (2002). Plutonium chemistry: a synthesis of experimental data and a quantitative model for plutonium oxide solubility. J Nucl Mater 305, 187–201.
- Jégou, C., Caraballo, R., Peuget, S., Roudil, D., Desgranges, L. Magnin, M. (2010). Raman spectroscopy characterization of actinide oxides (U_{1-y}Pu_y)O₂: Resistance to oxidation by the laser beam and examination of defects. J Nucl Mater 405, 235–243.
- Kerleguer, V. (2020). Apport de l'étude de matériaux modèles U_{1-x}Pu_xO₂ à la compréhension des mécanismes d'altération des combustibles UOx et MOx en stockage géologique. PhD thesis, PSL Univ., MINES ParisTech (France), 199 p.
- Kerleguer, V., Jegou, C., De Windt, L., Broudic, V., Jouan, G., Miro, S., Tocino, F., Martin, C. (2020). The mechanisms of alteration of a homogeneous U_{0:73}Pu_{0:27}O₂ MOX fuel under alpha radiolysis of water. J Nucl Mater 529, 151920.
- Korzhavyi, P.A., Vitos, L., Andersson, D.A., Johansson, B. (2004). Oxidation of plutonium dioxide. Nat. Mater. 3, 225–228.
- Lemire, R.J., Garisto, F. (1989). The solubility of U, Np, Pu, Th and Tc in a geological disposal vault for used nuclear fuel, At. Energy Canada Limited, AECL.
- Liu, N., Wu, L., Qin, Z., Shoesmith, D.W. (2016). Roles of radiolytic and externally generated H₂ in the corrosion of fractured spent nuclear fuel. Environ. Sci. Technol. 50, 12348–12355.
- Liu, N., Qin, Z., Joël, J.J., Shoesmith, D.W. (2017). Modelling the radiolytic corrosion of adoped UO₂ and spent nuclear fuel. Journal of Nuclear Materials 494, 87–94.
- Liu, M., Kang, Q., Xu, H. (2020). Modelling uranium dioxide corrosion under repository conditions: A pore-scale study of the chemical and thermal processes. Corrosion Sc. 167, 108530.
- Lousada, C.M., Trummer M., Jonsson M. (2013). Reactivity of H₂O₂ towards different UO₂based materials: the relative impact of radiolysis products revisited. J. Nucl. Mater. 434, 434–439.
- Maillard, C., Adnet, J.M. (2001). Plutonium(IV) peroxide formation in nitric medium and kinetics Pu(VI) reduction by hydrogen peroxide. Radiochim. Acta. 89, 485–490.
- Marty, N.C.M., Bildstein, O., Blanc, P. et al. (2015). Benchmarks for multicomponent reactive transport across a cement/clay interface. Comput Geosci 19, 635–653.
- Merino, J., Cera, E., Bruno, J., Quinones, J., Casas, I., Clarens, F., Gimenez, J., de Pablo, J., Rovira, M., Martinez-Esparza, A. (2005) Radiolytic modelling of spent fuel oxidative dissolution mechanism. Calibration against UO₂ dynamic leaching experiments. J Nucl Mater 346, 40–47.
- Millero, F.J., Sotolongo, S. (1989). The oxidation of Fe(II) with H₂O₂ in seawater. Geochim Cosmochim Acta 53, 1867–1873.

- Neck, V., Kim, J.I. (2001). Solubility and hydrolysis of tetravalent actinides. Radiochim Acta 89, 1–16.
- Niedermayr A., Koehler S.J., Dietzel, M. (2013). Impacts of aqueous carbonate accumulation rate, magnesium and polyaspartic acid on calcium carbonate formation (6-40 degrees C). Chem. Geol. 340, 105–120.
- Nilsson, S., Jonsson, M., (2011). H_2O_2 and radiation induced dissolution of UO_2 and SIMFUEL pellets. J Nucl Mater 410, 89–93.
- Odorowski, M. (2015). Altération de la matrice (U,Pu)O₂ du combustible irradié en conditions de stockage géologique: Approche expérimentale et modélisation géochimique. PhD thesis, MINES ParisTech (France), 277 p.
- Odorowski, M., Jégou, C., De Windt, L., Broudic, V., Peuget, S., Magnin, M., Tribet, M., Martin, C. (2016). Oxidative dissolution of unirradiated Mimas MOX fuel (U/Pu oxides) in carbonated water under oxic and anoxic conditions. J Nucl Mater 468, 17–25.
- Odorowski, M., Jegou, C., De Windt, L., Broudic, V., Jouan, G., Peuget, S., Martin, C. (2017). Effect of metallic iron on the oxidative dissolution of UO₂ doped with a radioactive alpha emitter. Geochim Cosmochim Acta 219, 1–21.
- Pehrman, R., Trummer, M., Lousada, C.M., Jonsson, M. (2012). On the redox reactivity of doped UO₂ pellets – Influence of dopants on the H₂ O₂ decomposition mechanism. J Nucl Mater 430 (2012) 6–11.
- Poinssot, C., Ferry, C., Lovera, P., Jegou, C., Gras, J.-M. (2005). Spent fuel radionuclide source term model for assessing spent fuel performance in geological disposal. Part II: Matrix alteration model and global performance. J Nucl Mater 346, 66–77.
- Riba, O., Coene, E., Silva, O., Duro, L. (2020). Spent fuel alteration model integrating processes of different time-scales. MRS Advances, 10.1557/adv.2020.51.
- Shoesmith, D.W. (2000) Fuel corrosion processes under waste disposal conditions. J Nucl Mater 282, 1–31.
- Spahiu, K., Cui, D.Q., Lundstrom, M. (2004). The fate of radiolytic oxidants during spent fuel leaching in the presence of dissolved near field hydrogen. Radiochim Acta 92, 625–629.
- Stroes-Gascoyne, S., Garisto, F., Betteridge, J.S. (2005). The effects of alpha-radiolysis on UO₂ dissolution determined from batch experiments with Pu-doped UO₂. J Nucl Mater 346, 5–15.
- Tasi, A., Gaona, X., Fellhauer, D., Böttle, M., Rothe, J., Dardenne, D., Schild, D., Grivé, M., Colàs, E., Bruno, J., Källström, K., Altmaier, M., Geckeis, H. (2018). Redox behavior and solubility of plutonium under alkaline, reducing conditions. Radiochim. Acta. 106, 259–279.

- Ulrich, K.U., Singh, A., Schofield, E.J., Bargar, J.R., Veeramani, H., Sharp J.O., Bernier-Latmani, R., Giammar, D.E. (2008). Dissolution of biogenic and synthetic UO₂ under varied reducing conditions. Environ Sci Technol 42, 5600–5606.
- van der Lee, J., De Windt, L., Lagneau, V., Goblet, P. (2002). Presentation and application of the reactive transport code HYTEC. Computational methods in water resources Proceedings (Elsevier Ed.), 599–606.
- van der Lee, J., De Windt, L., Lagneau, V., Goblet, P. (2003). Module-oriented modeling of reactive transport with HYTEC. Comput Geosci 29, 265–275.
- Wu, L. Qin, Z., Shoesmith, D.W. (2014). An improved model for the corrosion of used nuclear fuel inside a failed waste container under permanent disposal conditions. Corrosion Science 84, 85–95.