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DELIVERABLE D5.1

Agreement of conditions to consider in the models: discussions between modelling and experimentalists

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1 Methodology

The discussions between WP5 partners (modelling) and the experimentalists groups on the parameters needed or “desired” to calibrate and/or develop the models started on the kick off meeting of the DISCO project on the 13th of June, 2017, in Brussels, Belgium.

The discussion session was led by Lara Duro (A21) and Enzo Curti (PSI), and it started with the presentation of the aims and needs of the WP5 partners. Here are summarised the issues discussed during de session, which were already included in DELIVERABLE D1.2: Kick-off minutes.

For thermodynamic modelling it is required to have as complete chemical composition of the materials as possible, both of the initial material and of any potential secondary solids. Regarding the aqueous solutions, the chemistry of the solution as a function of time is needed: not only the radionuclides but also the major elements and parameters.

Important data for the modelling of the dissolution process are volume/mass ratio, surface area (site density), information regarding the metallic particles (% of the surface area), solution composition, etc. Information concerning any change with time is relevant and important, for example the evolution of the chemical solution with time, for both major and minor elements. If possible, information concerning secondary precipitates should be transferred.

Therefore, the modellers need to know: What will the experimentalists be able to deliver and when. Some Issues that were brought up during the discussion are listed below.

*How to describe the metallic particles in the fuel: The size distribution is such that these particles are so small they cannot easily be imaged and therefore, it is hard to get data on the true size distribution or number of particles per surface area unit.

*Solution composition. Carbonate under reducing composition & Young cement water. Also, the NNL situation is oxidizing. The young cement water is hard to model. Regarding the formation of colloids, it is important to use filtration and ultrafiltration.

*Use of hydrogen in experiments without metallic particles. It could be argued that this does not produce the reducing effect at the surface: however, there are hypotheses and data indicating that hydrogen does in fact have a reducing effect on a surface even without metallic particles. The general purpose is to mimic the conditions and processes inside a canister in the repository.

*Kinetic modelling, ie rate of change with time, vs. modelling the equilibrium, ie the state where no change is thermodynamically favoured: If you have a system where nothing changes, you will not get kinetic information. Discussion regarding if you model equilibrium or kinetics: are you modelling change with time or is nothing changing. However, it should be remembered that the core of the problem is what is the fate of the oxidants produced by radiolysis. If nothing changes, if [U] does not increase, in a spent fuel or alpha doped system, it means something other than uranium is reducing the oxidants. Experiments will get both things changing with time and also some that do not change.

*The idea of a model: the model should predict an evolution. Thus, the model needs to consider the evolution of the oxidants and reductants.

*Temperature: the discussion needs to also involve temperature. The thermodynamic modelling of the oxygen potential in the fuel will consider high temperature. The second part of the modelling should be done at lower T: temperature extrapolation is a bit of a problem. 25 degrees will be used for the lower T since most data is available for that temperature. Increasing the T means increasing the uncertainty, because of the lack of data and need to extrapolate

*Radiolysis: we need to know the radiation field and yield of different oxidants in the different systems.

After this, the focus was turned more on the matrix prepared by WP5 (see Annex I): this had been circulated before the meeting for the experimentalists to consider. The modellers need to know exactly what data the different methods mentioned in the GA actually will be delivered & available for the modellers to use.

It was decided that A21 should prepare a list of parameters, a “wish list”, for their modelling needs, preferably done in an excel sheet, sent to every partner who will provide experimental data and when they expect to provide the data. The next step, would be for the experimentalists to fill in exactly what data they will deliver. It was agreed to be sent the excel file by around end of September.

The excel sheet with the list of parameters that WP5 partners (modelling) would like to obtain was sent to all partners in the first week of October. The WP5 partners were aware of the difficulty in obtaining all parameters in the list, although in that point, it was preferred to be extensive rather than limiting and also the experimentalist were encouraged to include in the list any possible additional parameters/observations. During the following weeks, the different experimentalist groups involved in WP2, WP3 and WP4 sent the excel sheet back with their corrections and observations in agreement with their capabilities in determining the solid phases and aqueous solutions.

The final excel sheet (included in Annex II) is a compilation of the information received from the different experimentalist groups and conforms a detailed description of the parameters expected by WP5 partners of each experiment considered in DISCO project.

Annex I: Preparatory work from WP5 for the Kick-off meeting of DISCO for discussion on the preparation of D5.1

In the following pages different matrices are presented, which are the result of crossing the information in WP2, WP3 and WP4 in the proposal. This is a draft document to be discussed during the afternoon session of the DISCO kick-off meeting to be held on the 13th June 2017 in Brussels.

The objectives are:

- to check that these are the experiments and the materials and conditions to use

- to discuss if and how the results are going to be considered in the models of WP5

- to open the discussion for the preparation of D.5.1. Agreement of conditions to consider in the models: discussions between modelling and experimentalists. Responsible: All partners. Due PM 6

Composition of the contacting solutions in the proposal:

Bicarbonate water: 1 to 2 10^{-2} M NaCl 1 to 2 10^{-3} M $NaHCO_3$	Young cementitious water with Ca, YCWCa, pH ~13.5: Na: $1.4x10^{-1}$M; K: 3.5 $x10^{-1}$M; Ca: $4.8x10^{-4}$M; Al: $6x10^{-5}$M; Si: $3x10^{-4}$M; SO_4^{2-}: $2x10^{-3}$M of SO_4^{2-}, CO_3^{2-}: $3x10^{-4}$M	Synthetic COx water (Callovo-Oxfordian Water)
Reducing (H_2), anoxic	Reducing (H_2), anoxic	with and without Fe

Cross matrix WP2-WP3-WP5

WP2 Hot cell work					**Use in experiments WP3**				WP5 USE IN MODEL
Fuel	**Burn-up**	**Form**	**Characterisation**	**Partner**	**solution**	**redox**	**partner**	**nr. Tests**	**WP5 partner**
MOX	38 GWd/THM	Two decladded fragments, one cladded segment (10mm).	Optical and electronic ceramography: grain-size, secondary phases and micro-cracking; gamma and Raman spectroscopy	KIT-INE	BW	reducing: Ar + 8%H2; 40 atm	KIT-INE	3	
MOX	40-60 GWd/THM	Cladded segment (2.5mm)	Optical and electronic ceramography: grain-size, secondary phases and micro-cracking; gamma spectroscopy	JRC	BW	anoxic: Ar	JRC	2	
Cr-doped	40-60 GWd/THM	Decladded fragments	Optical and electronic ceramography: grain-size, secondary phases and micro-cracking; gamma spectroscopy	JRC	BW	Reducing: 30bar H2 autoclave	JRC	1	
UOX	20-25 GWd/THM	Decladded fragments	Detailed characterisation of alteration products SEM, gamma spectroscopy	NNL					

No correspondence with WP3 experiments in the case of the MOX to be characterised by NNL has been found. I do not know whether this implies that no dissolution tests will be done with this material or that I simply have not found them. For some experiments in WP3 no characterisation of the corresponding solid in WP2 has been identified. I believe that the reason is that the solid comes from the First-Nuclides Project and was already characterised during it. They correspond to the experiments by Studsvik and CTM, the ones with a red square below (table taken from WP3 proposal).

Leachant	Conditions	Fuel	Burn-up (GWd/t_{HM})	# tests	Sample	Institution	Focus
Bicarbonate water ($pH \approx 8.3$)	Anoxic	MOX	40-60	2	cladded segment (2.5 mm)	JRC	IRF and Matrix
	Reducing with the presence of dithionite as reductant agent in anoxic atmosphere	UO_2	60	1	cladded segment (2.5 mm)	CTM	IRF and Matrix
	Reducing with the presence of H_2 atmosphere	MOX	38	3	cladded segment (10 mm) and fragments	KIT-INE	IRF and Matrix
		UO_2	57.1	1	decladded fragments	Studsvik	Matrix
		UO_2-Cr&Al doped	59.1	1	decladded fragments	Studsvik	Matrix
		UO_2-Cr doped	60	1	decladded fragments	JRC	Matrix
Young Cement water with Calcium ($pH \approx 13.5$)	Oxidising, equilibrated with air	UO_2	60	1	cladded segment (2.5mm)	CTM	IRF and Matrix
	Reducing with the presence of	UO_2	60	1	cladded segment	CTM	IRF and Matrix

Cross matrix WP2-WP4-WP5

The same cross matrix but, in this case, for WP2-WP4-WP5. Two matrixes are included: one for alfa work and another one for inactive work.

WP2 α-glove box

model solid	α-doping	simulation	characterisation	partner	Use in experiments WP4: solution	redox	WP4 partner	WP5 USE IN MODEL: WP5 partner
UO_2 ref	238Pu/233U	1e4 y	Alpha-enabled SEM, FIB and TOF-SIMS to take advantage of the model system approach.	. JUELICH . SCK-CEN . VTT	BW	H_2	. JUELICH . SCK-CEN . VTT	
					YCWCa	H_2	. JUELICH . SCK-CEN	
					Natural GW	Fe	. VTT	
UO_2 + Cr/Al	238Pu	1e4 y	Alpha-enabled SEM, FIB and TOF-SIMS to take advantage of the model system approach.	. JUELICH . SCK-CEN . VTT	BW	H_2	. JUELICH . SCK-CEN . VTT	
					YCWCa	H_2	. JUELICH . SCK-CEN	
					Natural GW	Fe	. VTT	
$(Pu,U)O_2$ 25 wt% Pu	^{238}Pu ~ 2.2*10^9 Bq/g		Samples already available will be annealed to restore stoichiometry, which will be checked with XRD and Raman spectroscopy.	CEA	COx		. CEA	

As with experiments with fuel, there are some materials here where no experiments with the material have been identified (in yellow in the previous table) and the other way round, i.e., some tests indicated in WP4 with no identification of the solids that will be used (red squares in table below, table taken from WP4 proposal).

Samples	**Bicarbonate water reducing, anoxic (H_2)** **(derived from WP3)** **(+/- additional components)**	**Cementitious water (YCWCa) pH ~13.5, Reducing, anoxic (H_2)** **(derived from WP3)**	**Synthetic COx water Callovo-Oxfordian Water) (+/- Fe(0))**	**Natural ground water, with Fe(0)**
UO_2 (reference sample)[1)]	JUELICH, SCK-CEN, USFD	JUELICH, SCK-CEN		
UO_2 + α-dopant (Pu-238/U-233)	JUELICH, SCK-CEN, VTT	JUELICH, SCK-CEN		VTT
UO_2 + Cr/Al[1)]	JUELICH, SCK-CEN, CIEMAT, USFD	JUELICH,SCK-CEN, CIEMAT		
UO_2 + Gd[1)]	CIEMAT	CIEMAT		
UO_2 + Cr/Al + α-dopant (Pu-238/U-233)	JUELICH, SCK-CEN, VTT	SCK-CEN, JUELICH		VTT
UO_2 + Gd + α-dopant (Pu-238/U-233)	CIEMAT	CIEMAT		
Homogeneous unirradiated MOX ($U_xPu_{1-x}O_2$) (high α)			CEA	
MOX ($U_xTh_{1-x}O_2$) [1)]	UCAM	UCAM		

Annex II: list of parameters (in excel format) to calibrate and/or develop the models to be delivered from the experimentalists.

The format of the document is an excel file, therefore, in the present document it is only shown a figure of the sheet with all the experiments included in DISCO whose parameters are detailed in other sheets of the excel file.

EXPERIMENTS											
Experimental La	**Solid**	**Water**	**Atm**	**WP2**	**WP3**	**WP4**	**Laboratory**	**Description**	**Kinetic measurement**	**Methods /Analyses**	**spreadsheet**
1	UO2 ref	BW	H2	x		x	USFD	?	?	SEM, EBSD, XRD	WP4-model systems
1_1	UO2 ref	BW, YCW	Ar + H2O2	x		x	Juelich	accelerated experimer	relative effects of H2O2, C	SEM, EBSD, XRD, solution analyses	WP4-model systems
2	UO2+Cr+Al	BW	H2	x		x	USFD	?	?	SEM, EBSD, XRD, ED	WP4-model systems
3	UO2+Cr	BW, YCW	H2	x		x	CIEMAT	?	?	Raman, XRD, SEM, SIMS	WP4-model systems
3_1	UO2+Cr	BW, YCW	H2	x		x	Juelich	accelerated experimer	relative effects of H2O2, C	Raman, XRD, SEM, SIMS	WP4-model systems
4	UO2+Gd	BW, YCW	H2	x		x	CIEMAT	?	?	Raman, XRD, SEM, SIMS	WP4-model systems
5	(U,Th)O2	BW, YCW	H2	x		x	UCAM	?	?	XRD, SEM	WP4-model systems
6	UO2 ref - 238Pu/233U	BW, YCW	H2	x		x	Juelich, SCK-CEN	MD	MD rates	SEM, solution analyses	WP4-alpha model systems
7	UO2+Cr/Al - 238 Pu/233U	BW, YCW	H2	x		x	Juelich, SCK-CEN	MD	MD rates	SEM, solution analyses	WP4-alpha model systems
8	UO2+Gd - 238 Pu/233U	BW, YCW	H2	x		x	CIEMAT	?	?	?	WP4-alpha model systems
9	UO2 ref - 238Pu/233U	Natural GW + Fe	?	x		x	VTT	?	?	?	WP4-alpha model systems
10	UO2+Cr/Al - 238 Pu	Natural GW + Fe	?	x		x	VTT	?	?	?	WP4-alpha model systems
11	(Pu,U)O2	COx	?	x		x	CEA	uMOX	?	XRD, Raman	WP4-alpha model systems
12	spent fuel UO2 (BU 60)	BW & YCW ± dith	H2/air	x	x		CTM	CS	IRF + MD	CER, SEM, EDS,GAM, ICP-MS	WP3-Hot cell
13	spent fuel UO2 (BU 57.1)	BW	H2	x	x		Studsvik	DF	MD	?	WP3-Hot cell
14	spent fuel Cr&Al-UO2 (BU 59.1)	BW	H2	x	x		Studsvik	DF	MD	?	WP3-Hot cell
15	spent fuel Cr-UO2 (BU 40-60)	BW	H2	x	x		JRC	DF	MD	CER, SEM, EDS,GAM, ICP-MS	WP3-Hot cell
16	failed UOX	pool water	air?	x	x		NNL	DF	?	SPH, GAM	WP3-Hot cell
17	MOX (BU 38)	BW	H2	x	x		KIT-INE	DF / CS	IRF + MD	CER, GSA, MCR, SPH, RAM,GAM	WP3-Hot cell
18	MOX (BU 40-60)	BW	anoxic	x	x		JRC	CS	IRF + MD	CER, SEM, EDS,GAM, ICP-MS	WP3-Hot cell
Legend	BU= Burnup in GWd/THM	BW=Bicarbonate Water						DF= Decladded Fragm	IRF = Instant Release Frac	ED = Electron Diffraction	
		GW= Ground Water						CS= Cladded Segment	MD = Matrix Dissolution	EBSD = Electron Backscattering Diffraction	
		YCW= Young Cement Water						uMOX= unirradiated MOX		SEM = Scanning Electron Microscopy	
		dith = dithionite								CER = optical and electronic ceramography	
		COx = Callovo-Oxfordien water (synthetic)								GSA = Grain size analysis	
										MCR = micro cracking	
										SPH = secondary phase analysis ?	
										GAM = gamma-spectrometry ?	
										EDS = Energy-dispersive X-ray spectroscopy	

EXPERIMENTS | WP4-model systems | WP4-alpha model systems | WP3-Hot cell