CHEMICAL EVOLUTION AND INTERACTION IN DISPOSAL CELLS

EURAD projects: ACED, CORI & FUTURE

14/09/2020 • Diederik Jacques & Norbert Maes (SCK CEN)

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GENERAL INTRODUCTION – WASTE PACKAGE – ENGINEERED SYSTEM – HOST ROCK

- **A disposal concept relies on 3 main safety functions**
  - Waste **containment**
  - Strong **retarded** transport of RN
  - **Isolation** of waste from the biosphere
- **Multiple barrier principle:**
  - Waste Package – Engineered Barrier System – Host Rock
- **Different materials -> chemical gradients -> interactions & E**
  - Impact on integrity of waste package
    - Organic degradation products
  - Impact on durability of EBS
  - Perturbations of the Near-Field of the host rock
  - Evolves afo time
- **Transport of RN**
  - Mobility f(geochemical conditions, complexing agents)
    - Through engineered barriers
      - Organics in the waste form/barrier materials
    - Through host rock

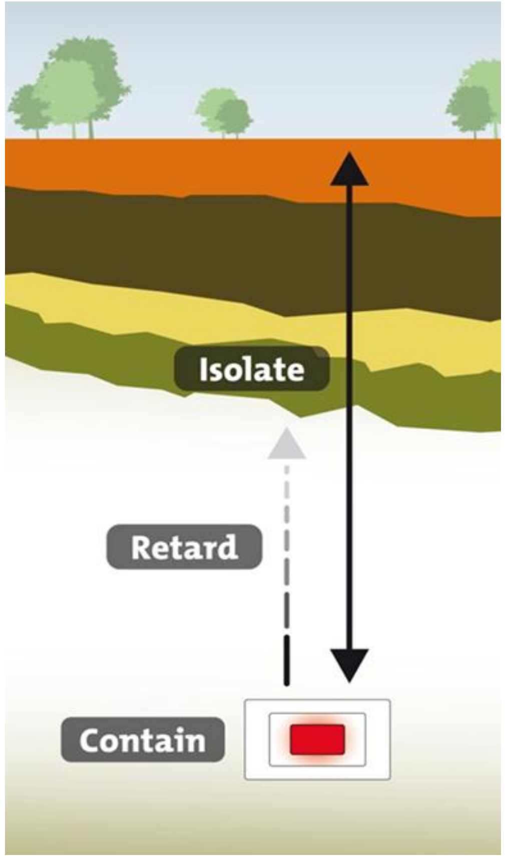
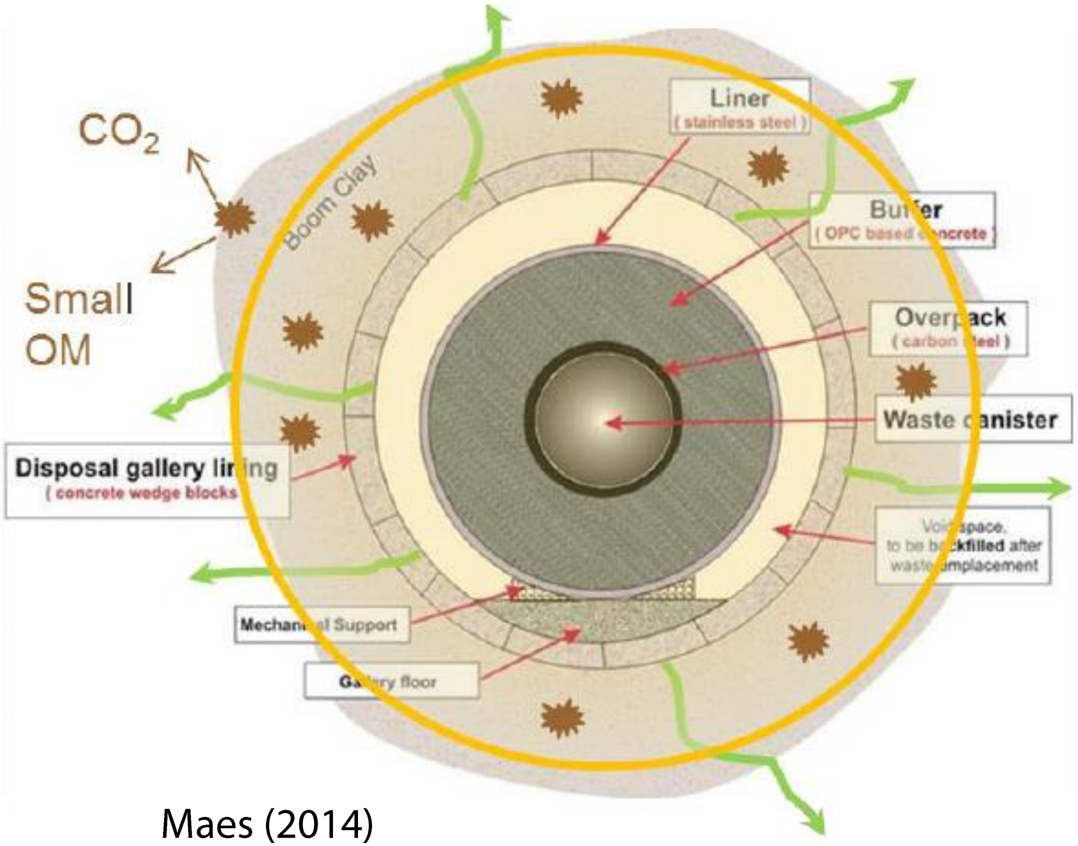


Figure from ONDRAF/NIRAS

ACED – ASSESSMENT OF CHEMICAL EVOLUTION IN A ILW OR HLW DISPOSAL CELL



Maes (2014)

- **DISPOSAL CELL.**
  - Intermediate level waste package
  - High level waste package
  - Immediate host rock surrounding (clay, crystaline)
- **CHEMICAL EVOLUTION**
  - Different materials (glass, steel, different types of cement-based materials, host rocks)
  - Chemical gradients – Transport
  - Disequilibrium – Geochemical reactions
- **ASSESSMENT**
  - Large structures
  - Long times

ACED – ASSESSMENT OF CHEMICAL EVOLUTION IN A ILW OR HLW DISPOSAL CELL

Long term chemical evolution forms an important input for the assessment of the evolution of a disposal system and the assessment of safety- and performance-related aspects

AIM – A better conceptual and mathematical representation of the chemical evolution to:

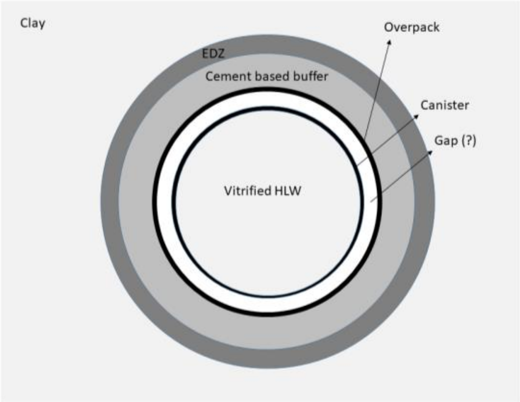
- Improve the assessment and quantification of generic safety functions such as isolation and containment of waste constituents
- Obtain a better substantiation of conservatism and reduction of uncertainty
- Increase the scientific basis for definition of requirements of materials

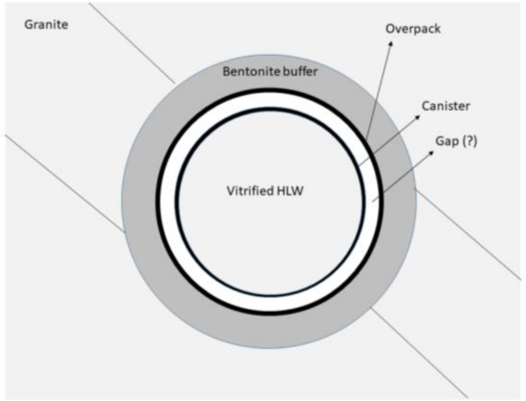
OBJECTIVE – For the assessment of the chemical evolution at the disposal cell scale:

- Improve methodologies for deriving multi-scale quantitative models for assessment of chemical evolution
- Derive robust models (including key processes)

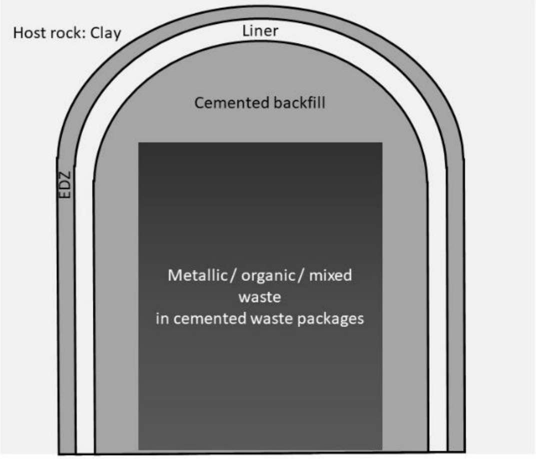
GEOLOGICAL DISPOSAL - REPRESENTATIVE DISPOSAL CELLS

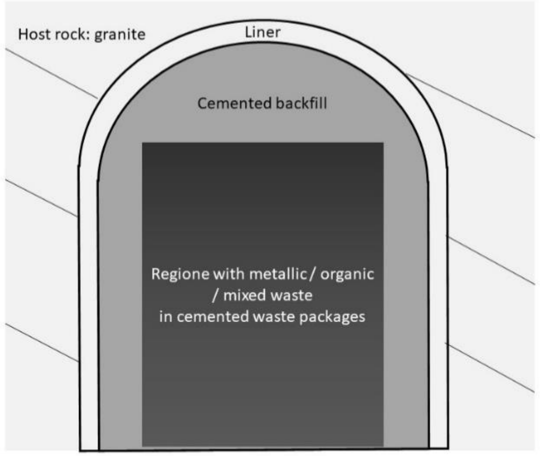
HIGH LEVEL ACTIVITY DISPOSAL CELLS





INTERMEDIATE LEVEL ACTIVITY DISPOSAL CELLS





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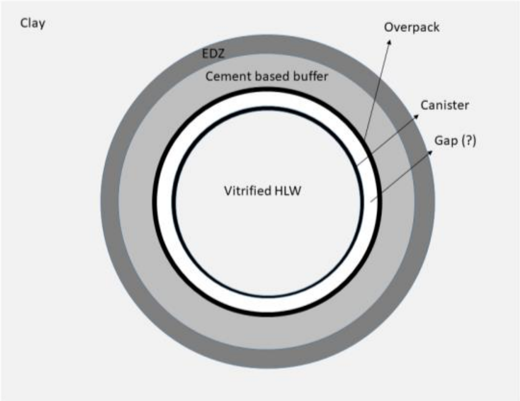

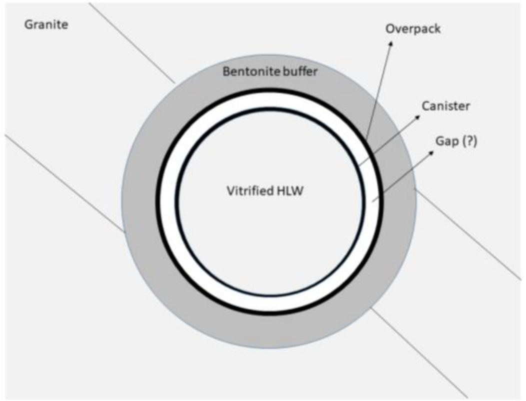

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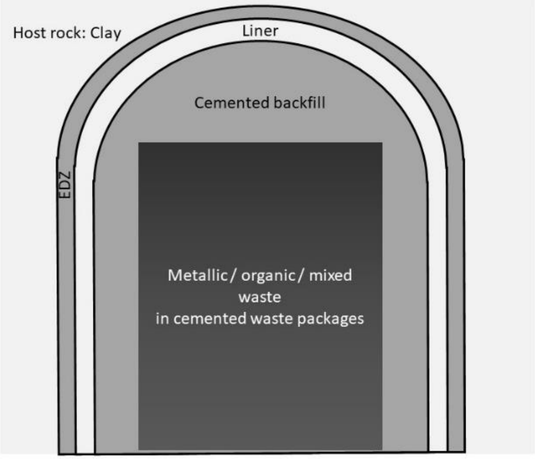

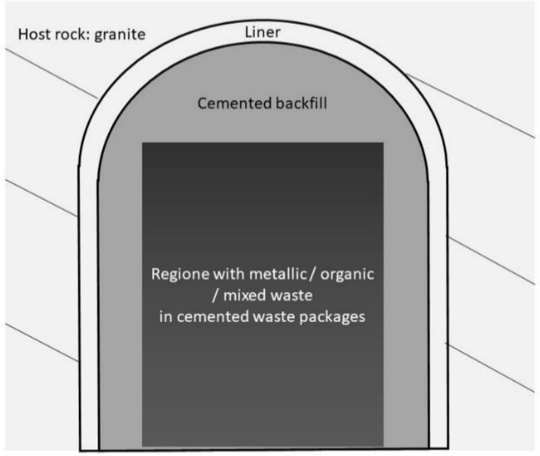

INTERFACES BETWEEN MATERIALS

Literature study on

- Glass-steel
- Steel-Cement
- Steel-Clay
- Steel-Granite
- Cement-Clay
- Cement-Granite

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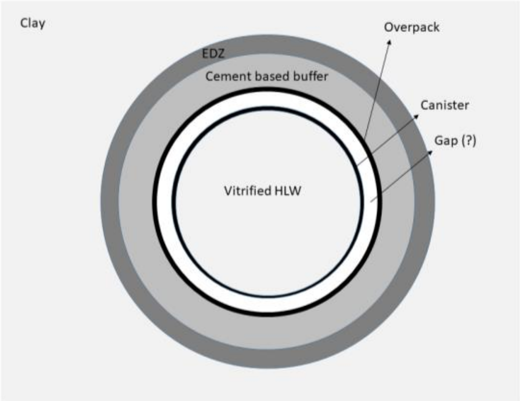

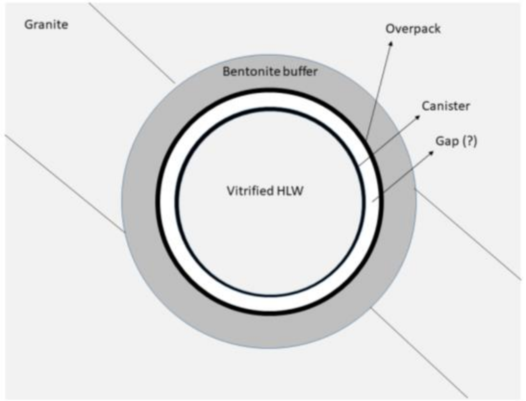

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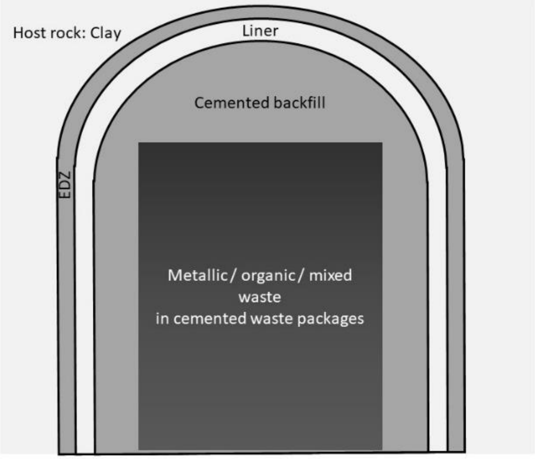

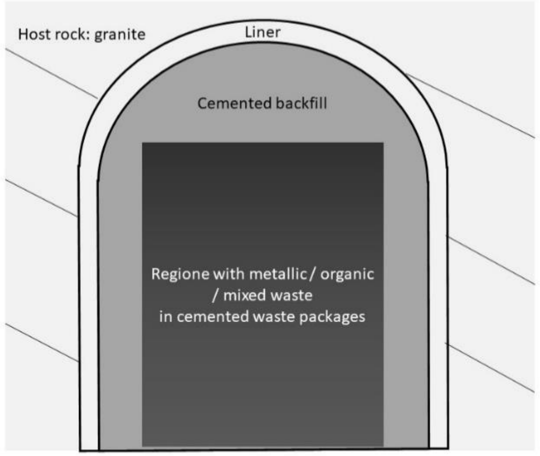

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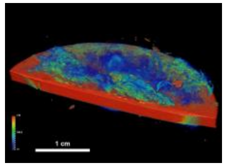
FOCUS ACED – STEEL-CONCRETE and STEEL-CLAY



Experimental study

Existing & new experiments

few months – several decades

To improve models

integration of knowledge

Input to larger scales

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FROM WASTE PACAKGE TO DISPOSAL CELL

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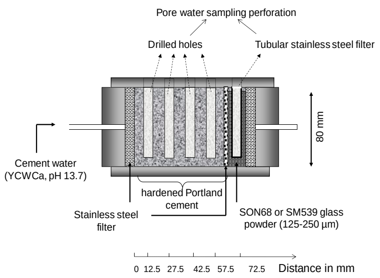
WASTE PACKAGE SCALE

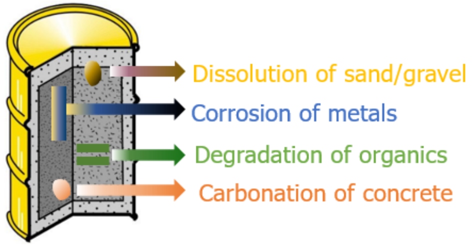
Experimental study existing data

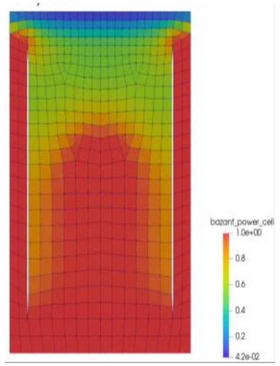


To improve models – Coupled reactive transport

integration of knowledge

Model abstraction for input to larger scales





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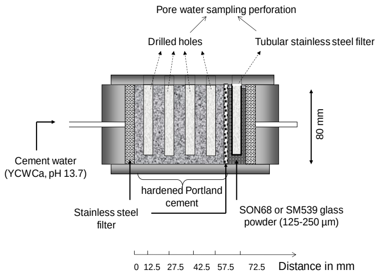

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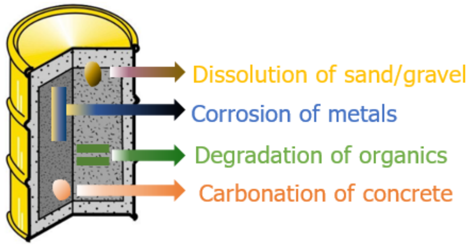

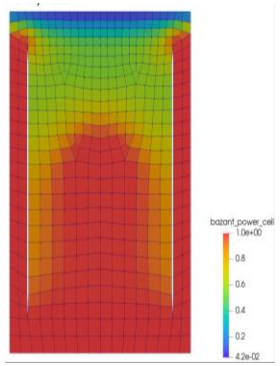

DISPOSAL CELL SCALE

Step I – Integration of state-of-art knowledge

upscaled information

full-scale coupled reactive model

Step II – Robust and manageable models

model abstraction

geometry / processes / parameterization …

benchmarking with full-scale model

reflect state-of-art and key processes

Step III – Model analysis and application

sensitivity

critical parameters

model performance

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FROM WASTE PACAKGE TO DISPOSAL CELL

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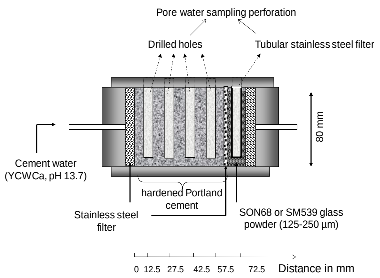

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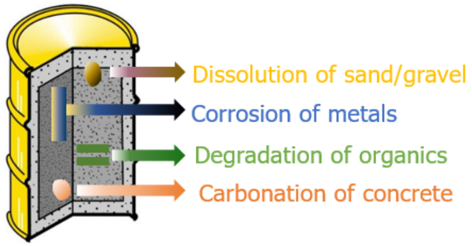

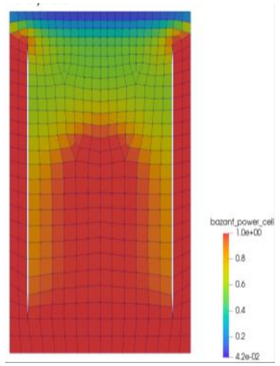

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END USERS

CORI: CEMENT ORGANICS INTERACTION

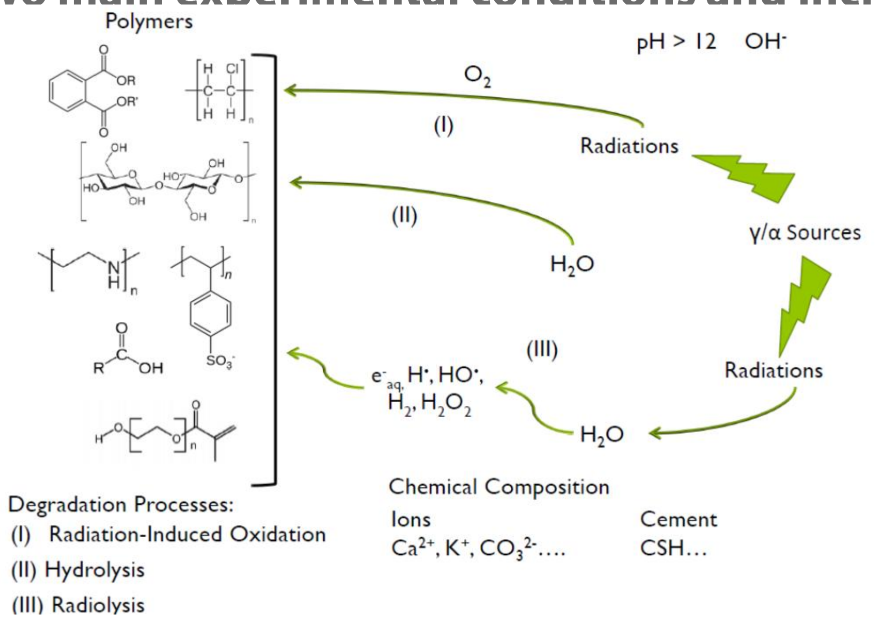
- **Objective:**
  - Improve the knowledge on the organic release issues which can accelerate the radionuclide migration in the post closure phase of repositories for ILW and LLW including surface/shallow disposal
- **Context:**
  - Organic materials are present in some nuclear waste and as admixtures in cement based materials and can potentially influence performance of disposal system
  - Potential effects are related to the formation of RN-organic complexes which
    - i) increase the RN solubility,
    - ii) decrease RN sorption
  - Cement based materials degrade afo time with distinct different alcaline conditions which affect RN speciation and interactions
  - Alcaline pH provide specific conditions under which organics can degrade, thus increasing their potential impact on repository performance

CORI: ORGANICS DEGRADATION

- **Improve knowledge of degradation of organic wastes in conditions representative of disposal facilities.**
- **Improve understanding of radiolytic/hydrolytic degradation of organic materials (PVC, cellulose, Ion exchange resins, superplasticizers).**
- **Provide characterization and quantification of soluble organic species generated by degradation.**

Degradation studies performed in CORI will focus on two main experimental conditions and include detailed analysis of the degradation products:

- Radiolytic degradation (gamma and beta, dry)
- Hydrolytic degradation (pH>12, non and pre-irradiated)
- Characterisation and quantification of soluble organic spe
- Gas measurements



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CORI: ORGANICS-CEMENT INTERACTIONS

- **Improve the understanding of the behaviour of anthropogenic organic molecules within cementitious systems.**

Study the sorption and transport properties of organic molecules that might be released from the organics inventories (incl. polymers and SuperPlasticizers) present in cement-based materials.

- Investigated organic molecules are
  - main degradation products like ISA (isosaccharinic acid), phthalates
  - EDTA and low molecular weight molecules
  - ^{14}C-bearing molecules from CAST
  - Other degradation products resulting from degradation studies
- Cement systems studied
  - CEM I and CEM V at different degradation states (including altered/carbonated states)
  - pure solid phases such as C-(A)-S-H and AFm-phases/ettringite.
- Impact of iron and calcium will be studied as potential competitors.

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CORI: RADIONUCLIDES-ORGANICS-CEMENT INTERACTIONS

- **Improving the knowledge on organic-radionuclide complexes mobility in cement-based systems**
- **Studying the competition or synergetic effect in ternary systems (organic/radionuclide/cement)**
- **Providing a mechanistic understanding of radionuclide interactions and quantitative transfer data in cementitious environments.**

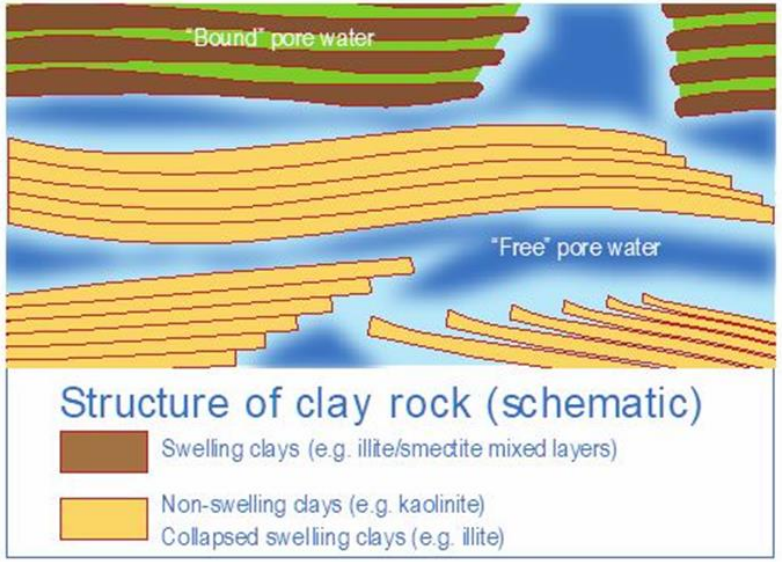
Experimental work is combining batch sorption, diffusion, column, speciation, solubility and advanced spectroscopic studies to allow fundamental model development and application-oriented analyses.

- Main radionuclides studied: Nickel, Uranium, Actinides(III/IV) and/or homologues.
- Organic and cementitious materials investigated are consistent with studies on organics-cement systems
  - ISA, phtalates, EDTA, LMW organics, ^{14}C-bearing molecules
  - CEM I, CEM V (different degradation states), C(A)SH, Afm-phases

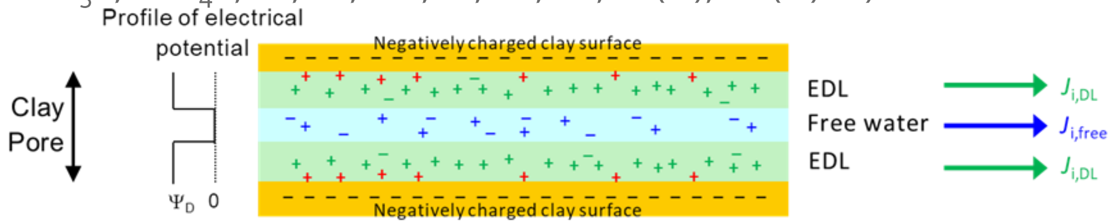
FUTURE: FUNDAMENTAL UNDERSTANDING OF RADIONUCLIDE RETENTION – SCOPE & OBJECTIVES

- **Objective:**
  - Broadening our scientific basis in the understanding of radionuclide *retention* and *transport* processes in *clay and crystalline host rock* based repository systems
- **Context**
  - Host rocks are the main barrier against transport of RN towards the biosphere, and they have to maintain this for geological time scales.
  - Suitable host rocks are selected because of favourable conditions for retaining RN and slow transport.
  - Understanding the processes of RN retention and transport, are therefore of primary importance for a reliable safety assessment.
    - Impact of chemical boundary conditions (pH, ionic strength) and the rock microstructures on radionuclide (RN) speciation, mobility and sorption reversibility in argillaceous and crystalline rocks.
    - Quantitative and mechanistic understanding of the impact of specific surface properties of materials, structural heterogeneity on the mobility.
    - Fundamental understanding of surface induced (heterogeneous) redox processes relevant for uptake of redox-sensitive radionuclides at Fe^{II}/Fe^{III} bearing minerals surfaces.

FUTURE: MOBILITY IN CLAYS



- **To enhance the quantitative and mechanistic understanding of the impact on radionu**
  - Charge effects (surface potential and electric double layer)
  - Microstructural effects (grain boundaries, water saturation, pore heterogeneity)
  - Solution characteristics (pH, ionic strength, competing elements)
- **To improve our fundamental understanding of adsorption mechanisms to elaborate state of art models and concepts for radionuclide behaviour in real systems**
  - Emphasis on reversibiliy of sorption and sorption competition
  - OQ wrt. Adsorption reversibility and it's mechanism that control retention in the long term: adsorption vs. "incorporation" (surface precipitation, neo-formation, solid solution)
- **Systems:**
  - "pure clays": Illite, montmorillonite //Host rock clays: Opalinus Clay, Callovo-Oxfordian clay, Boda Claystone
  - Weak to strong sorbing RN: I-, SeO_3^{2-}, SeO_4^{2-}, Ba, Ra, Mn, Ni, Co, Zn, Ln(III), An(III)-VI)



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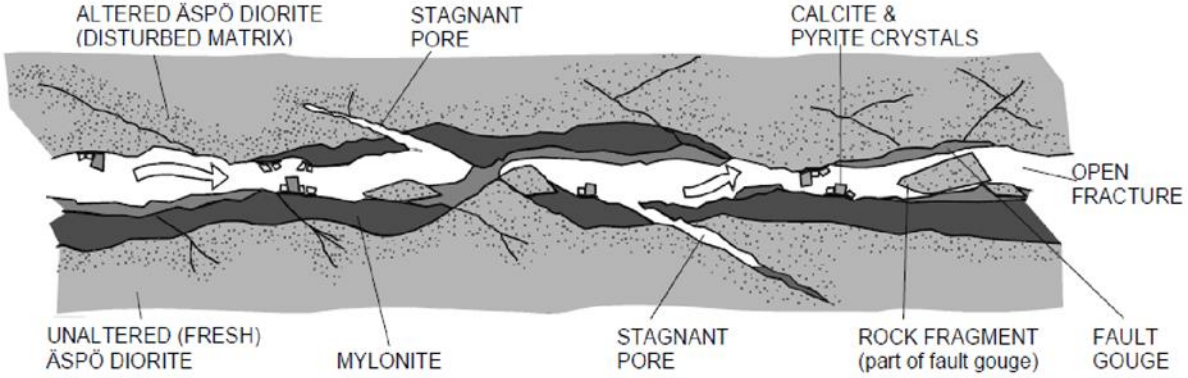
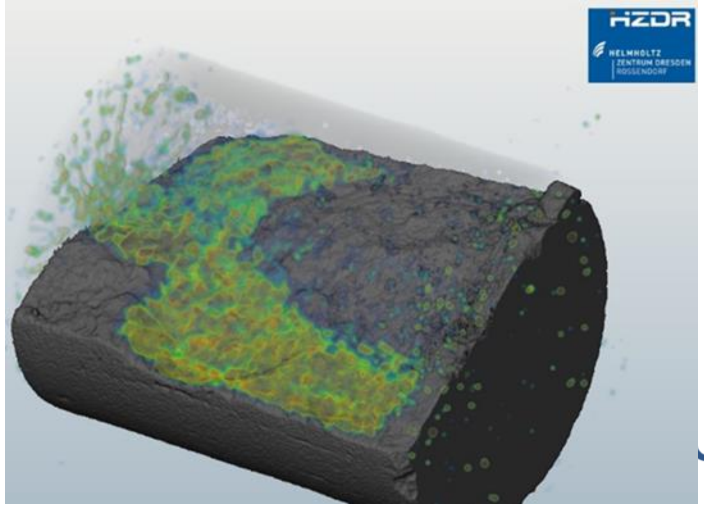
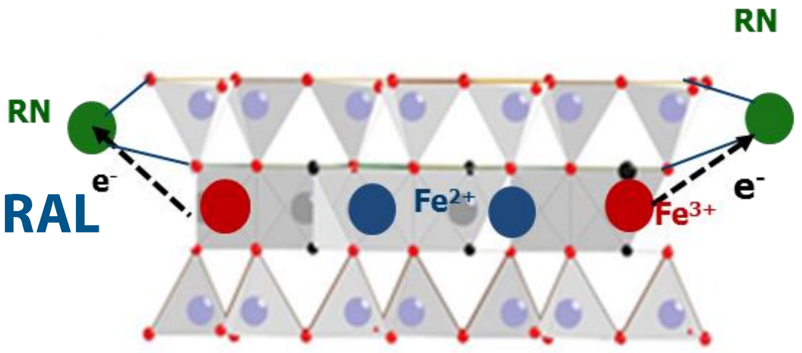
FUTURE: MOBILITY IN CRYSTALLINE ROCKS

- **How do microstructural and geochemical boundary conditions constrain the radionuclide transport pathways**
  - Role of pore geometry/pore network & fractures on flow field/transport
  - Role of fracture filling materials in retention
- **Systems:**
  - Rock: Grandiorite, migmatite, paragneis, gneiss, amphibolite, granites// fracture infill: lamprophyre, calcite, chlorite, kaolinite, illite…
  - I, Se, Sr, Ba, Ra, Ni, Eu





FUTURE: REDOX REACTIVITY OF RADIONUCLIDES ON MINERAL



- Improvement of the fundamental understanding (reduction of uncertainties) of **surface induced (heterogeneous) redox processes** with regards to coupled sorption and electron transfer interface reactions governing the retention of redox-sensitive radionuclides at Fe(II)/Fe(III) bearing minerals surfaces.

→ Limits to the current approaches used to quantify/thermodynamically describe the sorption of redox-sensitive elements

  - Frequent use of the "K_D" formalism, which assumes
    - Sorption reversibility
    - No change in the structure of the solid phase (nature of the sorption sites and of their density)
    - No change in the redox state of the "adsorbed" component
  - Difficulty to thermodynamically describe surface induced electron transfer reactions, mineral specific redox potential (often ≠ in solution)…

- Systems:
  - Fe containing minerals: illite, montmorillonite, nontronite, magnetite, green rust, goethite, COX, Tegulines clay, Red clay
  - Redox sensitive RN: Se, Tc, U, Np, Pu

CONCLUSION

The outcome of the projects ACED, CORI and FUTURE will improve our understanding of the performance of disposal concepts

- Evolution and interactions in disposal cells
- Impact of organic degradation products on RN mobility in cement barrier materials
- RN retention and transport in host rocks

Which entails us to improve safety assesments and increases our confidence in disposal concepts for a safe, final disposal of radioactive waste.