WP5 Innovations in liquid organic waste treatment and conditioning

Isabelle GIBOIRE, Kahina HAMADACHE and **Arnaud POULESQUEN** (CEA)
Work Package Leaders
Isabelle.giboire@cea.fr, kahina.hamadache@cea.fr, Arnaud.poulesquen@cea.fr

Management Team: **Stephen WICKHAM** (GSL), **Federica PANCOTTI** (SOGIN, **Mafalda GUERRA** (SOGIN), **Crina BUCUR** (RATEN), **Matthieu BRIFFAUT** (ECL), **John PROVIS** (USFD), **Rosa LO FRANO** (UNIPI)
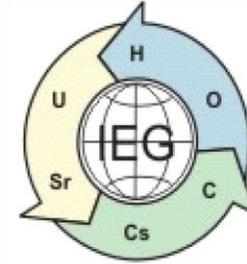
And all **great Partners**!

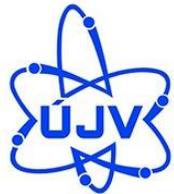*PREDIS May 2023 workshop in Mechelen, Belgium – Thu 25th presentation*

Partners

Objectives

- Implementing **geopolymers** and related **alkali-activated materials** (AAM) as **mineral binders**.

- Development of **direct conditioning solutions** for radioactive liquid organic wastes (RLOW) from **TRL 3 to TRL 6** including **validation tests** (real waste) and feasibility **scale-up** tests.

- Fulfilling **technical and economic** requirements related to RLOW:
  - robustness regarding **waste variability**,
  - easiness of **implementation** and **operation** (*e.g.*, mobile units),
  - capacity ranging from **small to large volumes** and limitation of secondary waste,
  - reduction of **disposal costs** by minimization of volumes (pre-treatment and waste loading).

PREDIS

Expected Impacts

- **Optimization** of geopolymers and AAM formulations for RLOW encapsulation, especially **waste loading** and **matrix performance**.

- Study of **geopolymers interactions with RLOW**.

- Leading to final wasteform showing **properties and performances compatible with safety and technical requirements** related to **disposal**.

- Process **robustness** regarding waste, raw materials and process variability including study of the **stability** and **durability** of the final wasteform.

- **Disposability assessment** related to Waste Acceptance Criteria (WAC) and scientific approaches for deeper physico-chemical understanding.

PREDIS

WP5 Structure

- Task 1 WP5 Management
- Task 2 Collection and review of waste, regulatory, scientific and technical data
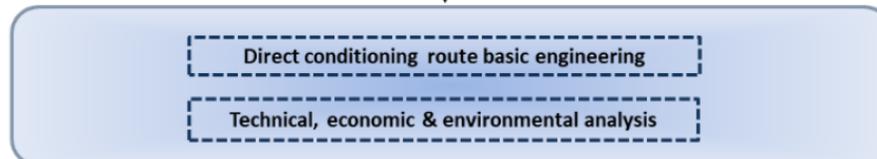- Task 3 Study of direct conditioning process
- Task 4 Study of conditioning matrix performances
- Task 5 Preliminary technical, economic and environmental analysis
- Task 6 Implementation and dissemination

Task 5.2. **Collection and review of data: reference waste**

- Identification of **reference wastes**, a combination of:
  Oils – Solvents – Scintillation cocktails
  (Cleaning and decontamination liquids – Organic effluents)

  - **common materials:** give continuity and permit **direct comparison**
    Oils: viscosity-controlled simple oils – Solvents: TBP, Dodecane – scintillation cocktails

  - **own partners materials:** directly applicable to national context

- **Description of RLOW inventories at European level** (owners, radiological and chemical compositions, volumes, storage conditions…) using questionnaires completed by WP5 partners and EUG members.

- A selection of raw materials and additives to formulate matrices:
  Locally-sourced **Metakaolin** and **Blast furnace slag** – **"Mixes"** – **Polymers**

Task 5.3. **Study of direct conditioning process**

- Exchange and definition of **protocols** to apply consistent testing procedures.

- Identification of **reference formulations** based on metakaolin, blast furnace slags and a mix of raw materials (MK-BFS-fly ash) ➔ *MS34 in Nov 22*

- Selection of a limited number of optimized formulations to be tested with **actual RLOW** and for **process scale-up**
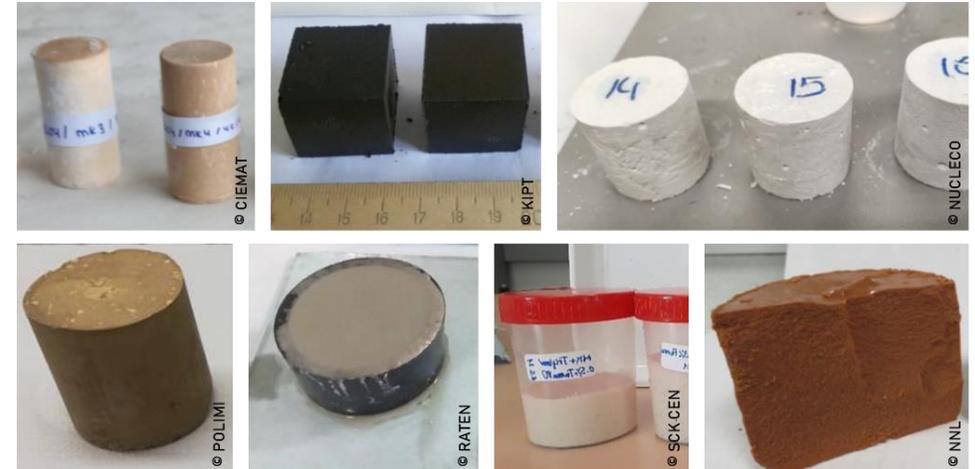
*Technical focus by **F. Pancotti (SOGIN) – Task 5.3 overview** and **A. Santi (POLIMI student) - Pre-impregnation of RLOW on polymers***

Task 5.4. **Study of conditioning matrix performances**

- Performed using **three reference formulations selected after Task 5.3** in close collaboration between pools of partners (each pool will be established depending on the considered matrix).

- Exchange and definition of **protocols** to apply consistent testing procedures.

- Study conditioning **matrix performances** (**durability !**) and behavior in relation with disposal, transport and prolonged storage requirements and specifications.

- **Assess disposability** according to RLOW radiological features and targeted disposal facilities.
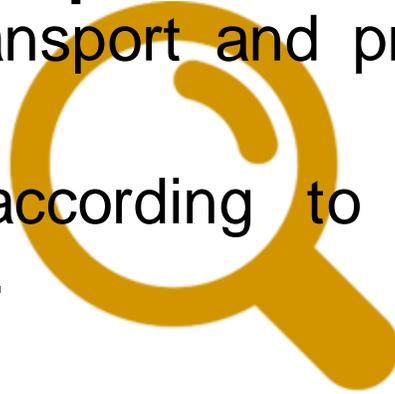
Technical focus by ***M. Briffaut (ECL) – Task 5.4 overview*** *and* ***T.N. Nguyen (SCK CEN student) - Study of conditioning matrix durability under various conditions***

Task 5.5. **Preliminary technical, economic and environmental analysis**

- **Information and data exchange with WP2**: LCA/LCCA case studies have been provided comparing cementation process against geopolymer conditioning matrices developed in WP5 ➔ *MS37 in Oct 22*

- Assessment criteria ranging to cover **impacts**:
  - environment (e.g., carbon footprint, emissions, energy use),
  - technical (e.g., TRL, waste loading, product performance),
  - strategic impact (e.g., disposability, process throughput),
  - cost (e.g., infrastructure cost, raw materials cost).

PREDIS

Task 5.6. **Implementation and dissemination**

- Availability to **disseminate the projects results** by disclosing them to the public during specific events (ICEM®2023, NWM2023).

- Project to collect papers to request a **Special Issue** in reputed journals, such as *Energies* or *Nucl. Sci. Tech., Sci. Technol. Nucl. Install.*

OPEN

Alteration in molecular structure of alkali activated slag with various water to binder ratios under accelerated carbonation

Check for updates

Thi Nhan Nguyen[1,5✉], Quoc Tri Phung[1✉], Ziyou Yu[2], Lander Frederickx[1], Diederik Jacques[1], Dimitrios Sakellariou[2], Alexandre Dauzeres[3], Jan Elsen[4] & Yiannis Pontikes[5]

Carbonation of alkali activated materials is one of the main deteriorations affecting their durability. However, current understanding of the structural alteration of these materials exposed to an environment inducing carbonation at the nano/micro scale remains limited. This study examined the evolution of phase assemblages of alkali activated slag mortars subjected to accelerated carbonation

PREDIS

Pre-disposal management of radioactive waste

WM SYMPOSIA 2023 · EDUCATION & OPPORTUNITY IN RADWASTE MANAGEMENT · A NON-PROFIT ORGANIZATION

Innovations in liquid organic waste treatment and conditioning

PREDIS Work Package 5 Management Team: I. Giboire[1], K. Hamadache[1], M. Fournier[1], C. Bucur[2], F. Pancotti[3], M. Guerra[3], M. Briffaut[4], R. Lo Frano[5], J. Provis[6], S. Wickham[7]

[1]CEA, DES, ISEC, DPME, Marcoule, France
[2]Institute for Nuclear Research Pitesti, Campului no. 1, 115400 Mioveni, Arges, Romania
[3]SOGIN SpA, via Marsala 51/C, 00185 Rome, Italy
[4]Ecole Centrale Lille, Cité Scientifique, 59650 Villeneuve-d'Ascq, France
[5]Università di Pisa, Lg L. Lazzarino, 1- 56126 Pisa, Italy
[6]University of Sheffield, Department of Materials Science & Engineering, Sheffield S1 3JD, UK
[7]Galson Science Ltd, Grosvenor House, Melton Rd, Oakham LE15 6AX, UK

The EU-project PREDIS targets the development and implementation of activities for pre-disposal

10 reports:
deliverables,
milestones,
M. Sc. thesis

PREDIS

PREDIS

Technical focus

- WP5 Summary, Isabelle GIBOIRE (CEA)
- Study of direct conditioning process, Federica PANCOTTI (SOGIN)
- *Pre-impregnation of RLOW on polymers, Andrea SANTI (POLIMI student)*
- Study of conditioning matrix performances, Matthieu BRIFFAUT (ECL)
- *Study of conditioning matrix durability under various conditions, Thi Nhan NGUYEN (SCK CEN student)*

Thank you for your attention!

WP5 T5.3 - Study of direct conditioning process

PREDIS MAY 2023 WORKSHOP

MECHELEN, 25/05/2023

FEDERICA PANCOTTI (SOGIN)

T5.3 – STUDY OF DIRECT CONDITIONING PROCESS

			Year 1											Year 2											Year 3											Year 4											
			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
WP 5	Innovations in liquid organic waste treatment and conditioning	CEA																																																		
T5.3	Study of direct conditioning process	RATEN&SOGIN																																																			
5.3.1	Definition of experimental protocols																																																				
5.3.2	Formulation: feasibility study & screening conditioning options (5 to 10)										M		M																																							
5.3.3	Formulation: optimization & robustness of reference formulations																												M																						
5.3.4	Investigation of reference formulations for real waste																																																			
5.3.5	Investigation of direct conditioning process scale-up																																																			
5.3.6	Synthesis of experimental results																																							D												

- Definition of experimental guidelines and protocols (materials, methods and selecting acceptance criteria) - T5.3.1 (completed)

- Assess conditioning options and develop the most promising reference geopolymer formulations to be further studied - T5.3.2 (completed)

- Optimisation and robustness of the reference formulations - T5.3.3 (completed)

- Consolidate the reference formulations from tests with real RLOW - T5.3.4 (on-going)

- Investigate feasibility of scale-up from exploratory pilot scale tests - T5.3.5 (on-going)

- Elaborate a technical report including key results, information and data obtained – T5.3.6 (on-going)

PREDIS

T5.3 – Main Achievements to date

- A number of conditioning options were studied for the incorporation of **RLOW** (high and low viscosity **Oils**, **Scintillation liquids**, **TBP-dodecane** mixture) and **3 reference formulations** (based on **MK**, **BFS** and **MIX** of raw materials) were identified as the most promising
- **Fresh grout** and **hardened materials properties** were tested (bleeding, setting time, workability, viscosity, compressive strength, heat release and flexural strength)

Qualitative evaluation of proposed formulations based on pre-defined set of criteria

	Option	Formulation	Waste	Criteria	WL (vol%)	surfactant	bleeding	supplying materials	robustness	heat release	setting time	compressive strenght	workability (slump/mini slump test)	viscosity	calorimetric data	flexural strenght
				Priority	H	M	H	H	M	M	H	H	H	H	M	M
OIL	1	MK - Metamax	Nevastane oil		green	green	red	green	green	red	green	green	green	green	green	green
	2	MK - Argicem	Nevastane oil		green	green	orange	green	green	orange	green	green	green	green	green	green
	3	MK - Metamax	Repsol supertauro 100 oil		green	green	green	green	green	green	green	green	green	yellow	yellow	green
	4	MK-BFS-FA (Ukr)	Nevastane oil		green	green	green	green	green	green	green	green	green	yellow	yellow	green
	5	MK-BFS-FA (Ukr)	Shellspirax oil		green	red	green	green	green	green	green	green	green	yellow	yellow	green
	6	MK-BFS-FA (metamax-Ecotrade-FA IT)	Nevastane oil		green	red	green	red	green	green	green	orange	green	yellow	green	green
	7	MK-BFS-FA (metamax-Ecotrade-FA IT)	Shellspirax oil		green	red	green	red	green	green	green	orange	green	yellow	green	green
	8	MK-BFS-FA (metamax-Ecocem-FA IT)	Nevastane oil		green	green	green	green	green	green				green	green	yellow
	9	MK-BFS-FA (metamax-Ecocem-FA IT)	Shellspirax oil		green	green	green	green	green	green	green	green	green	green	green	yellow
	10	BFS + Sand	Nevastane oil		green	red	green	green	green	green	green	green	green	green	green	green
	11	BFS + Sand	Shellspirax oil		green	red	green	green	green	green	green	green	green	green	green	green
TBP-dodecane	12	MK - Metamax	TBP-Dodecane (70-30)		green	green	green	green	green	red	green	green	green	green	green	green
	13	MK - Argicem	TBP-Dodecane (70-30)		green	green	orange	green	green	orange	green	green	green	green	green	green
	14	MK-BFS-FA (metamax-Ecocem-FA IT)	TBP-Dodecane (30-70)		green	red	green	green	red	green				green	green	green
scintill cocktails	15	MK-BFS-FA (MK-BFS-FA IT)	scintill		orange	green	green	green	red	green	yellow	green	orange	yellow	yellow	yellow
	16	MK - Metamax	scintill INSTAGEL plus		green	green	green	green	red	green	yellow	green	green	yellow	yellow	yellow
	17	BFS + Sand	scintillation cocktail (UG AB)		green	green	green	red	green	green	yellow	green	green	yellow	yellow	yellow

Criteria	Range	Colour	Priority	
WL (% vol.)	≥30	green	High	!
	≥20	orange		
	<20	red		
Surfactant	Y	red	Medium	•••
	N	green		
Bleeding	N	green	High	!
	Y <1%	orange		
	Y >1%	red		
Supplying materials	easy	green	High	!
	difficult	red		
Robustness	tested	green	Medium	•••
	not tested	red		
Heat release	high	red	Medium	•••
	medium	orange		
	low	green		
	not tested	yellow		
Setting time	3 < t (h) < 48	green	High	!
	<3 or >48	red		
Compressive strenght	>10	green	High	!
	5 < Rc < 10	orange		
	< 5	red		
Workability	good	green	High	!
	bad	red		
Viscosity	< 1000 mPa.s	green	High	!
	not tested	yellow		
Calorimetric data	available	green	Medium	•••
	not available	yellow		
Flexural strenght	>1MPa	green	Medium	•••
	<1MPa	red		
	not tested	yellow		

PREDIS

T5.3 – MK formulation

Geopolymer formulations tested:

2 x metakaolin powders of varying chemical and physical properties:

Flash & Rotary Calcined MK with K Silicate/KOH activator:

MetaMax® - RC, SiO_2 = 51.48%, Al_2O_3 = 43.99%, D_{50} = 3 µm, Fineness = 3843 m²/kg

Argicem® - FC, SiO_2 = 73.79%, Al_2O_3 = 19.97%, D_{50} = 41 µm, Fineness = 670 m²/kg

K Silicate – K120, K_2O = 21.3%, SiO_2 = 30.38%, H_2O = 48.32% (SiO_2:K_2O = 2.23)

KOH – Pure flakes supplied by Fisher Scientific

RLOW Surrogates:

Nevastane EP 100 oil – Viscosity at 25°C - 2.2 Pa·s

TBP – subsequently TBP/Dodecane (70/30 vol/vol) –

Viscosity at 25°C – Dodecane = 0.0018 Pa·s, Tween 80 = 0.4 Pa·s , TBP= 0.0036 Pa·s

---

Based on baseline study for each geopolymer the following molar ratio envelope was tested:

- MetaMax GP
  - SiO_2:K_2O (1.0 – 1.4)
  - K_2O:Al_2O_3 (1.0 – 1.5)
  - H_2O:K_2O (11 – 15)

- Argicem GP
  - SiO_2:K_2O (1.0 – 1.4)
  - K_2O:Al_2O_3 (1.0 – 1.35/1.5)
  - H_2O:K_2O (11 – 14/15)
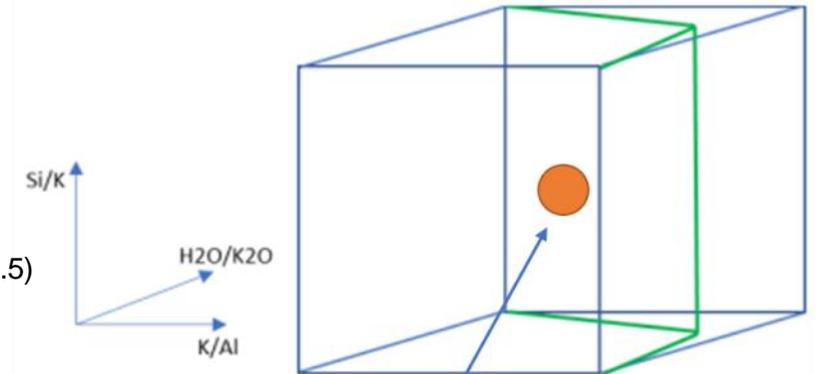
Mid-point formulation:
SiO_2:K_2O = <u>1.2</u> K_2O:Al_2O_3 = <u>13</u> H_2O:K_2O =<u>1.2</u>

Retardation and segregation of Argicem system at high water, high K/Al ratio point, required adjusted formulation envelope

T5.3 – MK formulation_
NNL Mixing Regimes at 4L scale

TBP/Dodecane trials

Nevastane trials

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

Mid-point formulation

Shear type	Oil loading (vol%)	Grout Temp at t=0 (°C)	Colflow Fluidity at t=0 (mm)	Viscosity descending (mPa·s)		Bleed (vol%)		Initial set (h)		Final set (h)	
				ASTM C1749 at 100 s^{-1}	UK Acceptance at 106 s^{-1}	At 24 h	At 48 h	Greater than	Less than	Greater than	Less than
High	20	27.4	>1020	261	304	0.5	1.25	6	22.75	6	22.75
High	20	24.6	960	405	314	<0.25	1	NM	22	NM	22
High	20	25.2	1020	246	271	0.25	0.75	5.5	22.25	5.5	22.25
Low	20	27.2	990	257	286	0.25	1	4	20.75	4	20.75
Low	20	21.0	>1020	207	279	<0.25	1	5	23	5	23
Low	20	21.2	>1020	204	280	<0.25	0.5	4.5	21.75	4.5	21.75
High	40	24.1	540	615	576	0	0.75	5	22.75	5	22.75
High	50	23.2									
Low	50	20.0	380	919	999	0	0.25	5	22	5	22

- Encapsulation of **up to 50 vol% loading** achieved

- **Low viscosity grouts** produced with good fluidity, **viscosity increased/fluidity decreased with increased oil loading**

- **Less than ≤1.25 vol% bleed at 48 h** on successful mixes, at higher loadings (50 vol%) mixing methodology important

- Relatively **high heats of hydration at 25°C** for MetaMax GP mixes will require assessment on scale-up

- High heat of dissolution

- Heat output > typical UK PC formulations (~100 kJ/kg)

- Small second polymerisation peak

- Effect of shear and oil loading negligible
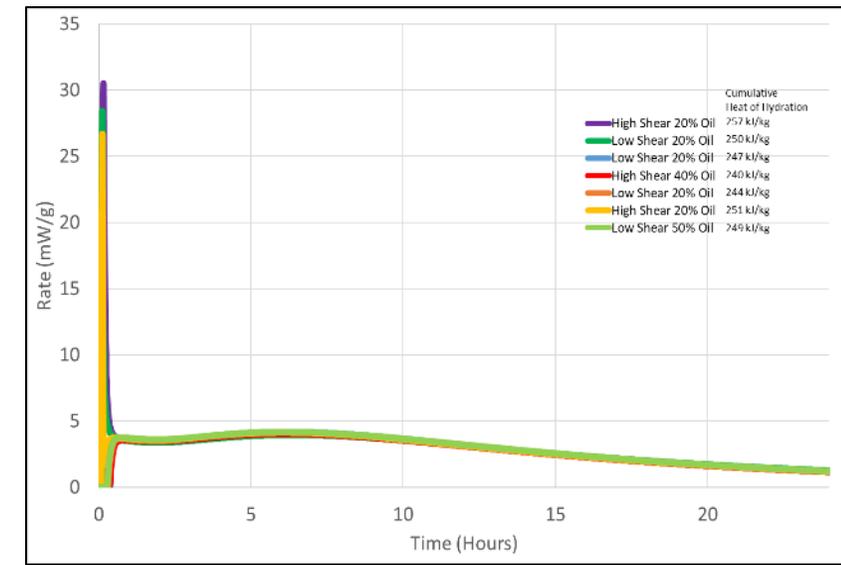
T5.3 – MK formulation_
MetaMax GP/Nevastane Product Properties

Compressive strength

Shear effects minimal (20% Loading)

Increased oil loading decreases strength (High Shear)
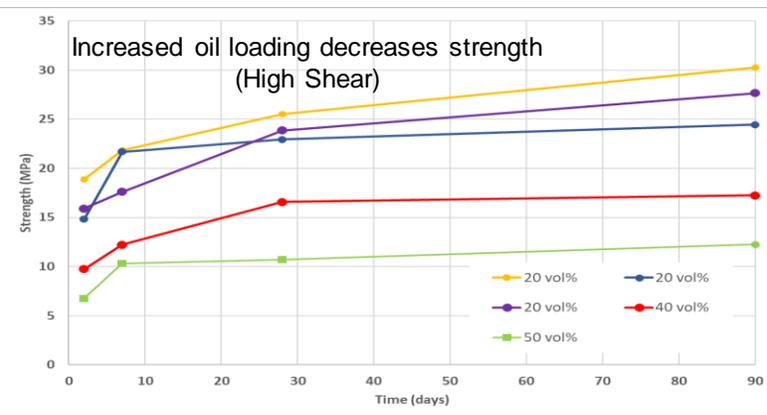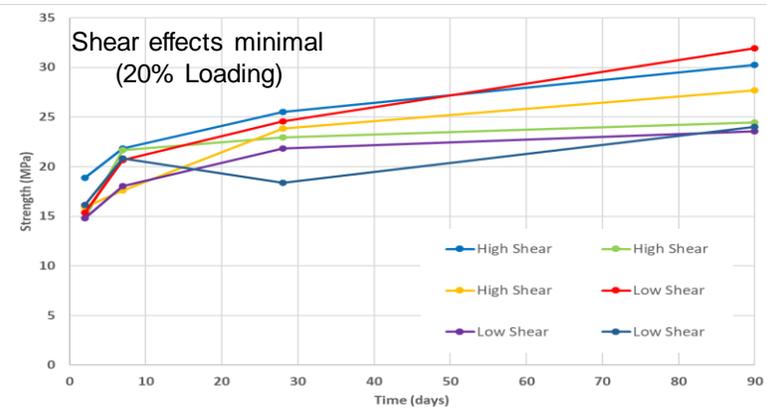
Flexural strength

Dimensional stability

- **Most compressive strength achieved by 7 d** – strengths acceptable

- **Flexural strengths >2 MPa** at 90 d curing

- Flexural strength **fluctuates over time at all oil loadings**

- **Small 0.03 - 0.11% shrinkage at 90 d** curing with negligible effect of shear for mid-point formulations

- Small number of formulations not stabilised at 90 d curing – **longer monitoring recommended**

MetaMax GP/TBP/Dodecane (70/30) Processing Results

Mid-point formulation

Mix No.	Surfactant loading (vol%) type	Oil loading (vol%)	Grout Temp at t=0 (°C)	Colflow Fluidity at t=0 (mm)	Viscosity descending (mPa·s)		Bleed (vol%)		Initial set (h)		Final set (h)	
					ASTM C1749 at 100 s^{-1}	UK Acceptance at 106 s^{-1}	At 24 h	At 48 h	Greater than	Less than	Greater than	Less than
507	2	20	25.1	500	539	490	0.5	1.25	4.0	20.7	4.0	20.7
515	2	20	25.2	550	545	484	<0.25	1	4.2	20.5	4.2	20.5
519	2	20	25.5	690	580	428	0.25	0.75	6.1	23.2	6.1	23.2

- **Tween 80** preferred surfactant of those trialled

- Encapsulation of up to 30 vol% loadings achieved with 1-3 vol% surfactant – **Mid-point only carried out at 20 vol% RLOW, 2 vol% surfactant**

- **Low viscosity grouts** produced <1000 mPa·s

- **Less than 1.25 vol% bleed at 48 h** on successful mixes

- Relatively **high heats of hydration at 25°C** for MetaMax GP mixes will require assessment on scale-up

Cumulative heat of hydration

1.2, 13, 1.2 20 vol% 2 vol% surfactant   247 kJ/kg
1.2, 13, 1.2 20 vol% 2 vol% surfactant   250 kJ/kg
1.2, 13, 1.2 20 vol% 2 vol% surfactant   248 kJ/kg

PREDIS
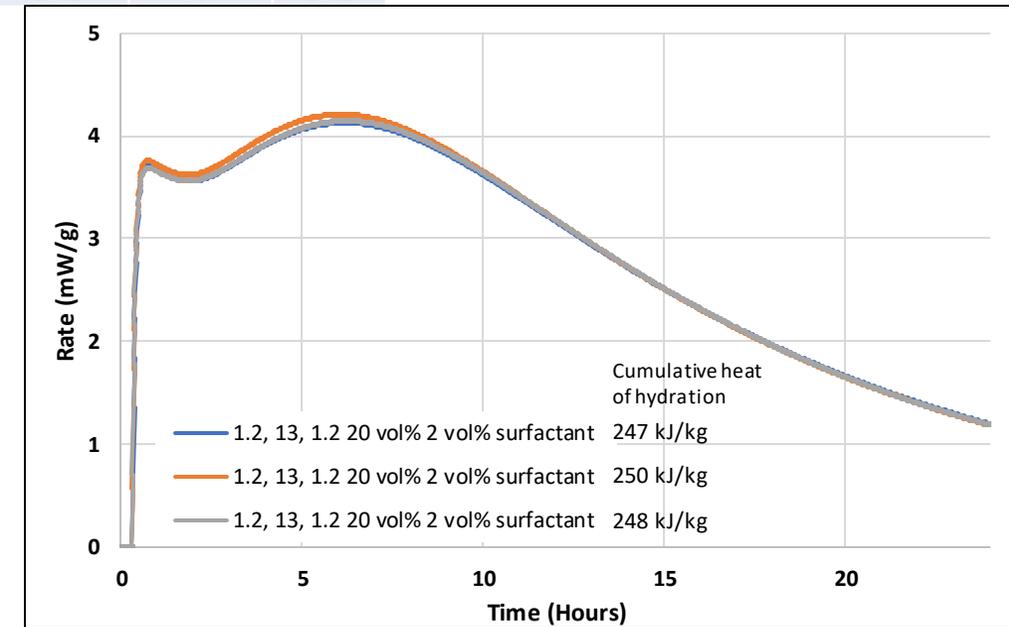
T5.3 – MK formulation_
MetaMax GP/TBP/Dodecane (70/30) Product Properties

Compressive strength
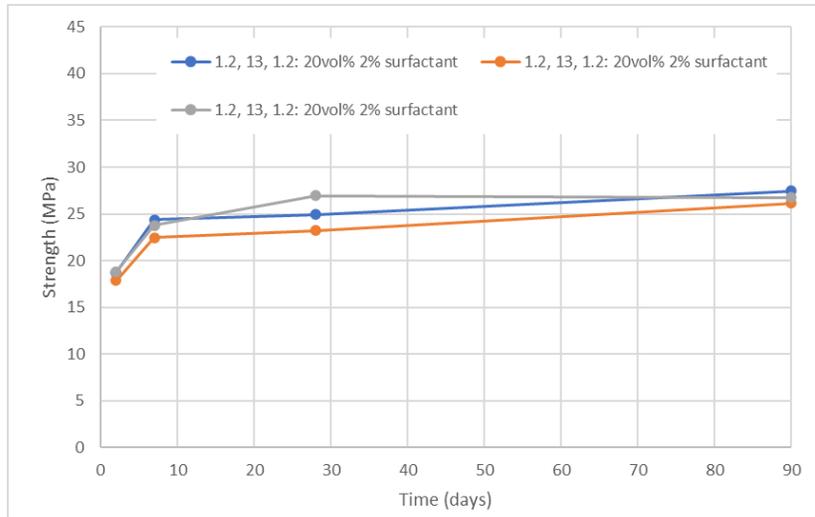
Flexural strength
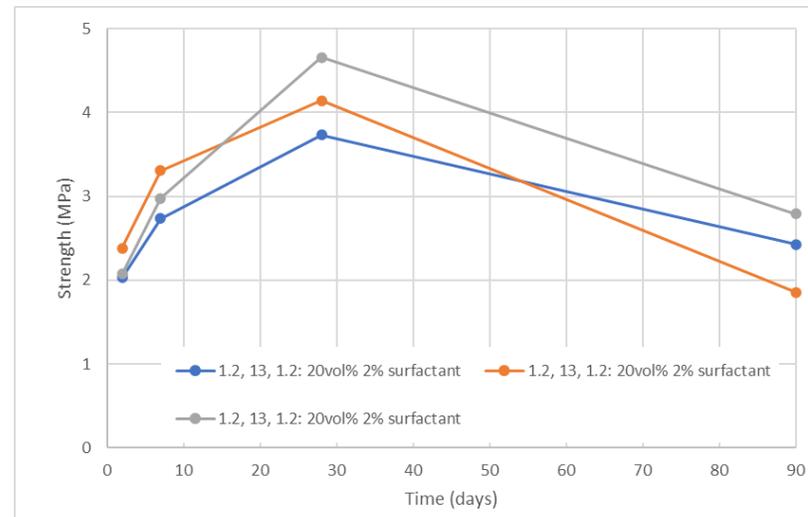
Dimensional stability
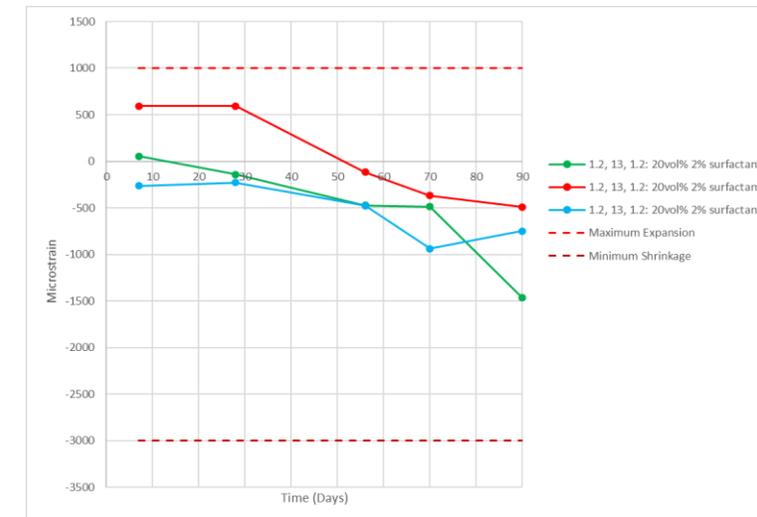
- Most strength gained by 7 d

- Mid-point formulations show reproducible strengths at 90 d

All strengths acceptable/typical GP performance

- 1.9-2.8 MPa at 90 days, considered acceptable but **drop from 28 to 90 d** - not observed in compressive strength

- **Shrinkage 0.05% - 0.15%** - within guidelines

- **Not reached stability over 90 d** although no obvious signs of loss of integrity

- **No evidence of organics expulsion** at 90 d curing

T5.3 – MK formulation_
MetaMax GP/Instagel sample preparation
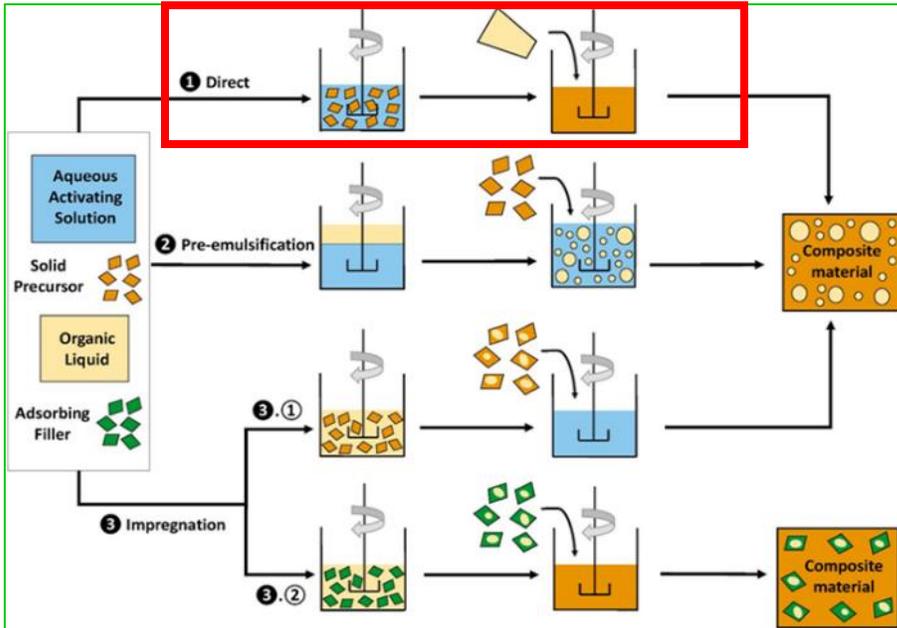
Procedure:
Geopolymer was prepared after 15 minutes of stirring in a planetary mixer. The activator was prepared 24 h before

Curing conditions:
In air at room temperature

RLOW Surrogates:
10 % - 30 % scintillation liquid Instagel plus
30 % - 40% Repsol Taurus Oil

- The mixture was **very liquid**
- The hardening time was similar as without waste, 4 h
- All the waste was immobilized. **No phase differences were observed**
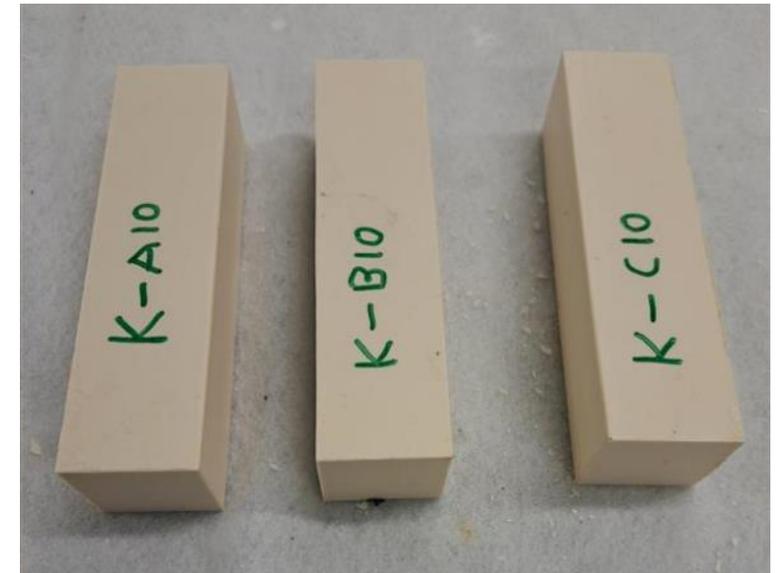
T5.3 – MK formulation_ MetaMax GP/Instagel Results

Compressive strenght
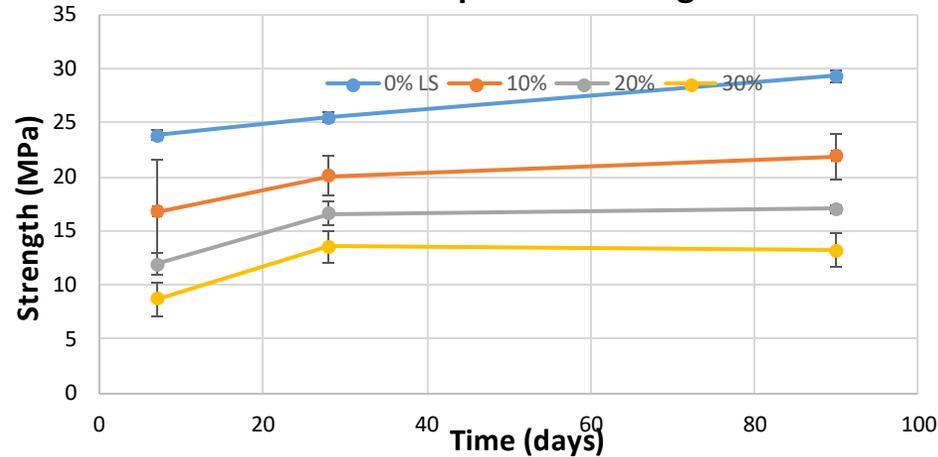
Leaching test - 30% Instagel
Leachate measurements in milliQ water
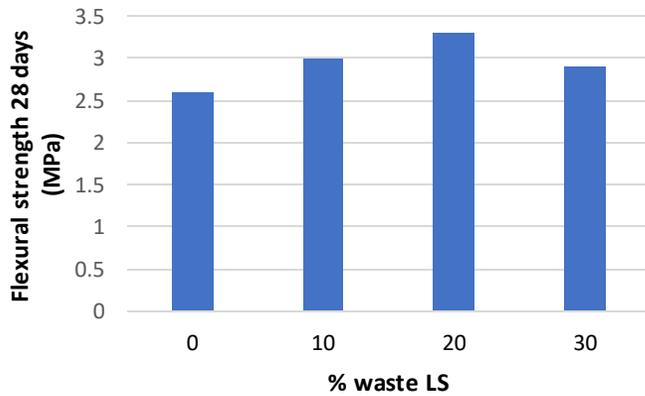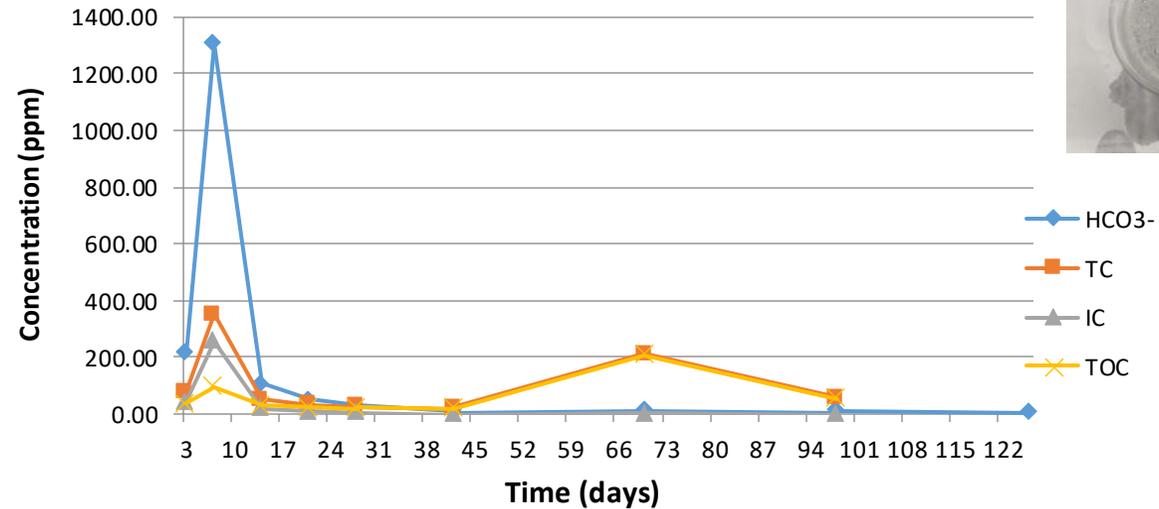
- **30% scintillation liquid was incorporated** with more than 10 MPa after 28 days of curing
- **Flexural strengths >2 MPa** at 28 d curing
- Leaching tests indicate that **samples containing scintillation liquid leach,** giving positive TOC values
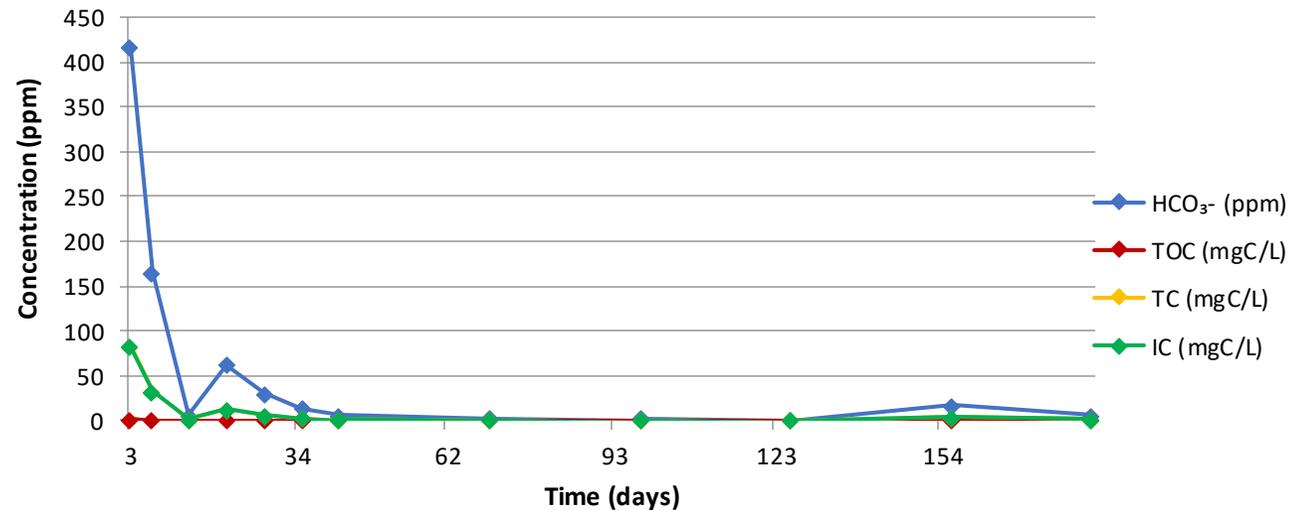- Samples with scintillation liquid **are not stable in water and appear cracks**

T5.3 – MK formulation_ MetaMax GP/Repsol Taurus Results

Compressive strenght
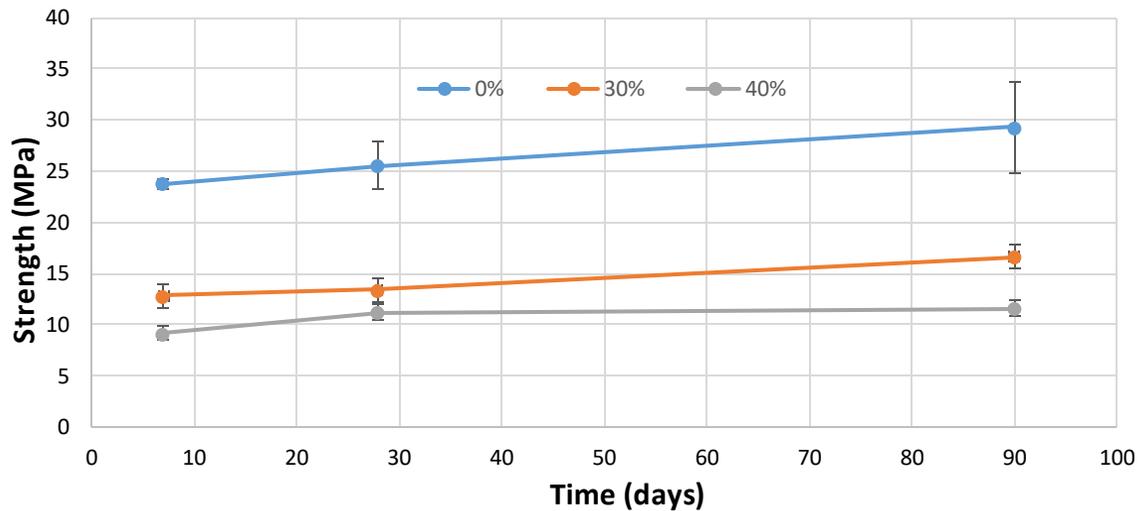
Leaching test - 40% oil
Leachate measurements in milliQ water

- **Stability over 90 d**

- **Not evidence of organics expulsion** at 28 d curing for more than 180 days of leaching test

T5.3 – BFS formulation

GGBFS (Ecocem Benelux)	Component											
	Loss of ignition	SiO_2	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Fe_2O_3
Content, wt. %	0.51	32.40	11.10	43.40	7.77	2.41	0.27	0.53	1.01	NA	NA	0.60

$Na_2O.2SiO_2 \cdot xH_2O$ (SILMACO, in powder form)	Component		
	H_2O	SiO_2	Na_2O
Content, wt. %	18.0	54.5	27.5

NaOH pellets (99% purity, VWR Chemicals)

River sand: <2 mm and density of 2.67 g/cm^3

Waste-forms

	Density (g/l)
Nevastane 100	**850**
Shellspirax	**885**
Tween 80	1060	→ surfactant

Reference mortars Fixed ~ 25wt.% river sand

Mortars	w/b*	SiO_2/Al_2O_3	SiO_2/Na_2O	H_2O/Na_2O
AAS 0.35	0.35	5.23	8.79	32.02
AAS 0.45	0.45	5.23	8.79	41.17
AAS 0.55	0.55	5.23	8.79	50.32

Waste-forms with oils
Trials

Mortars	Oil (wt.% of AAS mortars)	Tween 80 (wt.% of oil)
AAS 0.35		
AAS 0.45	10-25	3-8
AAS 0.55		

Ecocem BFS	RO BFS
Good workability and normal fluidity composition for all formulations	Good workability and normal fluidity composition for all formulations
Waste loading rates: up to 19%wt. for oil waste up to 10%wt. for liquid scintillator	Waste loading rates: up to 15%wt. for oil waste up to 9%wt. for liquid scintillator
Setting times ~ 18 hours	Setting times < 24 hours
Mechanical strength: between 5 -14 MPa for samples with oil waste	Mechanical strength: 5 - 6 MPa for samples with oil waste

Similar composition as Ecocem, but **the fineness of the BFS powder is important** – Ecocem much finer than Ro BFS (75µm)
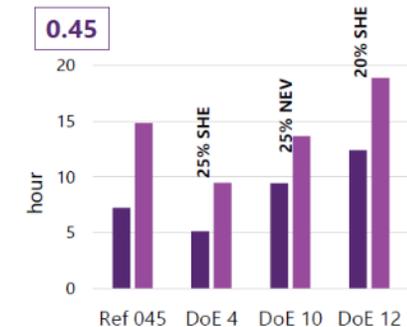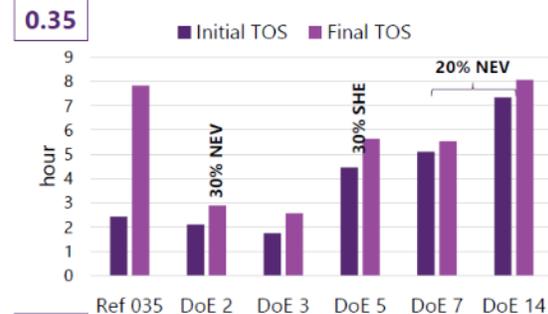
T5.3 – BFS formulation Results

After 1 day

w/b 0.35: 10 wt% oil | w/b 0.45: 20 wt% oil | w/b 0.45: 25 wt% oil | w/b 0.55: 20 wt% oil
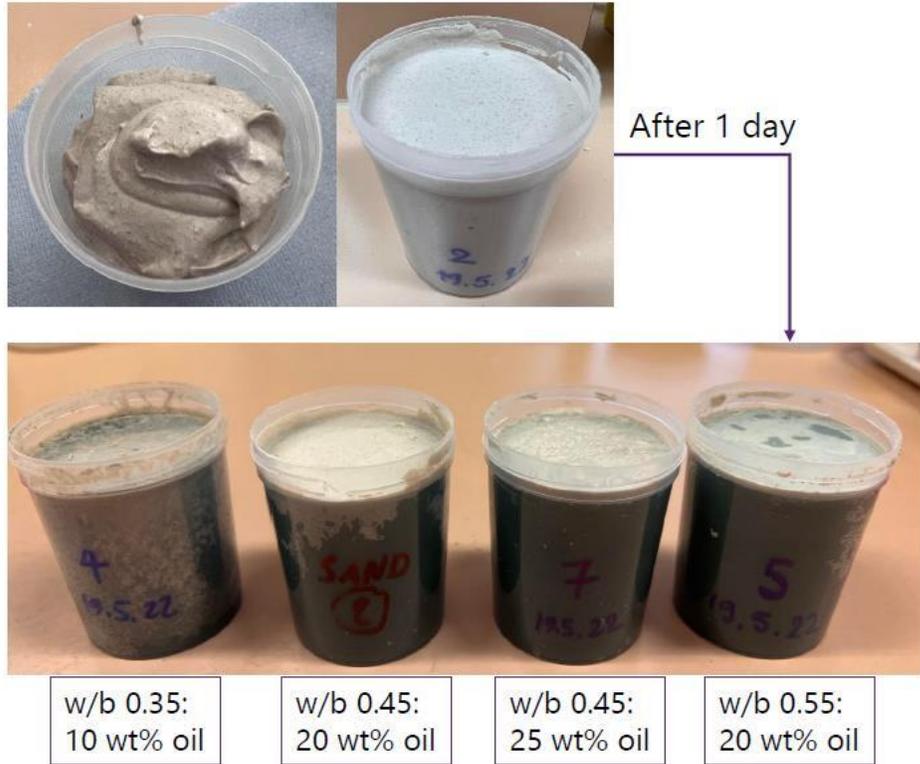
The oil mixed very well with AAS due to:

- Very **high viscosity** (100 mm^2/s at 40°C), high viscosity index (ISO VG of 111)
- Interact well with Tween 80 and geopolymers because of polar-heads (ester group)

Setting time

Sample ID	
High SS+NH	DoE 1
Low SS, high NH	DoE 2
Low SS, high NH	DoE 3
-	DoE 4
High SS, low NH	DoE 5
Low SS, high NH	DoE 6
Low NH	DoE 7
Low SS, low NH	DoE 8
High NH	DoE 9
-	DoE 10
High SS, low NH	DoE 11
Low SS+NH	DoE 12
High SS	DoE 13
High SS+NH	DoE 14
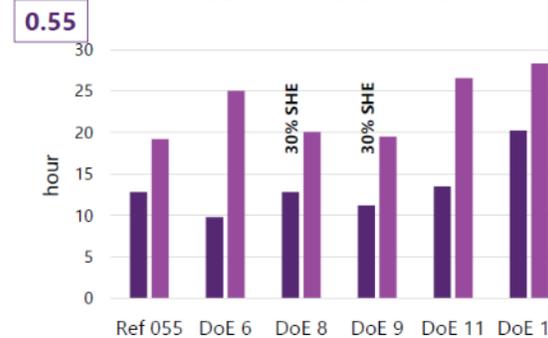
- The **w/b ratio** is the **main factor** affecting the setting time
- Alkaline activating concentration affects significantly the setting time: **high NH shortens** the setting while **high SS extends** the setting
- Oil type effect: **NEV** makes the setting **longer than SHE**
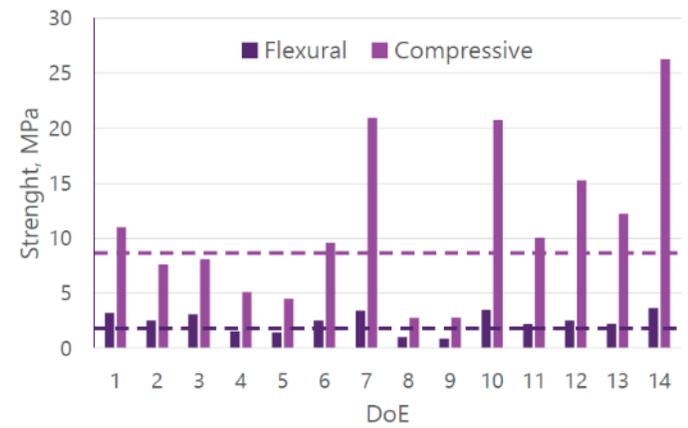- The effect of **waste loading is not significant**

T5.3 – BFS formulation Results
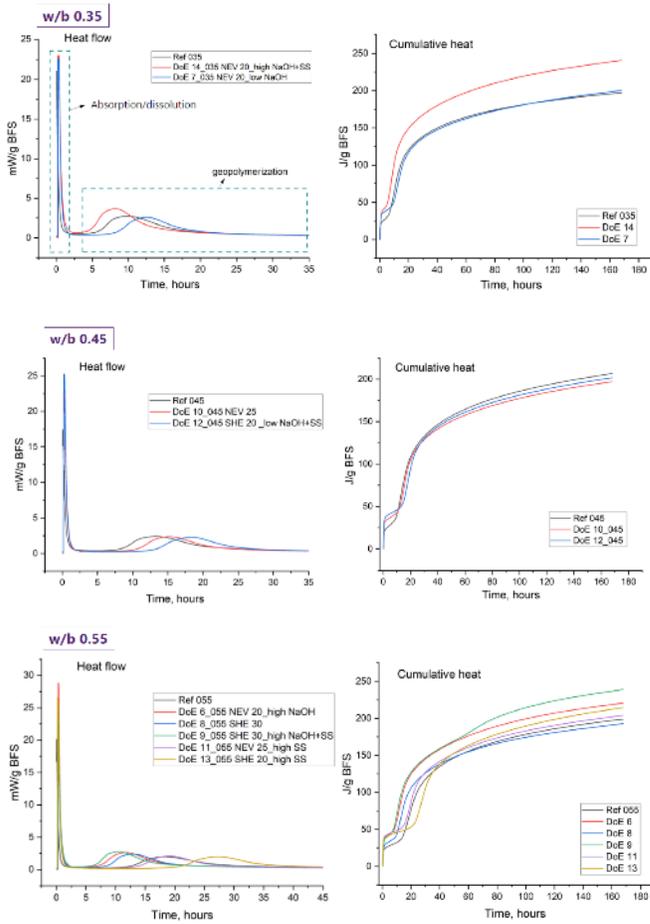
Heat release: Isothermal calorimetry

- The appearance of **oil delayed the geopolymerisation**

- **Oil** seems **not affect much the heat release** after ~7 days

- **High alkaline content accelerated** the geopolymerization and then heat release

Mechanical strengths

High SS+NH	DoE 1	0.45	30	3	NEV
Low SS, high NH	DoE 2	0.35	30	5	NEV
Low SS, high NH	DoE 3	0.35	25	3	SHE
-	DoE 4	0.45	25	4	SHE
High SS, low NH	DoE 5	0.35	30	4	SHE
Low SS, high NH	DoE 6	0.55	20	4	NEV
Low NH	DoE 7	0.35	20	3	NEV
Low SS, low NH	DoE 8	0.55	30	3	SHE
High NH	DoE 9	0.55	30	5	SHE
-	DoE 10	0.45	25	4	NEV
High SS, low NH	DoE 11	0.55	25	5	NEV
Low SS+NH	DoE 12	0.45	20	5	SHE
High SS	DoE 13	0.55	20	3	SHE
High SS+NH	DoE 14	0.35	20	5	NEV

- **Flexural strength**: higher than 2 MPa for most of the cases
- **Compressive strength**: higher than 8 Mpa for most of the cases with low WL and/or NEV oil
- The **strength** was **affected** much **by the w/b ratio and waste loading**

T5.3 – MIX formulation

Materials

KIPT Composition	wt.%
Fly ash (Ukr)	**34**
Slag (Ukr)	**20**
Metakaolin (Ukr)	**14**
Waterglass solution (UKRSILL 32)	**11**
KOH	9
H_2O	12
Water/binder	*0,23*
SiO_2/K_2O	*0,73*

Different Raw materials tested by CEA and NUCLECO

- Fly Ash: from Italy

- BFS (2 different types): ECOCEM (CEA) – ECOTRADE (NUCLECO) from France

- Metakaolin: Metamax (BASF)

- Waterglass solution (Betol K 5020 T)

Water/binder: 0,30

SiO_2/K_2O: 0,73

RLOW Surrogates:
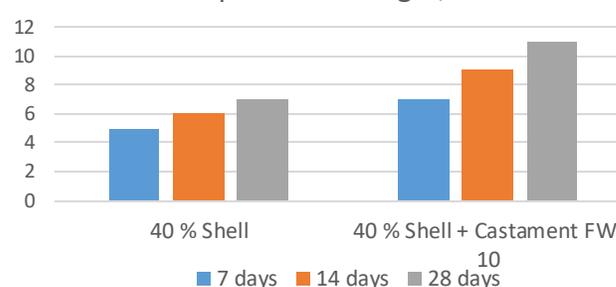- Nevastane EP 100 oil
- Shellspirax oil

T5.3 – MIX formulation Results

Compressive strength, MPa

Legend: ■ 7 days ■ 14 days ■ 28 days (categories: 10 % Shell, 10 % Nevastane, 20 % Shell, 20 % Nevastane, 30 % Shell, 30 % Nevastane)

Compressive strength, MPa

Legend: ■ 7 days ■ 14 days ■ 28 days (categories: 40 % Shell, 40 % Shell + Castament FW-10)

Rheology measurement

Legend: Paste without oil; Paste + 10% Shell Spirax; Paste + 20% Shell Spirax; Paste + 30% Shell Spirax; Paste + 40% Shell Spirax + 0,5% Castament FW 10
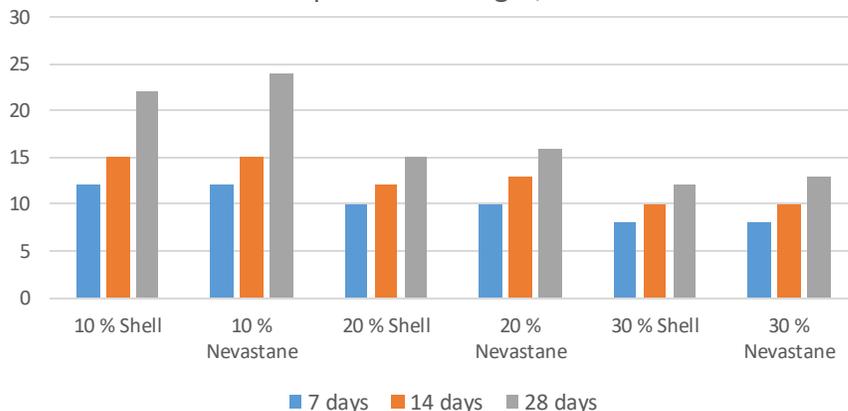
✓ **Up to 40 vol.%** of oil can be incorporated
✓ Tested materials show pseudoplastic behavior: **decreasing viscosity by increasing shear rate**
✓ **Viscosity o**f the paste (shear stress) **increase with the increasing of oil content**
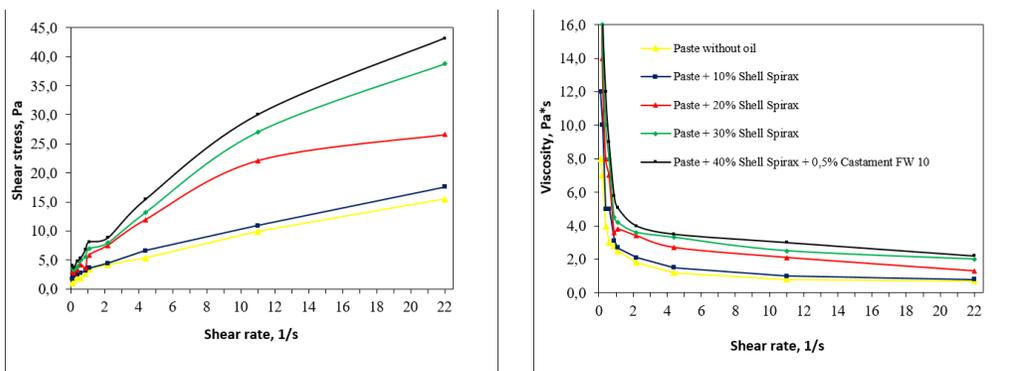
✓ The geopolymer paste with 40 vol.% of oil is the most structured (possible formation of pores). The use of **surfactant** (Castament 0,5%) **improves fluidity** (decreases viscosity) and provides quality samples **without large pores**
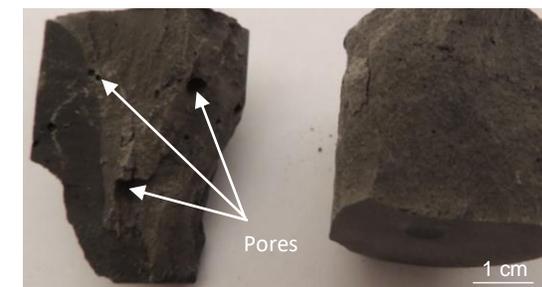
40% oil without (left) and with (right) surfactant

Parameter		Shell/Nevastane oils content, vol.%				
		10	20	30	40	40 + 0,5 % Castament FW 10
Setting time, h	Start	3/3	4/3	4/4	5/4	4/-
	finish	22/20	22/20	24/24	36/24	24/-
Density, g/cm³		2,10/2,12	1,96/1,98	1,88/1,90	1,65/1,8	1,82/-

T5.3 – MIX formulation Results

Robustness Nevastane oil
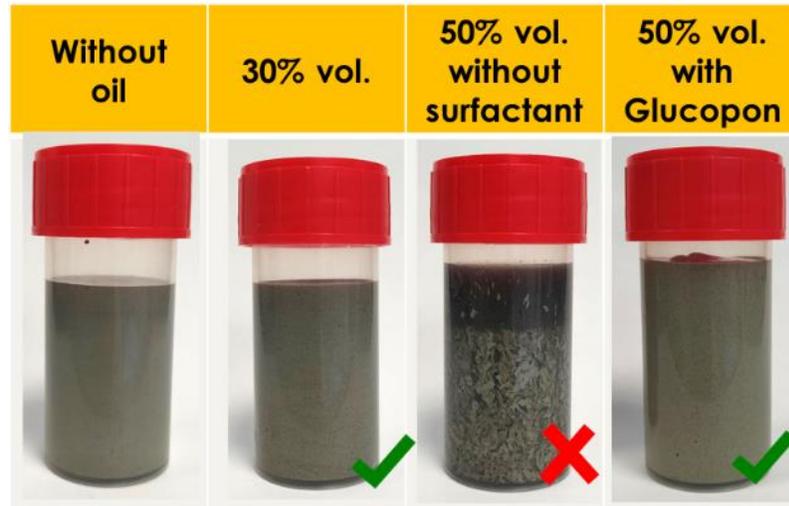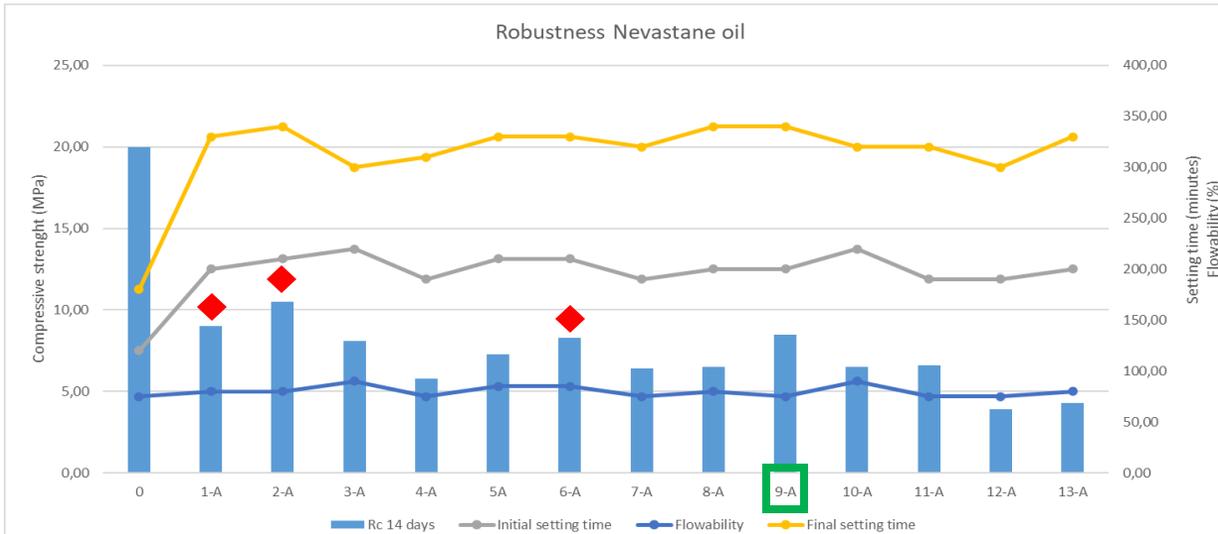
Without oil
$98^{\pm3}$ MPa

With 30% Nevastane
$33^{\pm2}$ MPa

Nucleco

- Robustness tests by varying recipe parameters by ± 2% (oil 30% vol.)
- Different Raw materials (BFS, MK, FA compared to KIPT and only BFS compared to CEA):
  - **Need for surfactant** (0,5% of SLS) to obtain workable samples
  - **Decrease in mechanical strength** (BFS Ecotrade)
- Bleeding observed in some formulations (+2% KOH)

CEA

- Nevastane EP100 (30% vol.) can be easily **incorporated without surfactant**
- The **mixing system has a crucial role** on the emulsification process
- **Storage conditions play a crucial role** on the mechanical properties (Temperature & relative humidity)

T5.3 – On-going work

Task 5.3.4 - Investigation of reference formulations with real ROLW

Consolidation and validation of the optimized reference formulations trough active tests with real liquid organic waste. It will be ascertained if the properties of the final matrix are affected by a real RLOW (by virtue of radionuclides and/or organic by-products content and/or other physical/chemical properties difference).

T5.3 – On-going work

Task 5.3.5 - Investigation of direct conditioning process scale-up

Consolidation and validation of the optimized reference formulations trough inactive preliminary scale-up tests to investigate the feasibility of the scale-up, study the influence of the mixing technology used to produce the fresh grout, ascertain if the properties of the final matrix are affected by scale-up of operation.

Isothermal calorimeter

Lab to drum scale
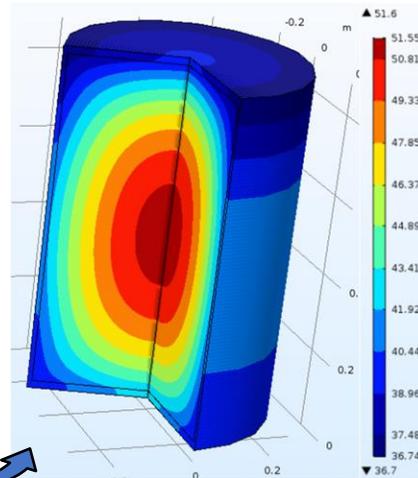
THANKS TO T5.3 PARTNERS

PREDIS   Thanks for your attention

Task 5.3
Conditioning of RLOW via pre-impregnation

PREDIS 4ᵗʰ Workshop
25ᵗʰ May 2023

Andrea Santi

Michele Brini, Eros Mossini, Gabriele Magugliani,
Elena Macerata, Marco Giola, Mario Mariani

Impregnation approaches

1) Impregnation

+

RLOW   ABSORBER   IMPREGNATED RLOW

2) Encapsulation

+

IMPREGNATED RLOW   MATRIX   WASTE FORM

VARIABLES

RLOW (TYPE, AMOUNT)
ABSORBER (TYPE, AMOUNT)
MATRIX (TYPE, AMOUNT, RHEOLOGY)

PARAMETERS

RLOW/ABSORBER RATIO
RLOW LOADING FACTOR
IMPREGNATION-ENCAPSULATION ORDER

Pre-impregnation with recycled polyurethane

- **Materials**
  - Waste: scintillation cocktail (UG) and tributyl-phosphate/kerosene (TK) mixture
  - Absorber: recycled polyurethane
  - Matrix: tuff-based geopolymer
- **Operating conditions**
  - Waste-to-absorber: 1:1 and 2:1 mass ratio
  - Loading factor: 10 and 20 wt.%
 - Procedure: mixing of pre-impregnated waste in matrix fresh grout
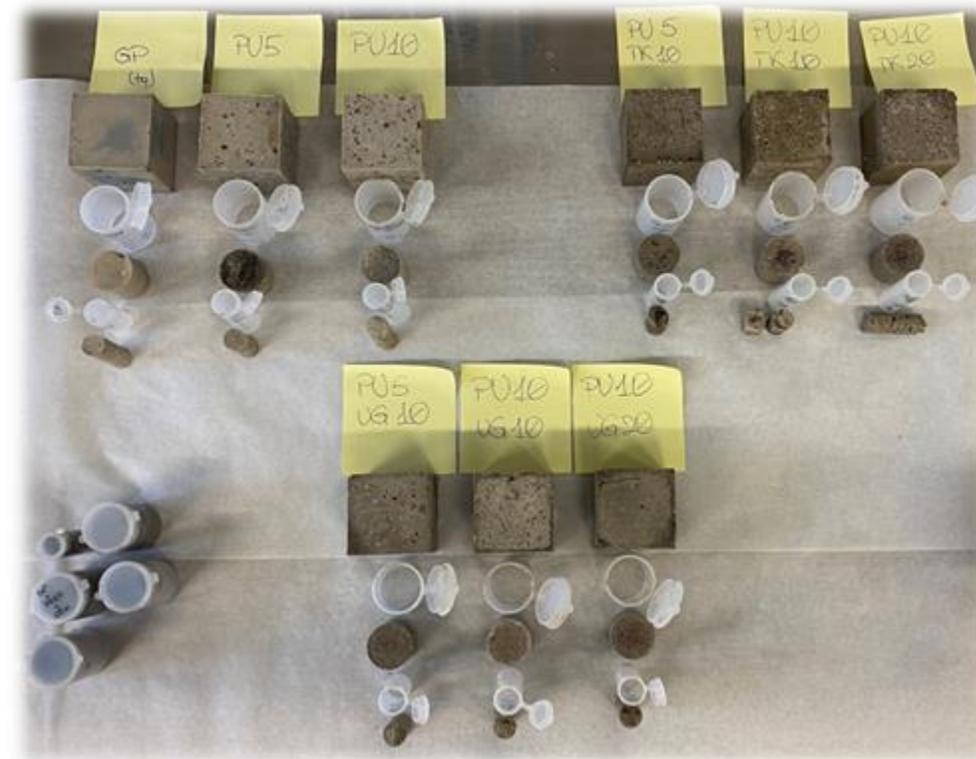
E. Mossini *et al*. «Pre-impregnation approach to encapsulate radioactive liquid organic waste in geopolymer» (under publication)

Pre-impregnation with recycled polyurethane

- Results
  - Swelling of fresh waste form → porous samples
  - Minor bleeding
  - Compressive strength < 2 MPa
  - Release of waste during immersion in water
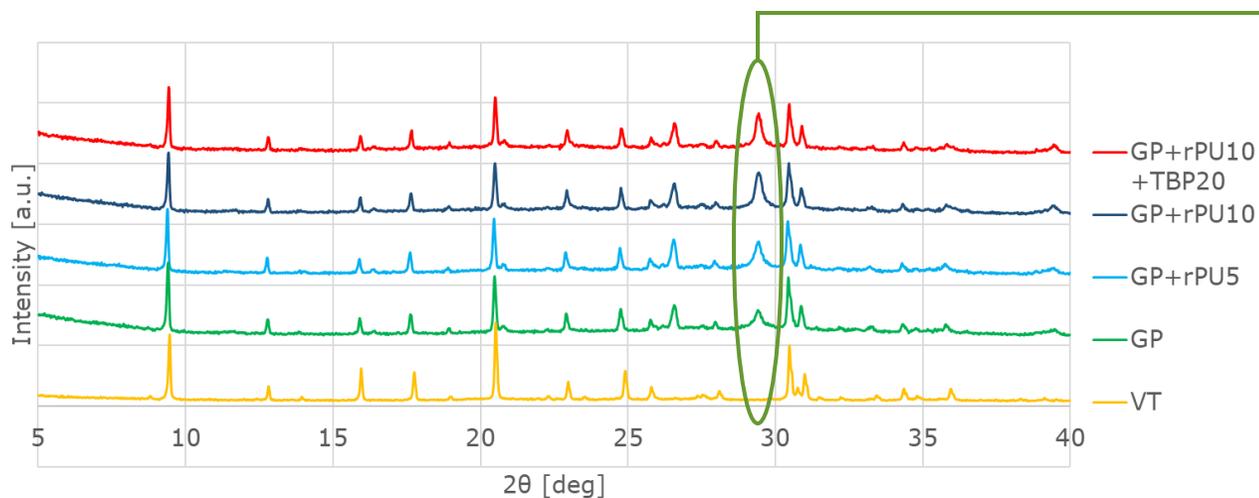
SODIUM CARBONATE PEAK

MATRIX-ABSORBER INCOMPATIBILITY
1) HYDROLYSIS OF URETHANE GROUPS
2) CARBONATION OF CO_2

Pre-impregnation with Nochar N910

- **Materials**
  - Waste: UG and TK
  - Impregnant: Nochar N910
  - Matrix: tuff-based and BFS-based formulation

- **Operating conditions**
  - Waste-to-impregnant: 3:1 mass ratio
  - Procedure: different orders of addition

Matrix	Technique	Loading Factor	Compressive Strength
Tuff-based	Impregnation	10 wt.%	~ 8 MPa
BFS-based	Impregnation	10 wt.%	~ 14 MPa
BFS-based	Emulsification	10 wt.%	~ 4 MPa

WP5 T5.4 – Study of matrix performances

PREDIS MAY 2023 WORKSHOP

MECHELEN, 25/05/2023

MATTHIEU BRIFFAUT (ECL : CENTRALE LILLE INSTITUT)

Objectives in terms of durability

- Capacity of the developed matrices (in WP5.3) to avoid RLOW release when immersed in a leaching solution :
  - Analysis of the leaching solution (global measurement)
  - Analysis of the matrix strength evolution (global measurement)
  - (Analysis of local matrix damage (indentation or permeability))

- Capacity of the developed matrices to resist high temperature

- Capacity of the developed matrices to resist irradiation

WP5 Progress

Active working months																																																		
				D Deliverable								**M** Milestone																																					
								Year 1								Year 2								Year 3								Year 4																		
WP 5	Innovations in liquid organic waste treatment and conditioning	**CEA**	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
T5.4	**Study of conditioning matrix performances**	**ECL&USFD**																																																
5.4.1	Definition of experimental protocols										**M**																																							
5.4.2	Study of conditioning matrix durability in endogeneous conditions																																																	
5.4.3	Study of conditioning matrix durability in aerated conditions																																																	
5.4.4	Study of conditioning matrix durability in acid & alkaline liquid lixiviation conditions																																																	
5.4.5	Study of conditioning materials behaviour under irradiation																																																	
5.4.6	Study of radionuclides binding and leaching																																																	
5.4.7	Study of Thermal behaviour & fire hazard																																																	
5.4.8	Synthesis of experimental results																																								**D**								
5.4.9	Disposability assessment																																										**M+D**					

- Definition of experimental protocols (materials, methods) - T5.4.1 (completed)

- Study of conditioning matrix durability in endogenous conditions - T5.4.2 (on-going)

- Study of conditioning matrix durability in aerated conditions - T5.4.3 (on-going)

- Study of conditioning matrix durability in acid & Alkaline liquid lixiviation - T5.4.4 (on-going)

- Study of conditioning materials behavior under irradiation - T5.4.5 (partially on-going)

- Study of radionuclides binding and leaching – T5.4.6 (on-going)

- Study of thermal behavior & fire hazard – T5.4.7 (work remaining to be performed by the end of the year)

Partners tasks involvements (organization)

Task	Formulation MK (NNL)	Formulation BFS (SCK-CEN)	Formulation MIX (KIPT)	RLOW surrogate
T5.3	CIEMAT + NNL/UoSF	RATEN + SCK-CEN	NUCLECO/SOGIN + KIPT	TBP Dodecane/scintill/oil
T5.4.2 to 5.4.4	CIEMAT + ECL/CEA	SCK-CEN/IRSN + CVRez	ENEA + SIIEG	TBP Dodecane/scintill/oil
T5.4.5	IMT + POLIMI			TBP Dodecane/scintill/oil
T5.4.6	UJV + POLIMI			TBP Dodecane/scintill/oil
T5.4.7	UNIPI			TBP Dodecane/scintill/oil

- Partners involved in T5.3 and T5.4
  - Easiest starting -> no take-up time

- Partners involved only in T5.4
  - Formulation robustness testing (raw materials and equipment)
  - Samples transport robustness

PREDIS

CIEMAT / MK FORMULATION

OIL and INSTAGEL immobilization (first results)

Metamax: Al_2O_3=45% SiO_2=51%
K-Betol: SiO_2=31,5% K_2O=20,5 H_2O=48%

Optimized formulation:
SiO_2:K_2O=1.2
K_2O:Al_2O_3=1.2
H_2O:K_2O=13

Procedure:
Geopolymer was prepared after 15 minutes of stirring in a planetary mixer. The activator was prepared 24 h before.

Oil immobilization
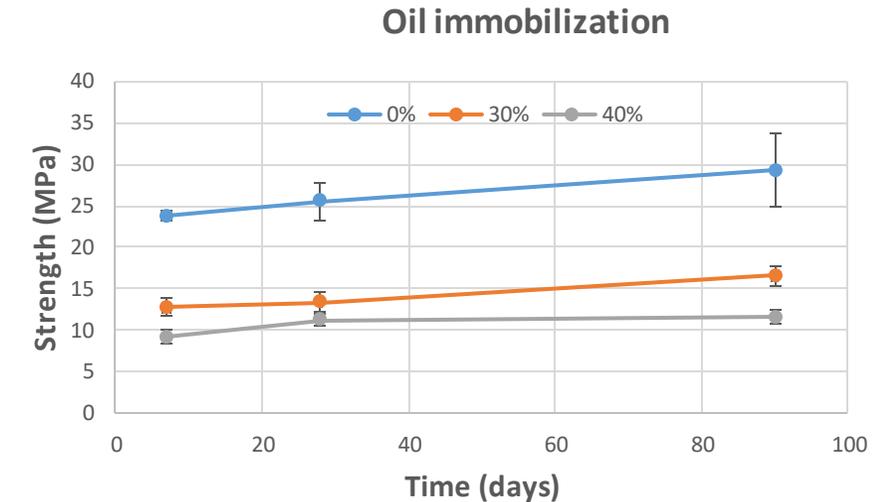
- Geopolymerization with this activator was highly exothermic
- The temperature reached was 46 °C at 4 h.
- Very fast setting
- No significant changes are seen with the introduction of OiL, similar times and T of setting.

CIEMAT / MK FORMULATION

OIL/INSTAGEL immobilization (first results of durability)

Instagel inmobilization
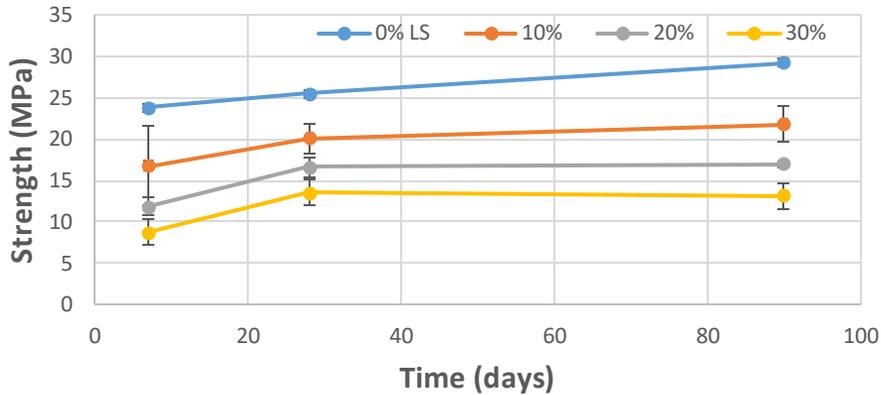
30% Instagel
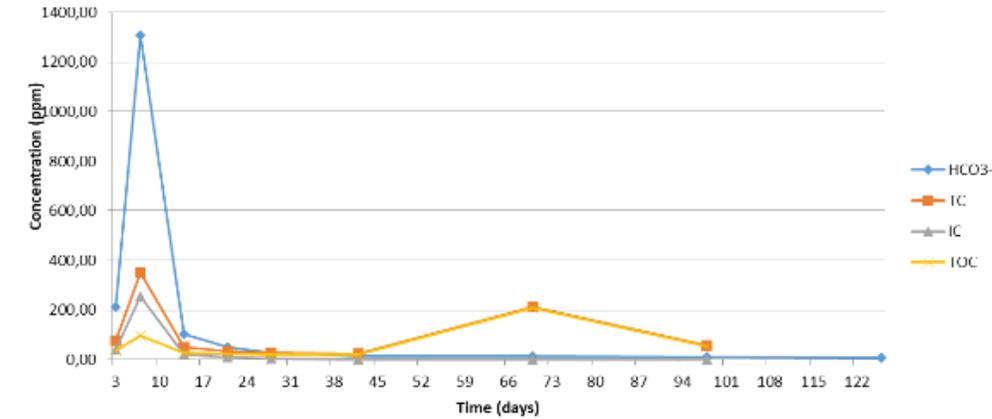
- Good mechanical strength results for both type of waste (negligible bleeding)

- Samples instability (cracking) when immersed in water (only after a drying)
- Oil release is observed in the case of Liquid scintillation samples

PREDIS

OIL (Nevastane) immobilization (first results of durability)

h = 3,3 cm

D = 2,7 cm
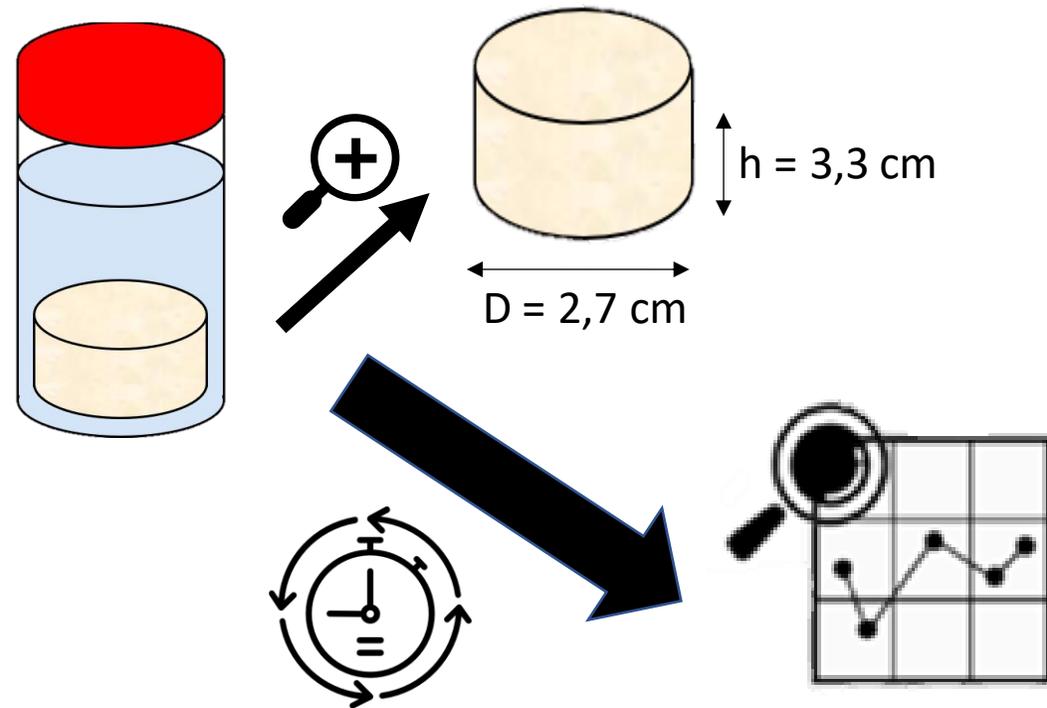
Solutions are periodically renewed :
3, 7, 14, 28, 56 & 90 days
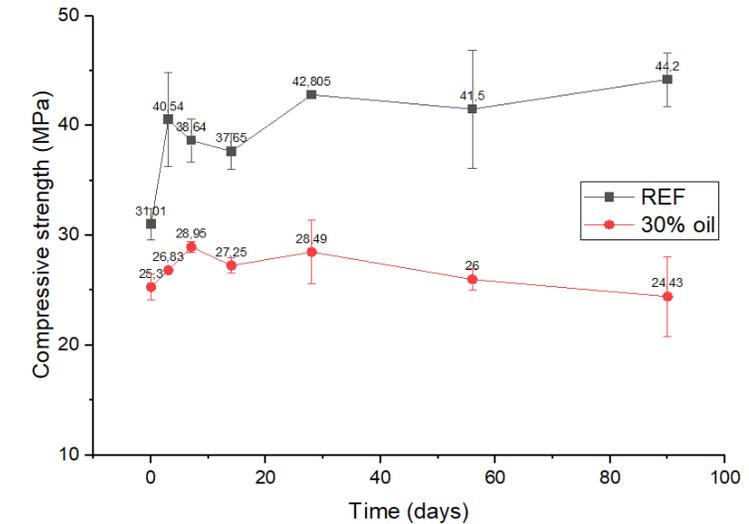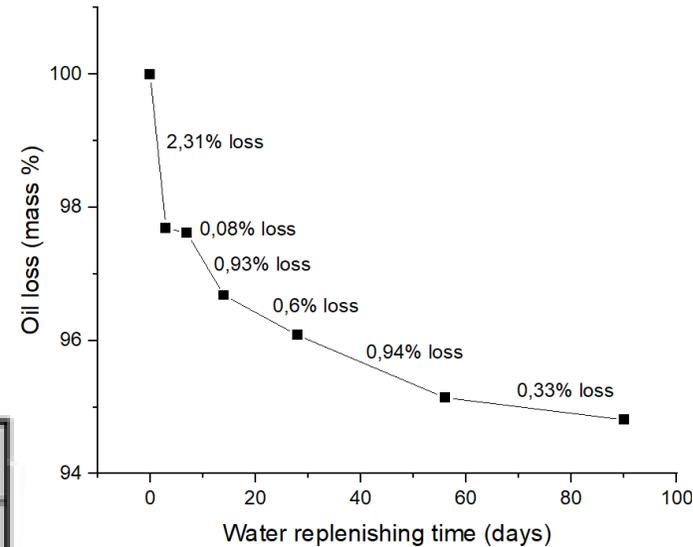
- Slight Oil release
- No effect of leaching on strength

PREDIS

OIL (Nevastane) immobilization (first results of durability)

- **No difference in crystalline phases** is observed before and after immersion (without oil : E and G or with oil : F and H

- The **amorphous hump does not seem to be shifted** towards lower diffraction angles

- XRD is executed on the outer layer of the sample leached (0-1 mm)

- Encapsulation seems to be more a physical phenomena that a chemical one

XRD pattern of reference and leached samples of GP. **E and G are with no oil**, **F and H are with 30% oil in volume**.
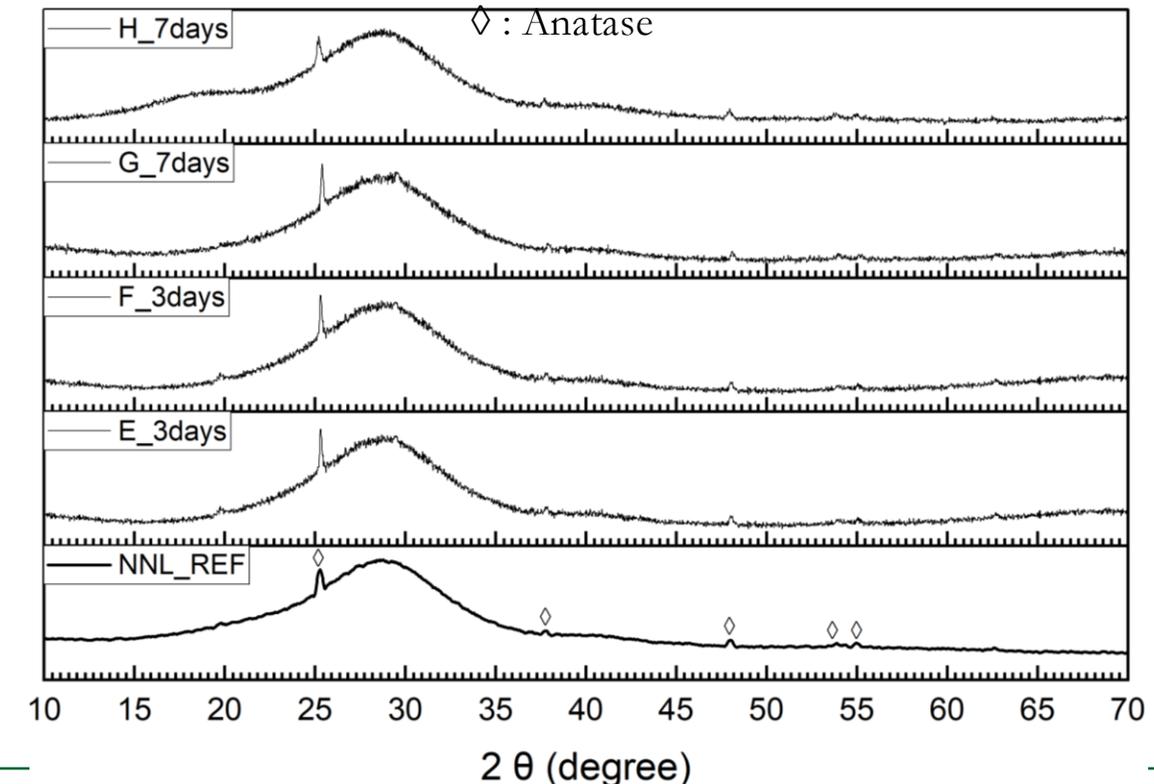
$\Diamond$: Anatase

2 θ (degree)

Turbine oil Mogul immobilization (first results)

BFS (SCK-CEN formulation) → materials: - BFS from SCK-CEN - BFS from CZ → Curing in different conditions: - dry - moist (sealed bag) → Bleeding tests Compressive strength

Sample characterisation → Leaching tests in demineralised water (day 2, 7, 14, 28, 56, 91) → - pH, conductivity - Si, Ca, Fe analysis - XRF analysis → Compressive strength - MTS 300 Exceed® -CSN EN 12390-3
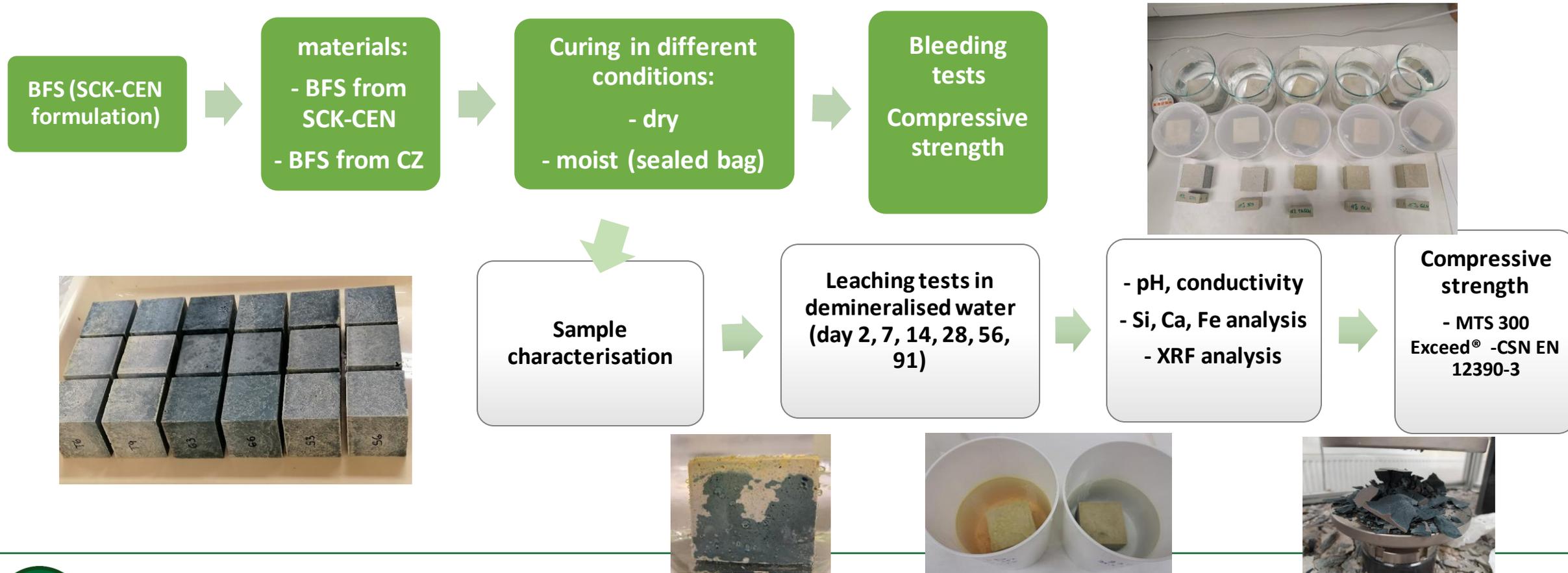
Turbine oil Mogul immobilization (first results)

- XRF : X-ray fluorescence

- Oil leaching
  - rapid decrease in the amount of oil leached from samples
  - no oil leaching after day 14
  - **less oil leaching at samples cured in a sealed bag**
- Decrease of leached Si from samples with time
  - significant difference between the samples cured in dry and wet conditions
- Increase of leached Ca from samples with time

48

Leaching in NH$_4$NO$_3$

	w/b	Waste vol. %	Oil
DoE 11	**0.55**	**25**	NEV
DoE 12	0.45	20	SHE
DoE 13	**0.55**	20	SHE
DoE 14	0.35	20	NEV

Leaching depth (28D), mm

DoE 11	DoE 12	DoE 13	DoE 14
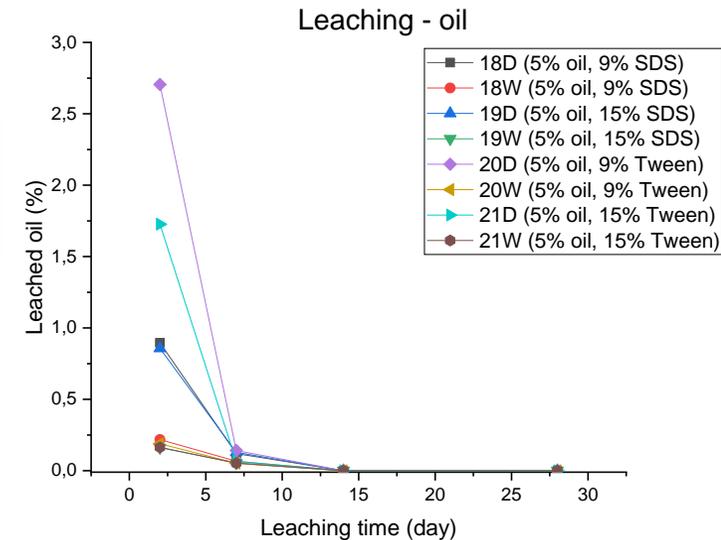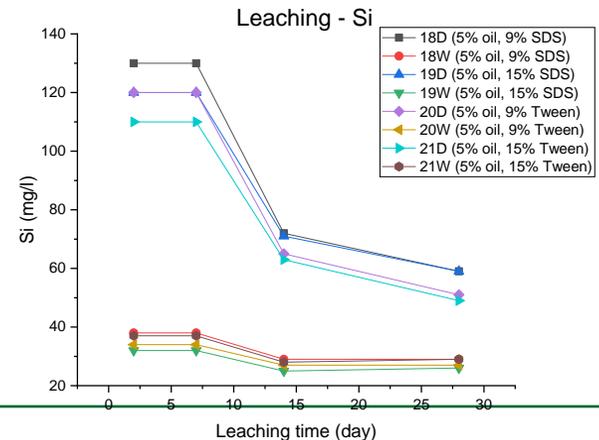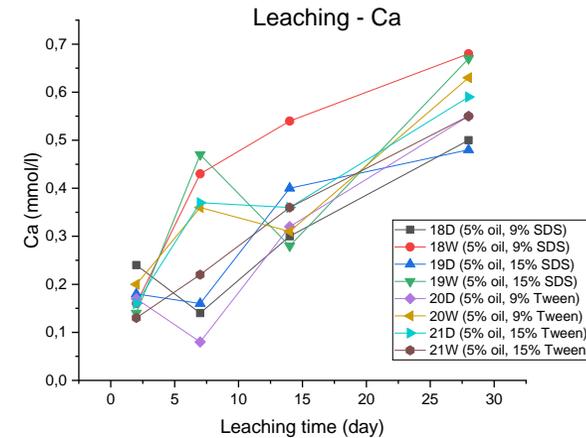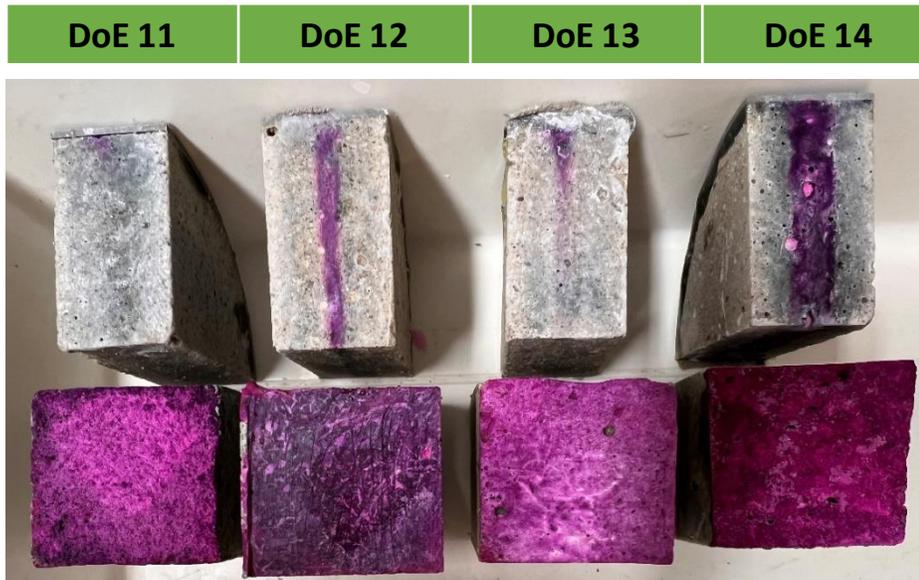
After 28d leaching

Before leaching

- Waste-forms are **more vulnerable** to leaching than AAS without oil
- Leaching resistance predominantly depends on **w/b ratio** and **waste loading**

49

Carbonation

| 0d | 7d | 14d | 28d |

DoE 11
NEV

DoE 12
SHE

DoE 13
SHE

DoE 14
NEV

$y = 1.8953x - 1.7083$
$R^2 = 0.9854$

$y = 3.1351x - 8.698$
$R^2 = 0.9797$

$y = 1.0093x - 0.8062$
$R^2 = 0.9741$

- Waste-forms with **SHE is more vulnerable** to carbonation than the waste-forms with NEV

- The higher waste loading and w/b ratio, the higher carbonation susceptibility

50

Matrix durability after irradiation

Emulsion:
Activation Solution + RLOW + Tween80

15 mins later
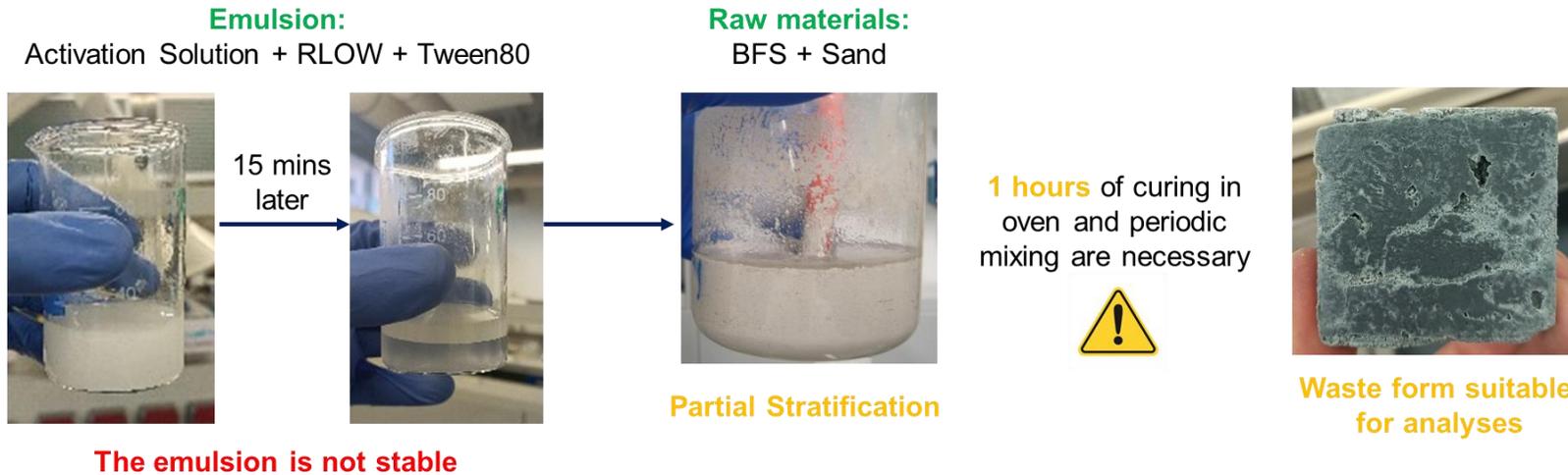
The emulsion is not stable

Raw materials:
BFS + Sand

Partial Stratification

1 hours of curing in oven and periodic mixing are necessary ⚠️

Waste form suitable for analyses

BFS-based formulation and protocol by **sck cen**

✓ **The emulsification step should be improved to avoid in-oven curing**

✓ Irradiations by **Co-60 source**

✓ Leaching following **ANSI-ANS**

✓ Release of matrix constituents, contaminants and organics

✓ Compression tests

Sample #A	Sample #B	Sample #C	Sample #D
Curing (28 d)	Curing (28 d)	Curing (28 d)	Curing (28 d)
Storage	Storage	**200kGy**	**200kGy**
Storage	**Immersion (28 d)**	Storage	**Immersion (28 d)**
Compression	Compression	Compression	Compression
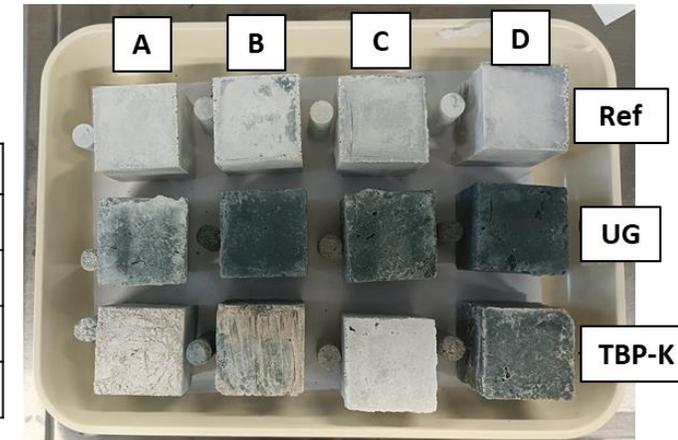
Matrix durability after irradiation

- R_c almost stable (around 50 MPa) following **irradiation at 200 kGy**.

- R_c reduced by about ≈20% following **2 months of water immersion** and >> 10 MPa.
  - ✓ **The compressive strength is poorly affected by irradiation and/or water immersion**

- R_c drops by ≈90% following high **organic liquid loading**.
  - ✓ **The compressive strength could compromised by RLOW loading**

- **Leachability indices of matrix constituents** (Ca, Na, K, Si, Al) **> 8** for reference and loaded samples.
- **Leachability indices of contaminants** (Cs, Sr, Ni, Co Ln, U, Th, …) **> 14** for reference and loaded samples.
- Irradiations does not affect contaminants and organics retention.
  - ✓ **The matrix resists to water immersion and irradiation.**

Durability after irradiation

Expected

$y = 4.5e\text{-}8\ x$

Result

$y = 1.98e\text{-}8\ x$

Figure: Cell test performed irradiating NaBr solution resulting   in confirmation of gas leakage from the cell.
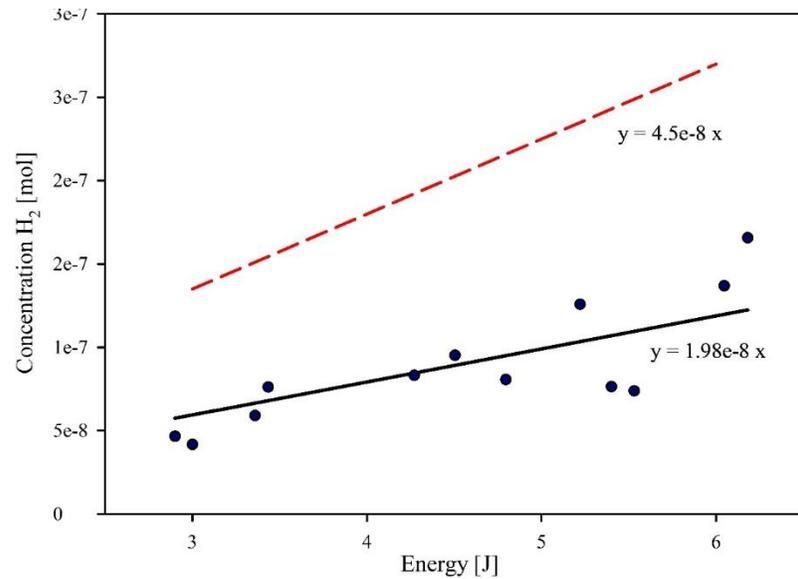
	Sample	Water [w%]	Dose [kGy]	H2 [ppm]
MK Based	GP Lille	17	8.39	7302
BFS Based	GP SCK-CEN (0.45)	17.7	9.18	11837
MIX Based	GP CEA	9.8	7.45	3133
	GP Rome	9.8	8.80	1933

Planned analyses

- Hydrogen release
- Morphology (XRD, SEM-EDX, Porosity)
- Mechanical Strength (Nano-Indentation)
- Leaching test
  (4 weeks – ICP and Ion chromatography)

First raw conclusions

- Curing conditions (endogenous or with drying) play a crucial role for :
  - Matrices stability (cracks) for MK based formulation
  - RLOW release rate for BFS based formulation
- Matrices (MK and BFS) seems unaffected by irradiation (< 200ky)
- Leaching solutions analysis (with different technics)
  - Oil release limited to the first day -> % threshold for incorporation?
  - Ions exchange with matrices -> consequences?

PREDIS

THANKS TO T5.4 PARTNERS

Thanks for your attention

PREDIS

WP5.3: robustness test

	Sample ID	SS (sodium silicate)	NH (NaOH)	WB (w/b ratio)	WL, Vol. % (waste loading)	SF, % (surfactant- Tween 80)	OIL type
High SS+NH	DoE 1	2.79	4.2	0.45	30	3	NEV
Low SS, high NH	DoE 2	2.59	4	0.35	30	5	NEV
Low SS, high NH	DoE 3	2.59	4.2	0.35	25	3	SHE
-	DoE 4	2.69	4	0.45	25	4	SHE
High SS, low NH	DoE 5	2.79	3.8	0.35	30	4	SHE
Low SS, high NH	DoE 6	2.59	4.2	0.55	20	4	NEV
Low NH	DoE 7	2.69	3.8	0.35	20	3	NEV
Low SS, low NH	DoE 8	2.59	3.8	0.55	30	3	SHE
High NH	DoE 9	2.69	4.2	0.55	30	5	SHE
-	DoE 10	2.69	4	0.45	25	4	NEV
High SS, low NH	DoE 11	2.79	3.8	0.55	25	5	NEV
Low SS+NH	DoE 12	2.59	3.8	0.45	20	5	SHE
High SS	DoE 13	2.79	4	0.55	20	3	SHE
High SS+NH	DoE 14	2.79	4.2	0.35	20	5	NEV
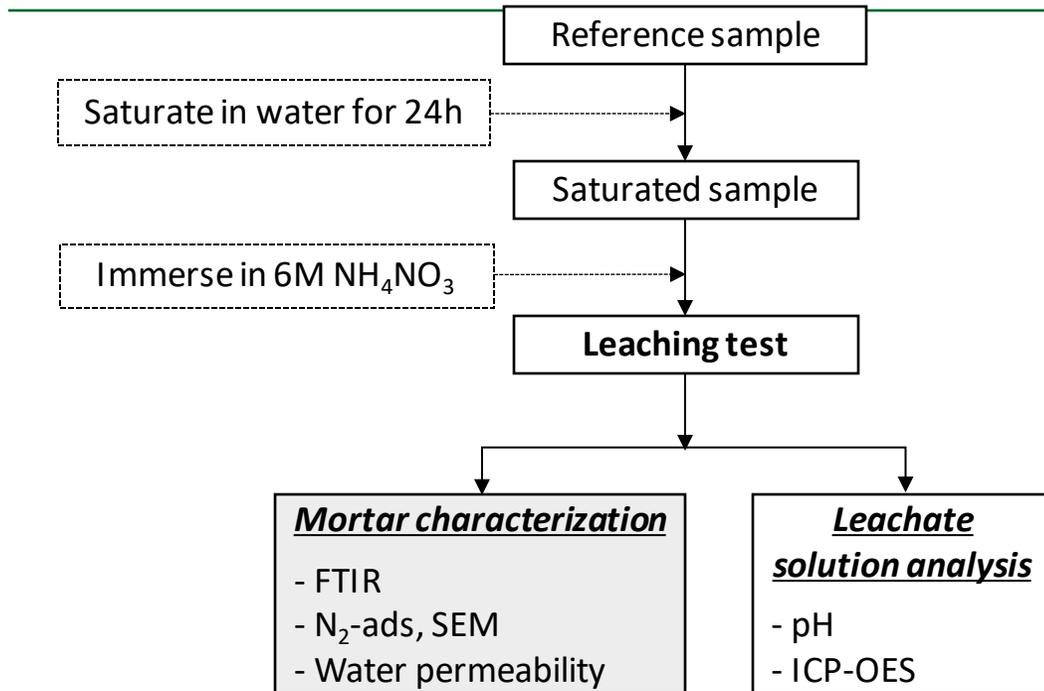
1. Magnetic stirrer
2. NH_4NO_3 vessel
3. N_2 gas line
4. Bubbler
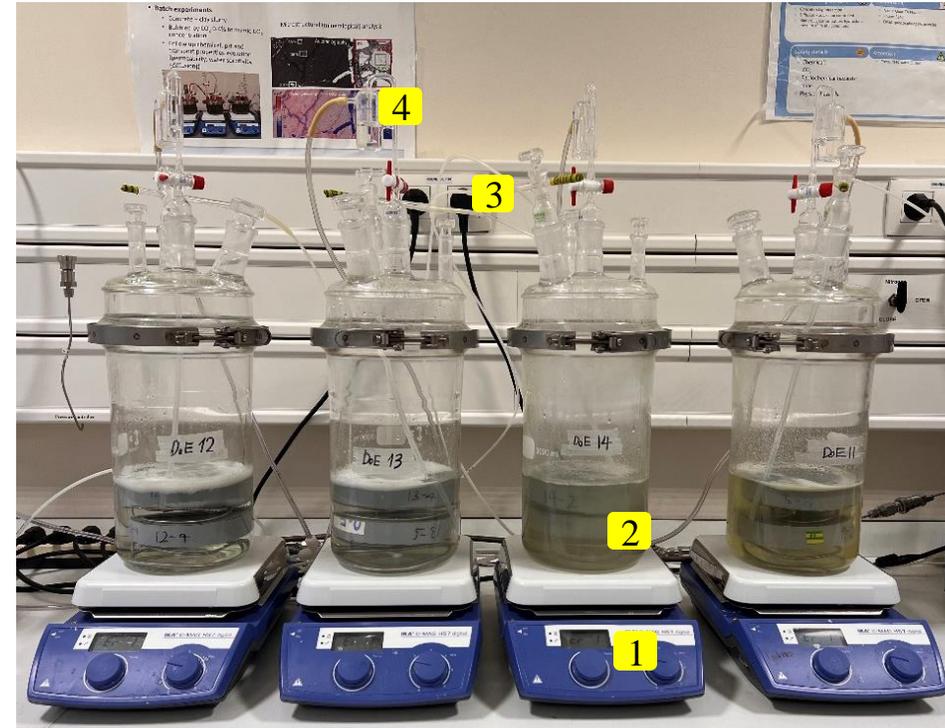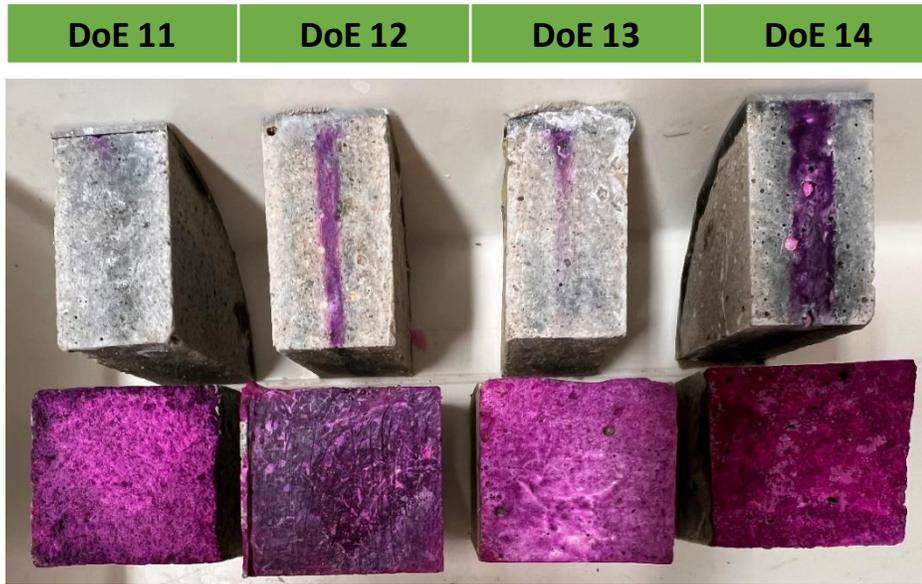
```
Reference sample
```

Saturate in water for 24h ┄┄┄→

```
Saturated sample
```

Immerse in 6M NH_4NO_3 ┄┄┄→

```
Leaching test
```

Mortar characterization

- FTIR
- N_2-ads, SEM
- Water permeability

Leachate solution analysis

- pH
- ICP-OES

PREDIS

WP5.4: Leaching in NH_4NO_3

High SS, low NH	DoE 11	**0.55**	**25**	5	NEV
Low SS+NH	DoE 12	0.45	20	5	SHE
High SS	DoE 13	**0.55**	20	3	SHE
High SS+NH	DoE 14	0.35	20	5	NEV

DoE 11	DoE 12	DoE 13	DoE 14

After
28d leaching

Before leaching

Leaching depth (28D), mm

- Waste-forms are **more vulnerable** to leaching than AAS without oil

- Leaching resistance predominantly depends on **w/b ratio** and **waste loading**

PREDIS

pH of leachate solution

High SS, low NH	DoE 11	0.55	25	5	NEV
Low SS+NH	DoE 12	0.45	20	5	SHE
High SS	DoE 13	0.55	20	3	SHE
High SS+NH	DoE 14	0.35	20	5	NEV

ICP-OES

Concentration (mg/l)	L-DoE 11	L-DoE 12	L-DoE 13	L-DoE 14
Al	<50	<50	<50	<50
Ca	15000 ± 380	12750 ± 320	12650 ± 320	12140 ± 310
Fe	<80	<80	<80	<80
K	480 ± 270	400 ± 270	400 ± 270	390 ± 270
Mg	<100	<100	<100	<100
Na	4900 ± 700	4000 ± 700	4200 ± 700	4400 ± 700
Si	<60	<60	<60	<60
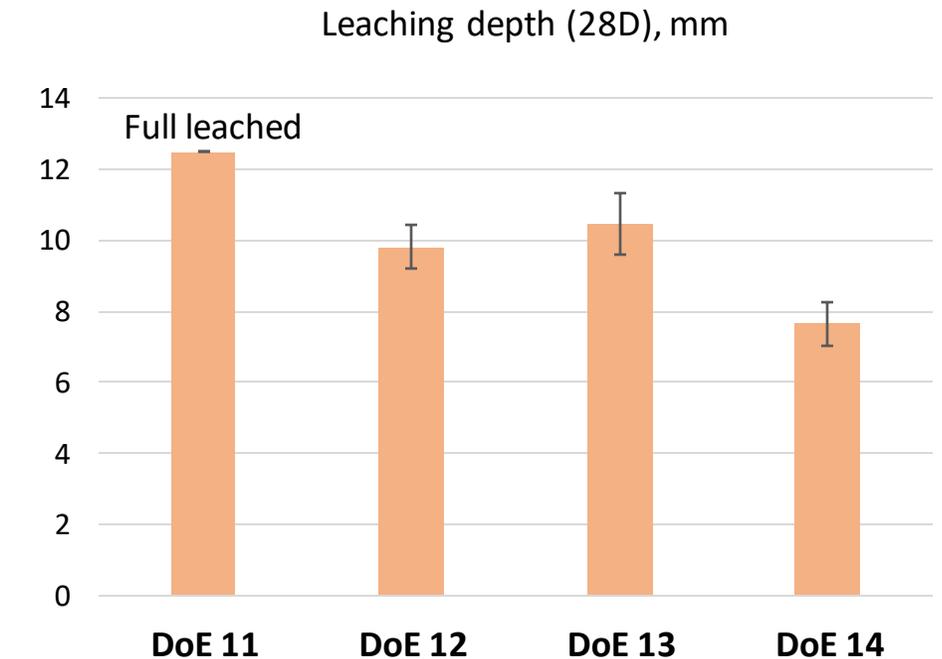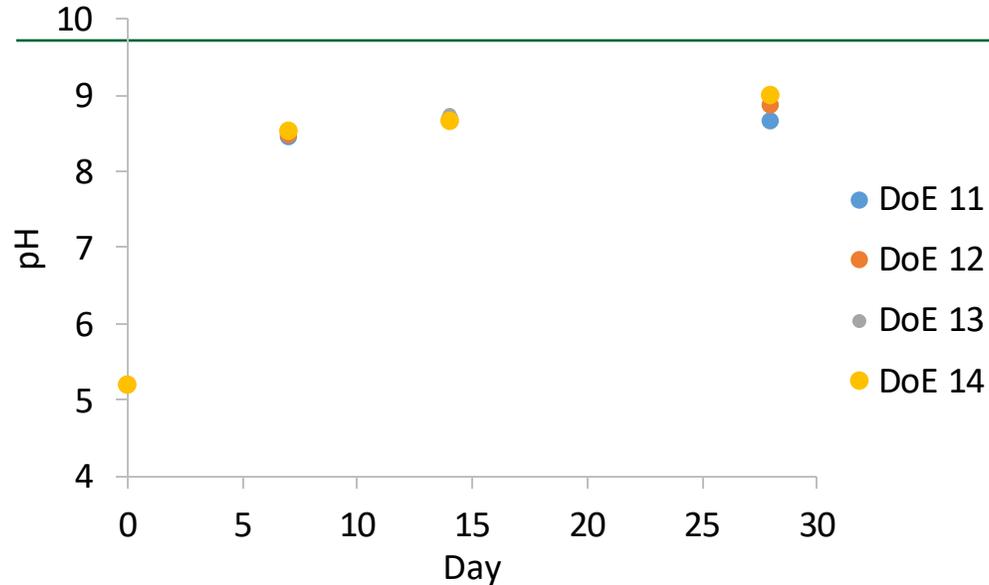
- The pH of leachate solution during entire leaching test <9.25 → NH4+>> NH3

→ no need to renew the leachant solution

- The **quasi-equilibrium** state is promptly reachable (after 7d leaching)

- Main leachable elements: **Ca, Na**

- C=C, C-H → **oil** is **leached out** of waste-forms

- N-H → NH_4^+ may **exchange to Na^+/Ca^{2+}** as the charge balancing role for C-A-S-H gel as seen by ICP-OES

- C=O (carbonyl) → unavoidable natural carbonation due to mixing/sampling

- Si-O-T shifts to higher wavenumber → **C-A-S-H gel becomes siliceous** after leaching
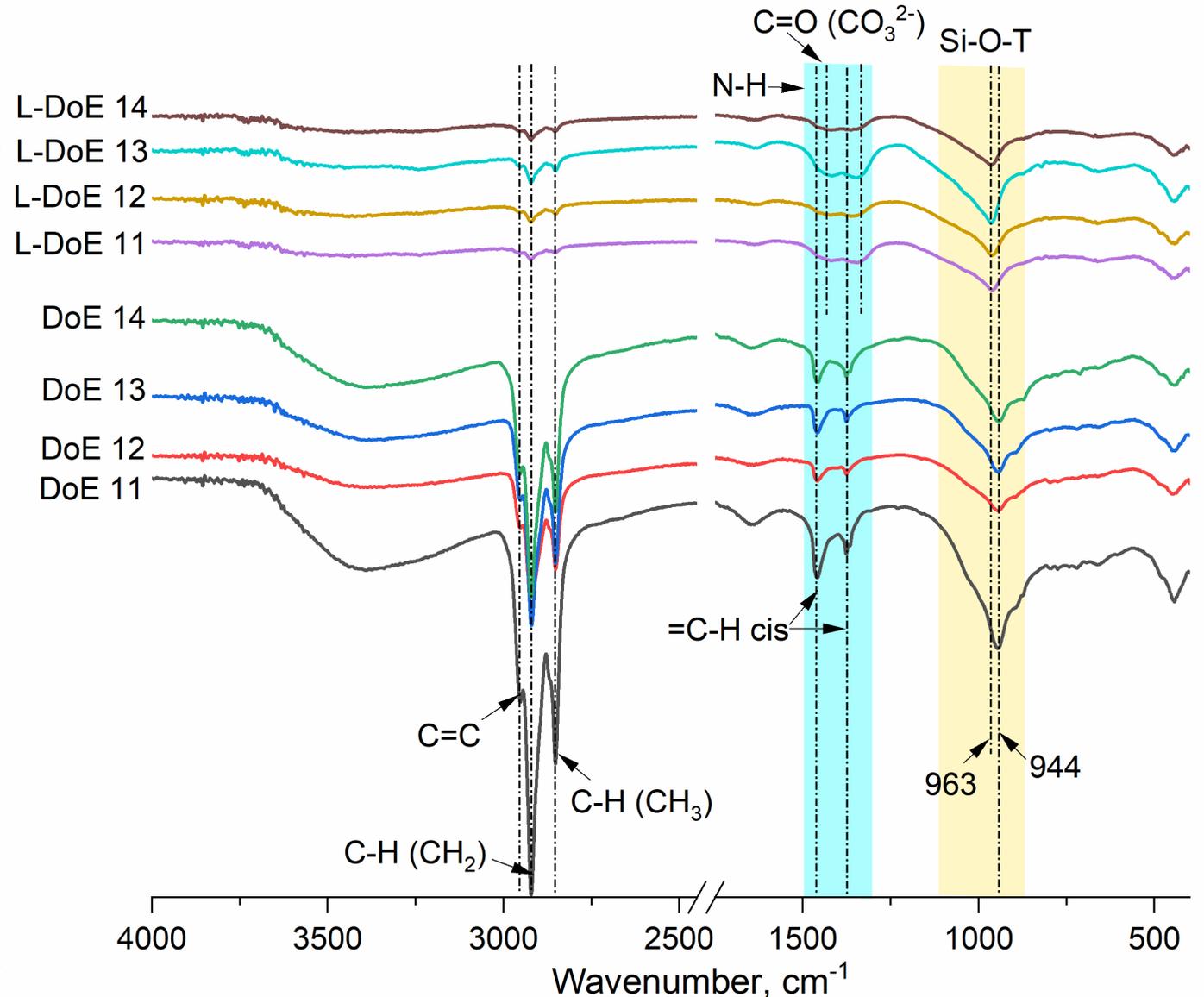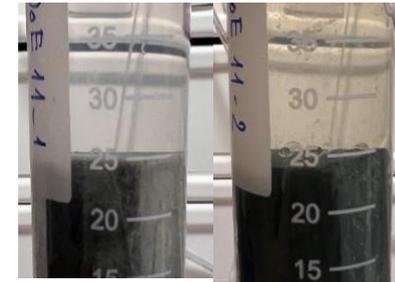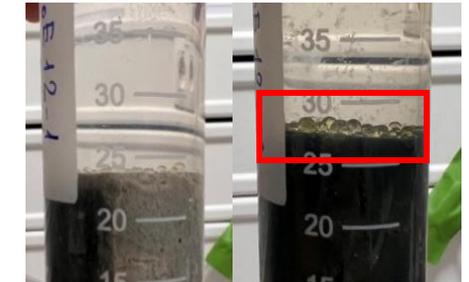
BSE
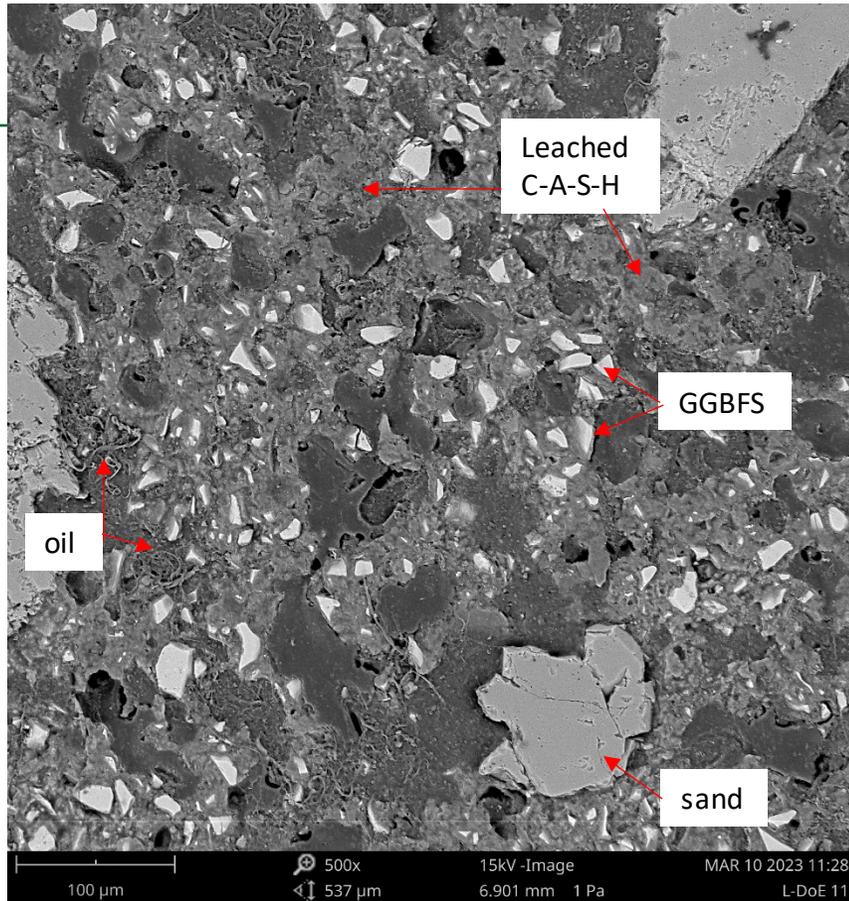
L-DoE 11

Small-volume leaching
→ determine the leaching of oil

DoE 11

DoE 12

DoE 13

DoE 14

Characterization: SEM/EDS, N_2-ads, MIP → on-going
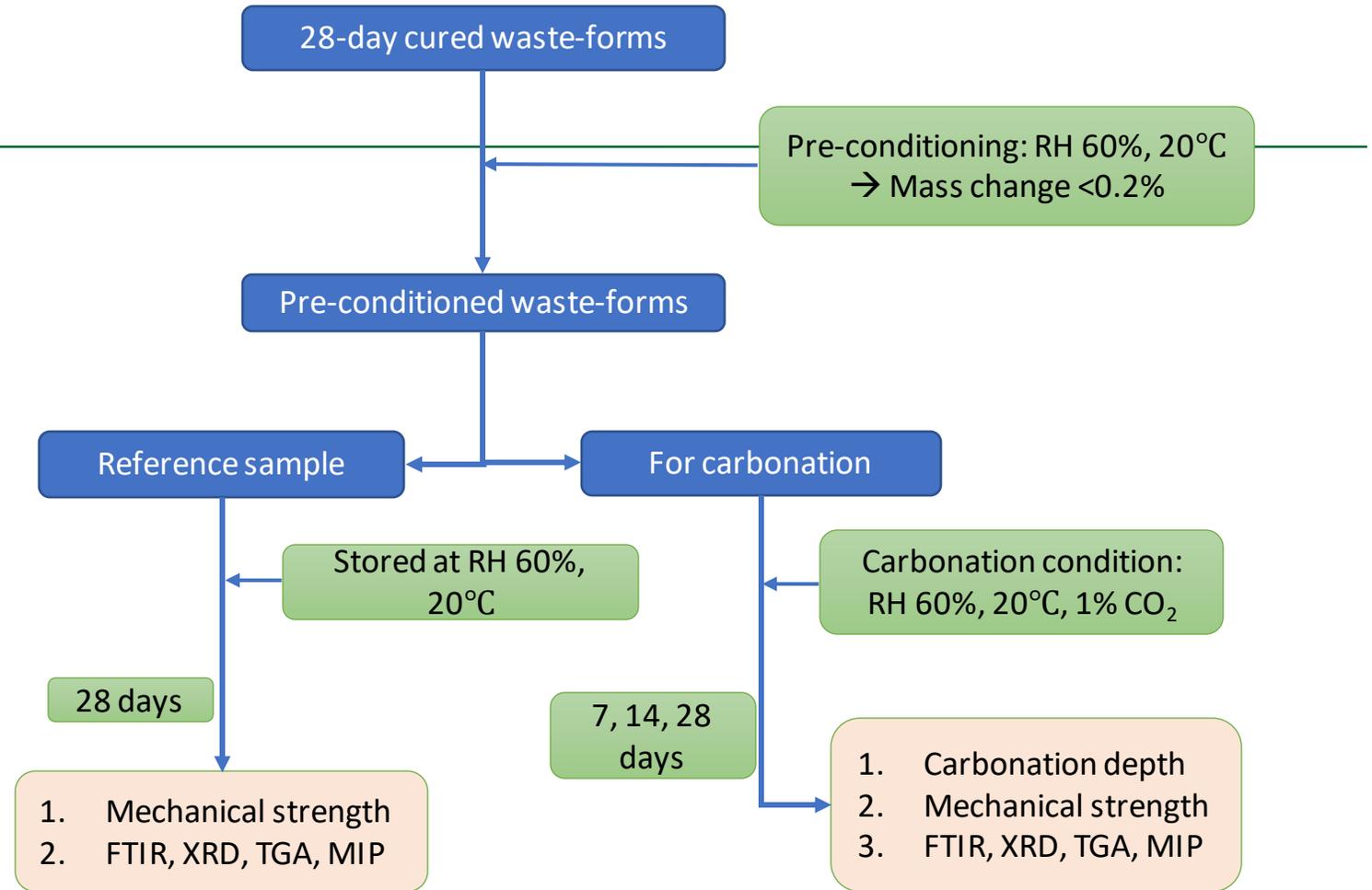
WP5.4: Carbonation
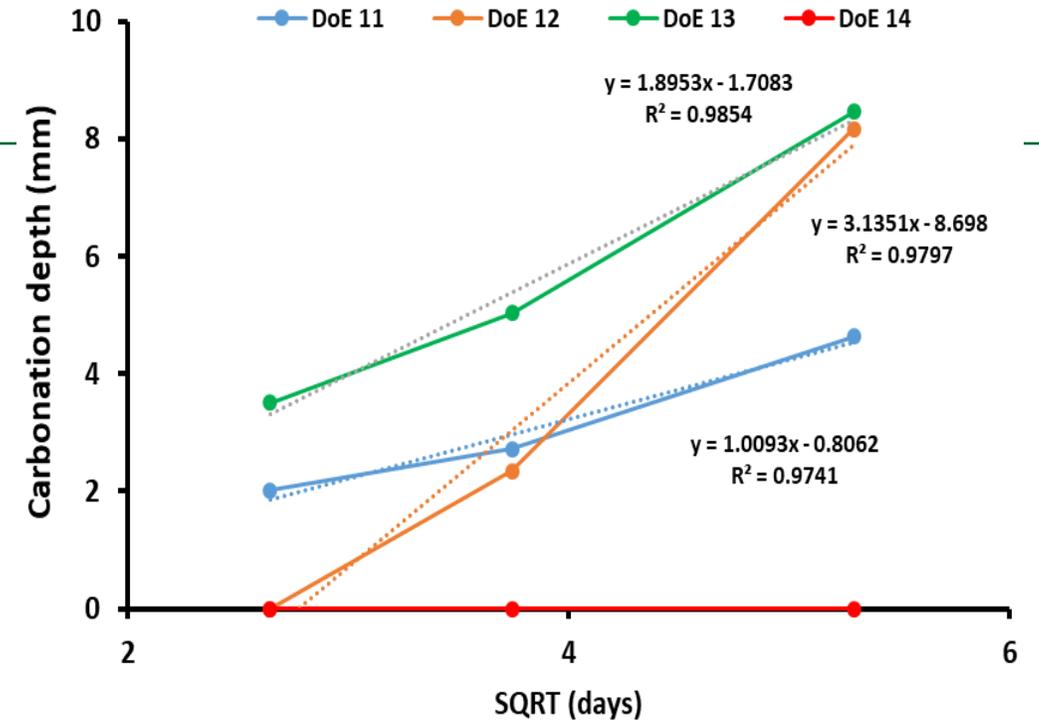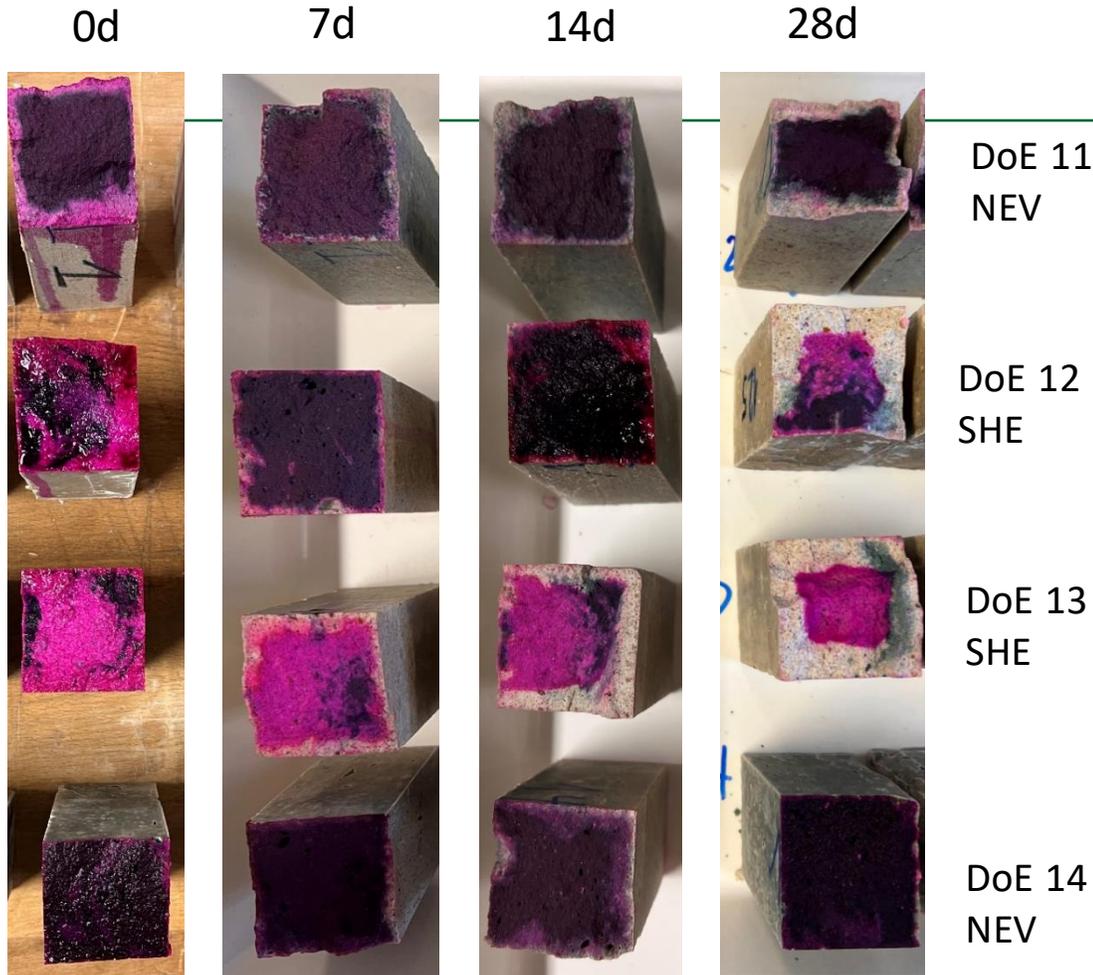
28-day cured waste-forms

Pre-conditioning: RH 60%, 20℃ → Mass change <0.2%

Pre-conditioned waste-forms

Reference sample

For carbonation

Stored at RH 60%, 20℃

Carbonation condition: RH 60%, 20℃, 1% CO_2

28 days

7, 14, 28 days

1. Mechanical strength
2. FTIR, XRD, TGA, MIP

1. Carbonation depth
2. Mechanical strength
3. FTIR, XRD, TGA, MIP

0d	7d	14d	28d	
				DoE 11 NEV
				DoE 12 SHE
				DoE 13 SHE
				DoE 14 NEV

$y = 1.8953x - 1.7083$
$R^2 = 0.9854$

$y = 3.1351x - 8.698$
$R^2 = 0.9797$

$y = 1.0093x - 0.8062$
$R^2 = 0.9741$

- Waste-forms with **SHE is more vulnerable** to carbonation than the waste-forms with NEV

- The higher waste loading and w/b ratio, the higher carbonation susceptibility
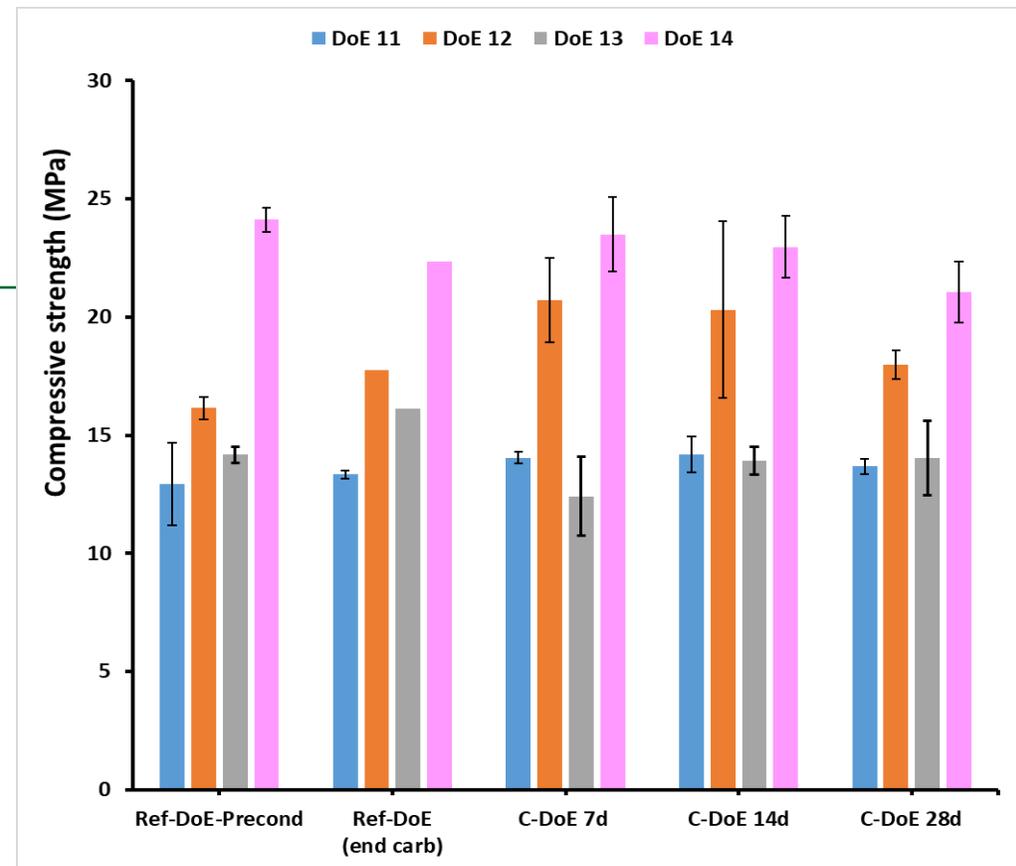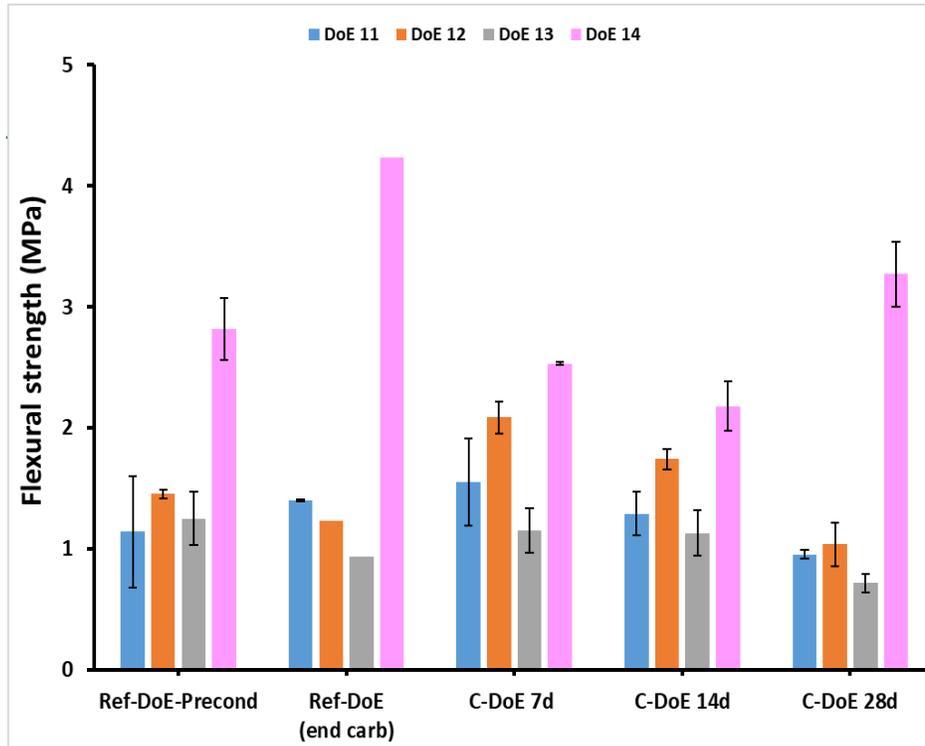
WP5.4: Carbonation

- Carbonation slightly **decreased the flexural** strength of all waste-forms

- Longer (28+28) days of curing did not affect much the flexural strength, except for DoE 14.

- Compressive strengths of all waste-forms were **less affected** by carbonation

→ Mechanical strengths of waste-forms tend to be more stable than that of reference AAS (without oil) under carbonation [1]

- Accelerated leaching and carbonation of AAS-oils have been finished and revealed interesting findings:

  - Both **carbonation** and **leaching** resistance of waste-forms depended significantly on **oil type, waste loading** and **w/b ratio**.

  - Leaching was significantly affected by the **w/b ratio**. **Ca** and **Na** were main leachable elements of waste-forms in 6M NH_4NO_3.

  - Carbonation was predominantly affected by **oil type**. Waste-forms with NEV showed better carbonation resistance than that with SHE.

  - Mechanical strengths of waste-forms seemed **stable** under carbonation (1% CO_2, 20 °C, 60% RH)

PREDIS

Copyright © SCK CEN

PREDIS

Thanks for your attention

And to all WP5 partners!