LONG-TERM RADIONUCLIDE RETENTION IN THE NEAR FIELD: COLLABORATIVE R&D STUDIES WITHIN EURAD FOCUSING ON CONTAINER OPTIMISATION, MOBILITY, MECHANISMS AND MONITORING

Marcus ALTMAIER, (WP CORI), Johan BERTRAND (WP MODATS),
Sergey CHURAKOV (WP FUTURE), Nikitas DIOMIDIS (WP CONCORD)

INTRODUCTION

- This presentation summarized work performed in the EURAD WPs CONCORD, FUTURE, CORI and MODATS.
- Research aims to deepen understanding regarding the long-term behaviour of key components in the repository near-field, assess specific radionuclide retention processes as well as developing methods for monitoring safety relevant parameters of repository systems.
- WPs investigate topics to meet implementation needs and contribute to Safety Cases in Europe at the highest level of scientific excellence.
- Work is fully integrated into the EURAD concept, emphasizing interactions between different WPs, involvement of End Users, assuring the link to national programmes and contributing to overarching features like Knowledge Management, Training and Education, or European Integration.

CONCORD

contributes to the optimization of container performance and of its assessment and evaluates novel container materials.

WP15 Concord motivation & goals

Long-lived disposal containers for SF/HLW have been shown to be feasible and safe.

- Can they be optimised?
- Can the prediction of their lifetime become more accurate and robust?

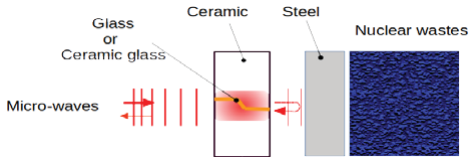
ConCorD aims to:

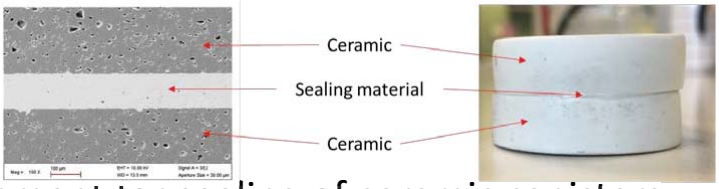
- Explore the potential of novel container materials and of optimisation of container design and performance within the engineered barrier system.
- Deepen the understanding of coupled interfacial processes influencing container performance under repository-relevant conditions, with a focus on:
  - irradiation-accelerated corrosion,
  - microbial activity
  - degradation during nearfield transients, and at varying scales.
- Improve performance assessment by demonstrating mechanistic understanding and by developing predictive models.

CONCORD

Novel Materials

Development and texting of novel materials and processes, e.g.:





Process and material development for sealing of ceramic canisters

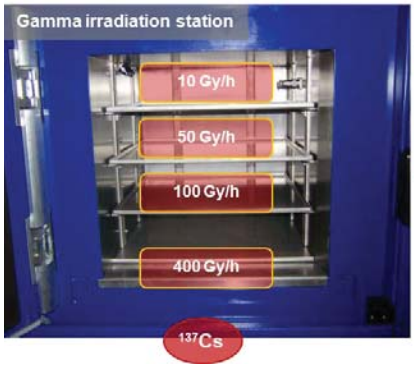
Development of Ti, Cr and Cu coatings by cathodic arc evaporation

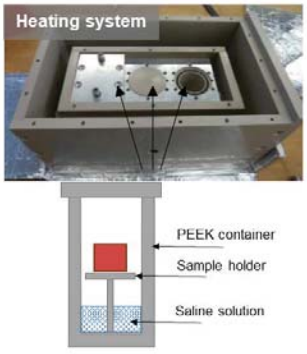
CONCORD

Corrosion under irradiation

Determine if dose rate or total dose is the parameter determining the corrosion damage:

- Cover several order of magnitude of dose rates and total doses
- Tests under realistic dose rate values and environments





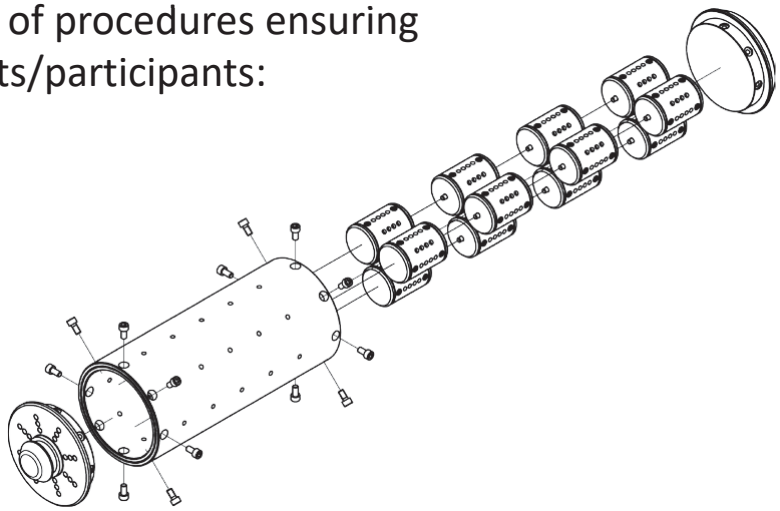
Duration of experiment (Hrs)	Dose Rate (Gy h^{-1})								
	0.0	0.1	0.2	1	2	10	20	100	1000
	Total irradiation dose (kGy)								
1	0 (S, C)								1 (S)
10	0 (S, C)							1 (S)	10 (S)
100	0 (S, C)					1 (S, C)		10 (S, C)	100 (S)
1,000	0 (S, C)			1 (S,C)		10 (S, C) + 2 with ben (S,C)		100 (S, C)	
5,000	0 (S, C)		1 (S, C)		10 (S)		100 (S)		
10,000	0 (S, C)	1 (S, C)		10 (S,C)		100 (S, C)			

CONCORD

Microbially influenced corrosion

- Coordination/testing/optimisation of procedures ensuring comparability between experiments/participants:
  - DNA extraction protocols
  - DNA amplification protocols
  - Cultivation

- In situ experiments deployed



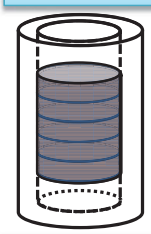
FUTURE

FUTURE

investigates the transport and retention mechanisms of radionuclides and provides mechanistic models for reactive transport simulations in “real” clays and crystalline rocks necessary for performance assessment studies.

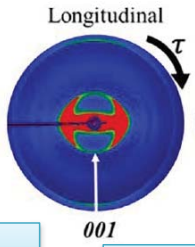
Effect of particle orientation on water diffusion

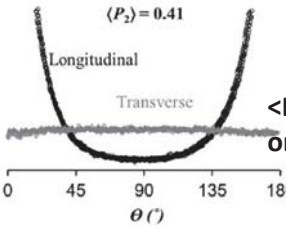
① Sample preparation



Vermiculite
Total porosity ~0.50

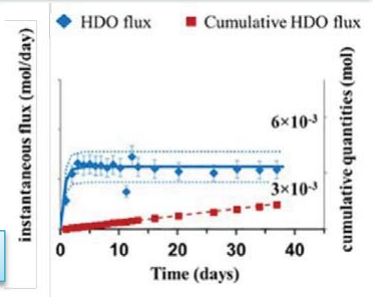
② X-ray scattering measurements



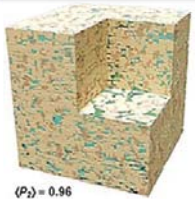


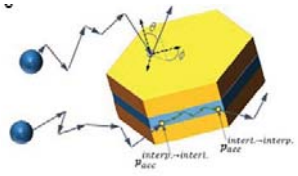
<P$_2$>= particle orientation

③ Through-diffusion experiments of water (HDO) tracer

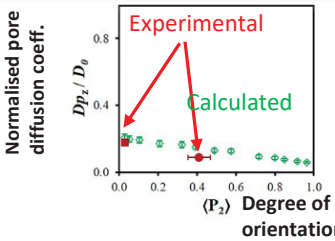


④ Brownian dynamics in representative virtual porous media





⑤ Comparison Experimental/calculated

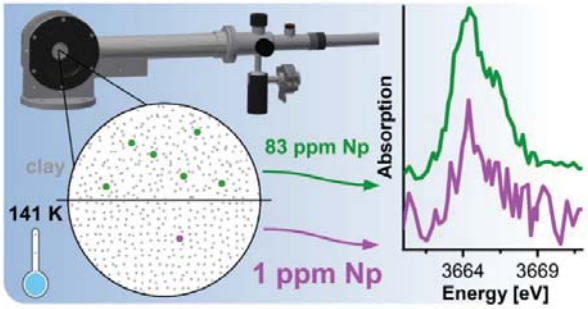


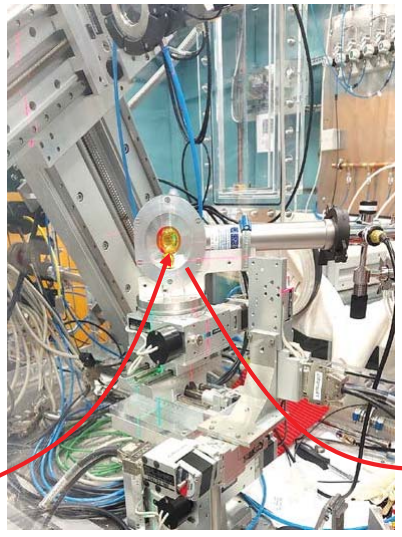
Take Home message

-Particle orientation is a primary parameter (as porosity) controlling water diffusion.

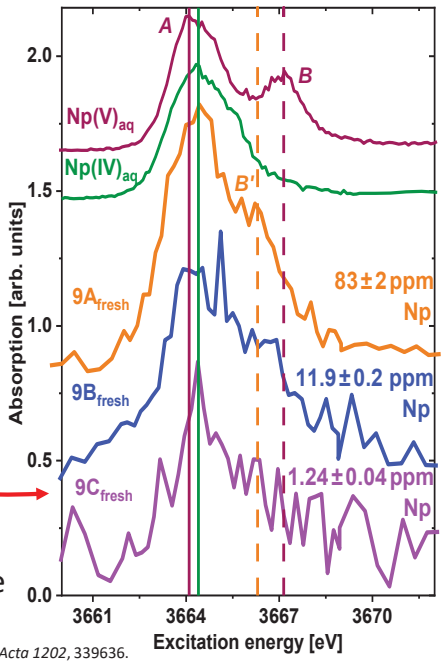
Asaad A., Hubert F., Ferrage E., Dabat T., Paineau E., Porion P., Savoye S., Gregoire B., Dazas B., Delville A., Tertre E. (2021) Applied Clay Science, 207, 106089.

Probing the NP oxidation state BY XAS at 1 – 80 ppm





ACT station at the KIT Light Source



Schacherl B., Joseph C., Lavrova P., Beck A., Reitz C., Pruessmann T., Fellhauer D., Lee J., Dardenne K., Rothe J., Geckeis H., Vitova T. (2002) *Anal. Chim. Acta 1202*, 339636.

Enigma of oscillatory crystal zoning: RN retention by Solid Solutions (Collaboration with DONUT WP)

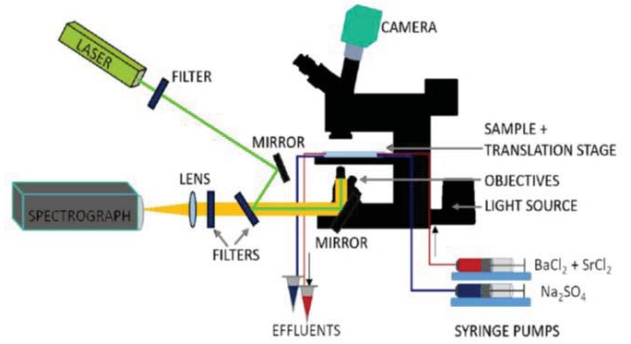
DONUT

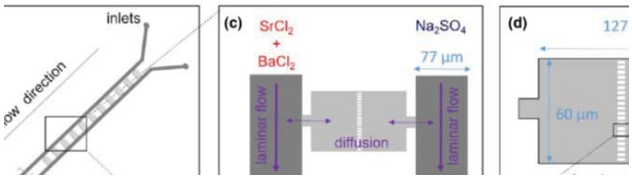
A lab-on-a-chip approach:

- in-situ characterization
- reactive transport modelling

Results:

- Classical nucleation theory predicts the composition of the nucleating solid solution phase
- Nucleation can be a competitive growth mechanism
- Crystal zoning is controlled by the limited diffusion of solutes and crystallization kinetics





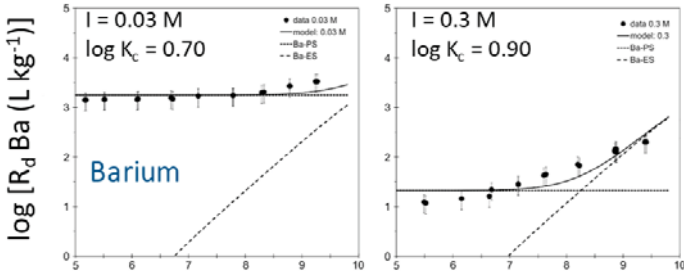
Poonoosamy J., Mahrous M., Curti E., Bosbach D., Deissmann G., Churakov S.V., Geisler T., Prasianakis N. (2021) Scientific Reports 11(1), 23678

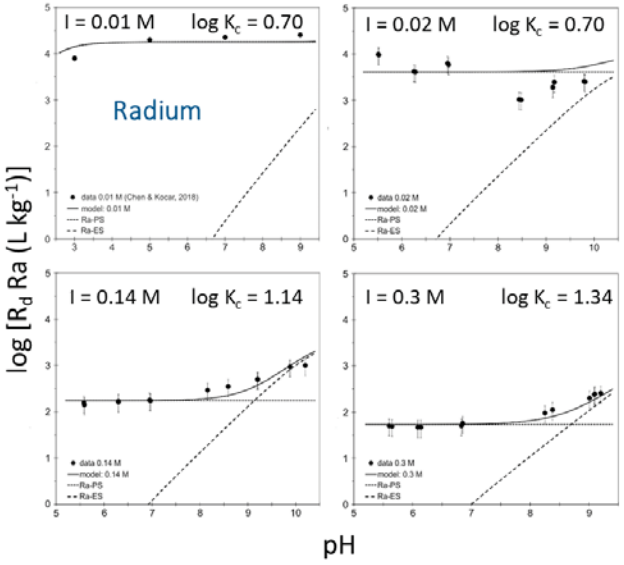
Adsorption of barium and radium on montmorillonite

Is Ba a good inactive analogue for ^{226}Ra?

- At low ionic strength: selectivity coefficients for Ba and Ra in good agreement (log K_c values vary between 0.70 and 0.84). At high ionic strength, the K_c (Ba-Na) slightly higher compared to the low ionic strength data.
- K_c (Ra-Na) exhibits a clear dependency on ionic strength

→ Ba is a good analogue for ^{226}Ra at I < 0.1 M and pH < 8





Klinkenberg M., Brandt B., Baeyens B., Bosbach D., Marques-Fernandes M. (2021) Appl. Geochem, 135, 105117.

CORI

CORI

improves understanding of the role of organics and their influence on radionuclide migration in cement-based systems with high organics inventories, being mainly relevant to LAW/ILW waste disposal.

CORI

- Organic materials are present in some nuclear waste and as admixtures in cement-based materials and potentially influence a geological disposal system.
- Potential effects of organic molecules are related to the formation of complexes in solution with some radionuclides of interest (actinides and lanthanides) which can (i) increase the radionuclide solubility and (ii) decrease the radionuclide sorption.
- Cement-based materials will be degraded with time in the context of waste disposal inducing a large range of alkaline pH conditions according to their degradation state. Alkaline pH provides specific conditions under which the organics can degrade, which contributes to increasing their potential impact on repository performance.
- Critical open topics and data needs required to better assess and quantify cement-organic-radionuclide-interactions are investigated in three R&D CORI Tasks:
  - **Organic Degradation**
  - **Organic-Cement-Interactions**
  - **Radionuclide-Organic-Cement-Interactions**

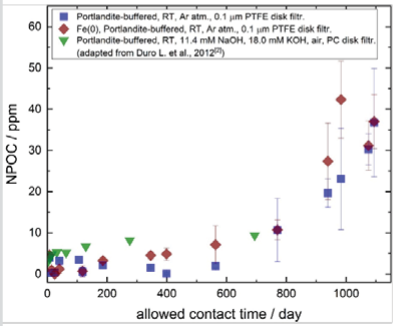
CORI State-of-the-Art report is available at the EURAD Website:
https://www.ejp-eurad.eu/publications/eurad-deliverable-31-cori-sota-cement-organic-radionuclide-interactions-content-lilw

CORI – example for technical work

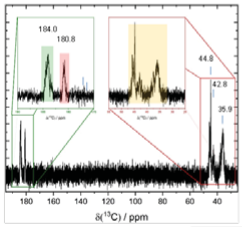
Task 2: degradation of UP2

- Degradation experiments on-going for > 3 years.
- Steady increase in UP2 degradation (based on NPOC values).
- Proxy ligands proposed as representative for UP2 degradation (inputs for Task 3 and 4).

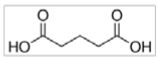
Degradation kinetics



Identification of deg. products: ^{13}C NMR

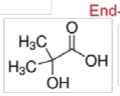


Bulk properties

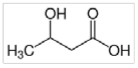


Glutaric acid (GTA)

End-groups



α-hydroxy-isobutric acid (HIBA)



3-hydroxy-butric acid (HBA)

CORI investigates degradation processes of selected organic materials:

(A) cellulose,
(B) PVC,
(C) Resins (incl. PAN),
(D) superplasticizer

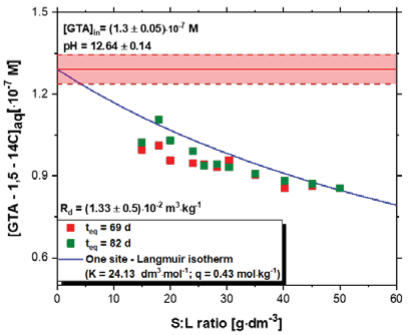
UP2: polyacrylonitrile-based (PAN) filter aid material used in nuclear power plants

CORI – example for technical work

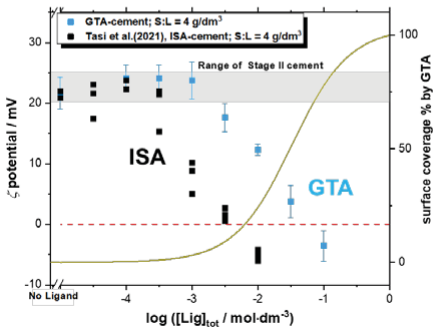
Task 3: uptake of organics

- Uptake of proxy ligands quantified for inactive and ^{14}C-labelled ligands.
- Very weak uptake observed for HBA and HIBA. Significantly higher uptake for GTA.
- Surface charge (quantified by zeta potential) affected by GTA. Impact on RN uptake?

Sorption of GTA – Langmuir isotherm



Zeta potentials (and comparison with ISA)



CORI investigates interactions of selected organic molecules with selected cement-based materials.
=> formiate, acetate, oxalate, adipate, glutaric acid, phthalate, α-hydroxy-butyric acid, 3-hydroxy - butyric acid, citrate, gluconate, ISA, EDTA, NTA, superplasticiser

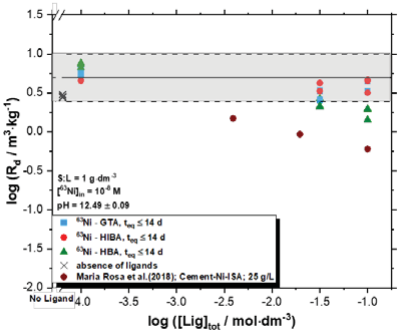
Methods:
- **Sorption studies (main)**
- **Diffusion studies**

CORI – example for technical work

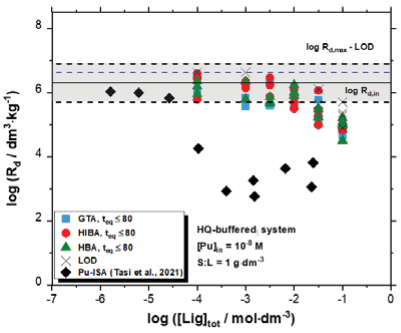
Task 4: uptake of radionuclides

- Impact of proxy ligands on solubility considered to assess RN upper concentration limits.
- Minor impact of proxy ligands on the retention of Ni, Eu and Pu.
- **Sorption experiments with degradation leachates on-going. Close-to-real conditions.**

Impact of proxy ligands on Ni uptake



Impact of proxy ligands on Pu uptake



CORI studies uptake of selected radionuclides in ternary systems consistent with Task 3 in terms or organics and selected cement phases.

Radionuclides focus on cationic species, spanning a larget set of relevant oxidation states
=> Ni(II), An/Ln(III), An/Ln(IV), U(VI),

Methods:

- **studies on speciation/solubility, retention and transport processes**

MODATS

MODATS

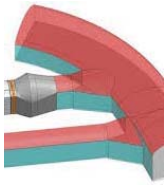
works to consolidate the implementation strategy for monitoring systems by developing methods through which confidence can be demonstrated in the data acquired and benefits derived for repository implementation.

MODATS

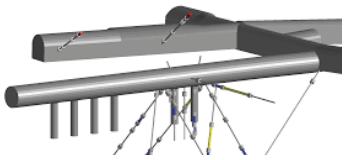
- The overall objective of the proposed MODATS R&D WP is to evaluate, develop and describe methods and technologies, and to provide the means to measure, treat, analyse and manage data in a consistent manner.
- Task 1: WP Management.
- **Task 2: Data Treatment for Increased Confidence in Repository Monitoring.**
- **Task 3: Novel and Optimised Monitoring Technology for Repository Monitoring.**
- Task 4: Communication and Project Synthesis

MODATS

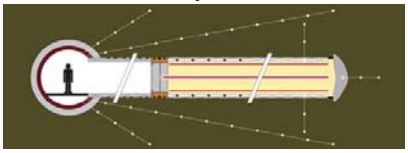
- Task 2 : Data Treatment for Increased Confidence in Repository Monitoring
  - The purpose of the Data Strand is to address the detailed questions regarding data that have been identified, but not resolved in previous EC projects
  - Use of URL Experiments data
  - this task aims to consolidate the implementation strategy for monitoring systems in repository facilities by developing methods through which confidence can be demonstrated in the acquired data and its analysis and benefits derived for repository implementation.



POPLU (Onkalo)

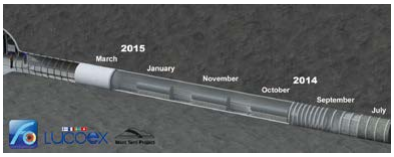


Prototype Repository, (Aspö)



Praclay, (Hades)

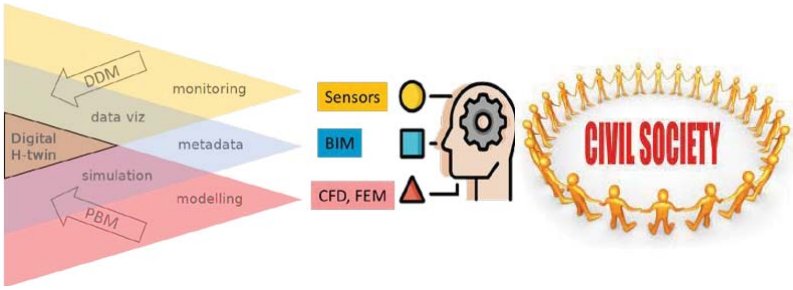
AHA105 (BURE)



FE, (Mont Terri)

Scope

- Combining DDM and PBM : Digital Twin
- **The physically based models (PBM)** are based on our understanding of the physics of the processes which control the catchment response and use physically based equations to describe these processes.



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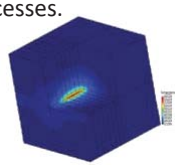
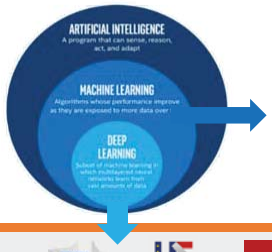
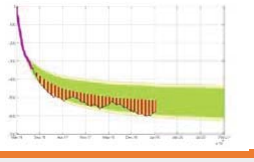
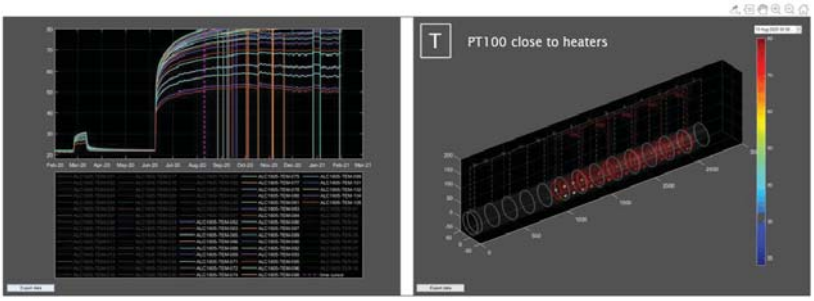


- A **data-driven model (DDM) is** based on the analysis of the data about a specific system. The main concept of data-driven model is to find relationships between the system state variables (input and output) without explicit knowledge of the physical behavior of the system.







ALC1605 HA cell demonstrator monitoring (started since 2019)

MODATS

- Task 3 : Novel and Optimised Monitoring Technology for Repository Monitoring

<u>Geophysics technics</u>

- Geophysical inversion
- CHENILLE (*Coupled beHaviour undErstaNdIng of fauLts : from the Laboratory to the fiEld*).
- Develop passive seismic monitoring and new methods for digital mapping of leakages
- Spectral induced polarization (SIP) method

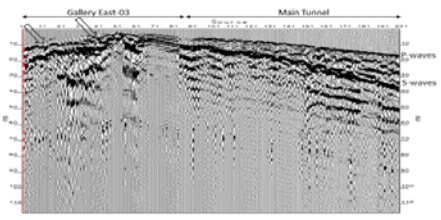
<u>Optical fiber sensors</u>

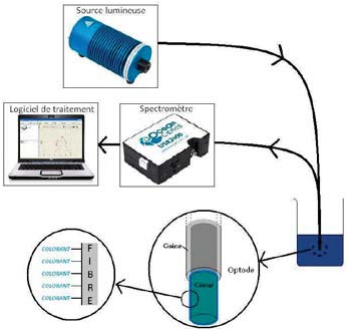
Radiation tolerant cable

Optode pH

Distributed temperature sensing

Calibration method for strain measurement





SUMMARY / CONCLUSION

- Expected key impact of the WPs is the generation of new scientific information.
- Results provide an improved technical basis for the Nuclear Waste Disposal Safety Case. This is including both new qualitative and quantitative data characterising the various systems studied, and also significantly improved scientific process and system understanding.
- All WPs include modelling of results, and offer potential links to further modelling activities in EURAD and beyond.
- New materials are tested and evaluated regarding performance and potential usability, and detailed concepts for monitoring repository evolution are developed, evaluated and tested.
- All the new information generated in CONCORD, FUTURE, CORI or MODATS will support the member states regarding decision making and planning within their respective national programs.

SUMMARY / CONCLUSION

- A dynamic dissemination strategy is realized both on an European and international level. The target is to provide information and scientific arguments to support activities contributing to the final disposal of nuclear waste, explicitly addressing different stakeholders.
- The technical/scientific results are first of all made available as open access peer-reviewed publications. Results also feed into the State-of-the-Art documents defined as public Deliverables in all four WPs
- The WPs are actively contributing to knowledge management tools established in EURAD, which offers a new quality of dissemination to ensure long-term access to the scientific and technical results generated in technical WPs like CONCORD, FUTURE, CORI or MODATS.
- Work in the EURAD WPs presented here is to a significant extent performed by young researchers and within PhD theses. This contributes to the continuing availability of highly trained specialists for implementers and regulators throughout Europe.

SUMMARY / CONCLUSION

EURAD contributes to European integration !

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