WP6 Innovation in Solid Organic Waste treatment and conditioning

CONSORTIUM MEETING, 25.05.2023

TH. MENNECART & WP6 PARTNERS

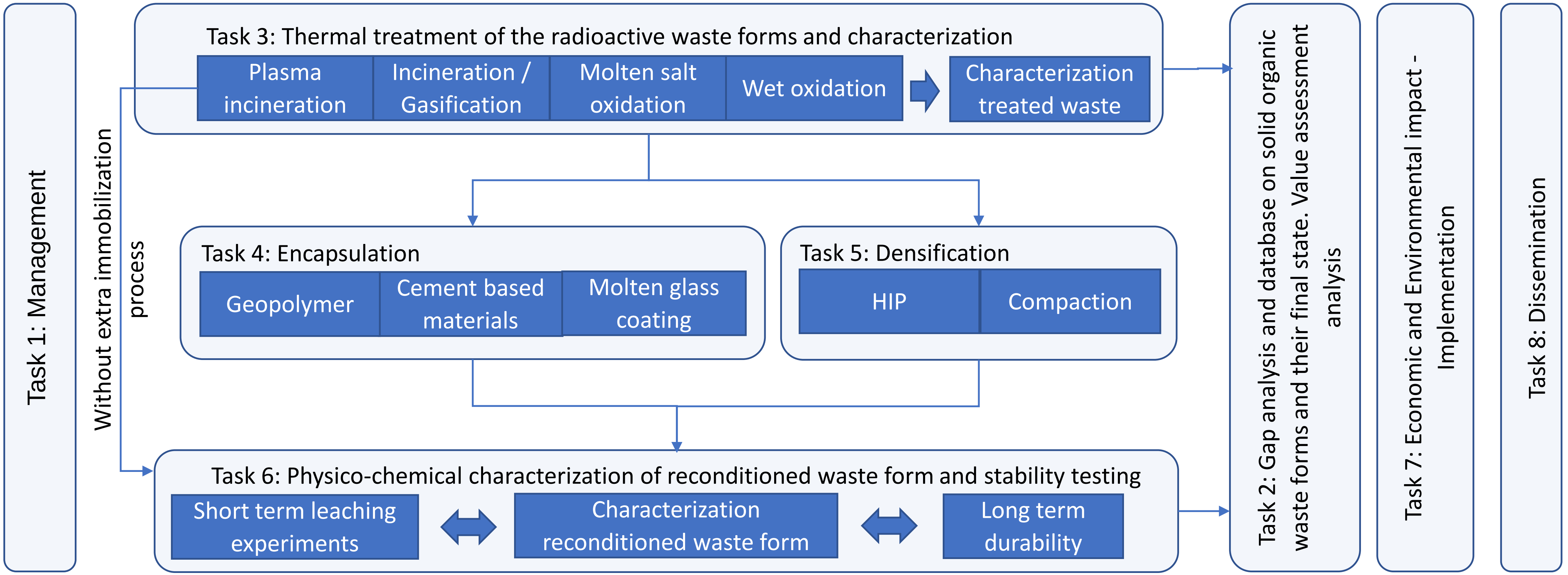
This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Overview of WP6 Objectives

- Perform a **gap analysis** during the first project year.
- **Demonstrate the reliability** of alkaline binders for conditioning of residues and secondary waste stemming from treatment of RSOW.
- **Verify the matrix performance** of conditioned final / ultimate waste according to a set of uniformed Waste Acceptance Criteria (WAC).
- **Improve understanding** of materials inventory before the thermal treatment and of the reconditioned waste once the conversion and immobilization has been achieved.
- Demonstrate **thermal treatment** methods leading to a significant **volume reduction** and to **safe reconditioned waste packages**.
- Deploy results for safe utilization by end users for **mathematical calculations** avoiding systematic experimental studies of the reconditioned waste.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Work Package 6 Structure

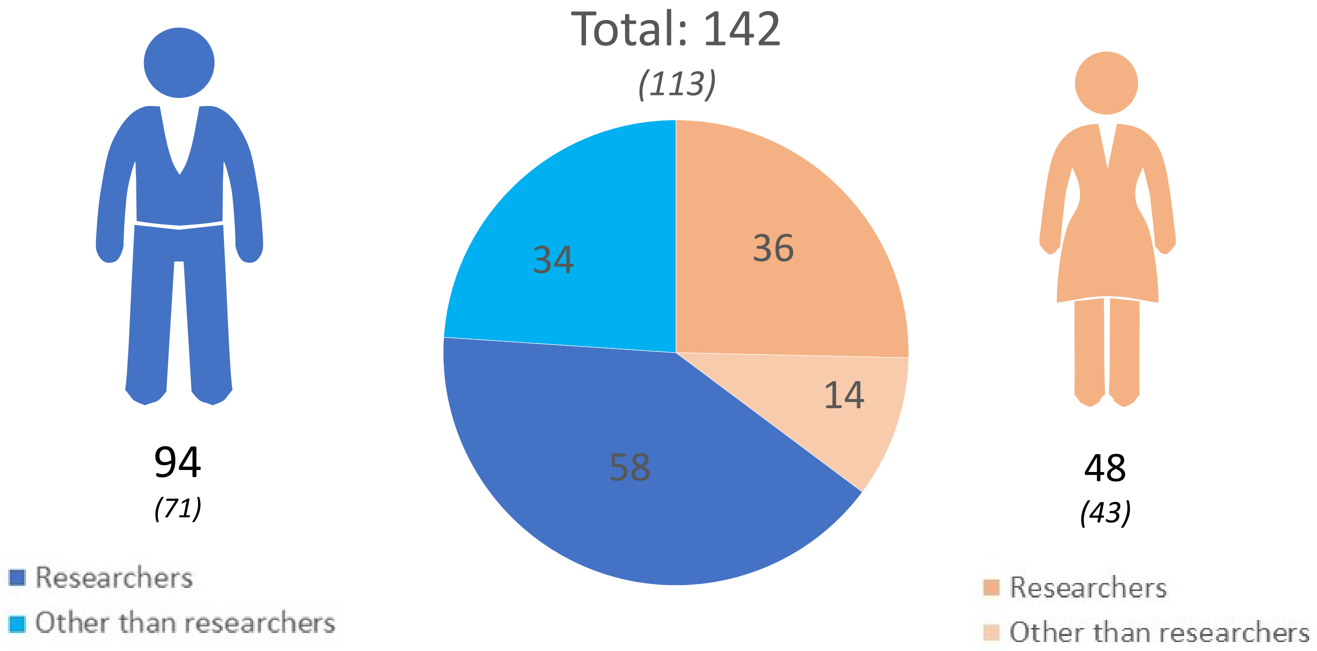


This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Partners of WP6

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Gender of researchers and other workforce



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Planning

D	*Deliverable = Intermediate report*
D-E	*Deliverable feeding to EURAD*
M	*Milestone = delivery of samples*
M-E	*Milestone feeding to EURAD*
	Active working months

			2020				2021												2022												2023												2024							
			september	october	november	december	january	february	march	april	may	june	july	august	september	october	november	december	january	february	march	april	may	june	july	august	september	october	november	december	january	february	march	april	may	june	july	august	september	october	november	december	january	february	march	april	may	june	july	august
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
			Year 1												Year 2												Year 3												Year 4											
WP 6	**Innovations in solid organic waste treatment and conditioning**	**SCK•CEN**	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
T6.1	**WP Management**	**SCK•CEN**																																										M						
T6.2	**Gap analysis and database on solid organic waste forms and their final state and value assessmen**	**GSL**																																														D	
T6.3	**Thermal treatment of the radioactive waste forms and characterisation of the treated / reconditio**	**CEA**																																		D												
6.3.1	Thermal treatment of the Radioactive Solid Organic Wastes	CEA																																M														
6.3.2	Characterisation of the thermally treated / reconditioned wastes	CEA																																														
T6.4	**Immobilisation of the treat wastes by geopolymer or cement-based materials encapsulation or by**	**CVR**																																		D												
6.4.1	Geopolymer	CVR																					M																									
6.4.2	Cement based materials	CSIC																					M																									
6.4.3	Molten glass coating	CEA																																														
T6.5	**Densification**	**USFD**																							M																						D	
T6.6	**Physico-chemical characterisation of reconditioned waste form and stability testing**	**VTT**																																													D	
6.6.1	Characterisation of reconditioned waste form	CIEMAT																												M																		
6.6.2	Short term leaching experiments under different exposed conditions	CIEMAT											M																																	M		
6.6.3	Long-term durability of reconditioned waste form	POLIMI																																												M		
T6.7	**Economic and Environmental impact - Implementation**	GSL																							M																		D					D	
T6.8	**Dissemination**	SCK•CEN																																														D
6.8.1	Reporting and guidelines																																															
6.8.2	Dissemination activities to the scientific community and public																																															

PREDIS

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Deliverables (> [M36])

- [**M36**], D6.1. Summary report: Description of the thermal processes used for the thermal treatment of the RSOW and the physical properties and chemical composition of the resulting treated wastes.
- [**M36**], D6.2. Conditioning of ashes from the thermal treatment of RSOW by geopolymer or cement based materials encapsulation or by molten glass coating.
- [**M42**], D6.3. Economic, environmental and disposability impacts of novel treatment technologies for low-level and intermediate-level solid organic wastes.
- [**M47**], D6.4. Implemented database: Matching the chemical composition of the investigated reconditioned wastes with the initial waste stream.
- [**M47**], D6.5. Densification techniques test report. Description of the process, the type of treated waste immobilised and the physical properties and chemical composition of the resulting materials.
- [**M47**], D6.6. Final report on the Physico – chemical characterisation of reconditioned waste form and stability testing.
- [**M47**], D6.7. Modelling tool to predict the behaviour of the reconditioned wastes based on the results obtained within the project.
- ✓ [**M48**], D6.8. Submission in scientific journals of at least 5 papers about the RSOW stability and durability tests after reconditioning.
- [**M47**], D5.7. Summary report “Use of geopolymer matrices for the immobilisation of liquid and solid radioactive organic wastes”.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Milestones

- ✓ [**M12**], M6.1. Definition of the leaching procedure for the short term experiments and the long term durability experiments (6.2 & 6.3).
- ✓ [**M22**], M6.2. Delivery campaign of the goepolymer samples.
- ✓ [**M22**], M6.3. Delivery campaign of the cement based materials samples.
- ✓ [**M24**], M6.4. Delivery campaign of wet oxidation samples for HIP tests.
- ✓ [**M24**], M6.5. Intermediate report on densification (HIP, compaction).
- ✓ [**M24**], M6.6. LCA Case Study Input to WP2.
- ✓ [**M29**], M6.7. Intermediate report on characterisation of the durability related properties of conditioned waste form.
- ➡ [**M34**], M6.8. Report on feasibility demonstration of the Wet oxidation and the Molten salt oxidation routes for the treatment of RSOW: Description of the processes and basic physico-chemical properties of the reconditioned waste form.
- [**M42**], M6.9. Value assessment workshop.
- [**M46**], M6.10. Final report on short term leaching experiments.
- [**M46**], M6.11. Final report on long term durability of conditioned waste form.

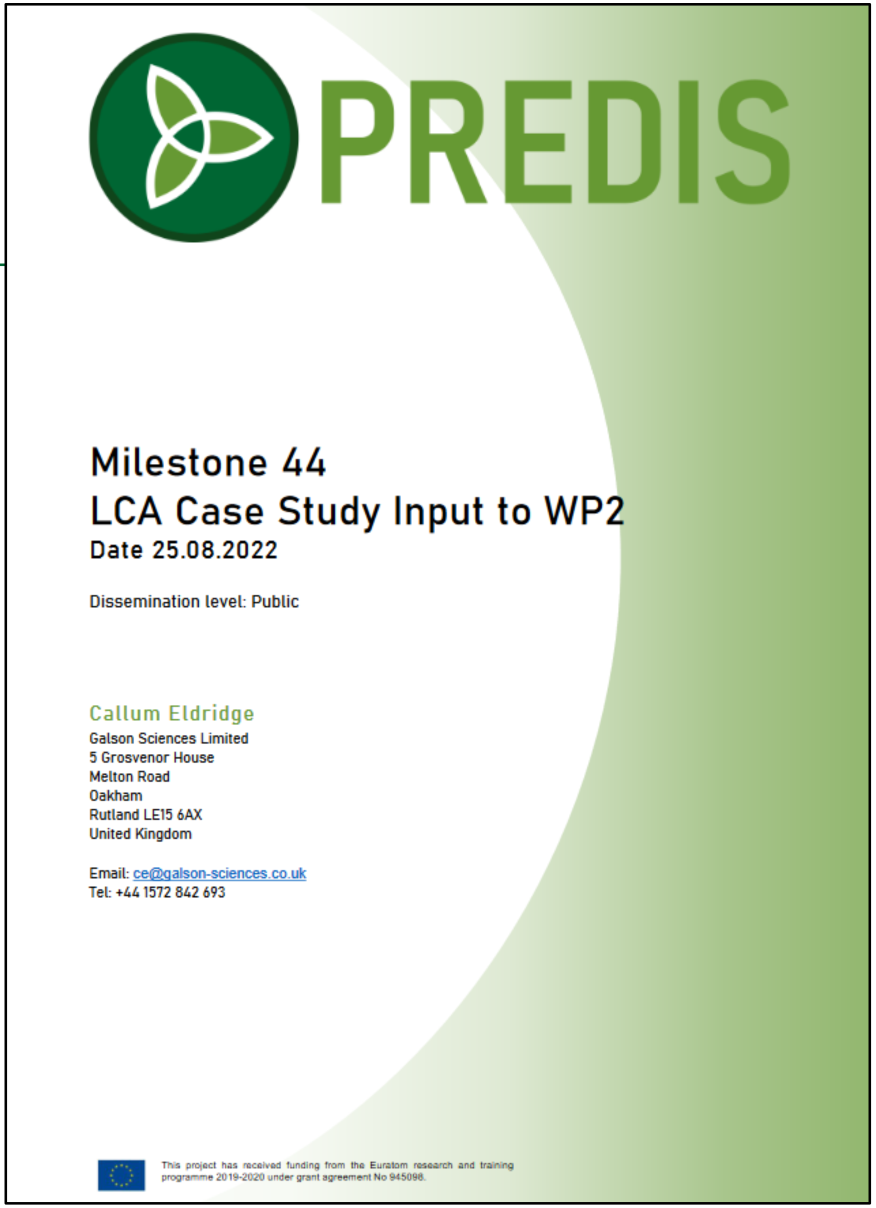
PREDIS

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Milestone 44 –
LCA case study input to WP2

- Focus on treatment of ashes arising from the IRIS process:
  - Hot-Isostatic Pressing (University of Sheffield)
  - Encapsulation in Geopolymer (Politecnico di Milano)
  - Compaction (CEA)

- Delivered in M24


PREDIS

Milestone 44
LCA Case Study Input to WP2
Date 25.08.2022

Dissemination level: Public

Callum Eldridge
Galson Sciences Limited
5 Grosvenor House
Melton Road
Oakham
Rutland LE15 6AX
United Kingdom

Email: ce@galson-sciences.co.uk
Tel: +44 1572 842 693

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Task 6.2 Gap analysis and database on solid organic waste forms and their final state and value assessment analysis (GSL)

- Gap analysis achieved during the 1st year of the project

- Strategic overview of RSOW initiated during Theramin (confidential report)
- A questionnaire was circulated in mid-December 2020 (joint questionnaire covering data requirements for several PREDIS deliverables across work packages)
  - Not enough answer to build a database
  - High level summary of waste rather a database

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

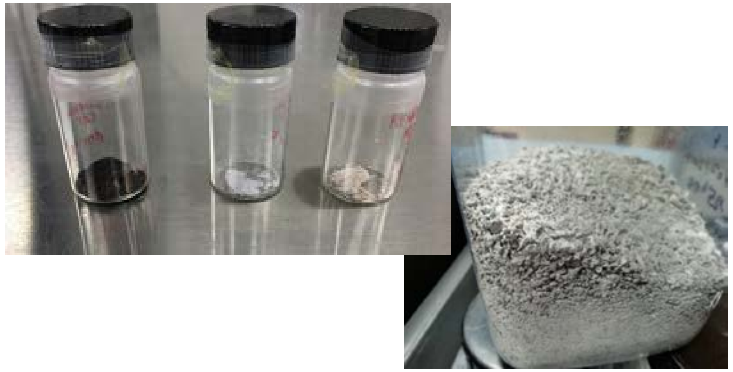
Task 6.3 Thermal treatment of the radioactive waste forms and characterization of the treated / reconditioned waste (CEA)

- Inventory of the available treated / reconditioned waste

- Sharing materials
  - IRIS ashes from CEA
  - MSO residues from CVRez
  - Thermally treated IERs from CIEMAT

- Characterization of the treated materials

Incineration / Gasification



Molten Salt Oxidation

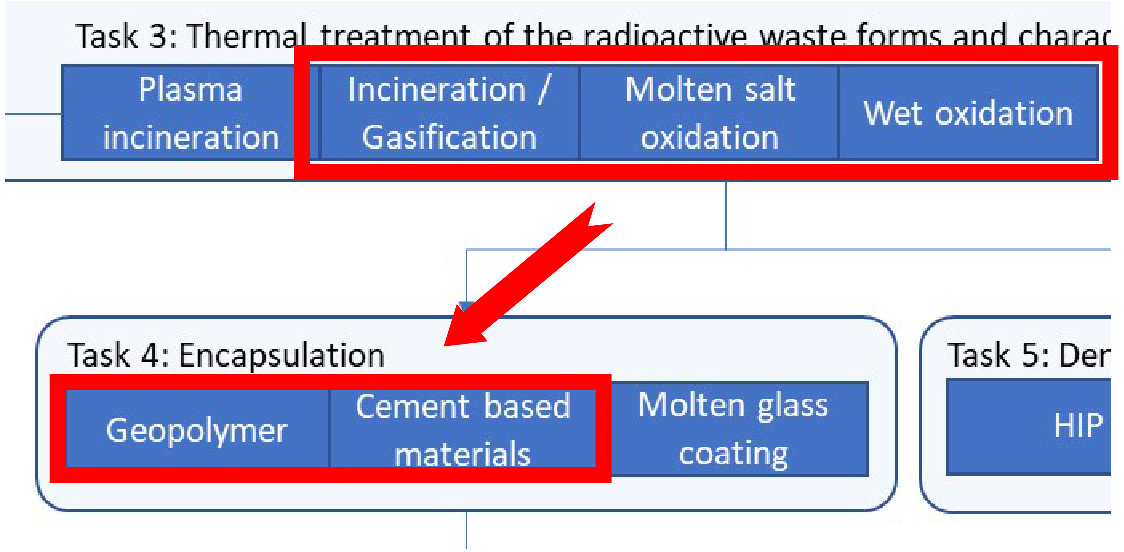
Plasma Incineration

Wet Oxidation

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Task 6.4 Immobilization of the treated waste by geopolymer or cement based materials encapsulation or by molten glass coating (CVRez)

Different treated waste requires different immobilisation matrices design



Cement based materials vs Geopolymer

Optimization of the formulation

Use of alternative materials

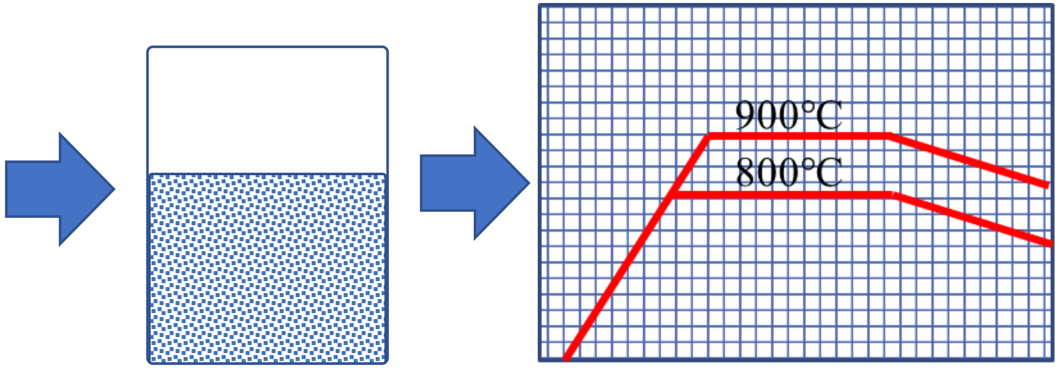
About 20 –30 % of waste loading whatever the option

CSIC Consejo Superior de Investigaciones Científicas · Ciemat · Helsingin Yliopisto Helsingfors Universitet University of Helsinki · CVŘ Research Centre Řež · Politecnico Milano 1863 · UAM Universidad Autónoma de Madrid · SCK CEN · VTT

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Task 6.4 Immobilization of the treated waste by geopolymer or cement based materials encapsulation or by molten glass coating (CVRez)

+



Mix ratio ashes/glass from 20/80 to 80/20

- ✓ Soft process
- ✓ Avoid radionuclide volatilization
- ✓ Coating of the waste
- ✓ No pressing, under air condition
- ✓ Obtaining a monolithic form

Weight load up to **40%w**

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Task 6.5 Densification (USFD)

- Compaction tests: pelletizing and granulation

- Hot Isostatic Pressing
    - IRIS ashes (4x formulations)
    - Polymer WIP
    - Wet oxidation sludge (in progress)
    - KIPT HIP at USFD

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Task 6.6 Physico-chemical characterization of reconditioned waste forms and stability testing (VTT)

- **Leaching experiments:**
  - Common protocol, national recommendation
  - After gamma irradiation, doped materials

About 400 samples

- **Harmonization of the results (proposition).** Excel file to calculate:
  - Normalized Loss
  - Cumulative Fraction Leached
  - Effective Diffusion Coefficient
  - Leachability Index

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Task 6.7 Economic and Environment impact - Implementation

Deliverables: Economic, environmental and disposability impacts of novel treatment technologies for low-level and intermediate-level solid organic waste [M42](GSL)

- Disposability Assessment Approach

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Dissemination and Reporting

Conferences & Workshops

- **NUWCEM** 2022, 4th International Symposium on Cement-Based Materials for Nuclear Wastes
- **FISA** 2022 **& EURADWASTE ’22**, 10th Euratom Conference on Reactor Safety & 10th Euratom Conference Radioactive Waste Management
- **CNMAT** 2022, XVI Congreso Nacional de Materiales,
- **NENE** 2022, 1st International Conference Nuclear Energy for New Europe
- **IGD-TP** Symposium and Webinar: The role of optimization in radioactive waste geological disposal programmes
- **NUMAT** 2022, The Nuclear Materials Conference
- **Materials Research Symposium** Fall Meeting 2022
- **Migration** 2023
- **6th International Workshop on Mechanisms and Modelling of Waste / Cement Interactions** & **EURAD** –WP CORI Final Workshop
- The 16th International **Congress on the Chemistry of Cement** 2023

13 presentations

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Dissemination and Reporting

Scientific papers

D6.8 (M48). Submission in scientific journals of at least **5 papers** about the RSOW stability and durability tests after reconditioning

1. "Fenton-like treatment for reduction of simulated carbon-14 spent resin", M.A. Hafeez, J. Jeon, S. Hong, N. Hyatt, J. Heo, W. Um

Journal of Environmental Chemical Engineering (2021), 9-1, https://doi.org/10.1016/j.jece.2020.104740

2. "Stability of $SrCO_3$ within composite Portland-slag cement blends", S.A. Walling, L.J. Gardner, D.P. Prentice, M.C. Dixon Wilkins, A.A. Hammad, W. Um, N.C. Hyatt

Cement and Concrete Composites, 135, 104823 (2023), https://doi.org/10.1016/j.cemconcomp.2022.104823

3. "Design of sustainable geopolymeric matrices for encapsulation of treated radioactive solid organic waste", A. Santi, E. Mossini, G. Magugliani, F. Galluccio, E. Macerata, P. Lotti, G. D. Gatta, D. Vadivel, D. Dondi, D. Cori, H. Nonnet, M. Mariani

Frontiers in Materials (2022), https://doi.org/10.3389/fmats.2022.1005864

4. "Solidification of molten salt from Molten Salt Oxidation technology", S V. Galek, A. Černá, P. Pražák, T. Černoušek, M. Vacek, V. Berger, J. Hadrava

In preparation

5. "Effect of the incorporation of a molten salt waste from nuclear power plants in the development of geopolymers and Portland cement systems", P. Perez-Cortes, I. Garcia-Lodeiro, F. Puertas, M. Cruz Alonso

In preparation in "Cement and Concrete Composites"

6. "Explorative scale-up of Fenton Oxidation and Geopolymer Encapsulation for the management of spent mixed bed ion exchange resins", F. Galluccio, E. Mossini, A. Santi, G. Magugliani, M. Giola, E. Macerata, G. D. Gatta, P. Lotti, D. Cori, G. Bilancia, P. Peerani, and M. Mariani

In preparation in "Nuclear Engineering and Technology Journal"

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Level technology – Ambition

Task	Technology (2019)	Ambition after 4 years	Current situation
3.1	Plasma incineration. Treatment of IER, cement concentrate, others	Increase the SHIVA technology level. **TRL from 5 to 6**	✗
3.1	Incineration / Gasification. Treatment of IER	Feasibility demonstration of the technology by incineration of (inactive) bituminized waste. **TRL from 2 to 4**	✗
3.1	Molten Salt Oxidation used for the treatment of Radioactive Liquid Organic Waste	Transposition of the technology to the treatment of RSOW (IER). Trials with (inactive?) IER and conditioning of the salt using goepolymer or cement based materials. **TRL from 4 to 6**	On-going
3.1	Wet Oxidation Route used for the destruction of dissolved organic contaminants	Development and optimization of the process for the destruction of IER leading to the complete recovery of the ^{14}C and associated radionuclide inventory into iron sludge. The sludge will be thermal treated for a complete immobilisation (task 5). **TRL from 2 to 3 - 4**.	On-going
4.1	Goepolymer immobilisation	Determination of the best geopolymer formulation for a safe and long term immobilisation of treated wastes after thermal treatment (e.g. ashes, salt). **TRL from 2 - 3 to 5**	On-going
4.2	Cement based materials immobilisation	Determination of the best cement based materials formulation for a safe and long term immobilisation of treated wastes after thermal treatment (e.g. ashes, salt). **TRL from 3 to 5**	On-going
4.3	New technique: Molten glass coating	Feasibility demonstration of the glass coating for the immobilisation of ashes after incineration of IER at the lab scale. **TRL from 1 to 4.**	On-going
5	HIP technology	Increase the technology level using radiotracers or radioactive samples. **TRL from 2 to 4**	On-going
5	Compaction assisted by thermal treatment	Feasibility demonstration of densification of ashes coming from incineration process by compaction, eventually with adjuvants and temperature. **TRL from 1 to 3 - 4**	On-going

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Scientific presentations – Flash talk

- “RSOW treatment using Molten Salt Oxidation process”
  Vojtech Galek (CVRez)

- “Immobilization of molten salt residue using alkali-activated and cement-based materials”
  - Lander Frederickx, Eduardo Ferreira, Quoc tri phung (SCK CEN)

- Flash talk
  - Gianni Vettese (UH)

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

RSOW treatment using Molten Salt Oxidation process

VOJTECH GALEK

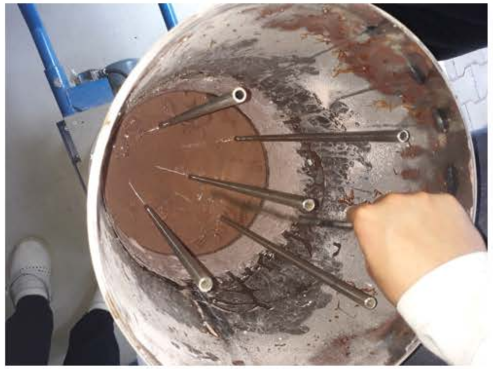
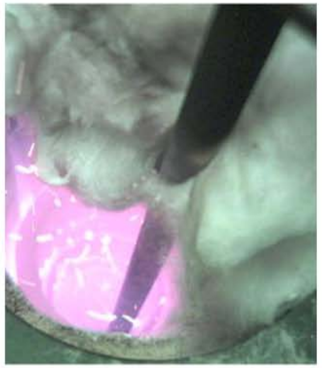
VOJTECH.GALEK@CVREZ.CZ

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Laboratory of Hazardous and Radioactive Waste Processing

CVŘ Research Centre Řež

- Molten Salt Oxidation (MSO) pilot plant for processing organic waste
- Evaporation/drying (ETL) of liquid waste (to the powder form)
- Equipment for solidification into geopolymer and polysiloxane matrices (GPS)

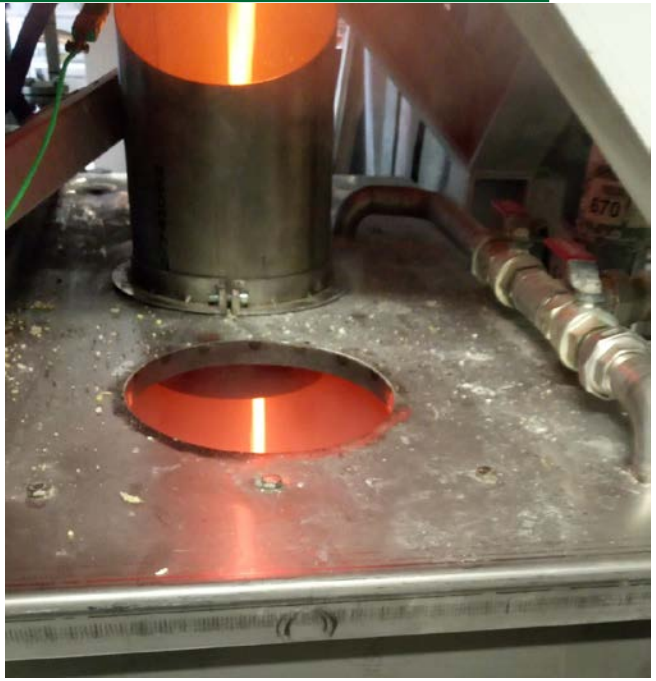





PREDIS

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

MSO Technology

- Volume reduction
- Flameless oxidation
- Alkaline-based carbonates
- Scrubber for acidic gases
- Stable heat transfer
- Catalyst-like environment



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

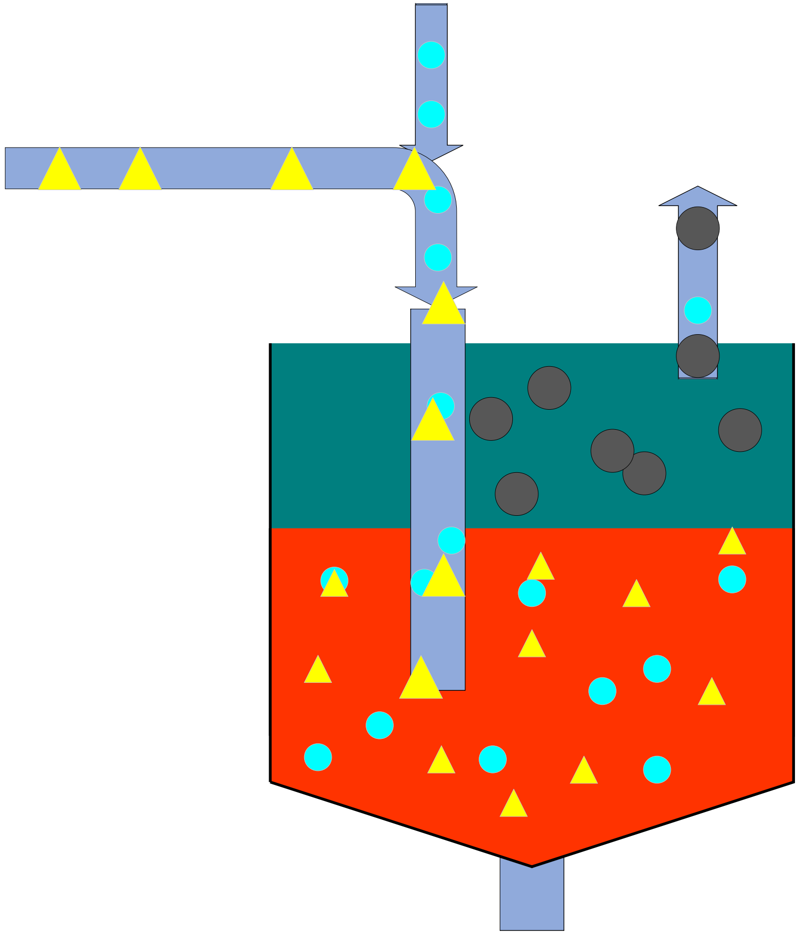
MSO Technology – Processed waste

- SORW: ion resins
- LORW: lubricants, organic solvents, scintillation liquids and decontamination liquids
- Hazardous waste: PCE, PCB, PVC, HCB, CFC-12, CN, PCDD/F
- Waste needs to be fully analysed


This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

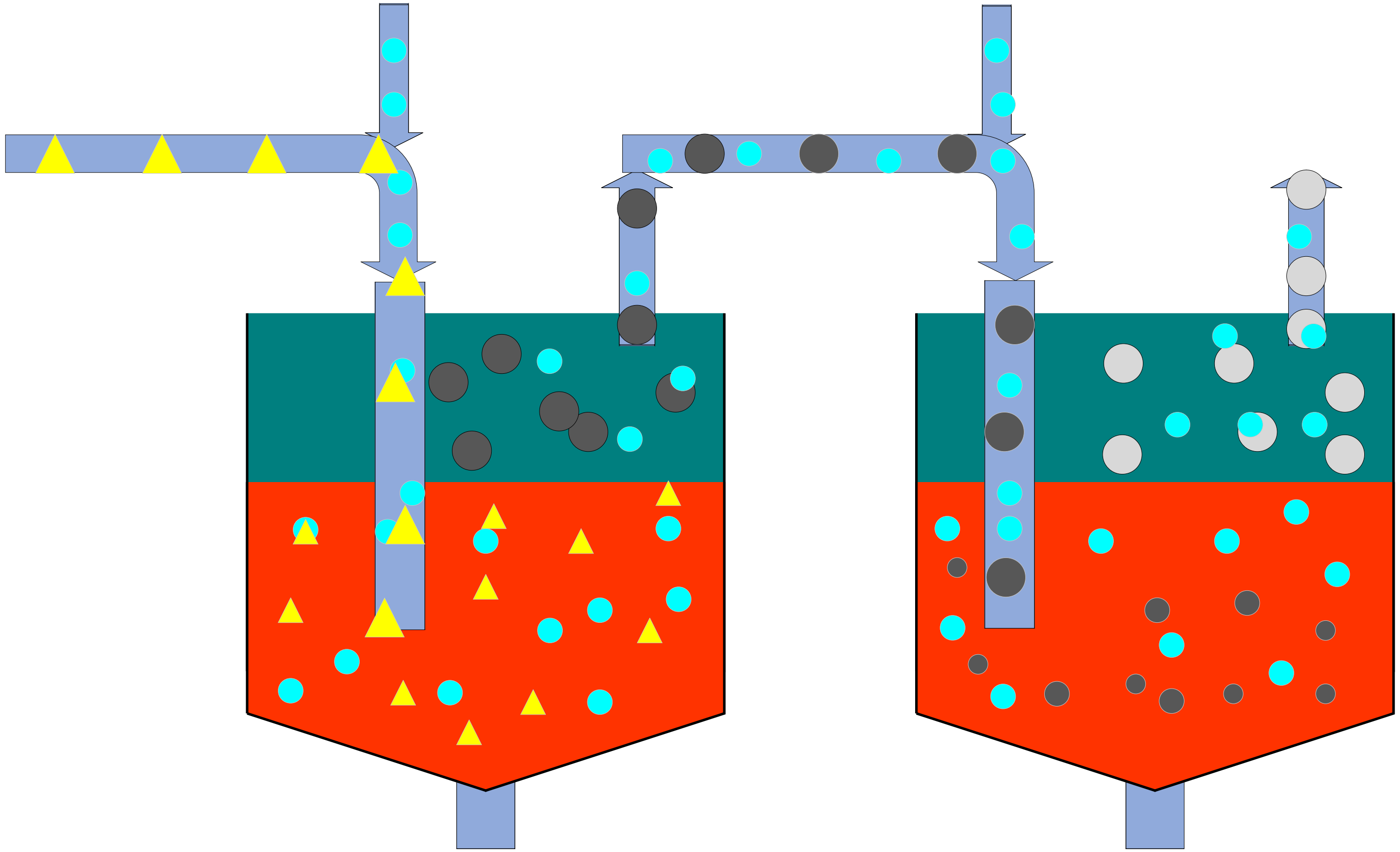
Principle of MSO

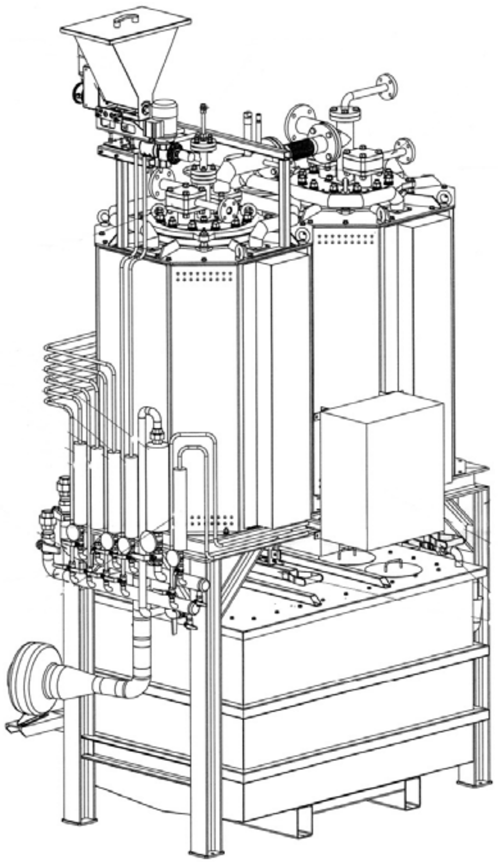
- Low dosing rate
- Low oxidation efficiency
- Increased time for total oxidation
- Low applicability



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

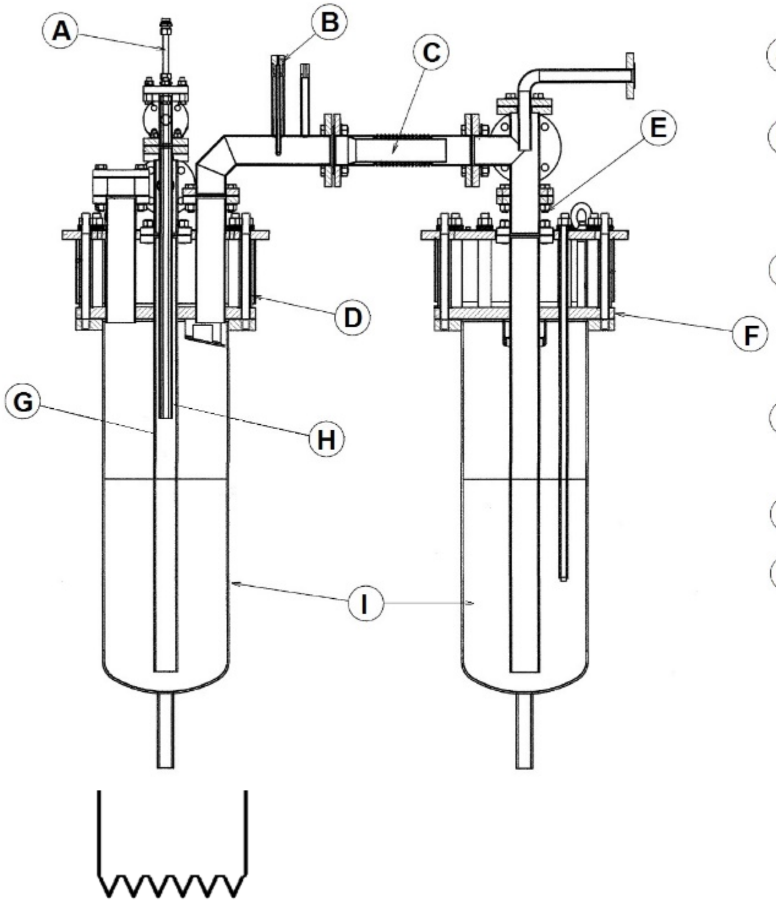
Principle of MSO

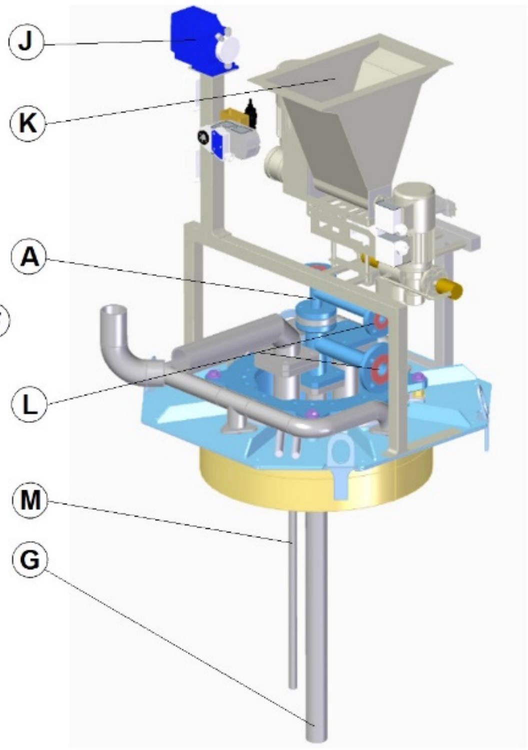




This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Principle of MSO



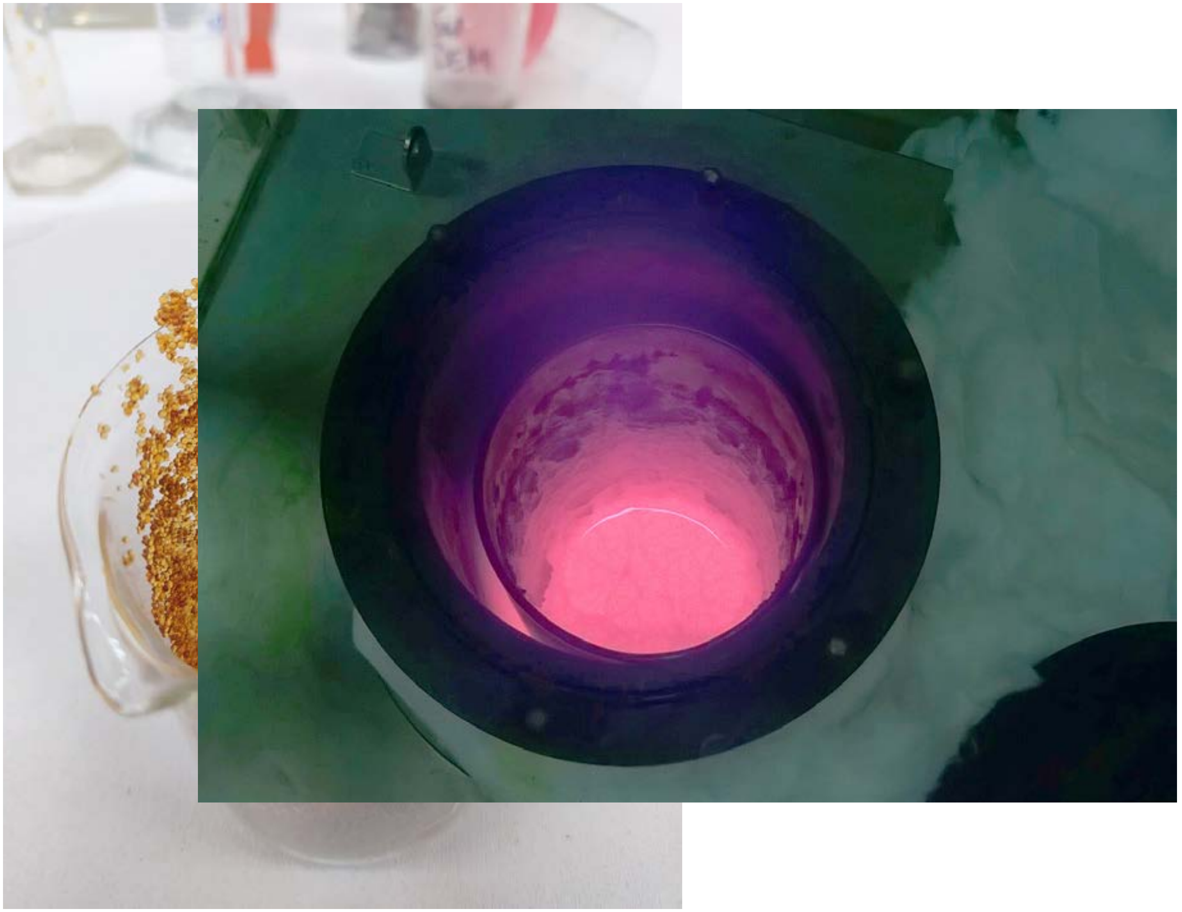


This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

What is the MSO waste

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

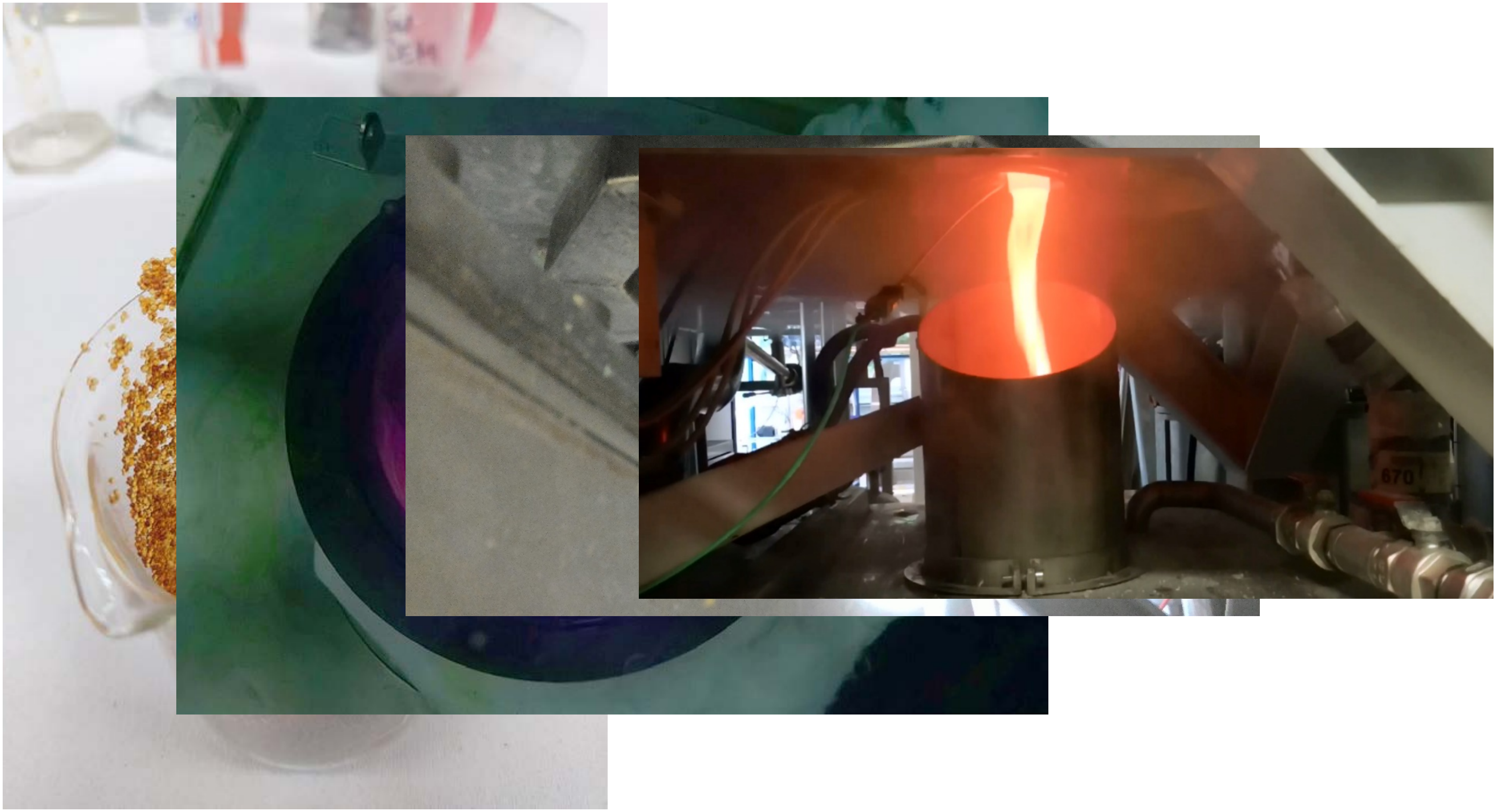
What is the MSO waste



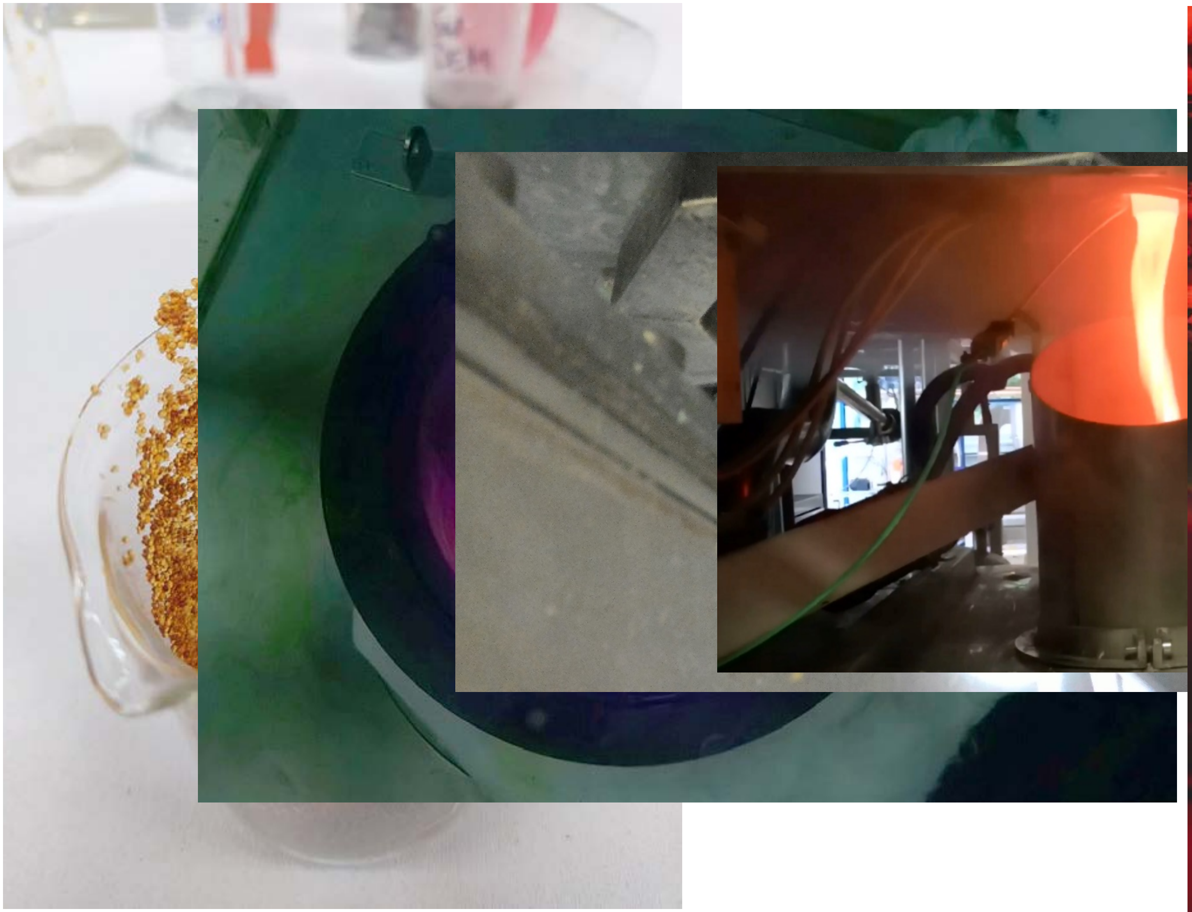
This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

What is the MSO waste

What is the MSO waste



What is the MSO waste

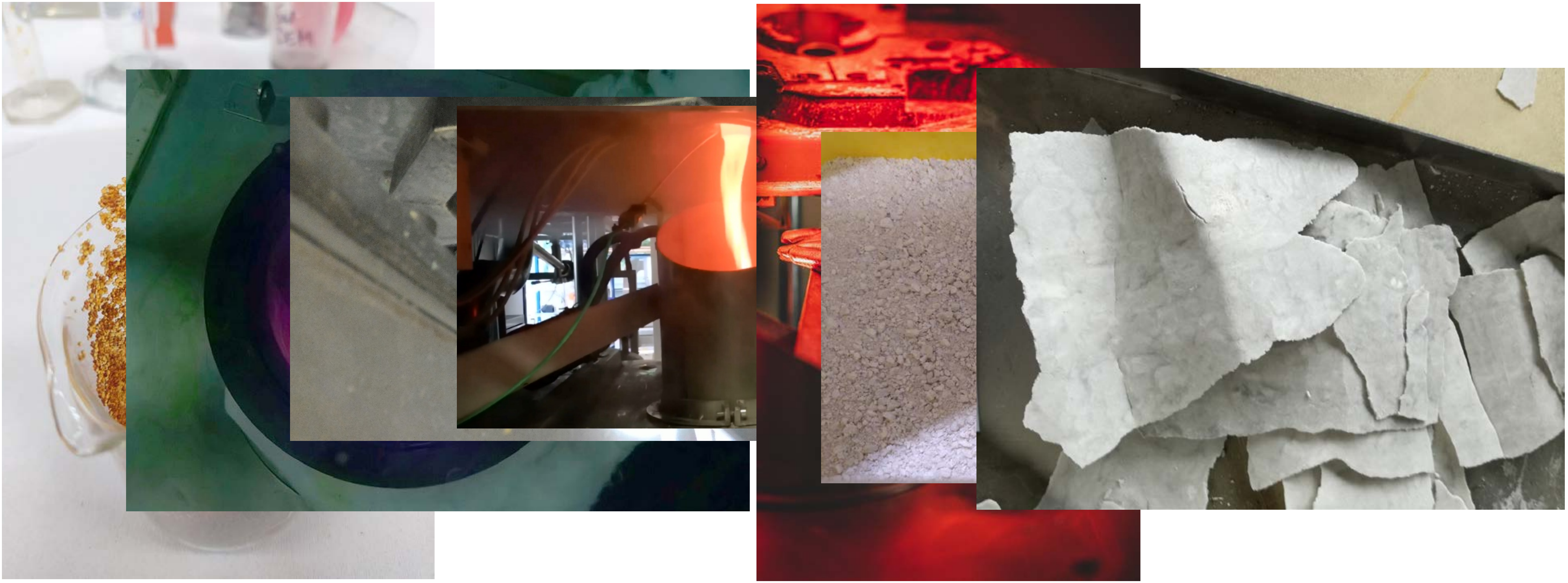


This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

What is the MSO waste

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

What is the MSO waste



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Immobilization of molten salt residue using alkali-activated and cement-based materials

LANDER FREDERICKX, EDUARDO FERREIRA, QUOC TRI PHUNG

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

PREDIS

Immobilization of molten salt: roadmap

Molten salt characterization

(Treatment of salt)

Immobilization

Compatibility with waste acceptance criteria

- Mechanical strength
- Low permeability
- Resistance to internal swelling reactions

Durability testing

- Carbonation
- Resistance to leaching
- Permeability
- Diffusion
- ASR resistance

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Matrices under consideration

Blended cementitious system

Alkali-activated materials

- CEM I / BFS / Silica fume / lime / limestone
- Varied waste loading and w/c ratio
- Proven matrix for other types of radwaste

- Metakaolin / BFS precursor
- Resistant to DEF/ASR
- Encapsulation of waste in 3D (C)NASH structure

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Pre-treatment is necessary!

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 \downarrow + 2NaCl$$

s = 75 g/L

$$Na_2CO_3 + Ca(NO_3)_2 \rightarrow CaCO_3 \downarrow + 2NaNO_3$$

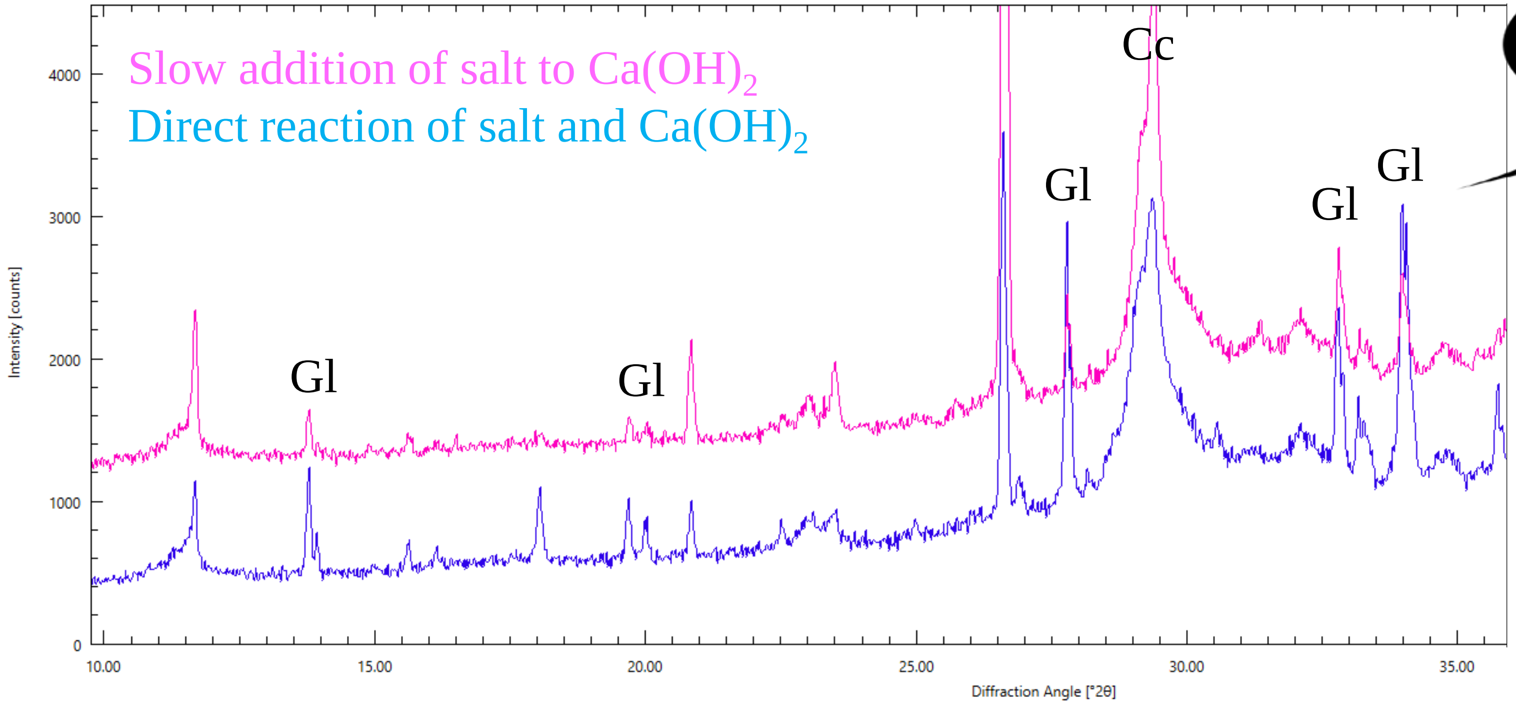
s = 1212 g/L

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2NaOH$$

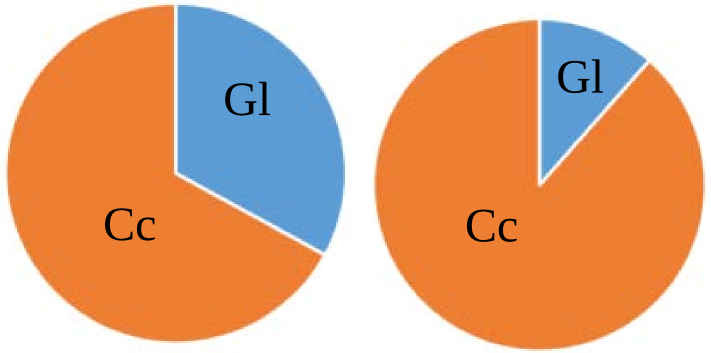
s = 1.73 g/L

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Transformation of salt by $Ca(OH)_2$

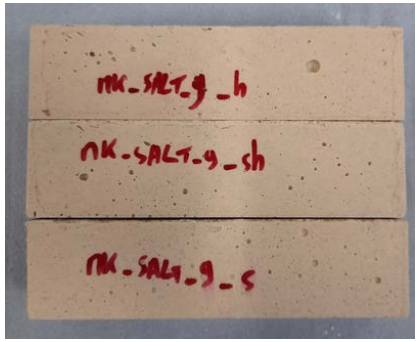


Gaylussite
$Na_2Ca(CO_3)_2 \cdot 5H_2O$



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Immobilization of $Ca(OH)_2$ treated waste



Metakaolin geopolymer prisms with 10 wt.% salt, converted by $Ca(OH)_2$

Alkali-activated BFS prisms with 10 wt.% salt, converted by $Ca(OH)_2$

Blended system cubes with 10 and 14 wt.% salt, converted by $Ca(OH)_2$

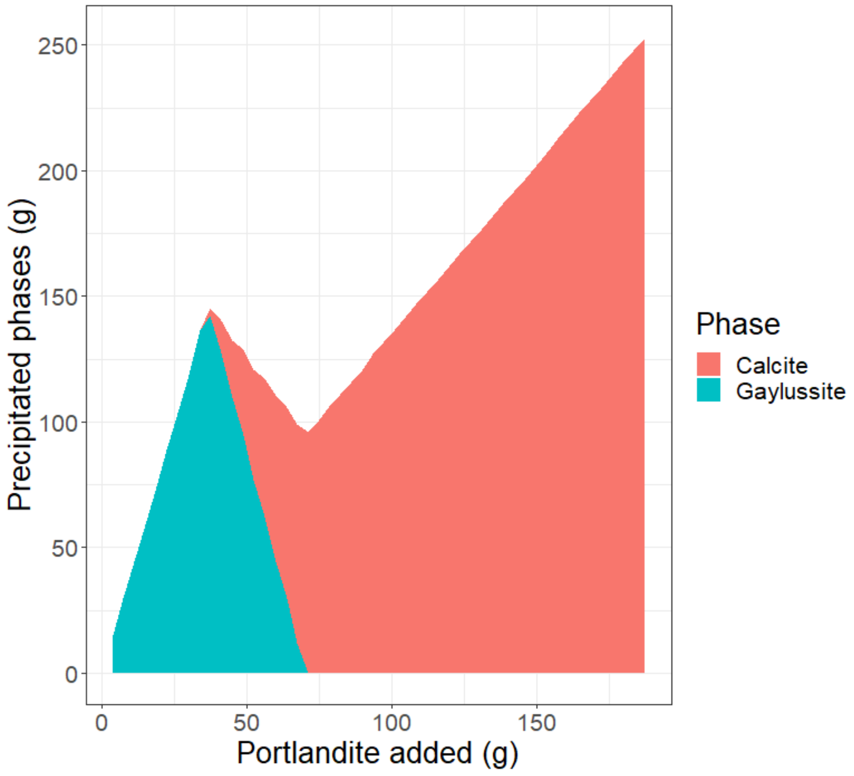
	Metakaolin		BFS		Blended system	
Waste loading (%)	10	15	10	20	10	14
Compressive strength (MPa)	25±1	13±2	42	37	15	15
Final setting time (hours)	>5 h	/	2h30m	1h15m	5h00m	1h17m
Notes	Efflorescence		/		/	

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

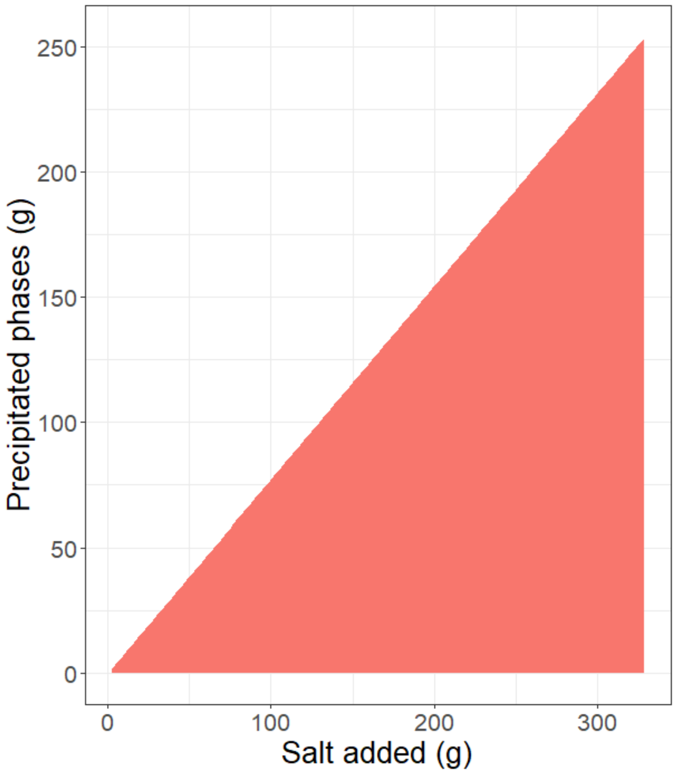
Thermodynamic modeling

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Speciation of carbonate phases after pretreatment



Stepwise addition of $Ca(OH)_2$ to salt



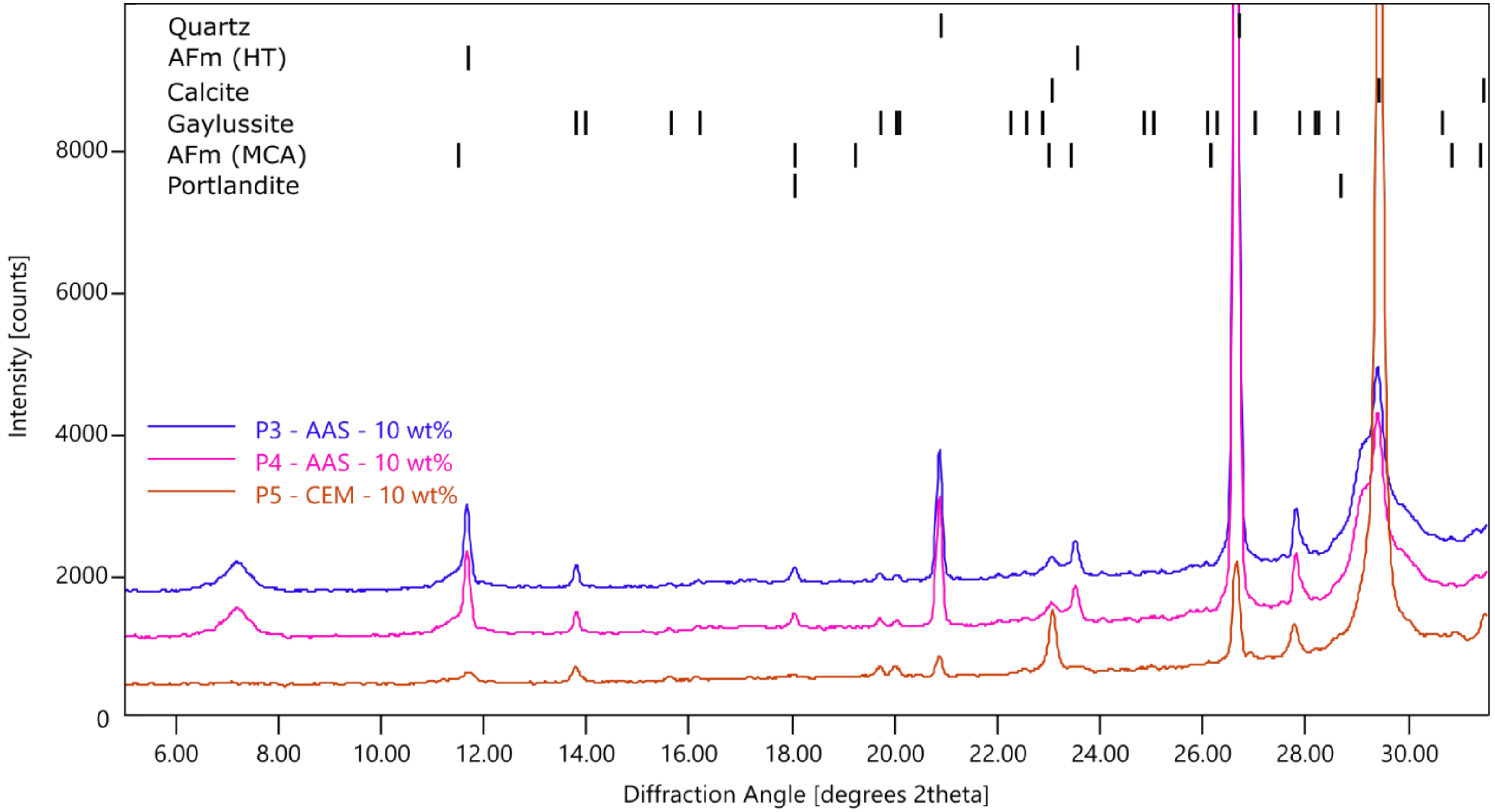
Stepwise addition of salt to $Ca(OH)_2$

- Unexpected presence of gaylussite after pretreatment
- Attributable to Na-rich environment in which $Ca(OH)_2$ is introduced
- Stepwise addition of $Ca(OH)_2$ promotes calcite formation

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Carbonate phases in matrix

	P4	P5
Portlandite	0.0	0.0
AFm	2.2	1.7
C(A)SH	51.1	47.1
Unreacted Slag	*17.3*	*10.4*
Gaylussite	12.2	0.0
Calcite (aggregate)	*0*	*21.6*
Calcite (salt)	3.3	16.4
Quartz	*13.9*	*2.9*



- Gaylussite still occurs even after stepwise addition of $Ca(OH)_2$
- AAM (P4): gaylussite is thermodynamically stable
- Cementitous materials (P5): gaylussite is not stable

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

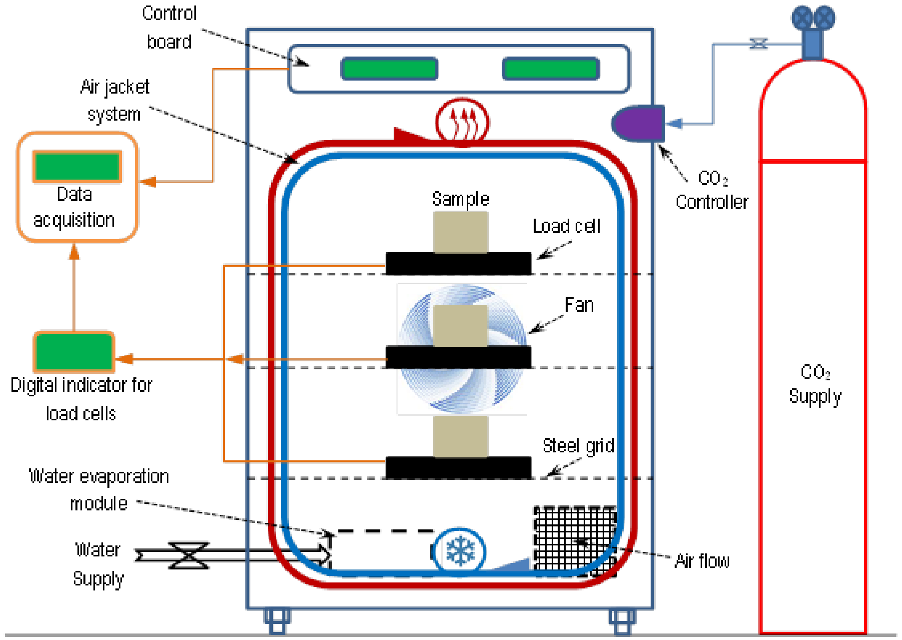
Durability

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Carbonation experiments

- Samples cured for 28 days
- Preconditioning at 60% RH, 20°C until achievement of stable mass
- Exposure to 1% CO_2, 60% RH, 20°C
- 3 Months
- Intermediate follow up
  - Measurements: strength, length
  - Characterization

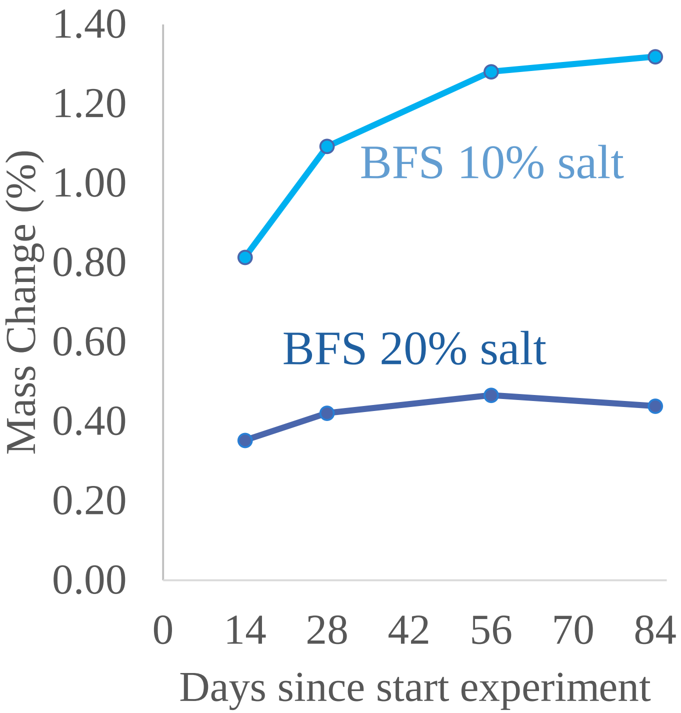
Setup

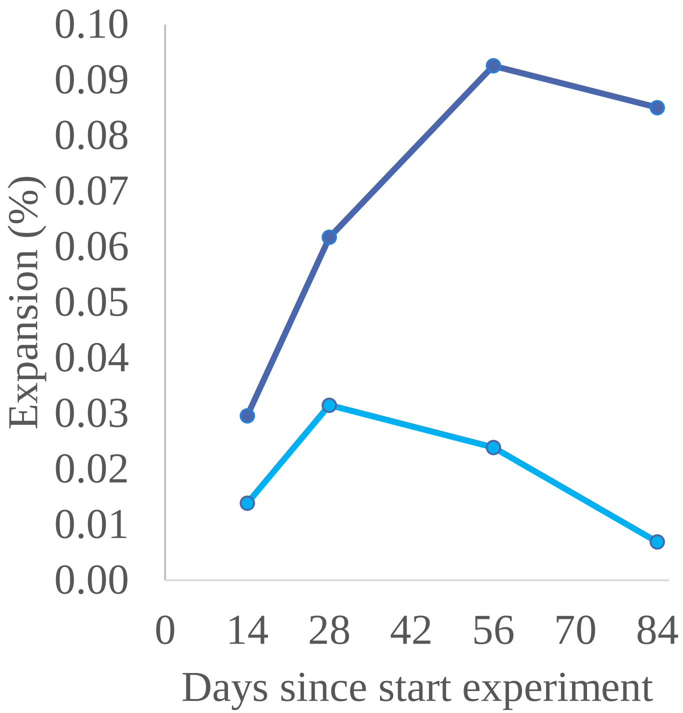


This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Carbonation experiments

Mass & Length





Mass increase

≈

Ingress of CO2

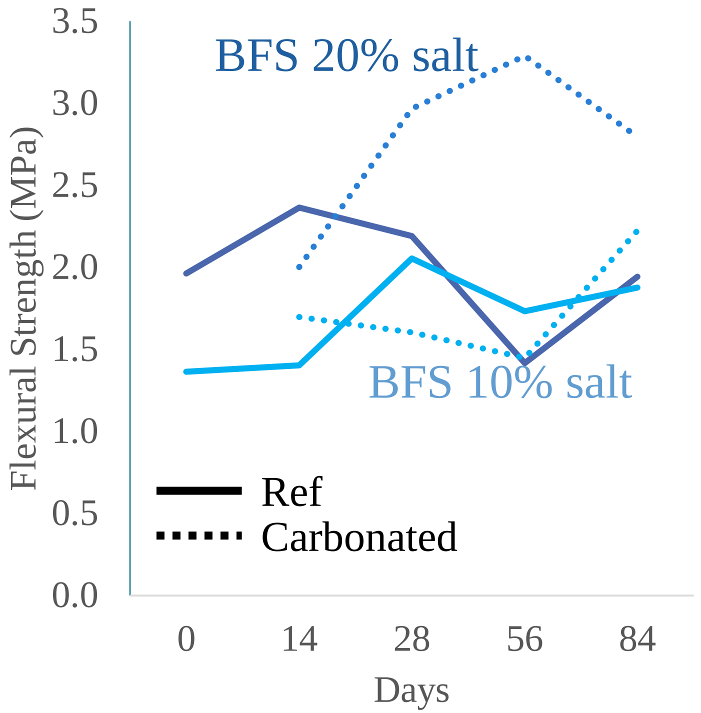
≠

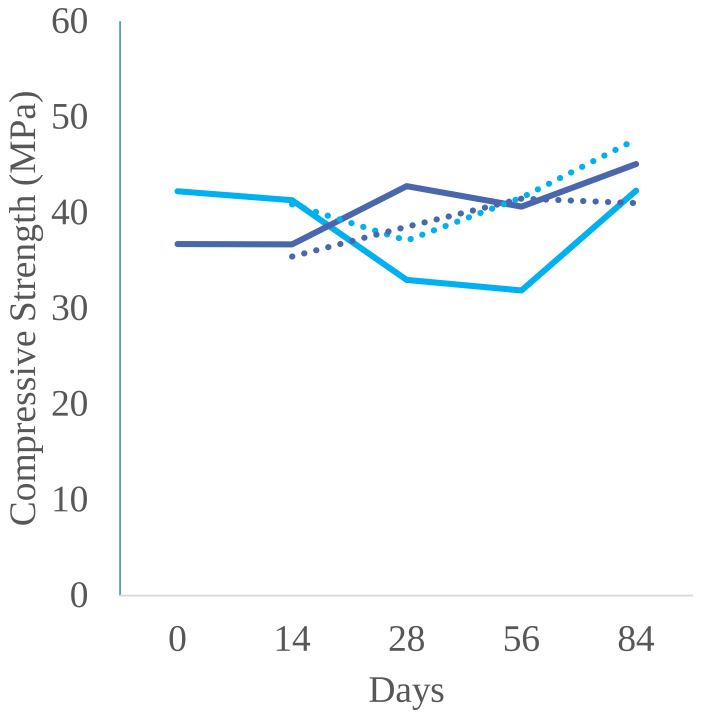
Expansion of samples

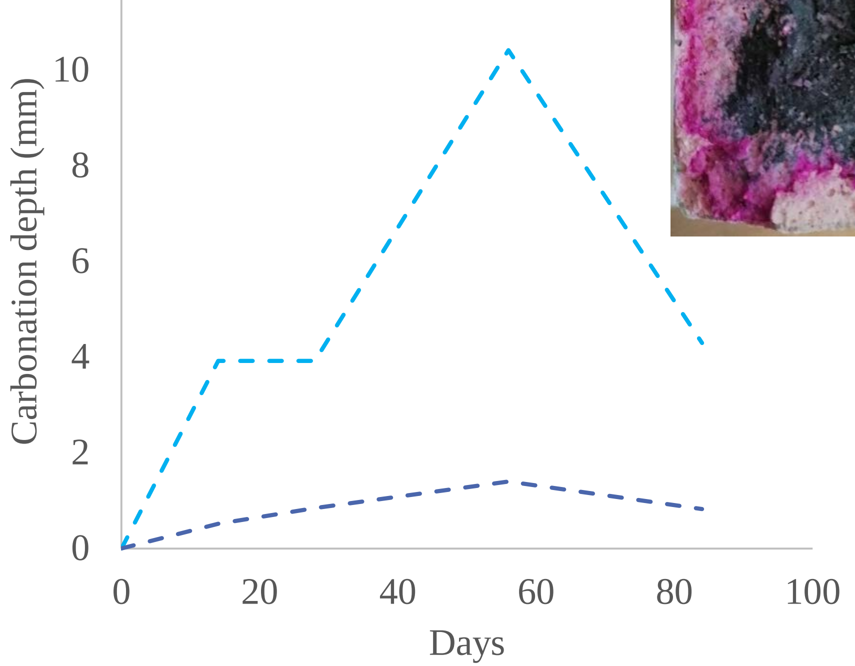
This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Carbonation experiments

Strength & carbonation depth



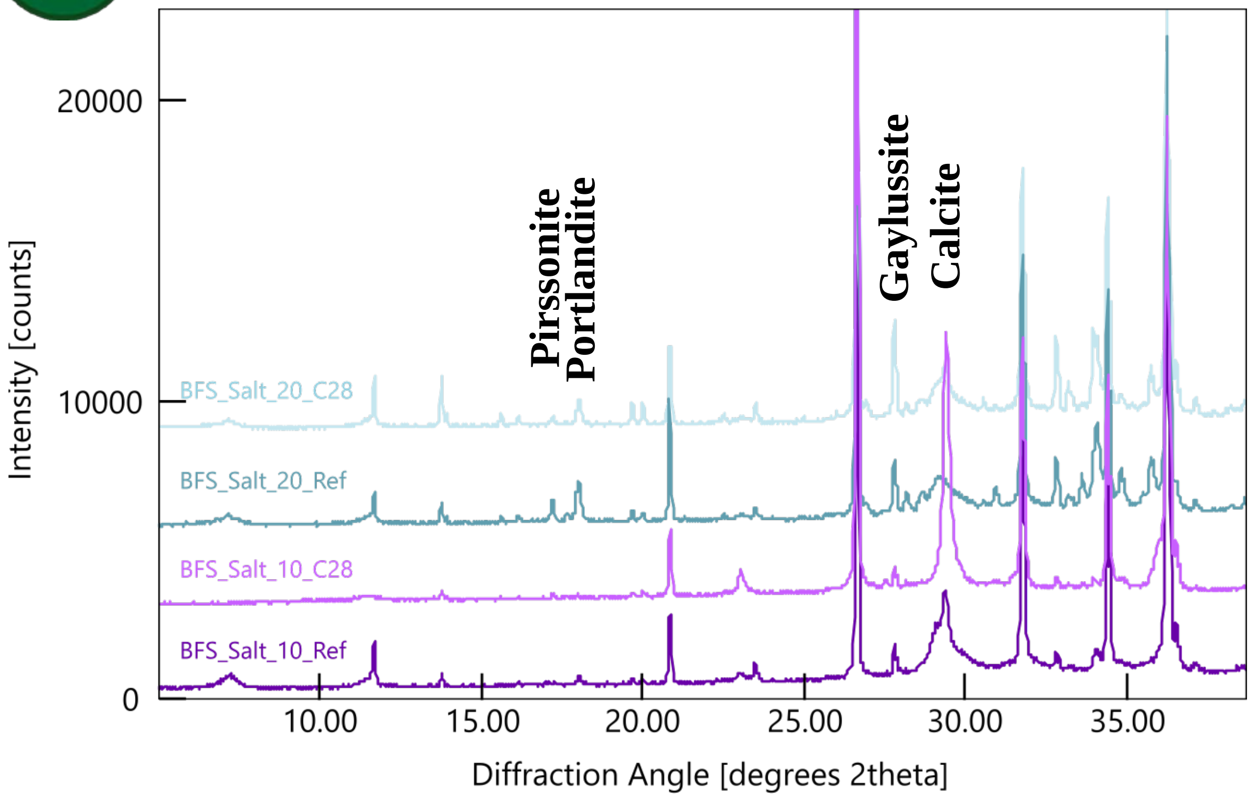




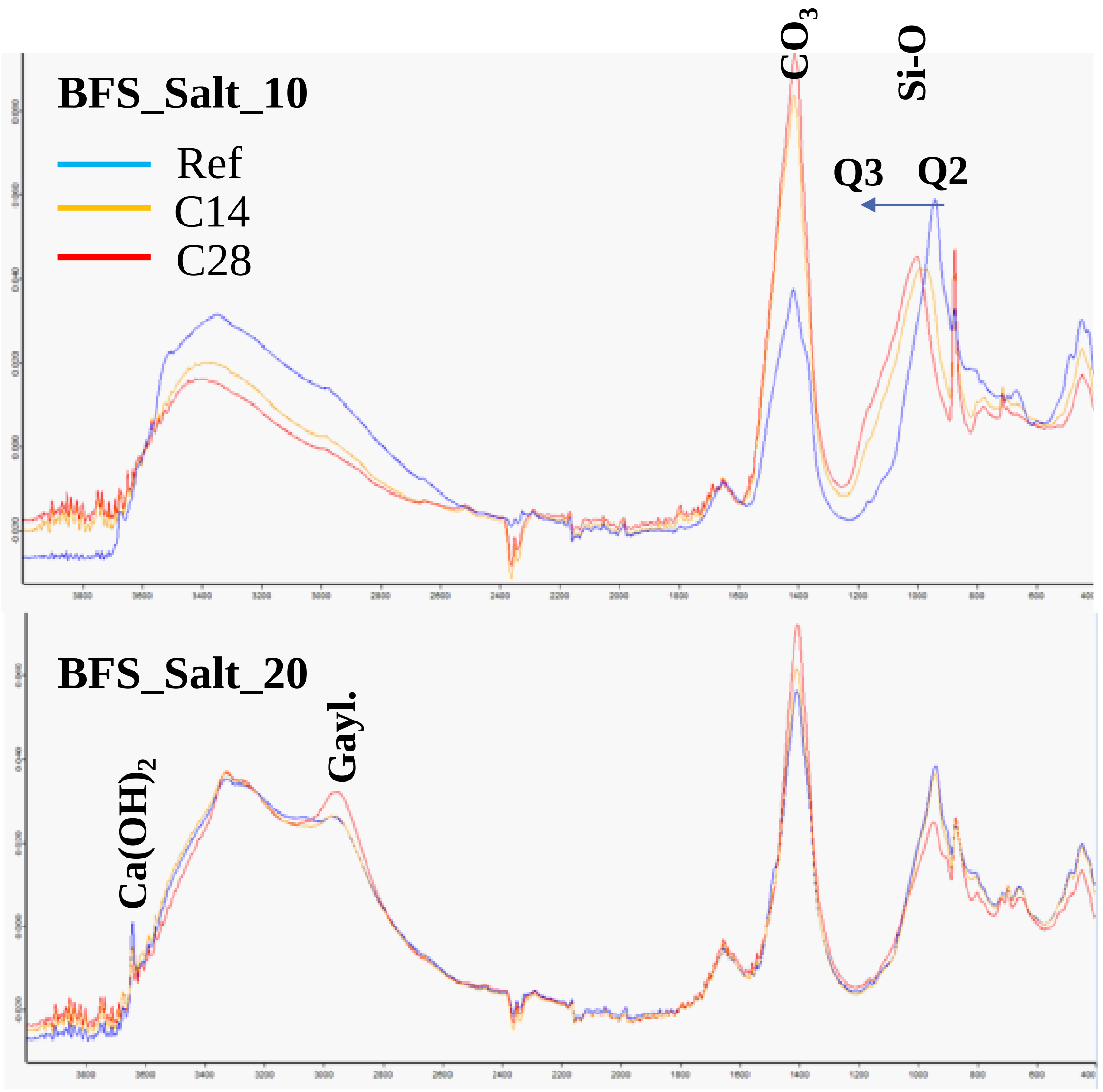
This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Carbonation experiments

Characterization



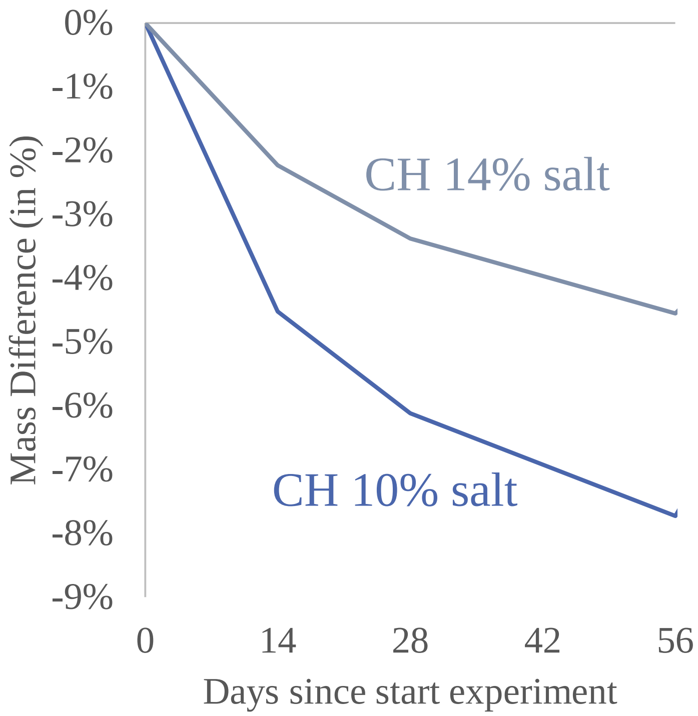
	Amorph	AFm	Cc	Gayl.	Pirss.	$Ca(OH)_2$	Qz
BFS Salt 10 Ref	71	8	3	3	0	1	14
BFS Salt 10 C28	62	2	20	3	0	0	14
BFS Salt 20 Ref	52	8	0	7	13	4	15
BFS Salt 20 C28	49	8	1	14	9	3	17

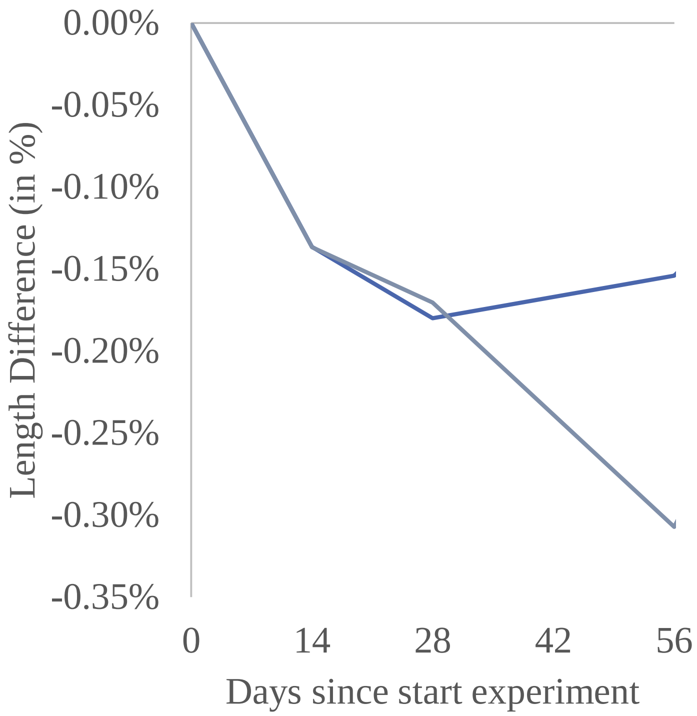


This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Carbonation experiments

Mass & Length





Mass decrease

Water release > CO2 intake

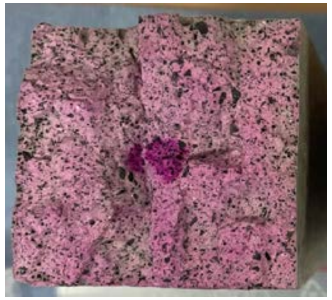
=

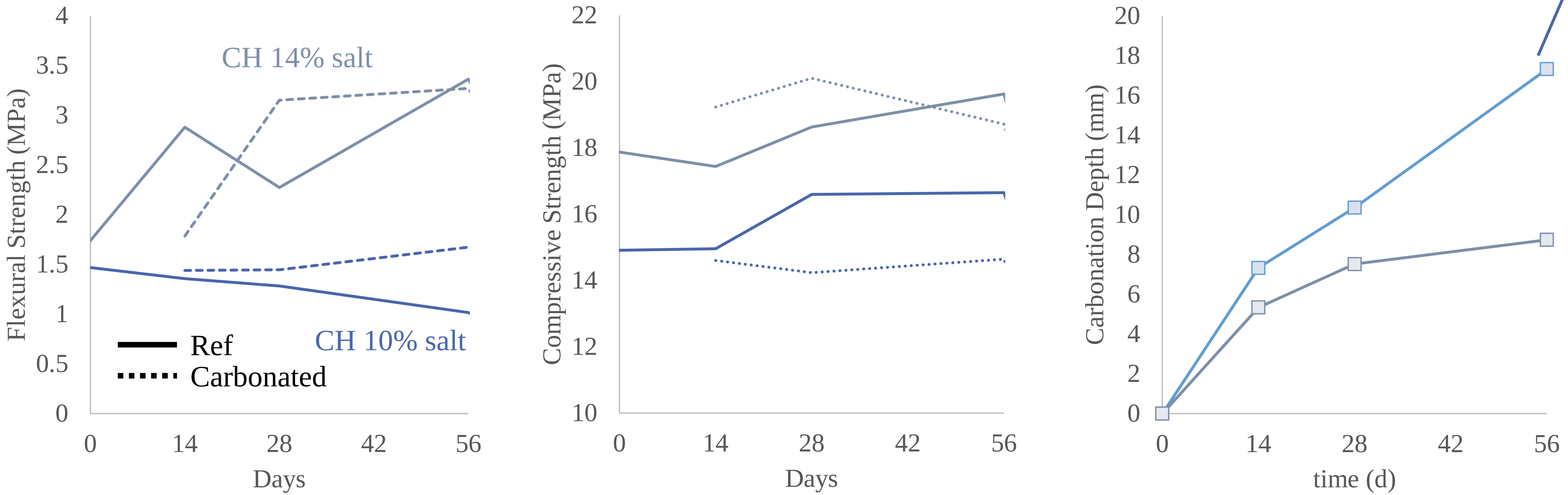
Shrinkage of samples

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Carbonation experiments

Strength & carbonation depth





This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Leaching experiments

PREDIS 6 - protocol

- Leaching in glovebox
- Intermediary analyses leachate:
  - TIC-TOC
  - pH, resistivity
  - ICP analysis
- Leachant composition:

g/l	Na	Ca	K	SO4	Si	Al	pH
Expected:	0	0.02	2.80	1.09	0	0	12.70
Measured:	1.48	0.02	0.84	1.08	0.01	0	12.99

Accelerated leaching

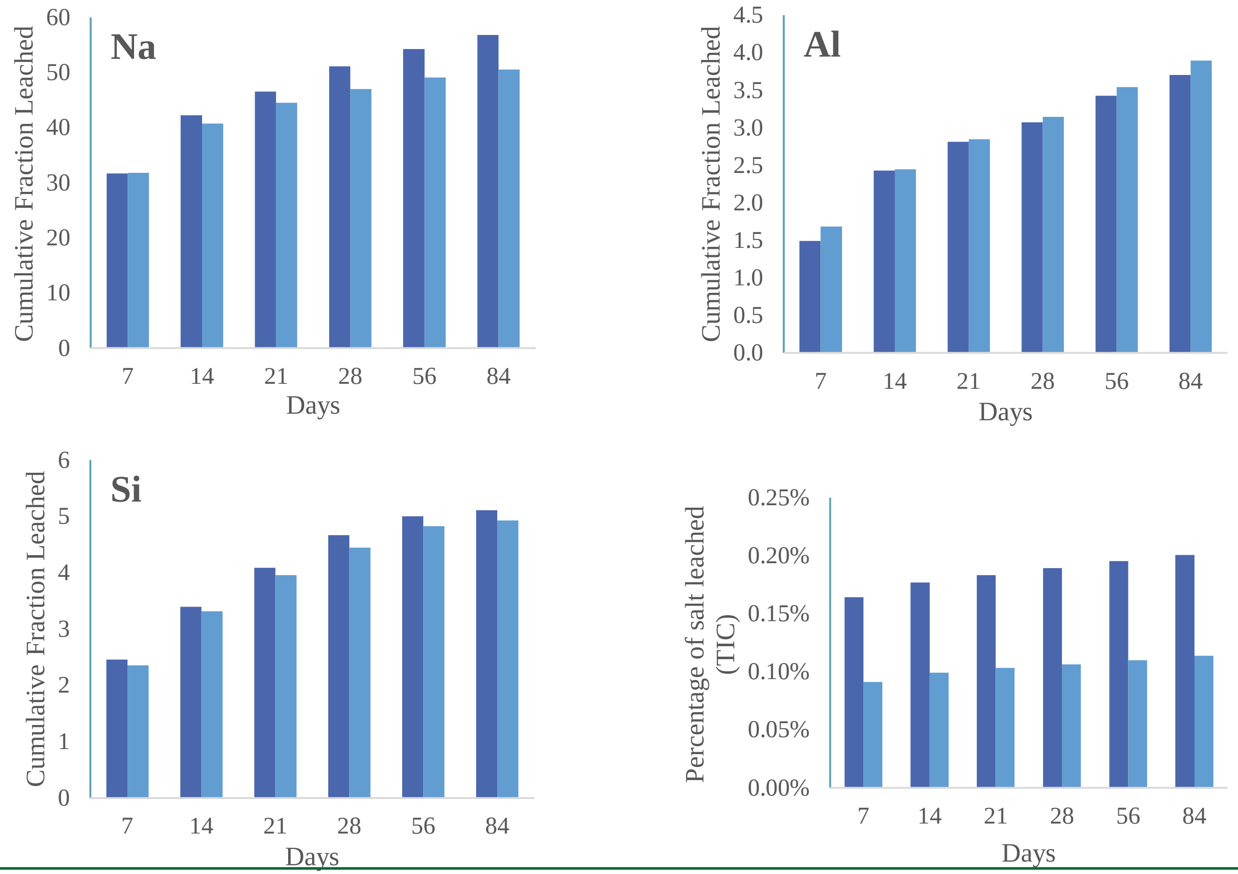
- Leaching in reaction vessel bubbled with N_2
- Intermediary analyses leachate:
  - ICP analysis
- Leachant: 6M NH_4NO_3

Post-Mortem

- SEM analyses
- Indentation of leached surface

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

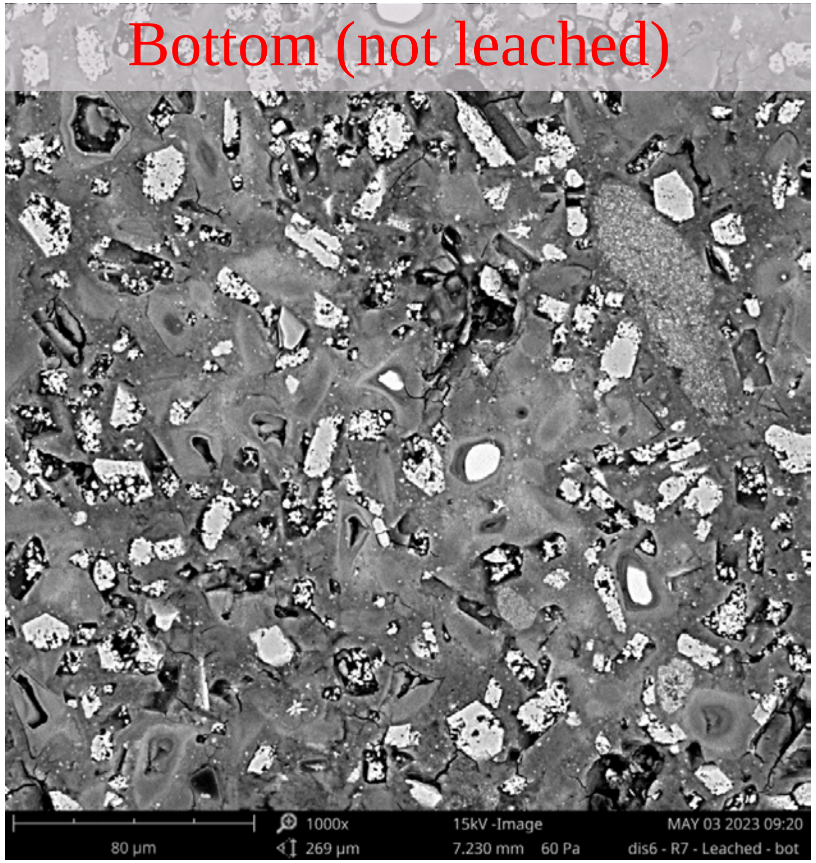
Leaching – preliminary results

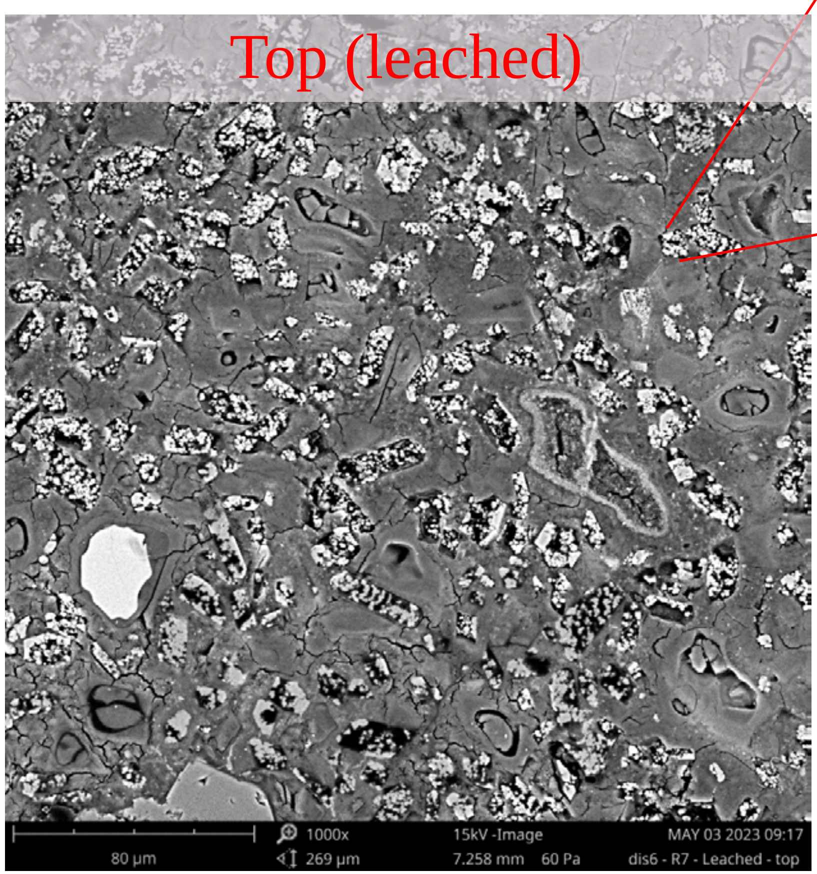


- Initial sample composition to be determined (estimated for CFL calculation)
- TIC and Na do not arrive at similar leaching rates

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Leached samples - SEM



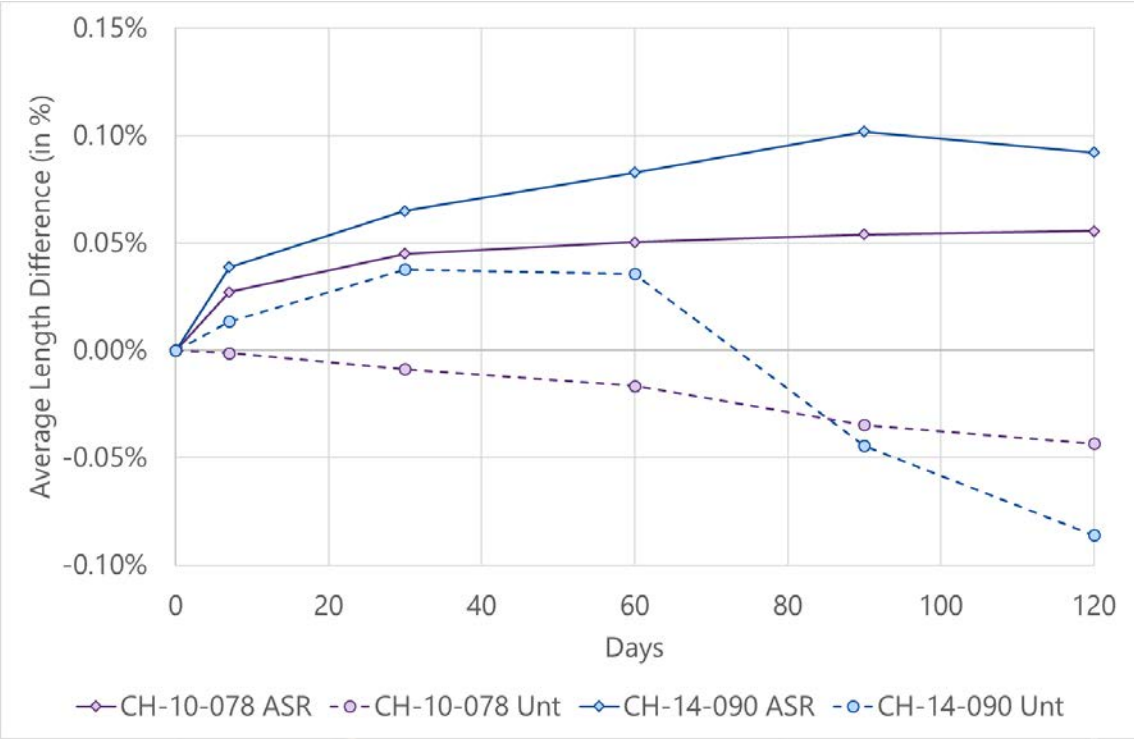


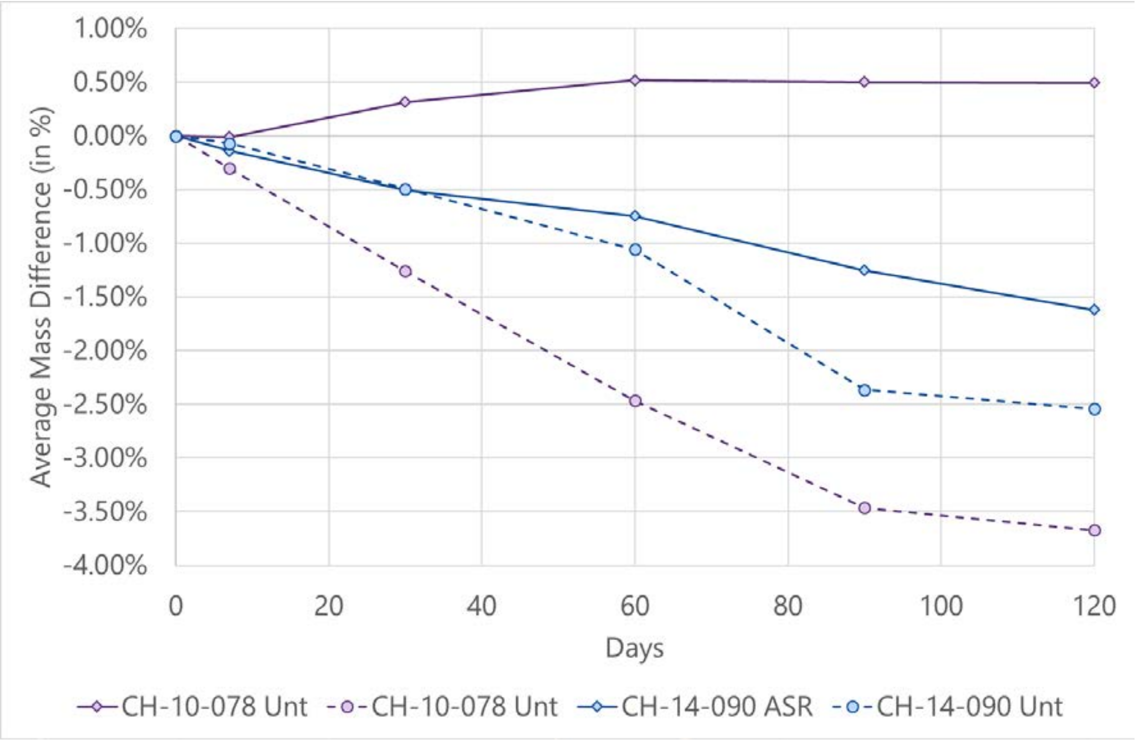
Carbonate crystals

- Precipitation of carbonate crystals in voids
- Less carbonate crystals in voids near leaching front
- Degree of dissolution needs to be quantified

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Long term ASR test – preliminary results





Expansion of samples under ASR

Retraction of samples in a sealed bag (Unt)

Mass loss of samples with 14 % salt

Mass gain of samples with 10 % salt

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Preliminary conclusions

Alkali-activated materials

- Na-Ca carbonate (gaylussite/pirssonite) is stable in a AAM matrix
- The carbonation resistance of AAM increases with increasing waste loading due to portlandite buffering
- Alkali leaching is significant (* needs to be verified) and could be associated with dissolution of carbonate crystals in voids

Cementitious materials

- Na-Ca carbonate (gaylussite/pirssonite) is a metastable phase in cementitious materials
- The carbonation resistance also increases with increasing waste loading: further microscopic analysis after the test
- Expansion due to ASR seems limited up to 120 days.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Lander.Frederickx@sckcen.be

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

UNIVERSITY OF HELSINKI
FACULTY OF SCIENCE

PREDIS VTT

Short-Term Stability and Physico-Chemical Characterisation of a Reconditioned Waste Form Relevant to LILW Radioactive Waste Disposal

Gianni F. Vettese[1]*, Taavi Vierinen[1], Tandre Oey[2] , Suvi Lamminmäki[2], Sami Hietala[1], Matti Nieminen[2], Markku Leivo[2], Tapio Vehmas[2] Jaana Laatikainen-Luntama[2], Emmi Myllykylä[2] & Gareth T. W. Law[1]

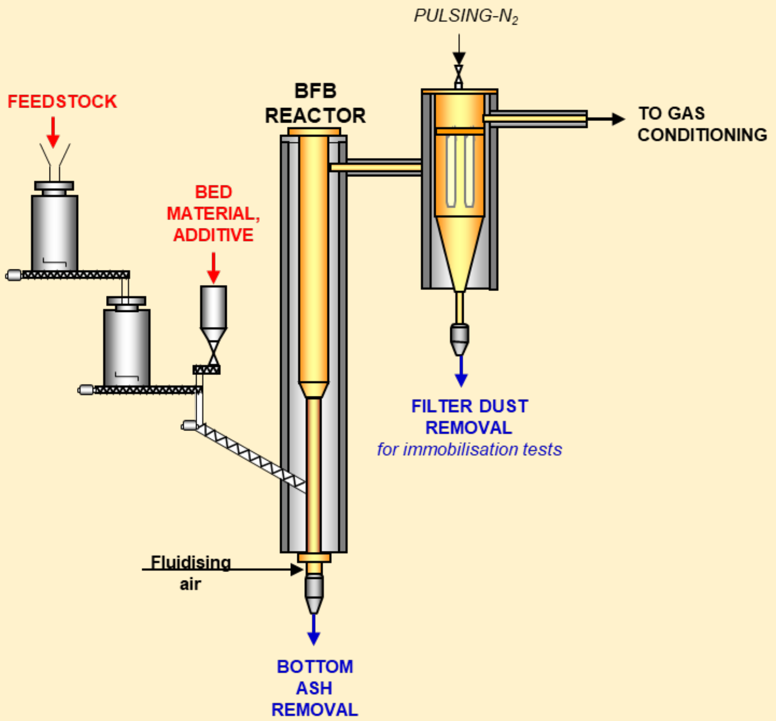
[1]The University of Helsinki, Radiochemistry Unit, Helsinki, Finland, [2]VTT Technical Research Centre of Finland, Helsinki, Finland

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

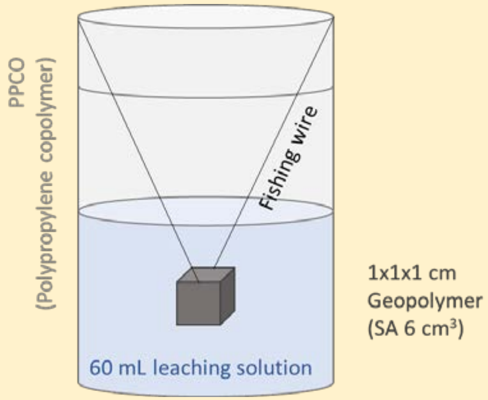
Methodology

1. Gasified Ion-Exchange Resin prepared by VTT using a Bubbling fluidized bed reactor (BFB) was used for gasification of organic ion-exchange resin doped with stable RN analogues.
2. Geopolymer ($1\%_{wt}$ ash loading).
3. Leaching experiments follow PREDIS WP6 protocol.

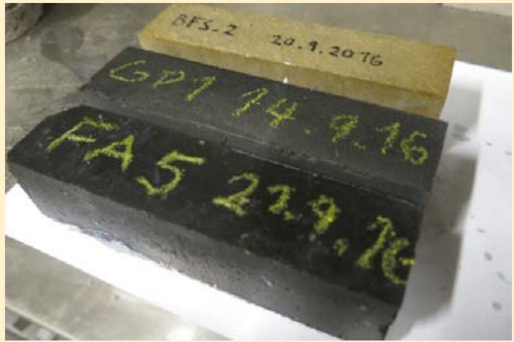
1.



3.



2.



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

UNIVERSITY OF HELSINKI
FACULTY OF SCIENCE

PREDIS VTT

Aims and Objectives

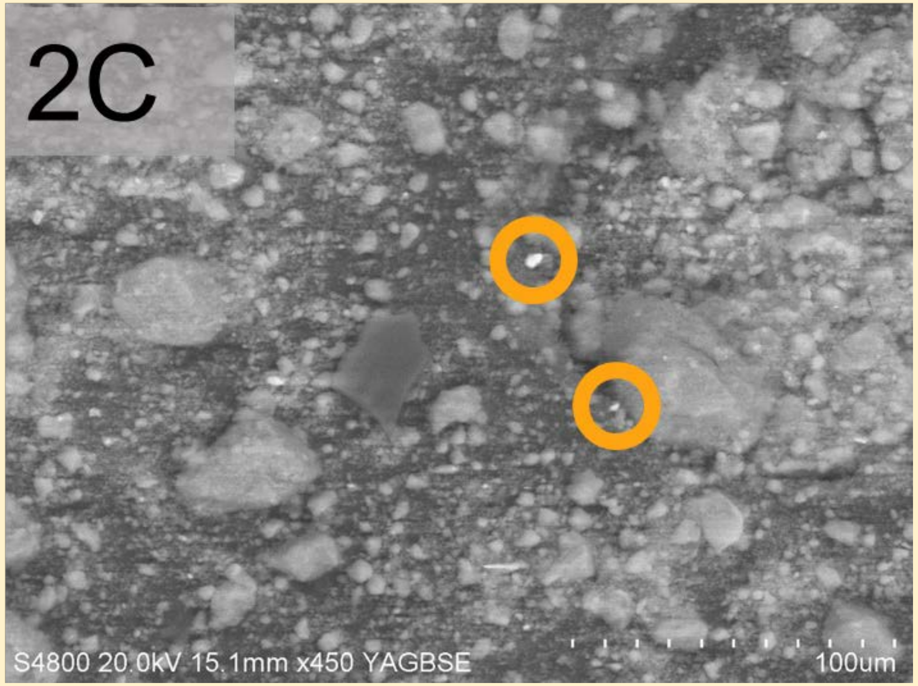
Overarching aim: Semi-dynamic leaching experiments assess the short- and long-term (1 month – 2 years) behaviour of the matrix and contaminants.

1. Pre-characterisation of the physico-chemical properties of geopolymer.
   - Elemental composition.
   - Structural information e.g., Imaging (SEM-EDX or EMPA) or ^{29}Si and ^{27}Al MAS NMR.
2. Assesment of leaching behavior of waste-form in repository conditions.
   - Elemental composition of leachate (MPAES / ICPMS).
   - Assessment of colloid formation (DLS / Zetasizer).
3. Post-mortem characterisation of the physico-chemical properties of the leached geopolymer.
   - 1, 6, 12 & 24 months.
   - Elemental composition.
   - Structural information e.g., Imaging (SEM-EDX or EMPA) or ^{29}Si and ^{27}Al MAS NMR.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

1. Pre-characterisation

- 1% ash in a metakaolin geopolymer.
- Contains stable isotopes of: Cs (200 mg/kg), Sr (20 mg/kg) Cr (3000 mg/kg), Co (40 mg/kg), and Ni (3000 mg/kg).
- Heterogeneous particles from ash are retained after encapsulation into the geopolymer matrix.



ESEM-BSE of metakaolin geopolymers. Circles highlight dense agglomerations.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

UNIVERSITY OF HELSINKI
FACULTY OF SCIENCE

PREDIS VTT

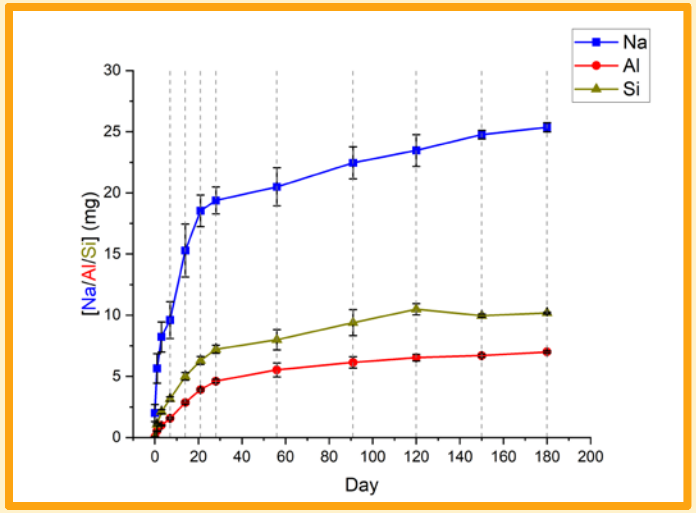
2. Aqueous Analyses

pH and **conductivity** remain **stable** at 12.5 and 8.5 mS/cm respectively. **No colloids** observed in leachate using dynamic light scattering.

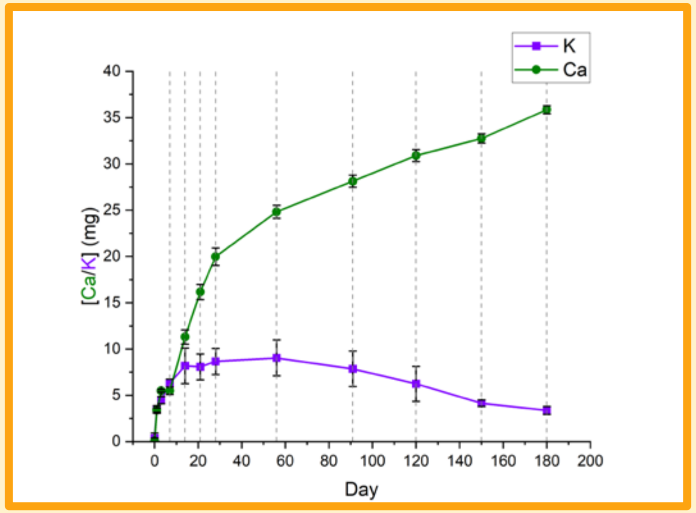
Bulk: Na (24.2 %), Al (5.9 %), and Si (2.9 %) leach into the solution, Ca (66 %) and K (0.8 %) are removed from solution into the geopolymer.

Trace: Cs (55 %) leaches into the solution. Leaching index (9.1) was significantly above waste acceptance criteria of (6.0) prescribed by US NRC for radioactive waste [ANSI 2019]. Co, Cu, Ni, Sr and Cr are retained within the geopolymer.

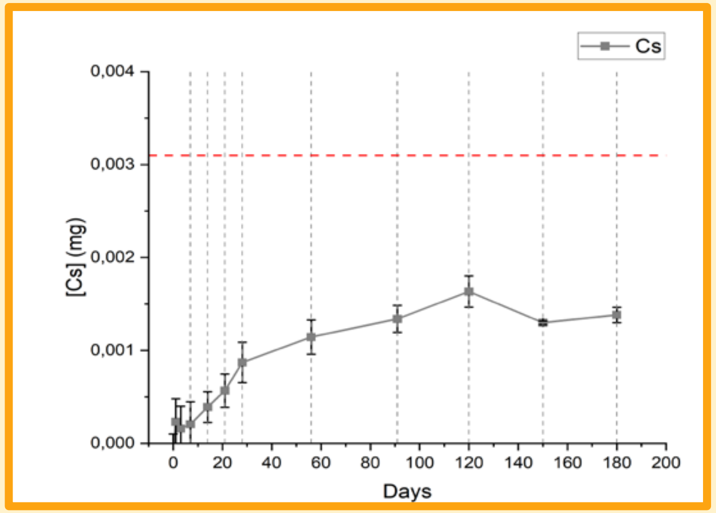
Leaching



Absorption



Leaching



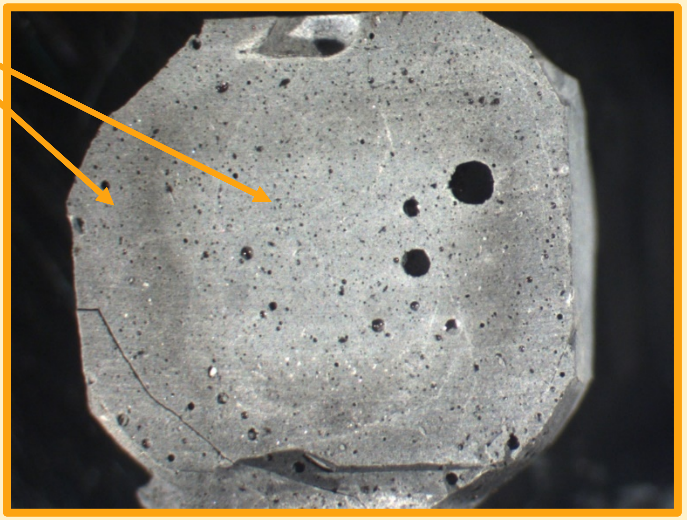
[left] Cumulative leaching of Al, Si, and Na; **[middle]** Cumulative absorption of K and Ca; **[right]** Cumulative leaching of Cs.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

3. Post-Mortem Analyses

Leached geopolymers are sacrificed, preserved, and dissected after 1, 6, 12 and 24 months.

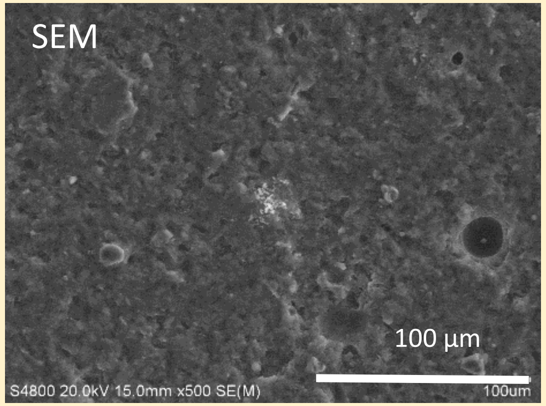
1. Different morphology
2. Weaker integrity
3. Change in geopolymer structure?



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

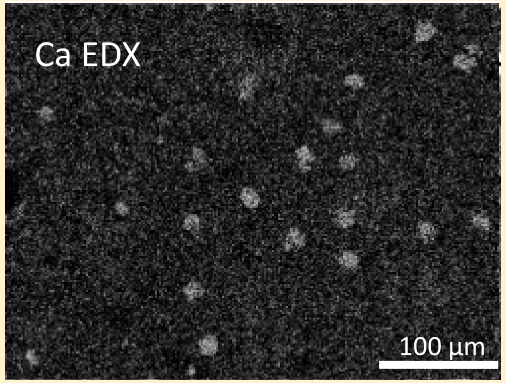
3. Post-mortem analyses

Unleached Geopolymer



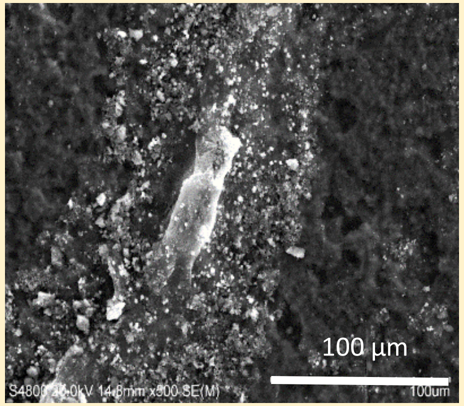
1 month

Increased cracking, change in morphology and growth of Ca rich secondary phases (5-20 µm). XRD confirmed as $CaCO_3$.



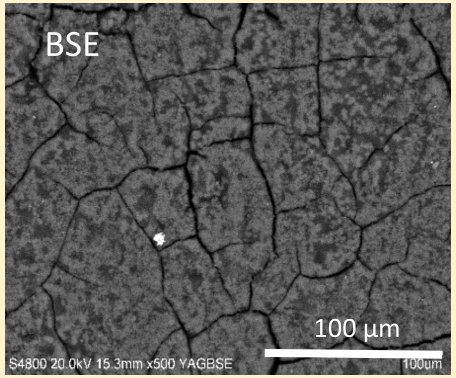
6 months

Continued change in morphology and growth of $CaCO_3$ secondary phases.



12 months

Continued change in morphology (now significant cracking) and growth of $CaCO_3$ secondary phases.



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Outlook

Conclusions

- Successfully developed experimental methodology for leaching experiments + post-mortem analyses.
- Assess change in geopolymer structure and its interactions with surrogate radionuclides.
- Leaching experiments show Cs was retained within the criteria to US NRC.
- Masters thesis + Expected Publications 2023/4.

Future work

- Completion and publication of 1st gen. geopolymer experiments (12 month).
- On-going experiments with 2nd generation leaching experiments. Doped with elevated RN and ash loadings (15, 50%).
- More complex, merits molecular-scale analysis to identify bonding mechanism(s). E.g., XAS, TEM, EPMA.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Thank you

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 945098.