BEHAVIOR OF SPENT NUCLEAR FUEL UNDER REPOSITORY CONDITIONS

Assessment of Key Parameters Governing the Mechanism of Dissolution During Leaching

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- **Experiments**
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WHY DO WE CARE?

Life Cycle of Spent Fuel

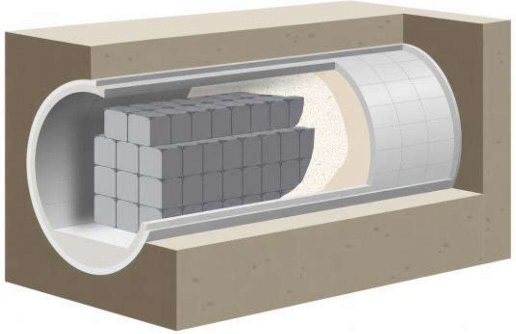
- Fuel Fabrication → Reactor Operation → Interim Storage → Geological Disposal

Spent nuclear fuel remains radioactive for very long periods.

Deep geological repositories can be considered the reference disposal solution.

Long-term safety assessment

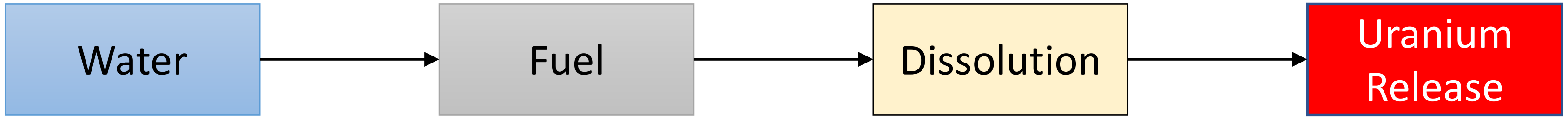
Picture of a facility that stores vessels filled with radioactive waste.[1]



Conceptual illustration of a cementitious disposal disposal gallery. [2]

[1] *Source: Wikimedia Commons*
[2] Smith, Front. Nucl. Eng., 5 (2026) 1840901.

PROBLEM DEFINITION



- How fast does UO_2 dissolve?
- Which conditions accelerate dissolution?
- Which conditions slow it down?

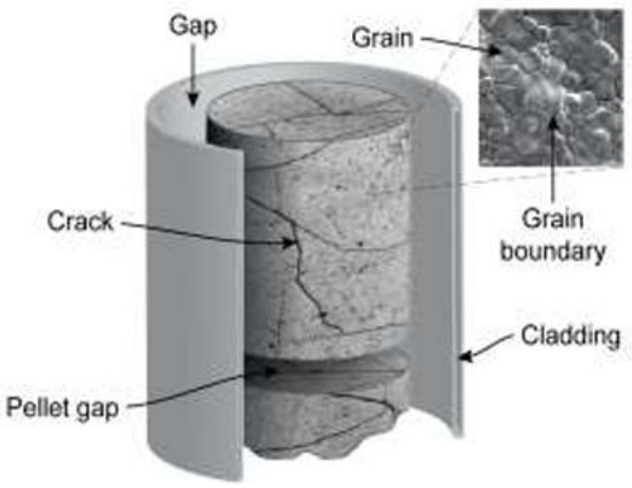
+

UO_2 dissolution has been widely studied.

−

Reducing conditions
Radiolytic effect
Long-term behaviour
Doped material effect

DISSOLUTION EXPERIMENTS



A schematic view of cracked spent fuel pellets, pellet-cladding gap and grain boundaries [2]

Leaching experiments are used to reproduce spent nuclear fuel dissolution under deep geological repository conditions

Experimental systems are designed to study radionuclide release from the fuel matrix into solution

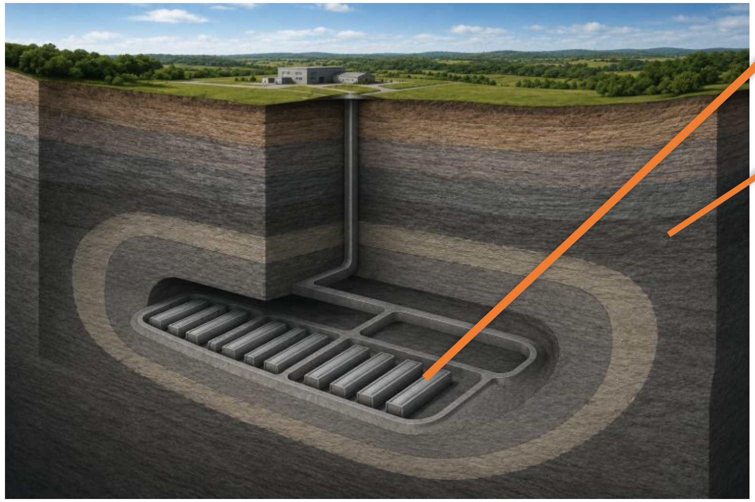
How do water chemistry, temperature, and radiolytic oxidants control UO_2 dissolution kinetics and uranium release under repository-relevant conditions?

[3] K. Spahiu, EURAD State of the Knowledge (SoK) Report (2021)

KEY PARAMETERS

Parameter	Conditions
Sample Type	*Powder / Pellet / Cr-doped Pellet*
Water Chemistry	*BC / PCW / COx*
S/V Ratio	*0.1–1* m^{-1}
Temperature	*RT (20–25°C) / 80°C*
Pressure	-
Radiolysis Conditions	*Gamma irradiation /* H_2O_2
Method	*Static*
Atmosphere	*Ar,* CO_2*/Ar*
Catalytic Materials	-
Sampling Intervals	*Determined*

WATER CHEMISTRY



Conceptual illustration of a deep geological disposal.
disposal.

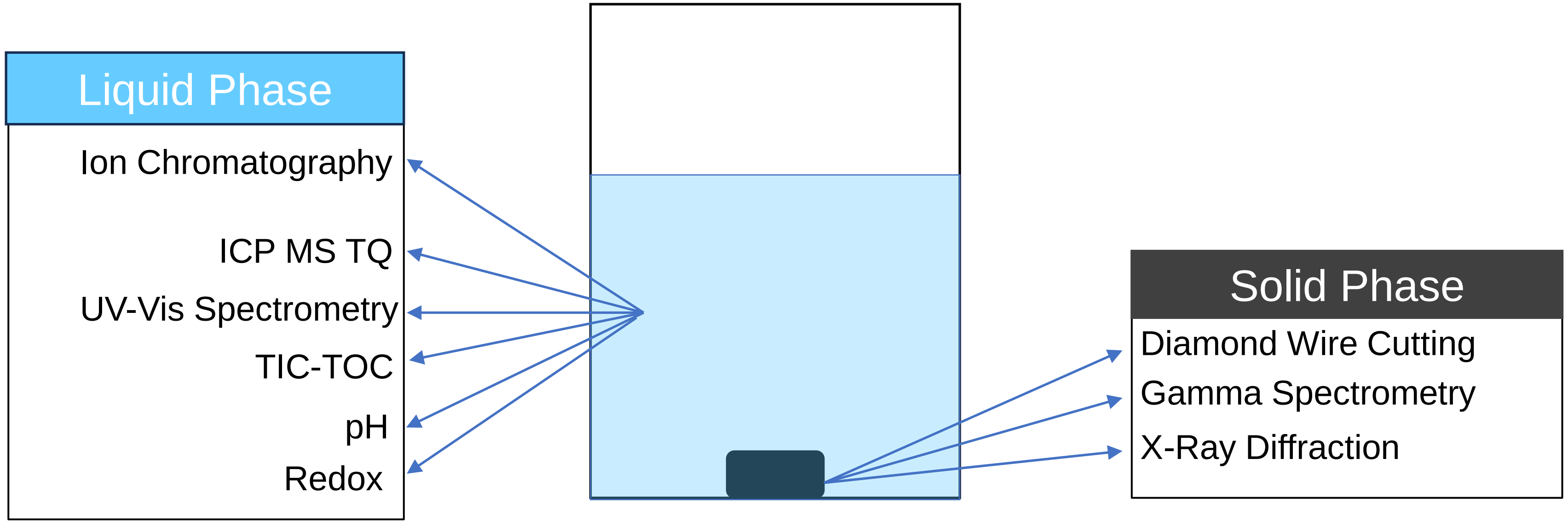
Water Type	pH	Role in Study
Portland Cement Water [3]	12.5	✓ Represents cementitious near-field conditions ✓ High pH alkaline environment ✓ Relevant for engineered barrier interactions
Callovo-Oxfordian Groundwater[4]	7.15	✓ Represents clay host-rock porewater ✓ Simulates reducing clay repository conditions ✓ Relevant for radionuclide transport in clay formations
BiC Water [5]	8.9	✓ Simplified bicarbonate system ✓ Reference solution for carbonate-controlled dissolution ✓ Used to isolate carbonate effects on UO_2 dissolution

[3] ANDRA, *Composition des solutions de type eaux cimentaires*, C.NT.ASCM.09.0010.
[4] ANDRA, *REC-CTEC-P01 – Preparation of COx Synthetic Water*, 2016.
[5] Rodríguez-Villagra et al., *J. Nucl. Mater.*, 606 (2025) 155635.

MODEL MATERIALS

Fuel Type	Composition	Role in Study
Precipitated UO_2 Powder	Uranium Dioxide (UO_2)	High surface area and rapid dissolution behavior
UO_2 - Pellet	Natural Uranium Dioxide (UO_2)	Conventional UO_2 reference material
Cr-Doped UO_2 - Pellet	UO_2 doped with Chromium Oxide (Cr_2O_3)	Influence of dopants on dissolution behavior

MATERIALS & METHODS



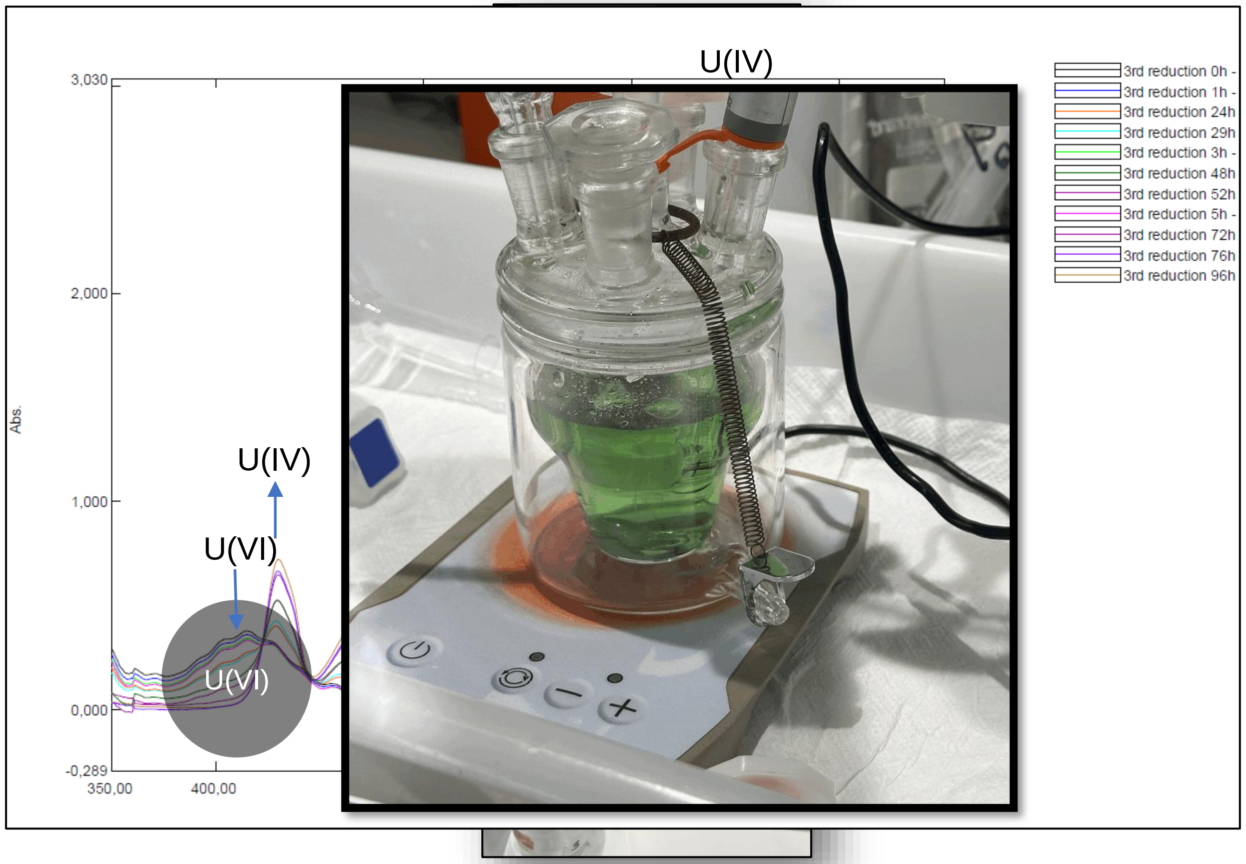
MODEL MATERIAL I

Precipitated UO_2 Powder

SAMPLE PREPARATION - FABRICATION OF UO_2 POWDER

Stock Solution (Uranyl nitrate) electrochemically reduced [6]

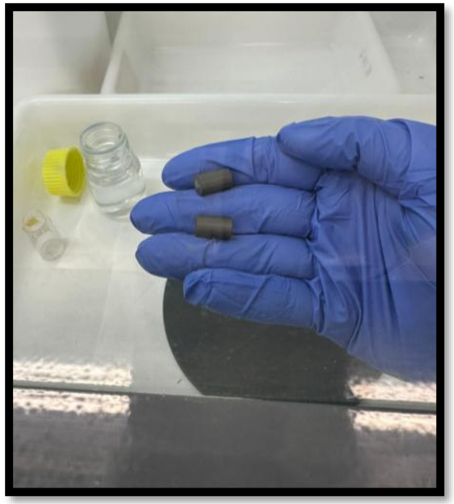
- Step 1 > Adding NaOH causes hydrolysis of U(VI)
- Step 2 > Filtration
- Step 3 > Adding HCl to dissolve solid phase
- Step 4 > Reduction of U(VI) to U(IV) by an Electrochemical Method
- Step 5 > Precipitation



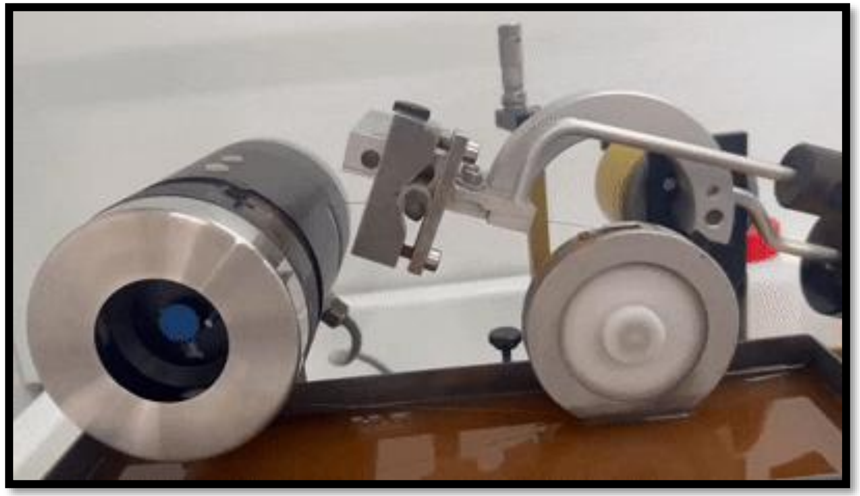
[6] Rousseau et al., Radiochim. Acta, 94 (2006) 517–522.

MODEL MATERIAL II
UO_2 PELLET

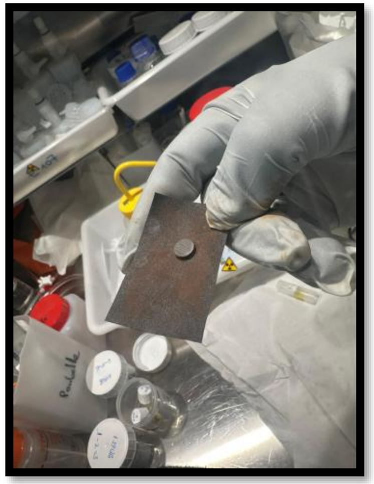
SAMPLE PREPARATION - CUTTING OF UO_2 PELLETS



Collection
UO_2 pellets obtained from
Subatech stock



Cutting
Pellets sectioned into
~2 mm slices



Polishing
Surface polishing to remove
oxidation and obtain
a homogeneous surface

Storage
Prepared samples
stored before
leaching experiments

PELLET CHARACTERIZATION - GAMMA SPECTROMETRY

- Activities of the UO_2 pellets were estimated by gam

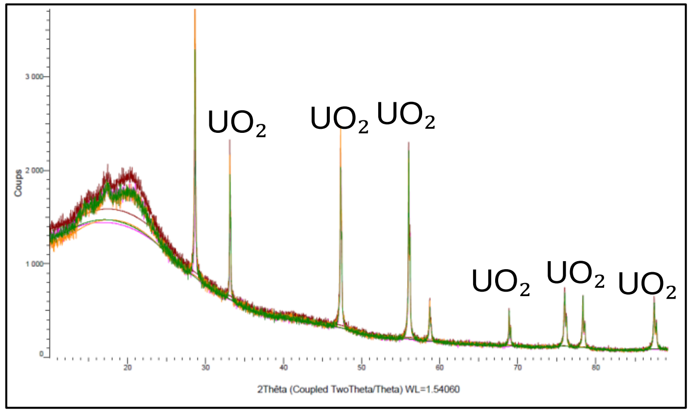
	Th-234 (Energy: 63.3 keV)		U-234 (Energy: 53.2 keV)	
Label	Energy (keV)	Activity (Bq /total)	Energy (keV)	Activity (Bq /total)
SS139UA	63.3	8.94E+04	53.2	1.13E+05
SS139UB	63.3	8.98E+04	53.2	1.11E+05
SS139UC	63.3	8.93E+04	53.2	1.12E+05
SS140UA	63.3	7.76E+04	53.2	4.50E+04
SS140UB	63.3	7.43E+04	53.2	4.45E+04
SS140UC	63.3	7.43E+04	53.2	3.99E+04

Label	Characteristic	Est. Activity	Diameter (mm)	Heigh (mm)	Mass (g)
139UA-1	Natural	3.18E+04	8.67	2.15	1.3065
139UA-2	Natural	2.88E+04	8.67	2.01	1.1816
139UA-3	Natural	2.52E+04	8.67	1.92	1.0325
139UA-4	Natural	2.88E+04	8.67	2.02	1.1822
139UA-5	Natural	2.95E+04	8.67	2.04	1.2116
139UA-6	Natural	1.15E+04	8.67	1.17	0.4724
139UB-1	Natural	2.91E+04	8.68	2.01	1.2146
139UB-2	Natural	2.85E+04	8.68	1.95	1.189
139UB-3	Natural	2.81E+04	8.68	1.92	1.172
139UB-4	Natural	2.92E+04	8.68	2.04	1.2183
139UB-5	Natural	2.86E+04	8.68	2.12	1.1912
139UB-6	Natural	1.01E+04	8.68	0.74	0.4224
139UC-1	Natural	2.82E+04	8.67	1.96	1.1651
139UC-2	Natural	2.89E+04	8.67	2	1.1951
139UC-3	Natural	2.87E+04	8.67	1.92	1.1832
139UC-4	Natural	3.04E+04	8.67	2.17	1.2541
139UC-5	Natural	2.89E+04	8.67	2.19	1.1939
139UC-6	Natural	1.25E+04	8.67	0.95	0.5154

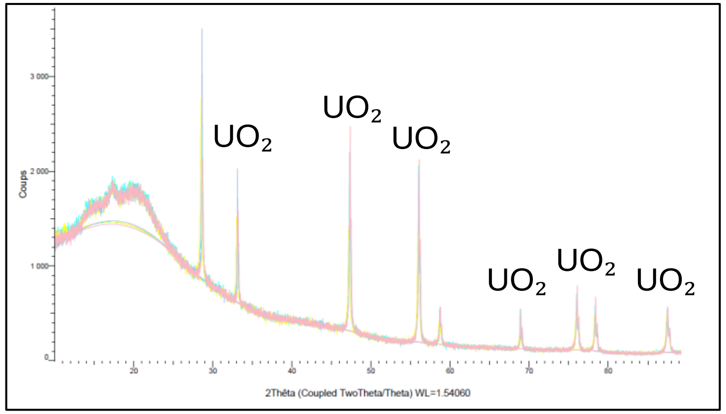
*These results were used to estimate the activity o

PELLET CHARACTERIZATION - XRD

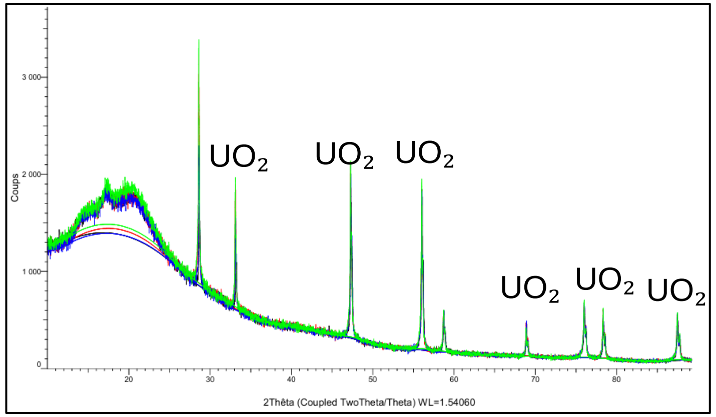
- XRD analysis performed before leaching experiments to characterize pellet surfaces



Results from Slice A1-A4



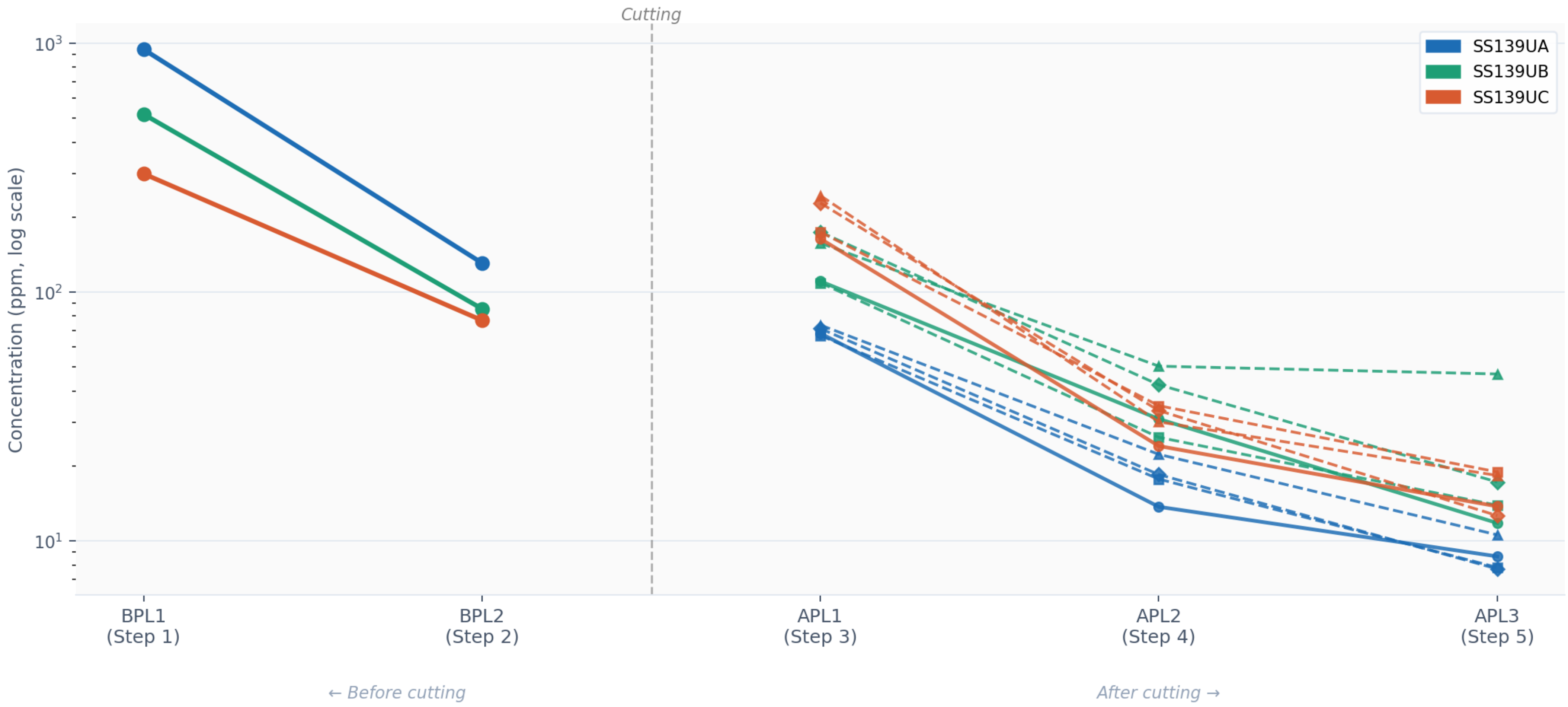
Results from Slice B1-B4



Results from Slice C1-C4

*XRD measurements will be repeated after leaching to monitor secondary phase formation

PRE-TREATMENTS



EXPERIMENTAL DESIGN

UO_2 PELLETS

EXPERIMENTAL DESIGN – LEACHING UNDER ARGON ATMOSPHERE

Atmosphere

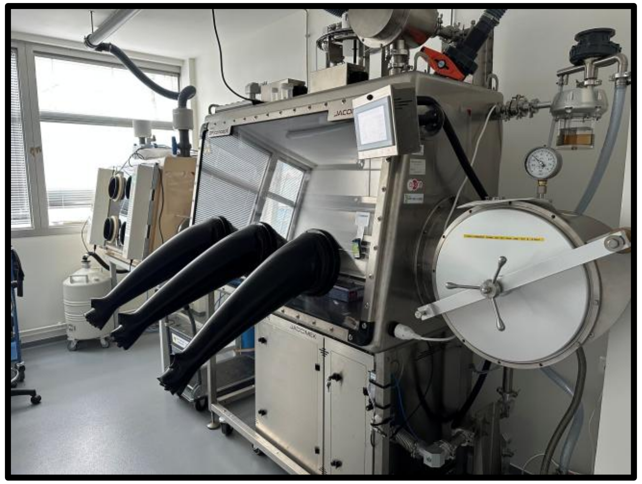
- Argon-controlled glovebox environment
- Minimization of oxidative air exposure

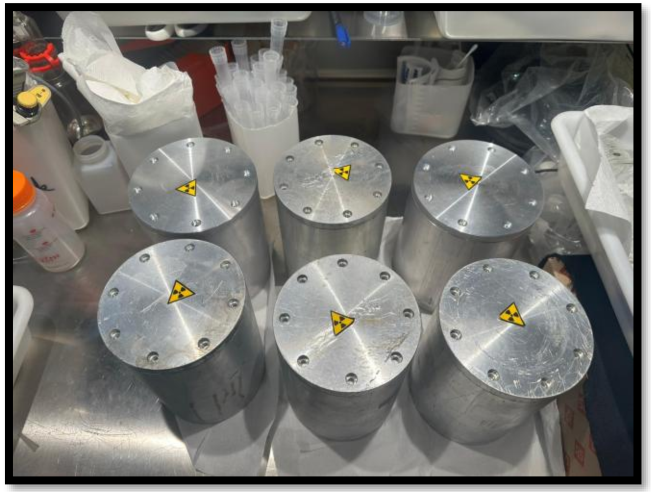
Reactors

- Teflon vessels for static leaching tests
- Stainless-steel autoclaves for closed-system experiments

Water Chemistry

- PCW to simulate cementitious repository conditions
- Bicarbonate solution to study carbonate effects on dissolution





EXPERIMENTAL DESIGN – LEACHING UNDER 1% CO_2/AR

Atmosphere

- Controlled 1% CO_2/Ar glovebox environment
- CO_2 atmosphere maintained to preserve carbonate equilibrium and near-neutral pH conditions

Reactors

- Teflon vessels used for static leaching experiments

Water Chemistry

- COx water used to simulate clay repository conditions
- Controlled CO_2 equilibrium maintained during experiments
- Near-neutral pH stabilized around ~7.2

EXPERIMENTAL DESIGN – LEACHING AT HIGH TEMPERATURE

Atmosphere

- Controlled Ar atmosphere maintained during experiments
- Limited interaction with atmospheric oxygen during heating

Reactors

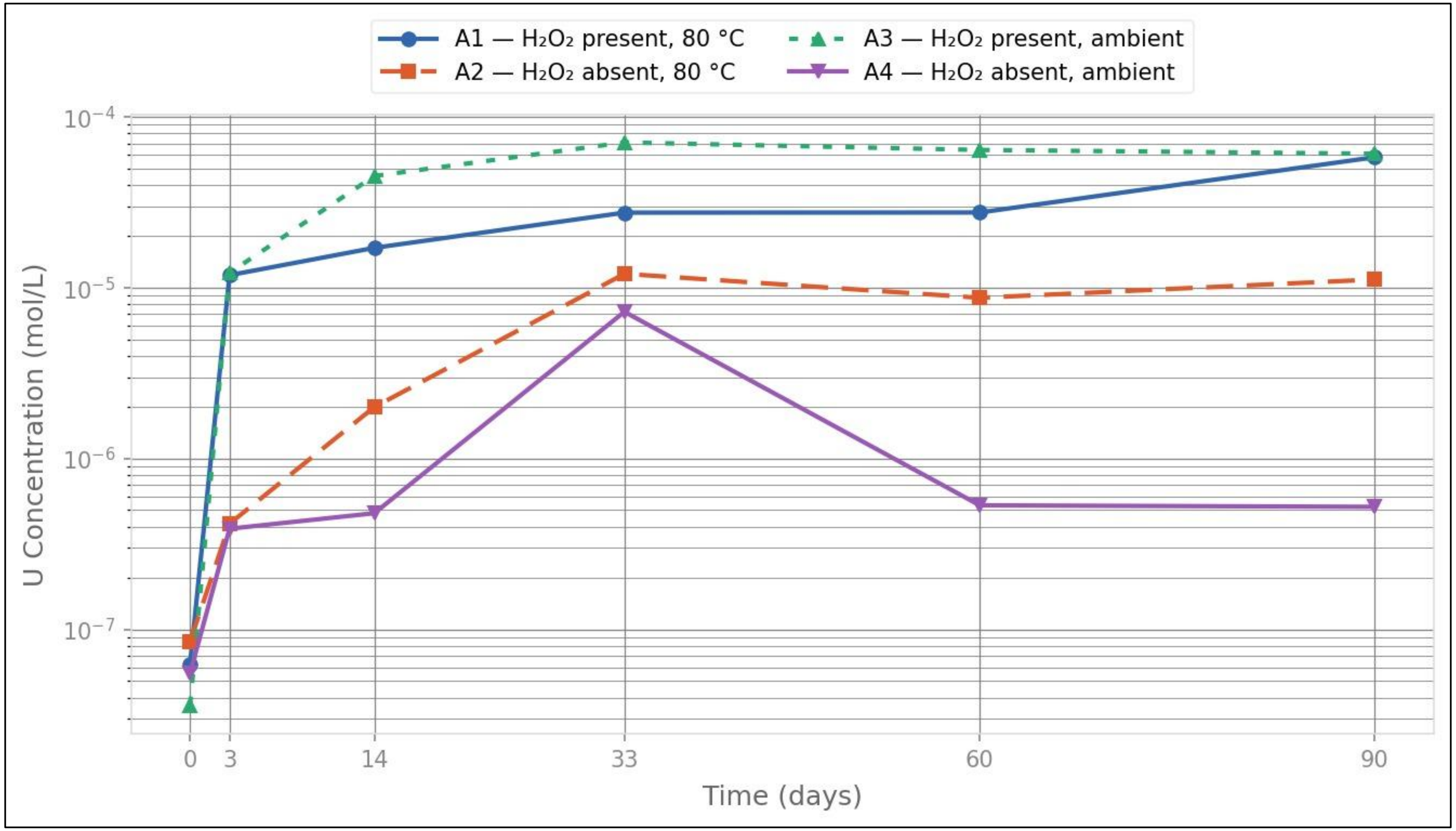
- Teflon vessels used for static leaching experiments
- Oven system used to maintain constant temperature at 80 °C

Water Chemistry

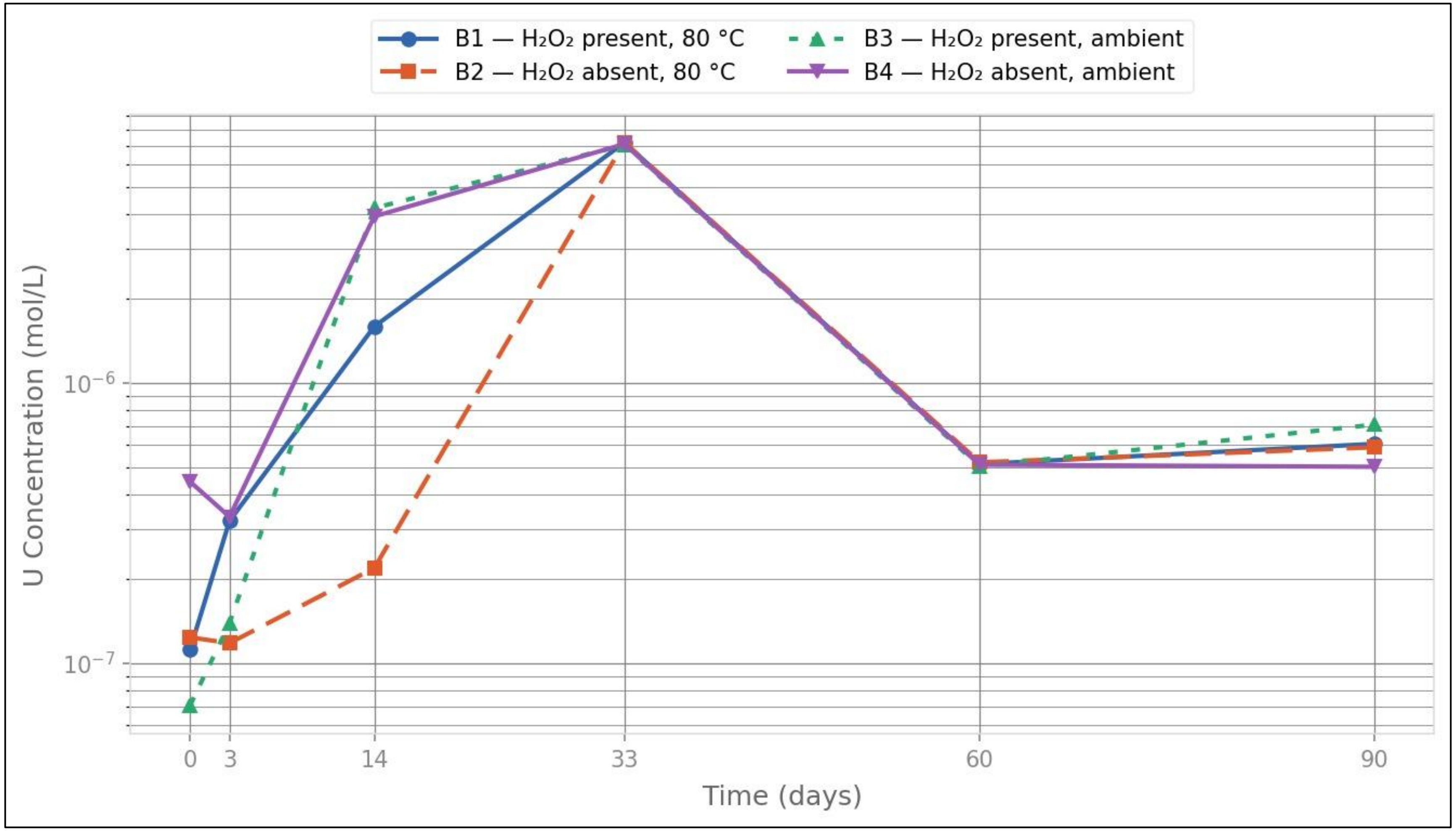
- Portland Cement Water and bicarbonate systems investigated at 80 °C
- A sealed COx configuration was used to preserve carbonate equilibrium.
- Evaluation of temperature effects on dissolution behavior

INITIAL RESULTS AT DAY 90

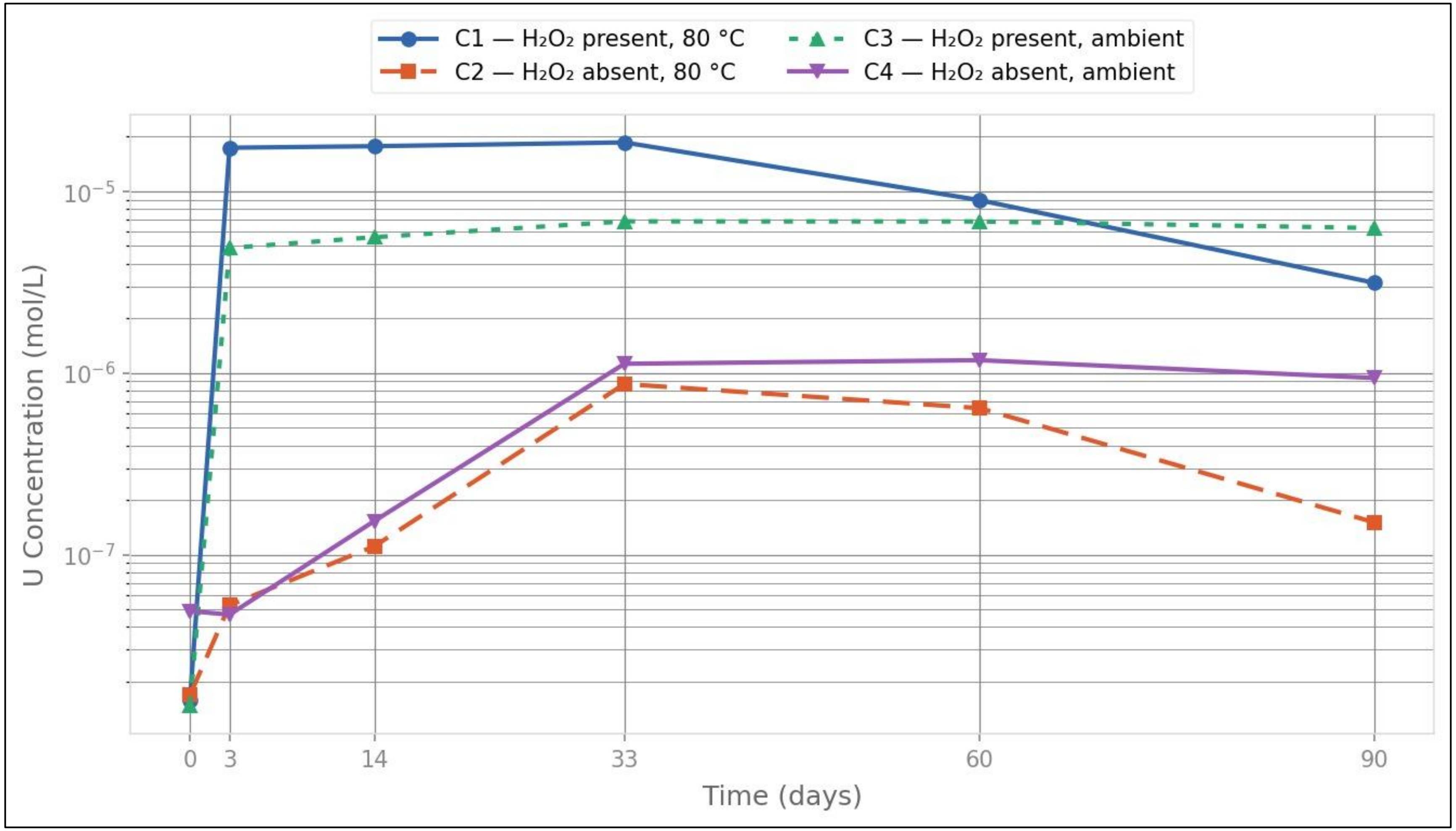
RESULTS – BICARBONATE - U CONCENTRATION IN 90 DAYS



RESULTS – PCW - U CONCENTRATION IN 90 DAYS



RESULTS – COX - U CONCENTRATION IN 90 DAYS



CONCLUSION

Dissolution experiments are being conducted on two UO_2 material forms:

Powder

- UO_2 powder successfully synthesized by electrochemical precipitation
- Awaiting additional characterization before leaching tests.
- Short-term dissolution experiments are planned

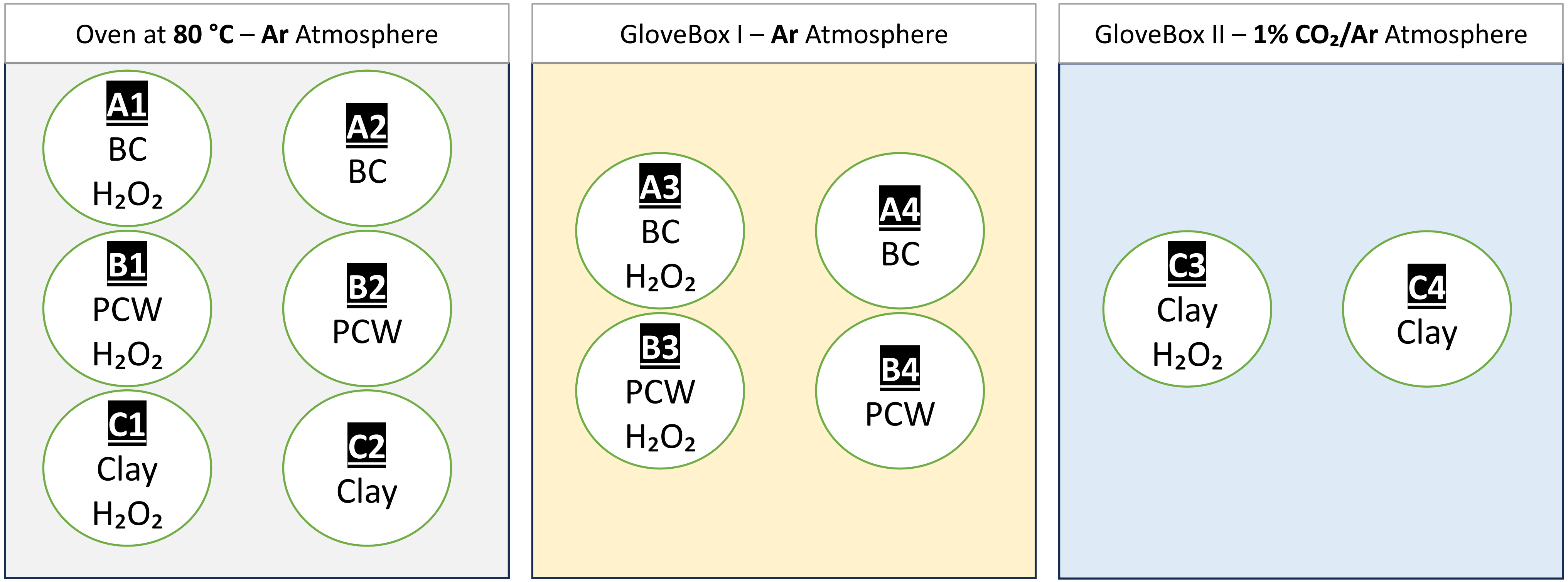
Pellets

- Pellet cutting and sample preparation completed
- Characterization and pre-treatment procedures performed
- Leaching experiments currently ongoing (Day 90)
- Initial analytical results under evaluation

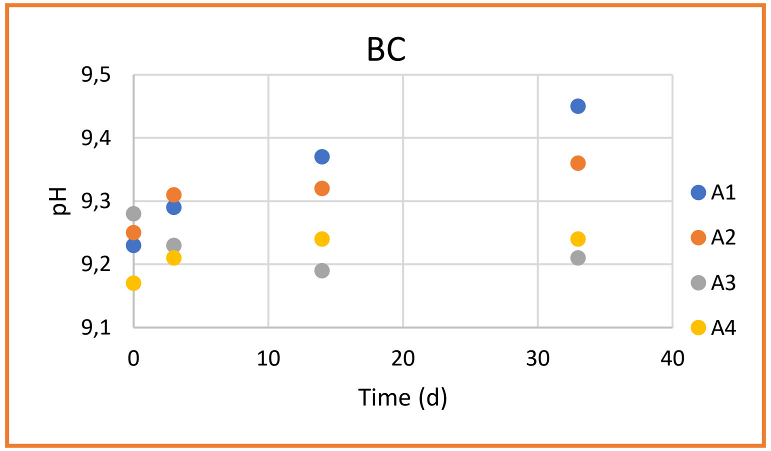
THANK YOU!

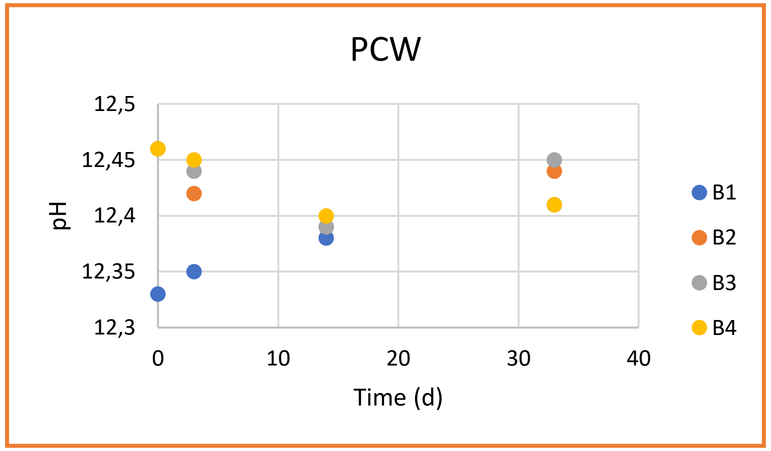
Appendix – Backup Slides

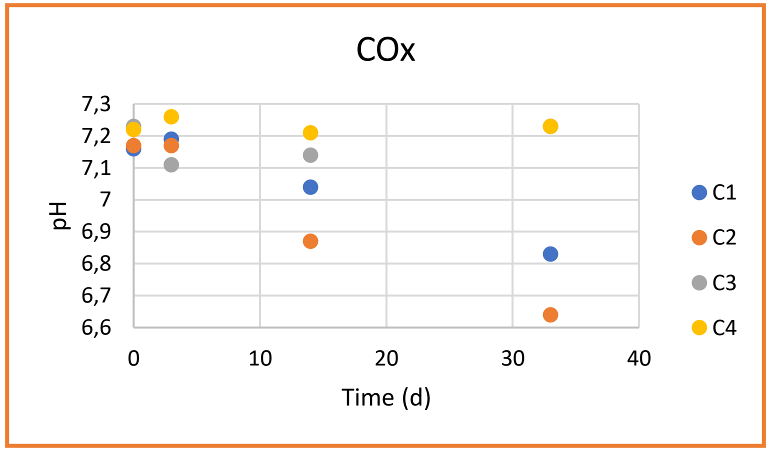
EXPERIMENTAL DESIGN – REACTOR SETUPS



RESULTS – PH DURING 33 DAYS





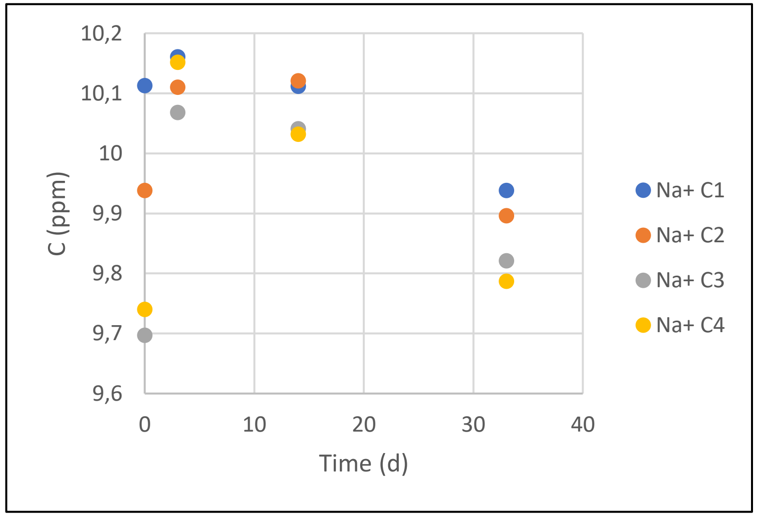


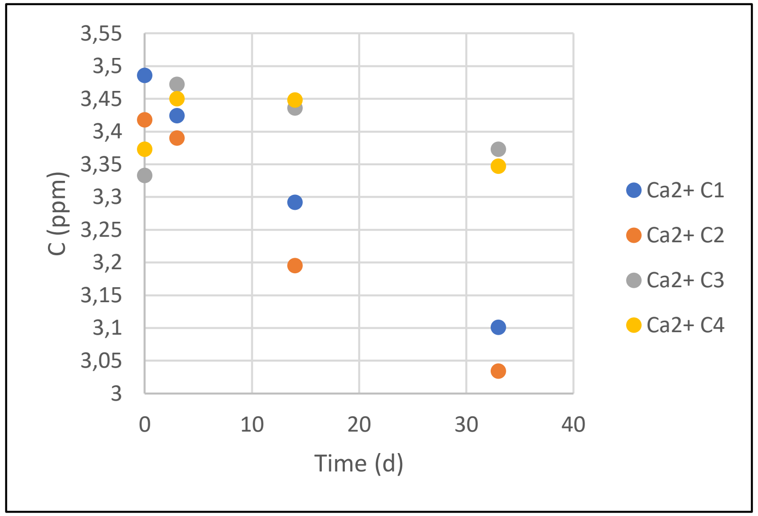
A1 – H_2O_2 is present at 80 °C.
A2 – H_2O_2 is absent at 80 °C.
A3 – H_2O_2 is present at ambient temperature.
A4 – H_2O_2 is absent at ambient temperature.

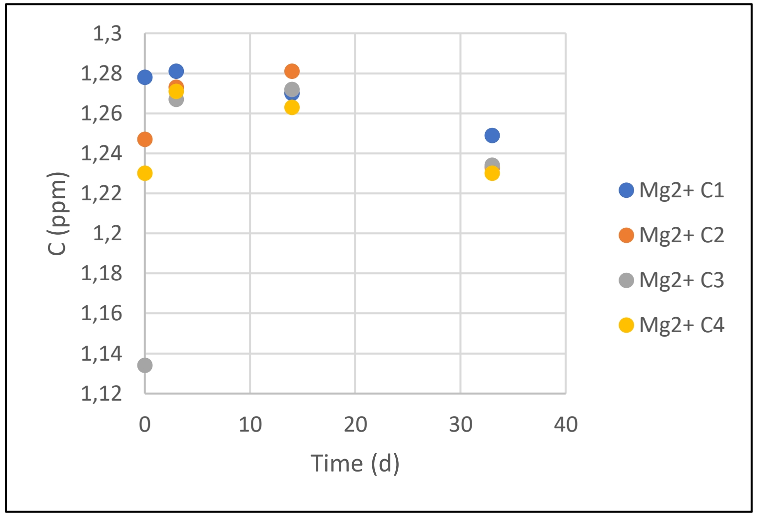
B1 – H_2O_2 is present at 80 °C.
B2 – H_2O_2 is absent at 80 °C.
B3 – H_2O_2 is present at ambient temperature.
B4 – H_2O_2 is absent at ambient temperature.

C1 – H_2O_2 is present at 80 °C.
C2 – H_2O_2 is absent at 80 °C.
C3 – H_2O_2 is present at ambient temperature.
C4 – H_2O_2 is absent at ambient temperature.

RESULTS – COX - WATER COMPOSITION IN 33 DAYS





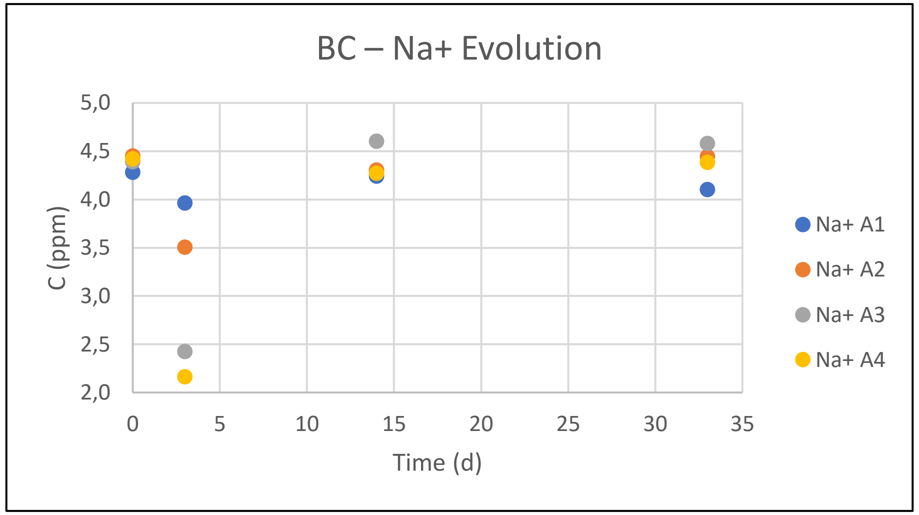


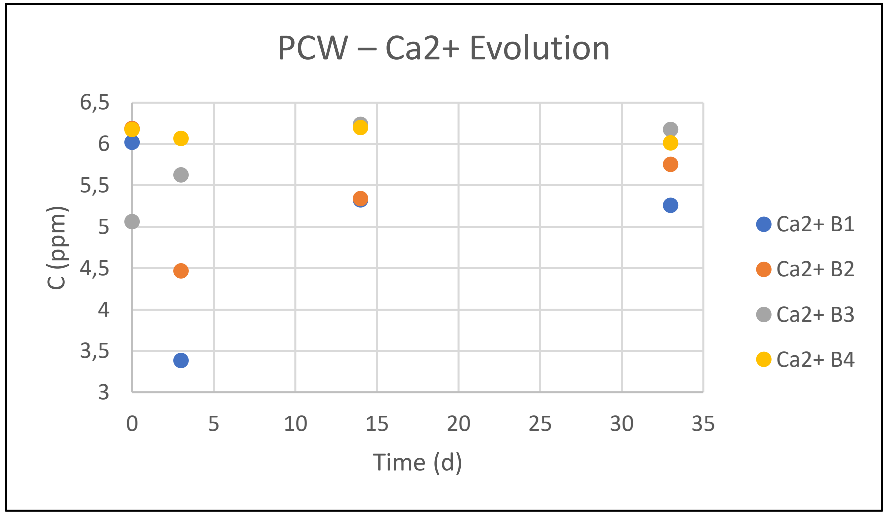
C1 – H_2O_2 is present at 80 °C.
C2 – H_2O_2 is absent at 80 °C.
C3 – H_2O_2 is present at ambient temperature.
C4 – H_2O_2 is absent at ambient temperature.

C1 – H_2O_2 is present at 80 °C.
C2 – H_2O_2 is absent at 80 °C.
C3 – H_2O_2 is present at ambient temperature.
C4 – H_2O_2 is absent at ambient temperature.

C1 – H_2O_2 is present at 80 °C.
C2 – H_2O_2 is absent at 80 °C.
C3 – H_2O_2 is present at ambient temperature.
C4 – H_2O_2 is absent at ambient temperature.

RESULTS – BC & PCW - WATER COMPOSITION IN 33 DAYS

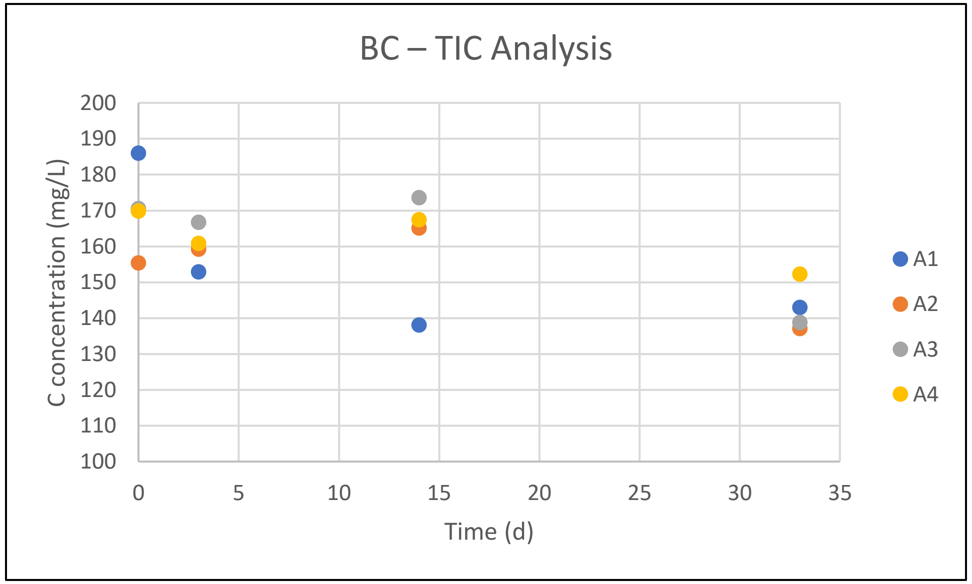


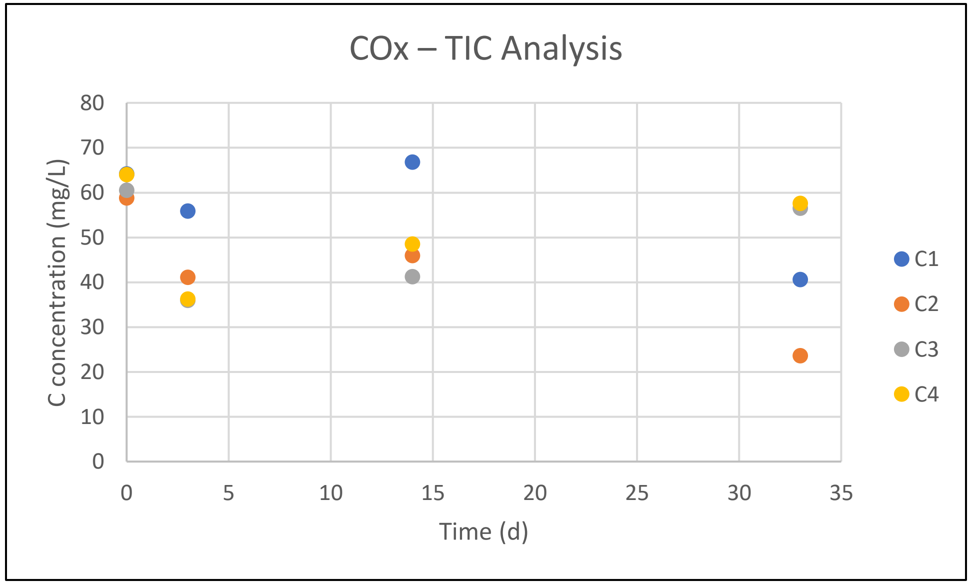


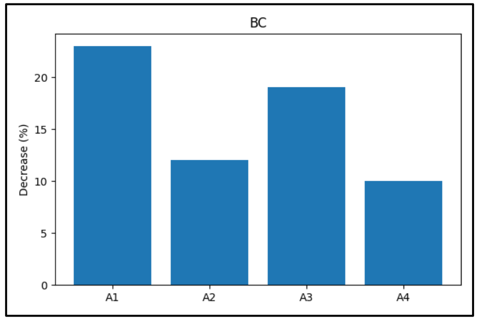
A1 – H_2O_2 is present at 80 °C. →
A2 – H_2O_2 is absent at 80 °C. →
A3 – H_2O_2 is present at ambient temperature. →
A4 – H_2O_2 is absent at ambient temperature. →

B1 – H_2O_2 is present at 80 °C. ↘
B2 – H_2O_2 is absent at 80 °C. ↘
B3 – H_2O_2 is present at ambient temperature. →
B4 – H_2O_2 is absent at ambient temperature. →

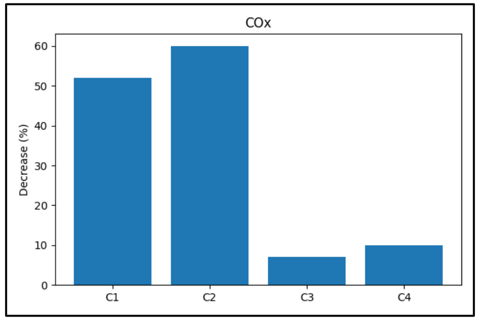
RESULTS – BC & COX - EVALUATION OF CARBON





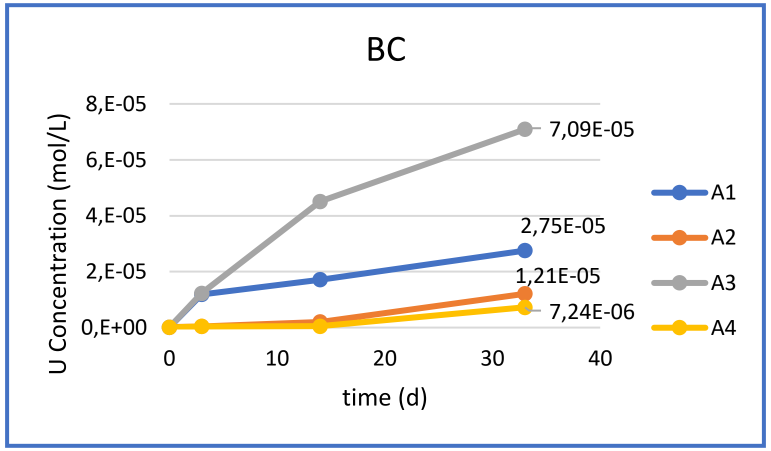


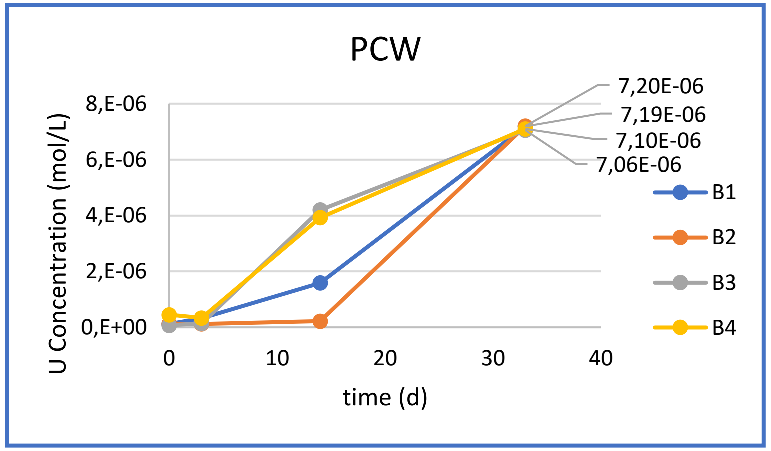
Decrease rate of C in BC

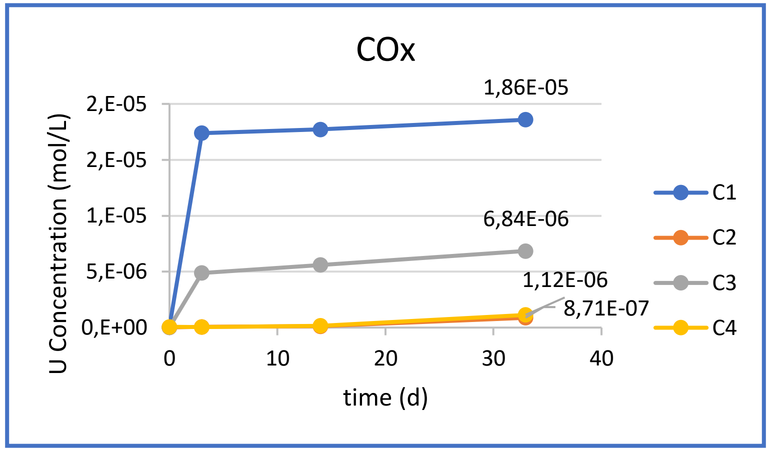


Decrease rate of C in COx

RESULTS – U CONCENTRATION IN 33 DAYS





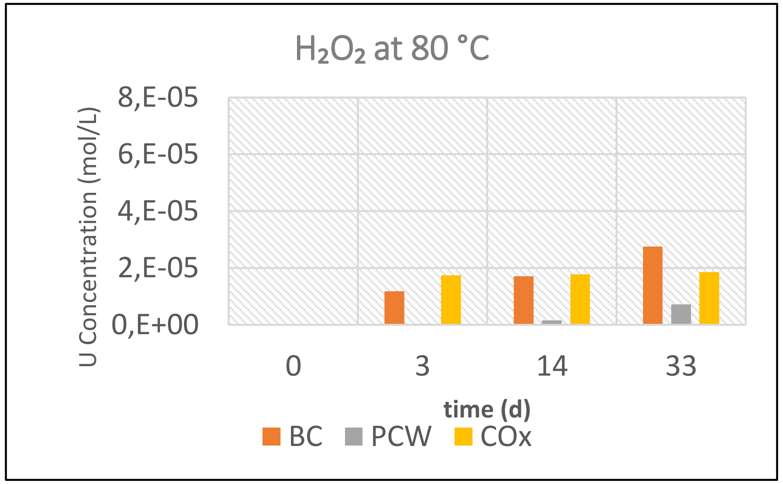


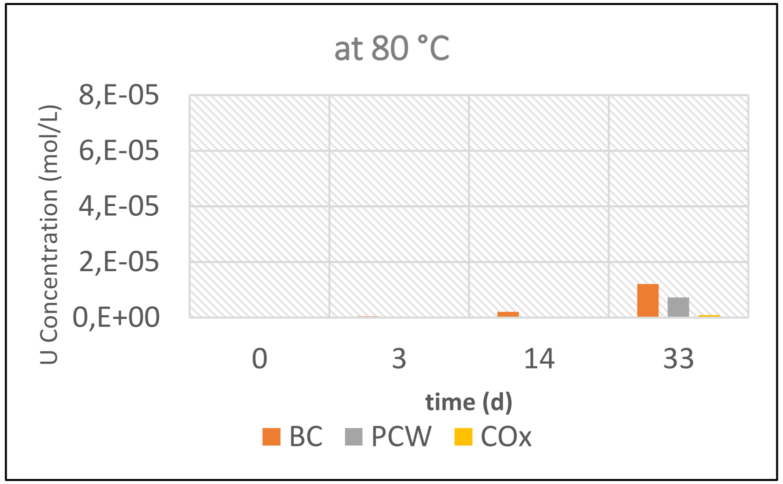
A1 – H_2O_2 is present at 80 °C. 2
A2 – H_2O_2 is absent at 80 °C. 3
A3 – H_2O_2 is present at ambient temperature. 1
A4 – H_2O_2 is absent at ambient temperature. 4

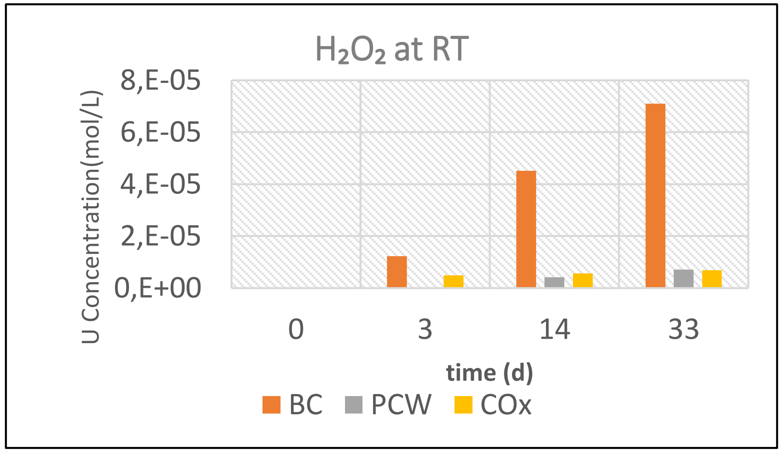
B1 – H_2O_2 is present at 80 °C. 1
B2 – H_2O_2 is absent at 80 °C. 1
B3 – H_2O_2 is present at ambient temperature. 1
B4 – H_2O_2 is absent at ambient temperature. 1

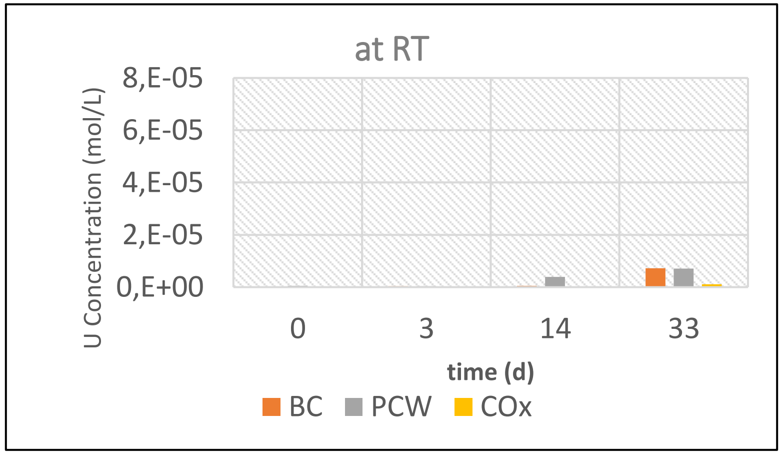
C1 – H_2O_2 is present at 80 °C. 1
C2 – H_2O_2 is absent at 80 °C. 3
C3 – H_2O_2 is present at ambient temperature. 2
C4 – H_2O_2 is absent at ambient temperature. 3

COMPARISON OF 4 EXPERIMENTAL CONDITIONS IN TERMS OF U DISSOLUTION









SAMPLE PREPARATION - FABRICATION OF UO_2 POWDER

- **Step 5 > Precipitation**

  Titration

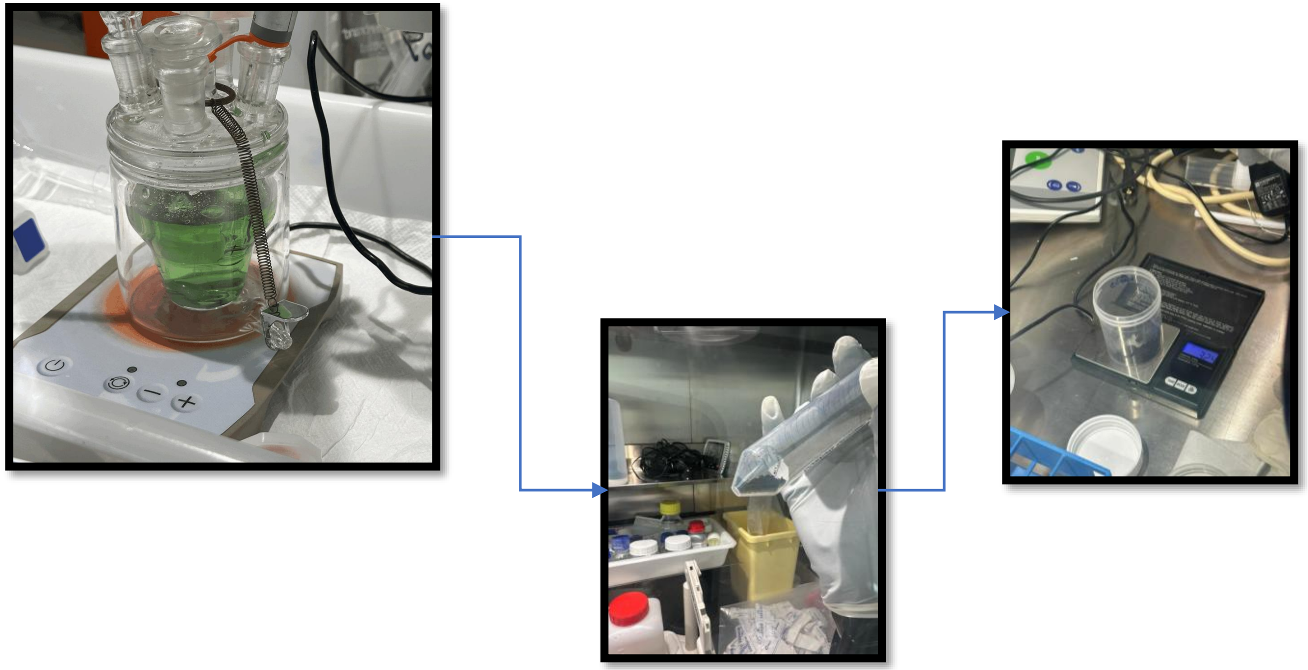
  pH: 0.15 - 5.6

- **Step 6 > Separation**

  Centrifuge –13500 rpm over 30 minutes

- **Step 7 > Stored ~3.2 g**

  Waiting for an extra characterization by Transmission Electron Microscopy



PRE-TREATMENTS - CHARACTERIZATION

Before Cutting

Label	BPL1 (ppm)	BPL2 (ppm)	Loss of the mass (mg)
SS139UA	943.67	130.75	64.94
SS139UB	517.88	85.60	36.47
SS139UC	298.63	76.92	22.70
SS140UA	4025.61	127.50	251.01
SS140UB	2019.02	693.19	163.92
SS140UC	1037.85	83.61	67.78

After Cutting

Label	PL1 (ppm)	PL2 (ppm)	PL3 (ppm)	Loss of the mass (mg)
139UA-1	68.17	13.70	8.66	1.37
139UA-2	66.84	17.71	7.82	1.40
139UA-3	73.64	22.26	10.57	1.61
139UA-4	71.24	18.47	7.71	1.47
139UB-1	110.43	30.88	11.79	2.31
139UB-2	108.83	26.06	13.90	2.25
139UB-3	157.19	50.33	46.82	3.84
139UB-4	174.16	42.39	17.24	3.53
139UC-1	163.69	24.04	13.76	3.04
139UC-2	174.13	34.91	18.92	3.44
139UC-3	243.95	30.06	18.31	4.42
139UC-4	227.74	33.37	12.63	4.14

SAMPLE PREPARATION - FABRICATION OF UO_2 POWDER

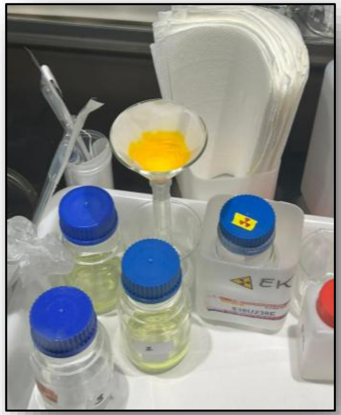
Stock Solution (Uranyl nitrate) electrochemically reduced [6]

- **Step 1 > Adding NaOH causes hydrolysis of U(VI)**

  $UO_2(NO3)_{2(aq)} + 2NaOH_{(aq)} \rightarrow UO_2(OH)_{2(s)} + 2NaNO_{3(aq)}$

- **Step 2 > Filtration**

  Solid phase is separated from liquid



- **Step 3 > Adding HCl to dissolve solid phase**

  $UO_2(OH)_{2(s)}+2HCl_{(aq)}\rightarrow UO_2^{2+}{}_{(aq)}+2Cl^{-}{}_{(aq)}+2H_2O_{(l)}$

6. Le Meur, M., *Protocole réduction U(VI) en U(IV) par voie électrochimique*.

SAMPLE PREPARATION - FABRICATION OF UO_2 POWDER

- **Step 4 > Reduction of U(VI) to U(IV) by an Electrochemical Method**
  - Static current = -1 mA
  - 96 hours for each batch (50 ml)
  - Characterization by UV Vis Spectrometry
- **Step 5 > Precipitation**

  Titration

  pH: 0.15 - 5.6