CONCORD

CONtainer CORrosion under Disposal conditions

25/10/2024 • Roberto GAGGIANO

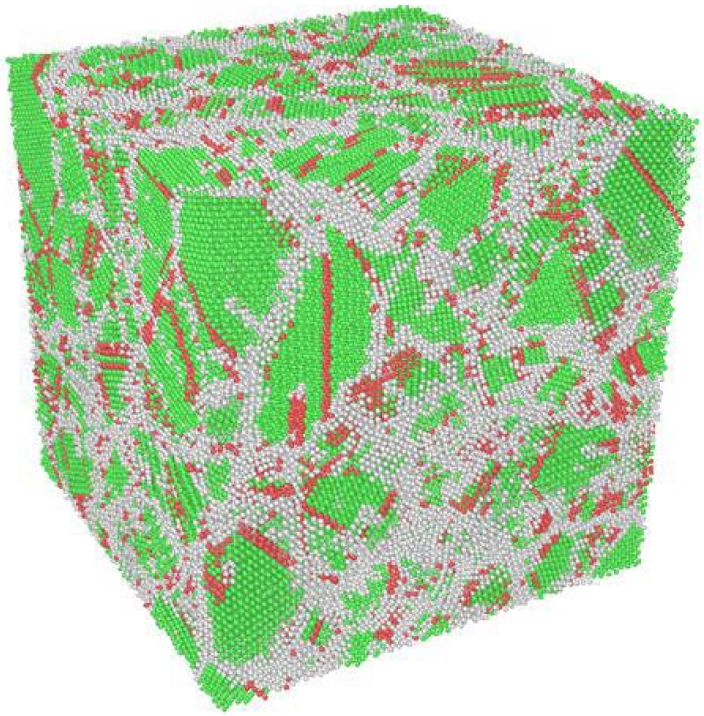
This project has received funding from the European Union's Horizon 2020 research and innovation programme 2014-2018 under grant agreement N°847593

MOTIVATION

- **Long-lived disposal containers for SF/HLW have been shown to be feasible and safe in several national programmes.**
  - Can they be optimised?
  - Can the prediction of their lifetime become more accurate and robust?

OBJECTIVES

1. **Explore the potential of novel container materials for the optimisation of container design and performance within the engineered barrier system.**
2. **Deepen the understanding of coupled interfacial processes influencing container performance under repository-relevant conditions, with a focus on:**
    1. irradiation-accelerated corrosion,
    2. microbial activity,
    3. degradation during near-field transients.
3. **Support performance assessment by demonstrating mechanistic understanding and by developing predictive models.**



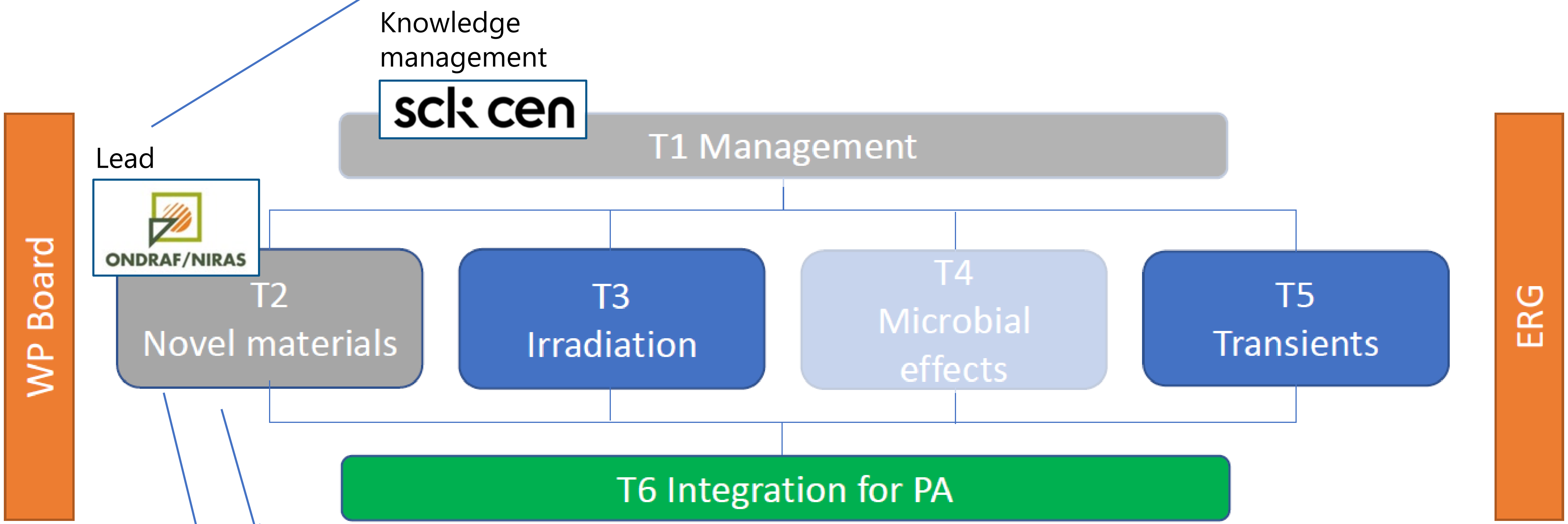
22 ORGANISATIONS FROM 12 COUNTRIES

WP STRUCTURE

Training materials (D15.4)

Initial and final SotA reports (D15.1 and D15.2)

ConCorD Synthesis Report (D15.14)

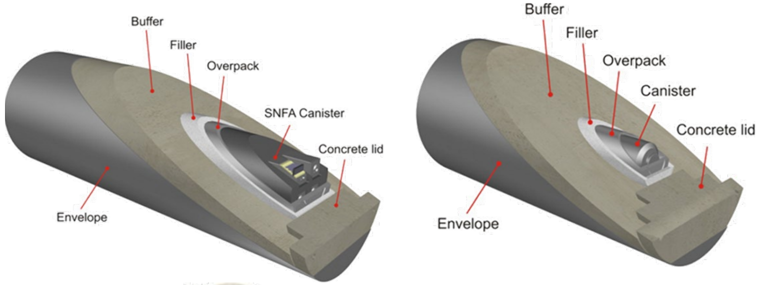


Novel materials and processes for the optimisation of long-term container performance (D 15.6)

Contribution to EURAD knowledge management

→ 3.2.3 "Containers using advanced materials (Novel Containers)"

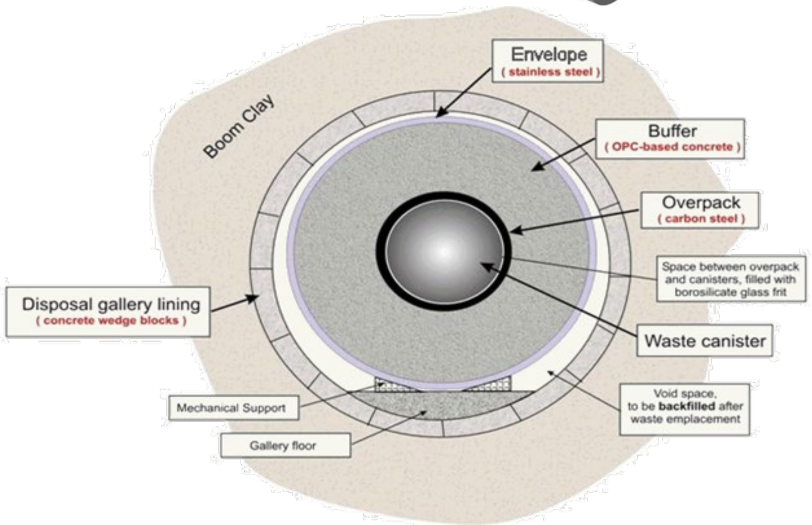
IMPORTANCE OF THE CONCORD WP FOR ONDRAF/NIRAS



- Up to now, *no specific rock has been selected as host for geological disposal* in Belgium and *the repository design itself is still generic to a large extent.*

- In addition, *cement formulation could change in the future*, towards lower pH cements

  → impact on the evolution of the environmental conditions



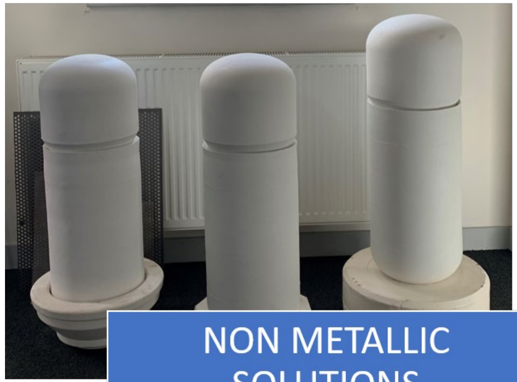
Long-term safety function of the overpack: total containment of the radionuclides during at least the thermal phase by preventing contact between the wasteform and the porewater coming from the host formation.

- **Important to:**
  - **Understand the general trends related to the corrosion behaviour of carbon steel in different environments**
  - **Keep an eye on alternative material soutions for the overpack**

SCIENTIFIC & TECHNICAL IMPACTS

- Pre-screening and preliminary optimisation of promising **novel materials**
- In depth understanding of the **relationship between irradiation and corrosion**
- Refined understanding of the **role of microbes** in canister degradation and identification of critical factors affecting viability
- Systematic exploration of **corrosion in an evolving environment**
- Developed **models** for interpretation of experiments and for canister lifetime predictions
- Synthesis of all the above for use in canister development and performance assessment programmes
- Addressed fundamental questions will lead to:
  - Better designed and **more focused future experiments**
  - Pave the way for **further canister optimisation**

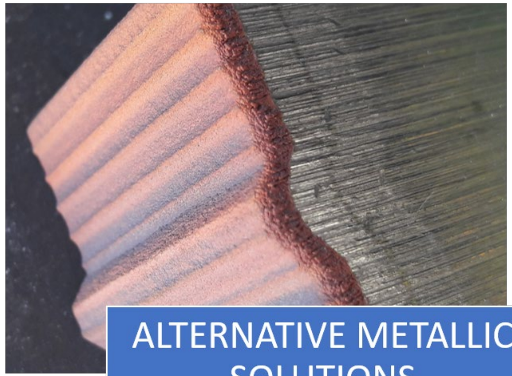
TASK 2: NOVEL MATERIALS



NON METALLIC SOLUTIONS

- Subtask 2.1 Ceramic Materials and Coatings
  - **Bulk materials:**
    - SiO_2/Al_2O_3 → sealing of ceramic container
    - Cr-doped SiC → sintering
  - **Coatings:**
    - TiO_2
    - CrN

    Process optimisation (porosities and flaws)



ALTERNATIVE METALLIC SOLUTIONS

- Subtask 2.2 Metallic materials and coatings
  - **Bulk materials:**
    - Cu alloy optimisation (+influence of impurities)
  - **Coatings:**
    - Cu, Ti, Cr,
    - Cu/Al_2O_3

    Process optimisation (porosities and flaws)

irCer institut de recherche sur les céramiques

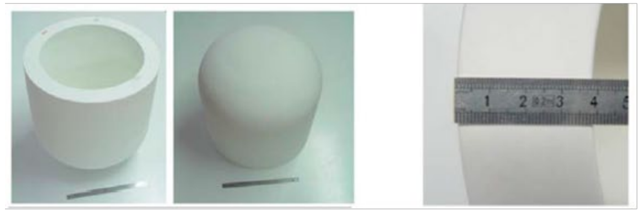
MINES Saint-Étienne

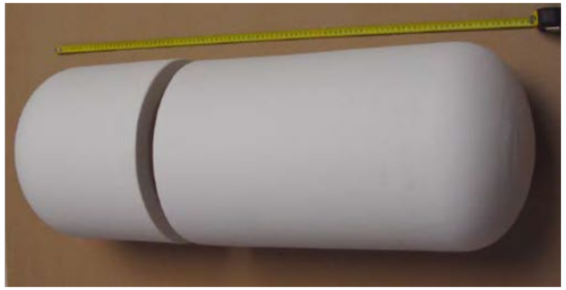
Activities:
- **Process optimization**
  - Coatings
  - sealing of ceramics
- **Determination of properties :**
  - physical/mechanical properties
  - leaching tests
  - simplified corrosion tests

KIPT

VTT

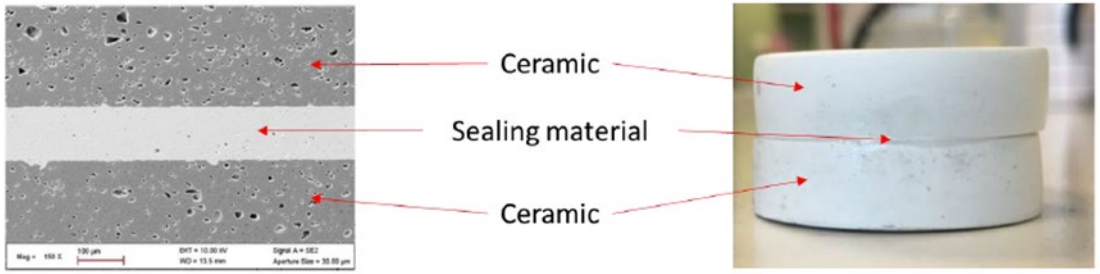
ALUMINA SOLUTIONS





Andra's half-scale model of Al_2O_3/SiO_2 VHLW container

- **Sealing by microwaves process**
  - Sealing materials previously achieved using specific *silica-based glass (T< 700°C)*



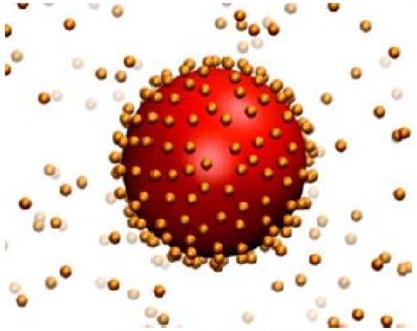
SEM micrograph of the interface between the sealing material and the ceramic canister

Picture of a sealing test

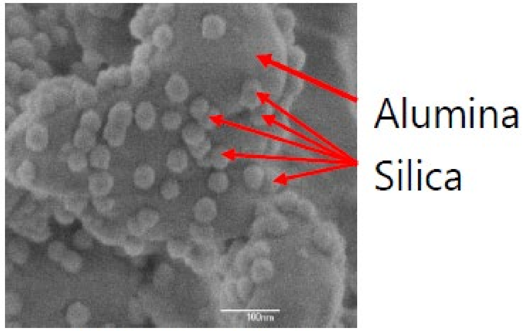
(Thesis - Greg KALFAYAN, 2019)

  - New materials targeted : **Glass-bonded ceramics**

- **Functionalization of particles by hetero-aggregation**



3D illustration of alumina/silica heteroaggregation
Orange : Silica particles
Red : Alumina particle



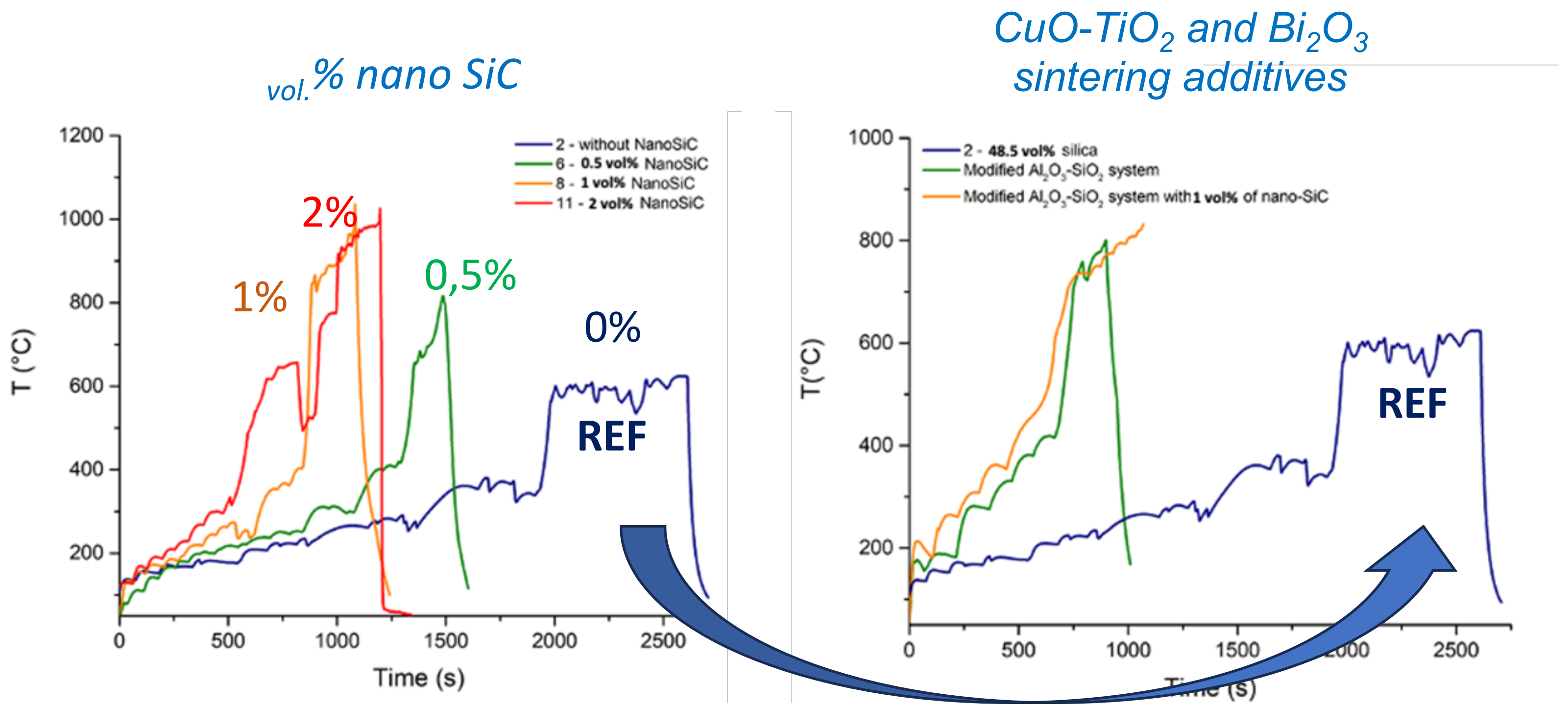
SEM micrograph of alumina/silica heteroaggregation

Sealing formulations based on silico aluminates with microwaves coupling

Objective: Improve the chemical affinities between the sealing material and the ceramic canister

ALUMINA SOLUTIONS

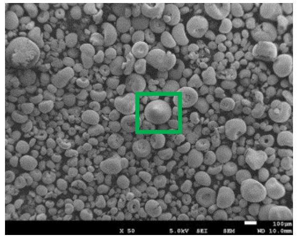
Al_2O_3+48,5% SiO_2 = reference composition → Different Al_2O_3/SiO_2 systems as sealing materials



Real breakthrough in the optimisation of microwave coupling for such type of formulations.

SILICON CARBIDE

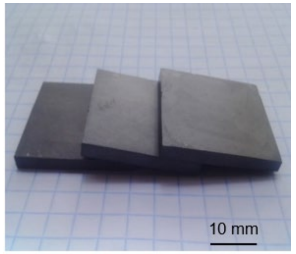
- **Focus on the optimization of the sintering process for the manufacture of composite materials based on SiC doped with Cr.**



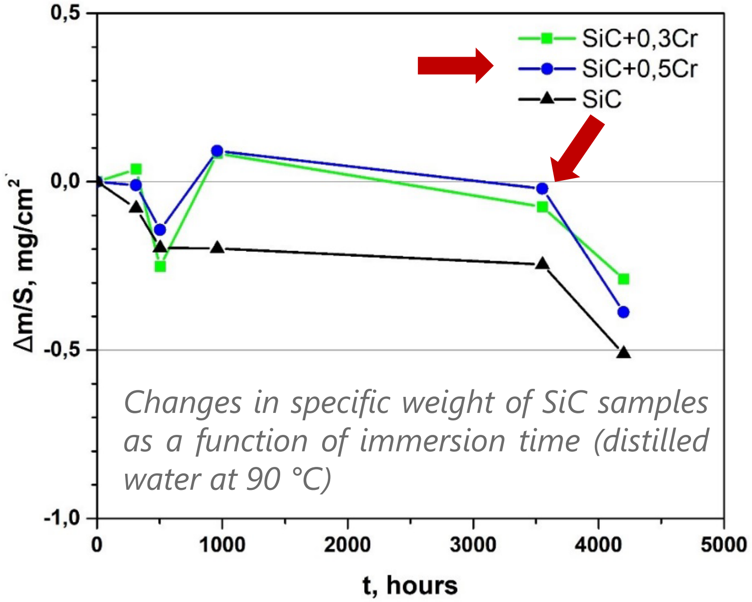
SiC powder (40÷100 µm)

Addition of Cr to the SiC powder (ball milling)

Hot isostatic pressing

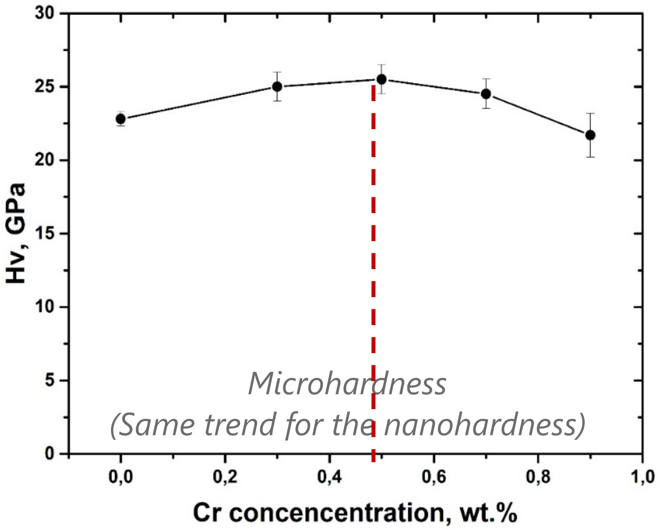


SiC(Cr) samples



Changes in specific weight of SiC samples as a function of immersion time (distilled water at 90 °C)

Samples	Measured density, g/cm³	From theoretic density of pure SiC,%
SiC (0 % Cr)	3.161	98.5
SiC (0.3 % Cr)	3.108	96.8
SiC (0.5 % Cr)	3.181	99.1
SiC (0.7 % Cr)	3.167	98.7
SiC (0.9 % Cr)	3.129	97.5



Microhardness (Same trend for the nanohardness)

Oxidation and dissolution of SiC in water:

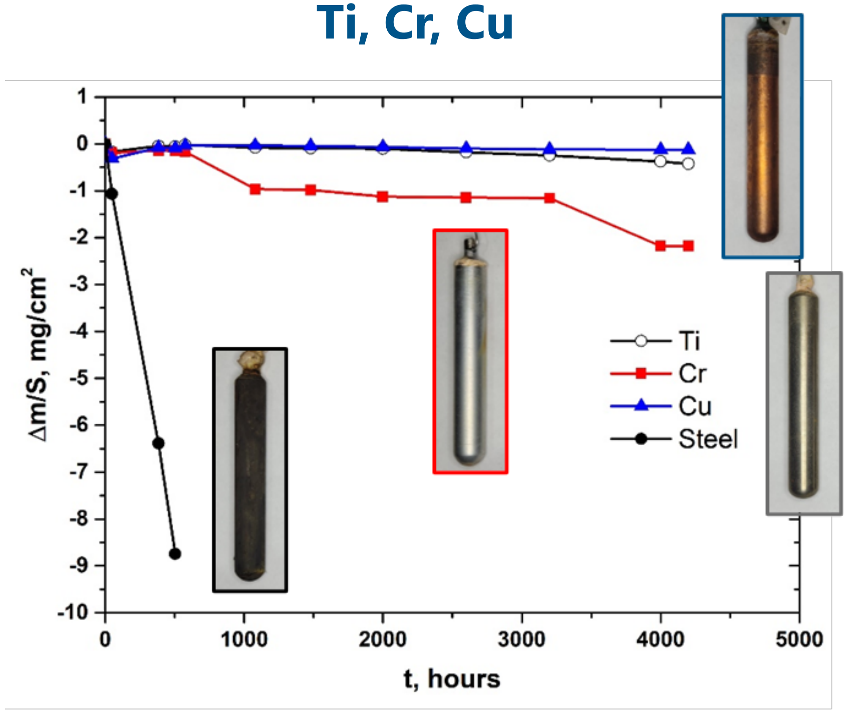
- $SiC + 2H_2O = SiO_2 + CH_4$
- $SiO_2 + 2H_2O = Si(OH)_4$

Cr forms a protective Cr oxide layer

CERAMIC AND METALLIC COATINGS

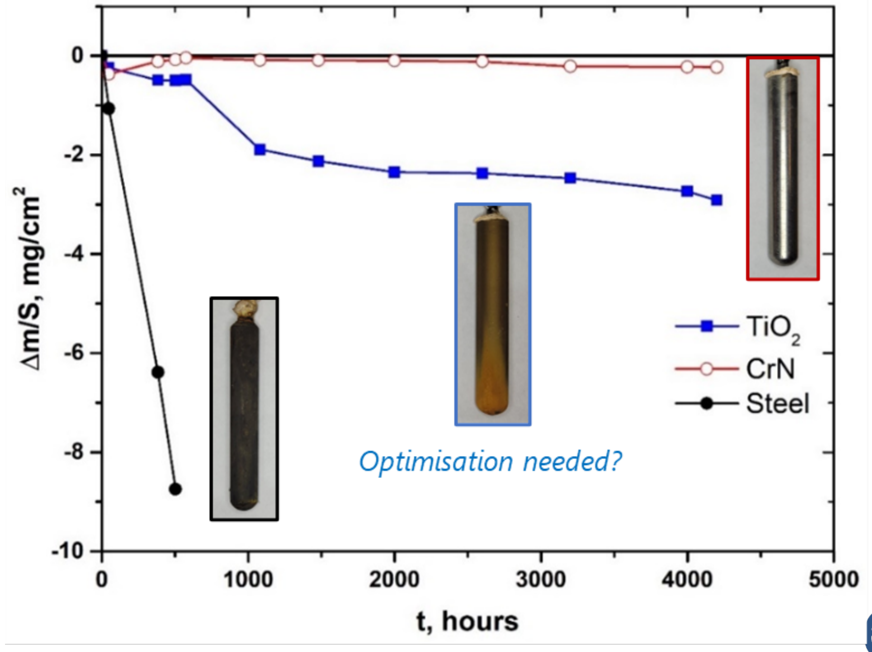
- Focus on optimization of the **PVD** method for coating production (thickness : **30 µm**)
- Good mechanical properties and a high degree of adhesion to the steel substrate at the **optimum bias potential.**

Ti, Cr, Cu



Changes in the specific weight as a function of immersion time in distilled water at 90 °C.

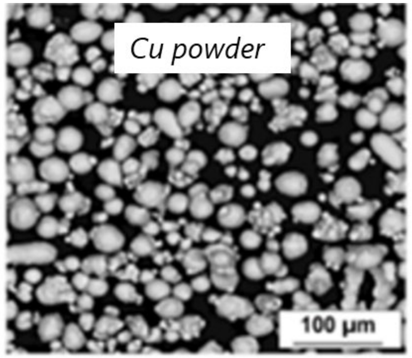
CrN and TiO_2

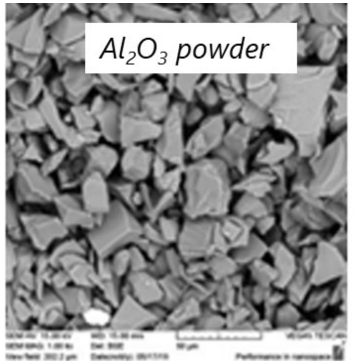


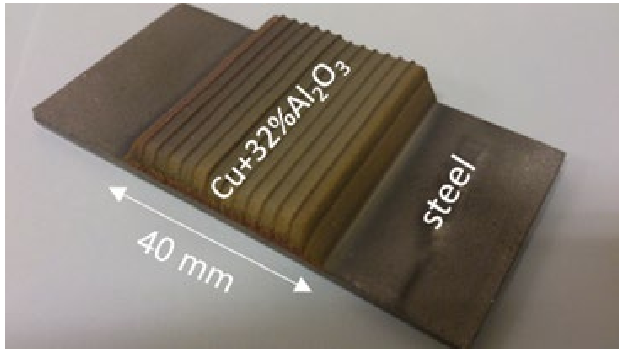
Changes in the specific weight as a function of immersion time in distilled water at 90 °C.

COPPER-ALUMINA COMPOSITE COATINGS

- **Cold spray coatings studied are produced from a mixture of powders Cu+32vol.%Al_2O_3.**

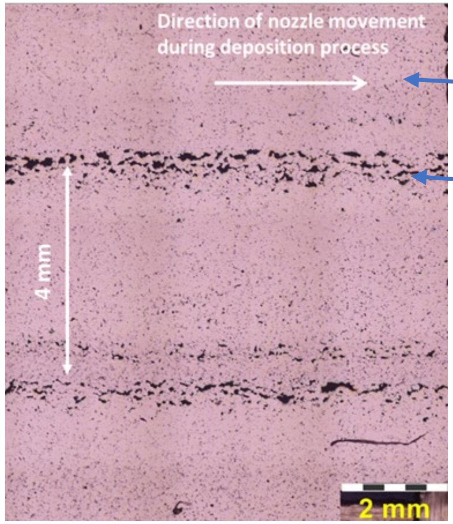






Composite cold spray coating coupon

- N_2 carrier
- 35 bars and 500°C
- 2 deposition speeds:
  - 20 mm/s
  - 40 mm/s



Light optical microscope image (cross-section parallel to the surface of the coating)

Low porosity in deposition lines (around 0.37%)

Higher porosity (2.47% to 3.31%) **in overlap zones**

Materials	*2 months (53-60 days)*	*3-4 months (87-120 days)*	*6 months (180 days)*
Wrought Cu	*14 µm/y*	*16 µm/y*	*23 µm/y*
Pure Cu CSC	*17 µm/y*	*13 µm/y*	*26 µm/y*
Composite Cu+32vol.%Al203 CSC (low strategy)	*21 µm/y*	*17 µm/y*	-
Composite Cu+32vol.%Al203 CSC (fast strategy)	-	*47 µm/y*	-

Corrosion rates vs. immersion time in synthetic goundwater at 90°C (50-100 ppb O_2)

TASK 3: CORROSION UNDER IRRADIATION

- **Goal: assess whether irradiation will contribute/accelerate the corrosion of candidate canister materials (steel and copper) under realistic conditions**
  - T3.1 Total dose vs. Dose rate
    - Experimental window of several orders of magnitude of dose rates, total doses and exposure durations using simplified model systems
  - T3.2 Repository conditions
    - Explore the influence of type of bentonite, nature of irradiation source, effect of bentonite saturation, limit dose rate where no irradiation effect is seen.

- **Activities**:
  - Corrosion tests in irradiation facilities
  - Post-mortem characterisation

TASK 3: CORROSION UNDER IRRADIATION

- **Goal: assess whether irradiation will contribute/accelerate the corrosion of candidate canister materials (steel and copper) under realistic conditions**
  - Focus on *bentonite buffer materials* with different saturation levels (FEBEX, MX-80, Ca-Mg Czech bentonite)
  - C-steel, copper, Ni-Alloy ; corrosion products
  - Groundwater compositions (SGW3, FEBEX, $NaHCO_3$)
  - Temperature (RT to 150°C)
  - Redox (aerobic, anaerobic)
  - Water saturation (full, partial, non saturated)
  - Nature of irradiation sources (Co-60, Cs-137)
  - Dose rates / Total dose (0-1000 Gy/hr ; 0-400 kGy)

Bentonite buffers are <u>not</u> representative for the current Belgian programme:

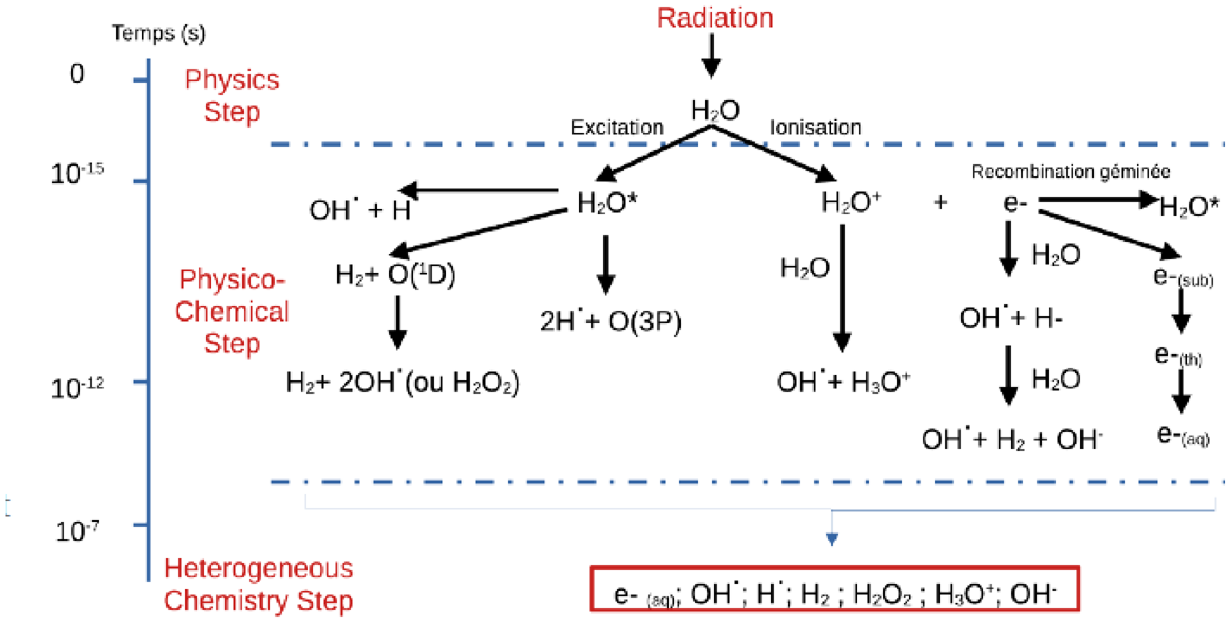
- pH from near-neutral to slightly alkaline
  → *active* corrosion
  → *film formation slowing down the corrosion rate with time*

However **irradiation affects water chemistry, generating oxydants**

Understanding the general mechanisms and trends remains relevant.

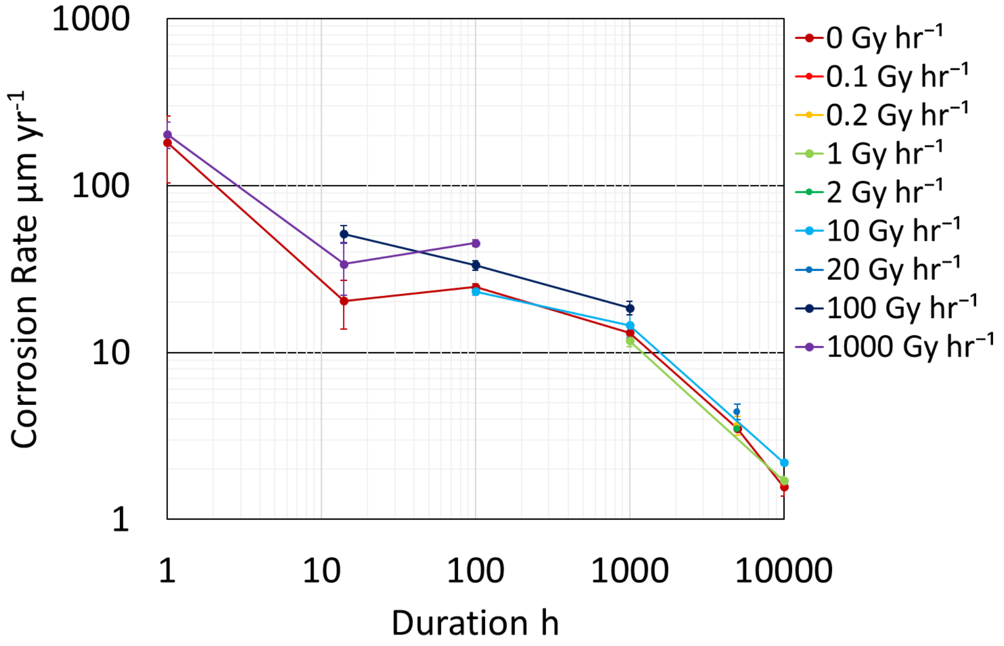
TASK 3: CORROSION UNDER IRRADIATION

- In terms results outcome:
  - A kind of **consensus** has been found **on corrosion products of C-steel with basically a mixture of *Fe-oxy-hydroxides and carbonate*** → the same "overall" mechanism?
  - **Corrosion kinetics were found to depend on the experimental parameters and conditions (water saturation, temperature)** → Link with expected repository conditions



TASK 3: CORROSION UNDER IRRADIATION

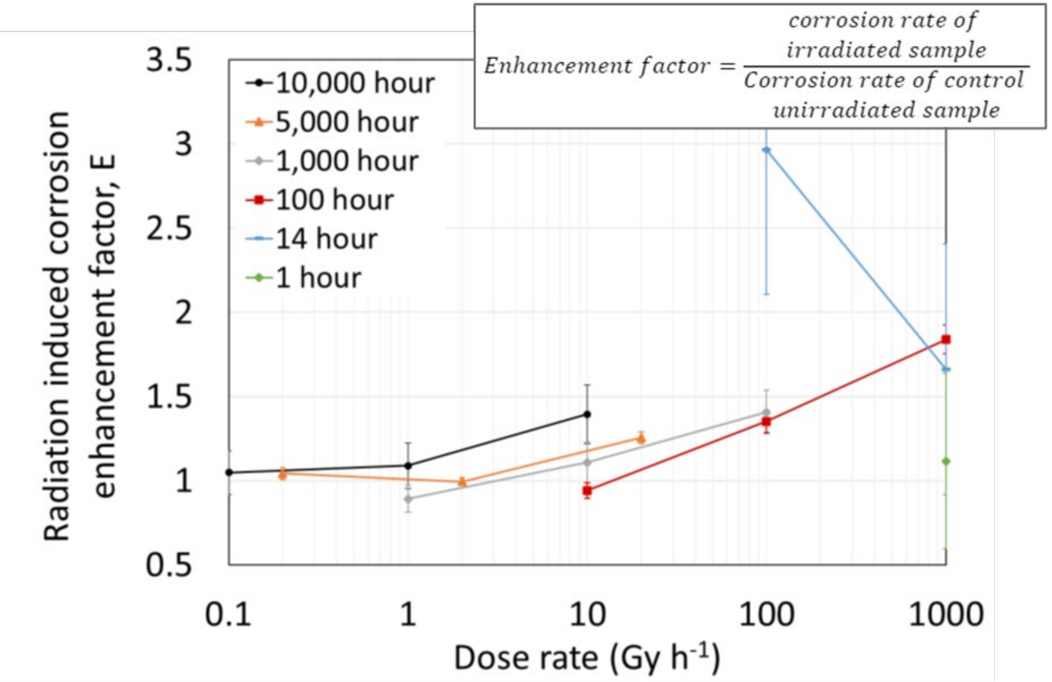
- The corrosion rate of **carbon steel** most strongly depended on exposure duration and could be loosely approximated by a power law relationship.



Average corrosion rate of carbon steel for set dose rates

TASK 3: CORROSION UNDER IRRADIATION

- The corrosion rate of **carbon steel** most strongly depended on exposure duration and could be loosely approximated by a power law relationship.
- A **significant increase in the corrosion rate** due to radiation exposure was only observed **at dose rates of 10 Gy/h or greater.**
- **At dose rates lower than 10 Gy/h no increase in corrosion rate associated with radiation was observed.**

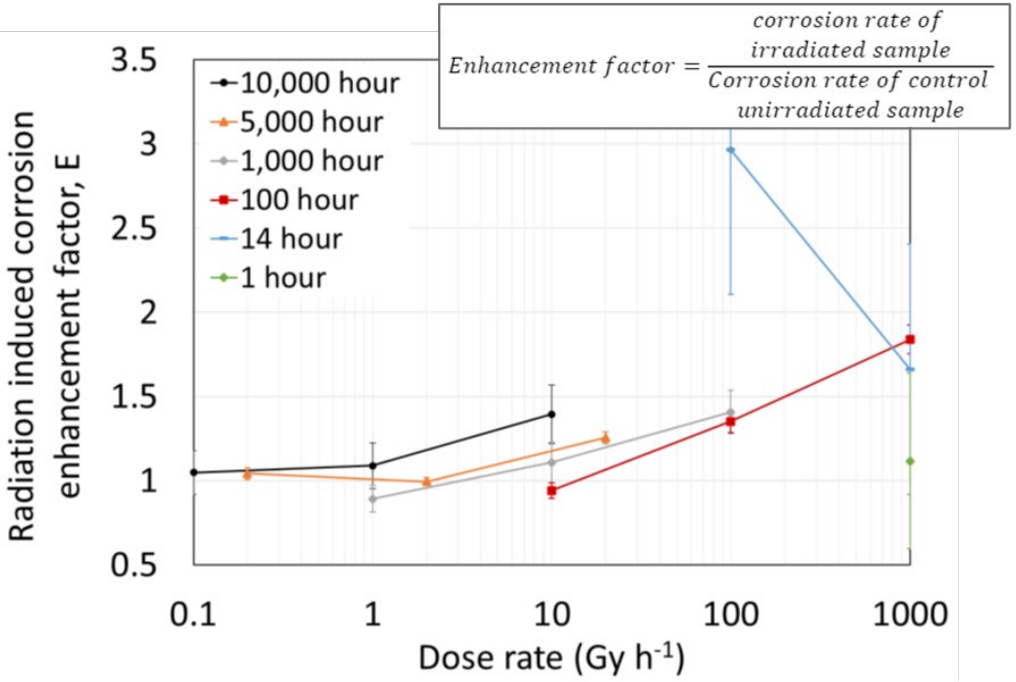


Influence of dose rate on the radiation induced corrosion enhancement factor, E.

TASK 3: CORROSION UNDER IRRADIATION

- The corrosion rate of **carbon steel** most strongly depended on exposure duration and could be loosely approximated by a power law relationship.
- A **significant increase in the corrosion rate** due to radiation exposure was only observed **at dose rates of 10 Gy/h or greater.**
- **At dose rates lower than 10 Gy/h no increase in corrosion rate associated with radiation was observed.**
- At durations longer than those explored here, it is expected that a significant increase in enhancement factor may be observed at dose rates lower than 10 Gy/h

Reference:
25 Gy/h at the surface of the overpack of the supercontainer



Influence of dose rate on the radiation induced corrosion enhancement factor, E.

TASK 5: TRANSIENTS

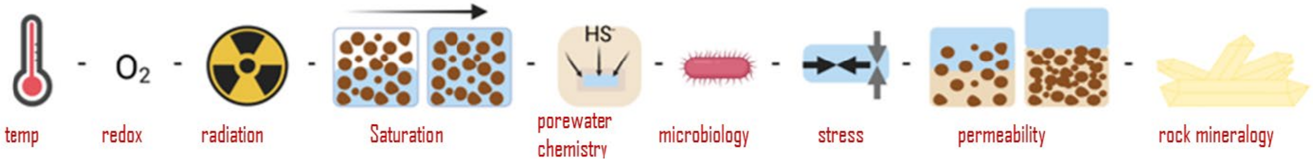
- Understand container **corrosion during transients** that would lead to chemo-mechanical interactions between the container material or coating (if present), corrosion products and buffer.

  → **Link to Task 3 and Task 4 activities**

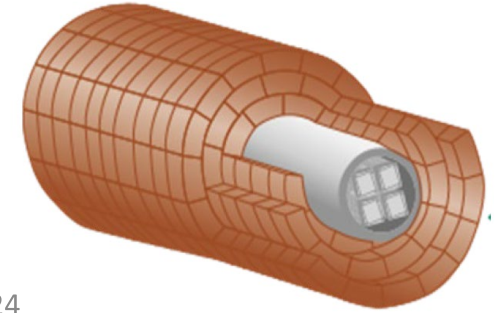
- To address existing **uncertainties** and to provide relevant experimental data to adequately account for these processes in performance assessment

  → **Link to Task 6 activities**

- Both laboratory and in-situ experiments



Focus: canister/bentonite interface



TRANSIENTS ANALYSED

- Thermal
- Redox
- Radiation
- Hydraulic (saturation)
- Chemical evolution
- Gas evolution

TASK 5: TRANSIENTS

- **Studied materials:**
  - **Carbon steel**
  - **Spheroidal graphite cast iron**
  - **Copper-nickel alloy** (Cu with about 30wt.% Ni)
  - **Cu-OFP**

- **Contact to different types of bentonites, hydration with waters of different salinity and nature:**
  - low salinity granitic waters,
  - bentonite porewater
  - sedimentary clay groundwater of high salinity.

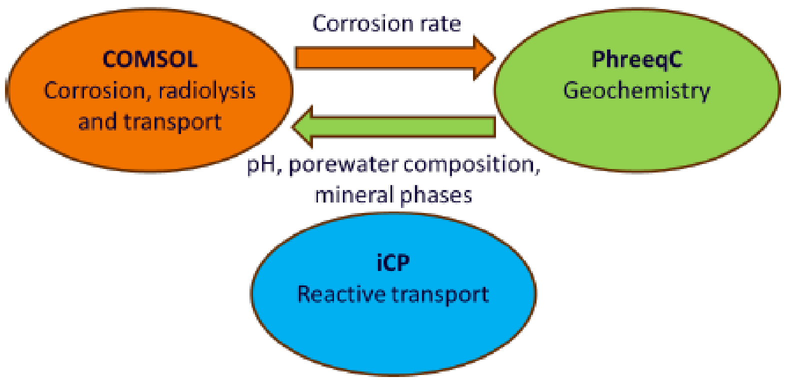
- **Carbon steel corrosion rate:**
  - increase at higher temperatures
  - enhanced by combining temperature and irradiation
  - strong influence of bentonite type and porewater salinity
- **Spheroidal graphite cast iron corrosion rate**
  - Dependence on bentonite environment and salinity
  - Higher values found combining a γ-radiation dose of 130 Gy/h and temperature
- **Very diverse corrosion products, highly dependent on the specific material and environmental conditions established at equilibrium.**

TASK 6: MODELLING

- **Modelling work:**
  - Reactive transport modelling – Links with Task 3 (irradiation) and Task 5 (transients)
  - Geochemical modelling with microbial activity – Links with Task 4 (microbial corrosion)
  - Repository scale modelling – contained within Task 6
- **Other work:**
  - ConCorD Synthesis Report (D 15.14) – Linked with all other Tasks

TASK 6: MODELLING

- **Development of modelling tools:**
  - Development of a water and chloride radiolysis model
  - Development of an electrochemical corrosion model for carbon steel
  - Integration of radiolysis and steel corrosion models into a reactive transport computational platform



- **Model application (Task 3 and Task 5)**
  - Simulation of irradiated experimental cells (carbon steel coupons embedded in compacted bentonite)
    - *Corrosion rate*
    - *Corrosion potential*
    - *Porewater chemistry*
    - *Precipitation of corrosion products*

EURAD-2

Innovative and new **Co**ntainer/canister materials under disposal field conditions: **Man**ufacturing feasibility and improved **D**urability

InCoManD (WP9)

InCoManD: Objectives

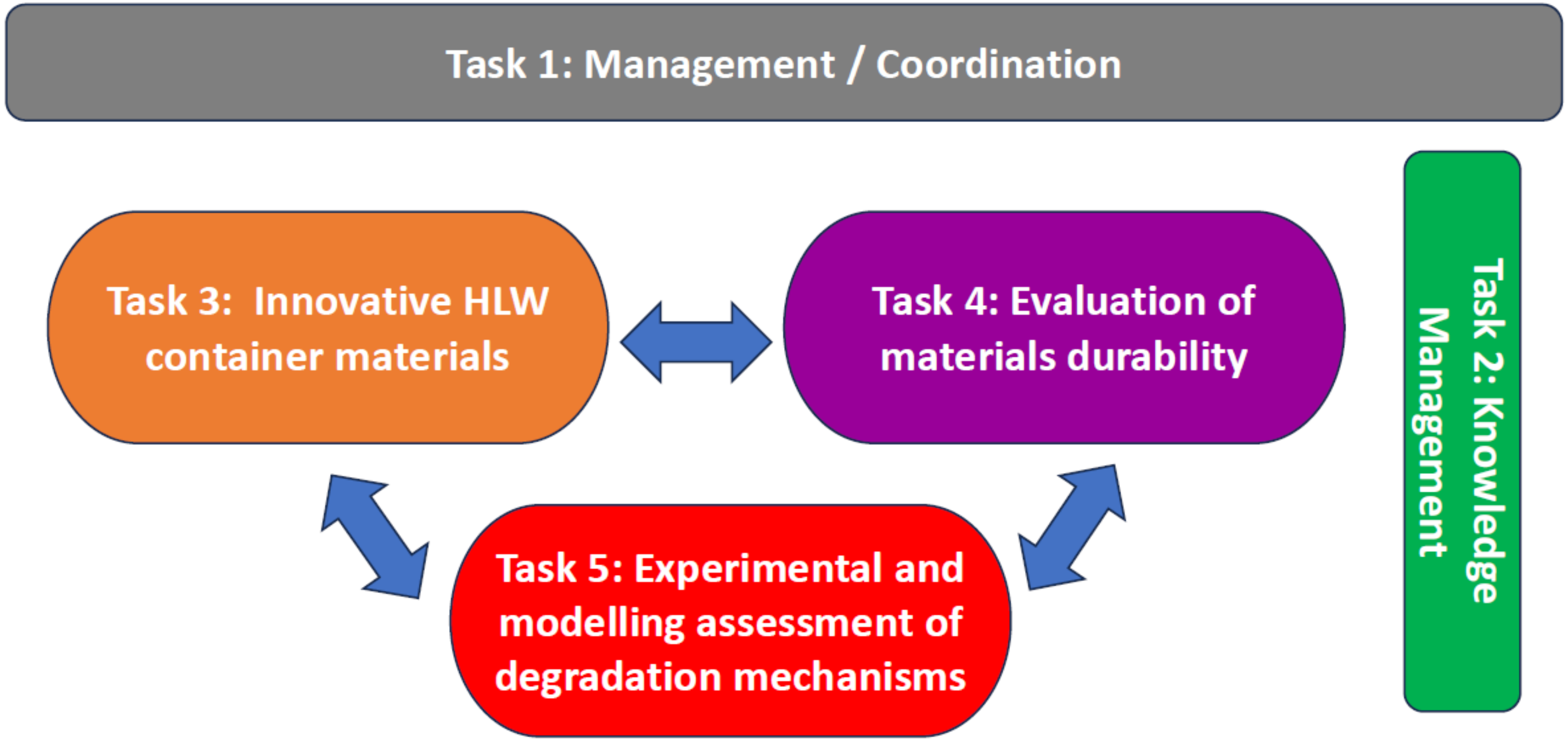
Innovative and new Container/canister materials under disposal field conditions: Manufacturing feasibility and improved Durability

→ **Innovative:** **solutions** (materials and/or processes) **never implemented or tested.**
→ **New:** **more traditional solutions** (materials and/or processes) **that need to be optimized, improved, tested in more realistic conditions…**
→ **Container and canister:** same meaning, can be referred to as **"component"**

- The WP aims* at **identifying and qualifying innovative solutions for the HLW containers/canisters**, as well as **providing a deep knowledge of the long-term durability** of **any selected material** in, as realistic as possible, field conditions.

*starting from the ConCorD project outcomes and going beyond…

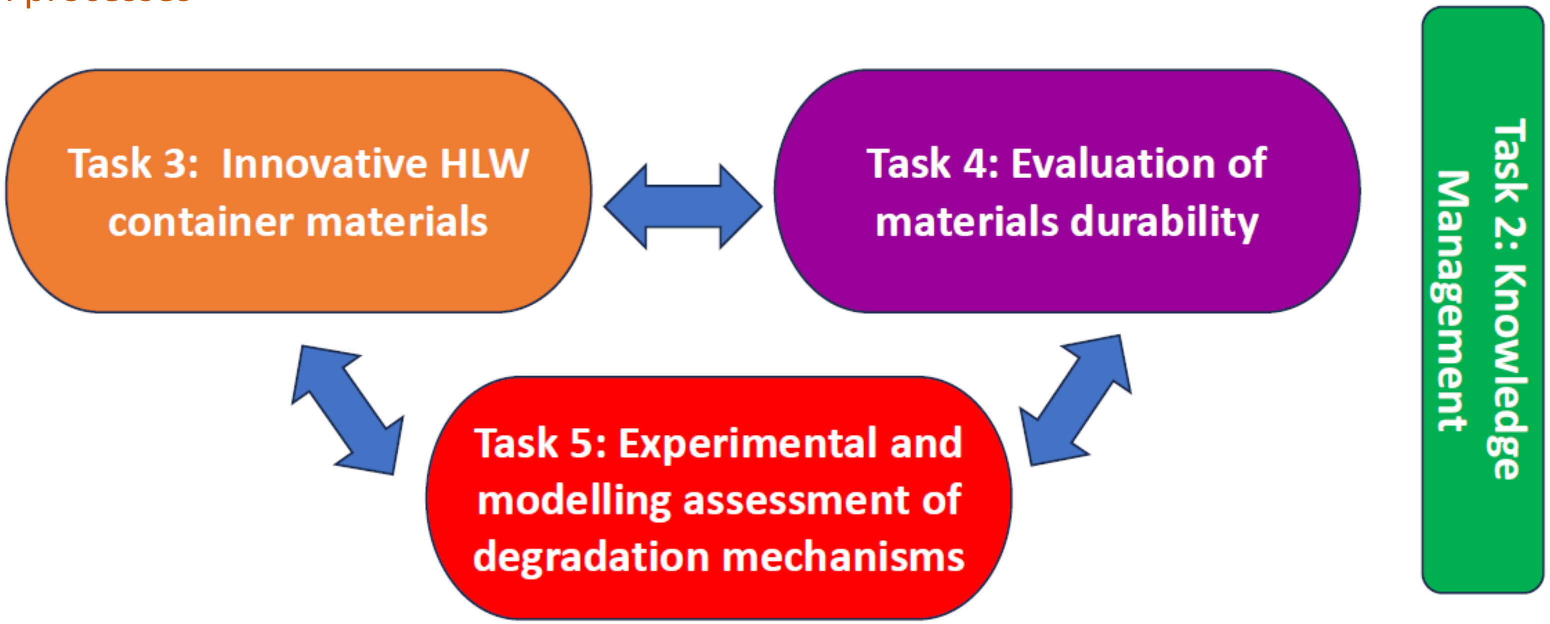
InCoManD: Organization in 5 Tasks



InCoManD: Organization in 5 Tasks

- Improve recently selected (within ConCorD) innovative bulk and coating materials
- Seek new options
  → Elaboration and optimization of fabrication processes

Evaluate the durability (i.e. corrosion resistance under **transients**) of the materials identified in Task 3 or previously recognized as reference materials
→ Identification of main degradation mechanisms



- Study of joint mechanical-corrosion degradation modes
- Determine threshold stresses for SCC
- Modelling of geochemistry and time-dependent transients

- Knowledge capture
- Knowledge transfer
- Additional KM activities: Summer School in Slovenia in 2027

THANK YOU FOR YOUR ATTENTION!

ANY QUESTION?