Deliverable 5.2
Report on Synthesis of formulation & process studies results

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Federica Pancotti (SOGIN) – Crina Bucur (RATEN)
Sogin SpA
Via Marsala 51/C, 00185 Rome, Italy

pancotti@sogin.it
+ 39 338 6397236

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Main author Federica Pancotti (SOGIN) – Crina Bucur (RATEN)	**Reviewed by** Giboire Isabelle (CEA), WP5 Lead	**Accepted by** Maria Oksa (VTT), Coordinator

Contributing authors Sciacqua Rossella (SOGIN), Sandalova Simona (SOGIN), Troiani Francesco (SOGIN), Samantha Irving (NNL), Martin Hayes (NNL), Carmen Manolescu (RATEN), Quoc Tri Phung (SCK-CEN), Thi Nhan Nguyen (SCK-CEN), Cori Davide (NUCLECO), Sergey Sayenko (KIPT), Yevhenii Svitlychnyi (KIPT), Esperanza Lara (CIEMAT), Vojtech Galek (CV-REZ) Sears Anna (CV-REZ), Petr Vecernik (UJV-REZ), Monika Kiselova (UJV-REZ), Eros Mossini (POLIMI), Gabriele Magugliani (POLIMI), John Provis (USFD), Poulesquen Arnaud (CEA)	**Pages** 200

Abstract

The Task 5.3 “Study of direct conditioning process” of the PREDIS WP5 was dedicated to study the direct conditioning process of radioactive liquid organic waste (RLOW) in geopolymer and related alkali-activated materials.

The partners involved in this task investigated basic formulations and processes for the direct conditioning of RLOW. All the promising conditioning formulations were further studied and grouped into three formulation families, based on – metakaolin (MK), blast furnace slag (BFS) and mixture of Fly Ash, BFS and MK (MIX). The optimisation and robustness of these formulations were studied with surrogates RLOW. The optimised reference formulations were further investigated with real RLOW and upscaled.

This Technical report summarises the work and results achieved by the partners in the scope of the Task 5.3.

Coordinator contact
Maria Oksa
VTT Technical Research Centre of Finland Ltd
Kivimiehentie 3, Espoo / P.O. Box 1000, 02044 VTT, Finland
E-mail: maria.oksa.@vtt.fi
Tel: +358 50 5365 844

Notification

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Abbreviations

PREDIS – Pre-Disposal Management of Radioactive Waste

RLOW – Radioactive liquid organic waste

WP – Work Package

TSO – Technical and Scientific Support Organization

RE – Research Entities

WMO – Waste Management Organisation

TBP – Tributyl Phosphate

DIPN – Di-Isopropyl Naphthalene

EDTA – Ethylene-Diamine Tetra-Acetic Acid

WAC – Waste Acceptance Criteria

RW – Radioactive Waste

GP – Geopolymer

MK – Metakaolin

BFS – Blast Furnace Slag

TBP – Tri-butyl phosphate

VT – Volcanic Tuff

CPM – Counts Per Minute

1 Introduction

Work package 5 (WP5) of the PREDIS project addresses the lack of available technologies for radioactive liquid organic waste (RLOW) treatment and conditioning by investigating and developing innovative technologies for direct conditioning of RLOW. The work package is divided into tasks focused on exploring the possibility of using geopolymers and related alkali-activated materials.

Task T5.3 is dedicated to the study of direct conditioning of RLOW. The main objective of this task is to develop and study most promising reference formulations that can be used for conditioning of various types of RLOW, identified in the Task 5.2 (Collection & Review of Waste, Regulatory, Scientific & Technical Data). The work within the Task T5.3 was organized in the following sub-tasks:

- Sub-task T5.3.1 – Definition of experimental protocols
- Sub-task T5.3.2 – Formulation of conditioning materials: feasibility study & screening of conditioning options (5 to 10)
- Sub-task T5.3.3 – Formulation of conditioning materials: optimization and robustness of reference formulations
- Sub-task T5.3.4 – Investigation of reference formulations with real RLOW
- Sub-task T5.3.5 – Investigation of direct conditioning process scale-up
- Sub-task T5.3.6 – Synthesis of experimental results

The list of partners involved in T5.3, describing the type of organisation and its involvement in different Sub-tasks, is presented in Table 1. It is important to note that in this Task various types of organisations, ranging from TSO's, waste management organisations and service providers to research organisations and universities were involved.

Table 1 *List of partners involved in PREDIS Task T5.3*

Project partner		**Country**	**Type of organisation**	**Sub-task**
Abbreviation	**Full name**			
RATEN	Regia Autonoma Tehnologii pentru Energia Nucleara – Institutul de Cercetari Nucleare Pitesti	Romania	RE	All - Task leader
SOGIN	Società Gestione Impianti Nucleari	Italy	WMO	All - Task leader
KIPT	National Science Centre Kharkov Institute of Physics and Technology	Ukraine	RE	T5.3.1 - T5.3.3, T5.3.6
NUCLECO	Nucleco Societa Per L'Ecoingegneria	Italy	Service provider	T5.3.1 - T5.3.4, T5.3.6
USFD	University of Sheffield	UK	University	T5.3.1 - T5.3.3, T5.3.6
NNL	The UK's National Nuclear Laboratory	UK	RE	T5.3.1 - T5.3.3, T5.3.6
CIEMAT	Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas	Spain	TSO	T5.3.1 - T5.3.3, T5.3.6
SCK CEN	Studiecentrum voor Kernenergie / Centre d'Etude de l'Energie Nucléaire	Belgium	RE	T5.3.1 - T5.3.3, T5.3.5, T5.3.6
CEA	Commissariat à l'énergie atomique et aux énergies alternatives	France	RE	T5.3.1, T5.3.3, T5.3.6
UJV Rez	ÚJV Rez, a.s.	CZ	TSO	T5.3.1, T5.3.4, T5.3.6
POLIMI	Politecnico di Milano	Italy	University	T5.3.1, T5.3.2, T5.3.4, T5.3.6
CV Rez	Centrum Vizkumu Rez	CZ	RE	T5.3.1, T5.3.5, T5.3.6

2 Radioactive liquid organic waste

2.1 Origin and characteristics

Radioactive Liquid Organic Waste (RLOW) are generated mainly by industrial nuclear entities such as nuclear power plants, spent nuclear fuel reprocessing plants, uranium enrichment plants, but also from research and medical applications.

Typically, the RLOW include oils (lubricating oils, hydraulic fluids, vacuum pump oils, cutting oils, thermal oils), solvents generated from different decontamination operations (toluene, carbon tetrachloride, dichloromethane, acetone, alcohols…), extraction solvents (the most used extraction solvent is tri-butyl phosphate diluted, usually with a light saturated hydrocarbon, often dodecane or a mixture of paraffins), scintillation liquids (toluene, xylene, hexane…)

For RLOW management not only radioactivity but also the chemical content has to be considered as both can affect the nuclear safety and have detrimental effects on human health and environment. RLOW are very mobile and will drain under gravity contributing to the spread of contamination, therefore they need to be effectively contained. Many types of RLOW are volatile and combustible or will support combustion of other waste. They can also provide a source of nutrients for microbial activity. Many organic fluids are immiscible with water and can be classed as nonaqueous liquids requiring special care due to their potential to rapidly migrate in environment (the lighter fraction can float on water whereas the dense fraction cannot). This distinction is significant for waste collection, storage, and processing. Furthermore, some of the decontaminants (chelating agents) can form water soluble complexes with radionuclides (especially the actinides) enhancing their mobility in near-field and geosphere.

In some cases, the RLOW have available management routes and incineration represents the main treatment option. Industrial incineration plants have WAC that cannot be accomplished by all the RLOW currently existing in different European countries. Because of the complex physico-chemical properties of the RLOW, many countries, partly including the EU Member States, still have their RLOW in storage and are working on development of an adequate management option. Table 2 contains the available information on the types of RLOW generated or stored by different organisations in EU member countries (adapted from the results of data collected using a specific questionnaire in the scope of Task 5.2 – D5.1 [1]). As it can be seen, the most common waste types are lubricants, organic solvents, and scintillation cocktails. The description of the different RLOW types as well as a further look on their origin is given in Table 2 below paragraphs.

***Table 2** Types of RLOW generated/stored by organisations in EU member states*

Organisation	Country	Lubricants	Organic solvents	Scintillation cocktail	Decontamination liquids	Sludge
KIPT	Ukraine	Y				
Sellafield Ltd.	UK		Y			
CV Rez	Czech Republic	Y	Y	Y	Y	
ÚJV Rez	Czech Republic	Y	Y	Y		
SOGIN	Italy	Y	Y			
RATEN (*)	Romania	Y		Y		
Cernavoda NPP (**)	Romania	Y	Y	Y		Y

(*) RLOW generated in RATEN are conditioned in a cement matrix (using emulsifiers) and conditioned waste packages are sent for final disposal in National Repository Baita Bihor.

(**) RLOW generated by Cernavoda NPP are solidified using NOCHAR polymers and sent for incineration at a European waste processor.

2.1.1 Lubricants

Lubricants include both oils and greases and are used in nuclear power plant and in other non-energetic application (for example in vacuum pumps used in different experimental facilities).

Radioactive oil waste produced in nuclear power plants consists of lubricating oils from primary heat transport pumps, hydraulic fluids from fuelling machines, and turbine oils. These are normally low-level waste containing only relatively small quantities of ß/y emitting radionuclides due to the contamination with volatile radionuclides or through their contact with radioactive materials. Furthermore, the lubricants used in nuclear power plants can contain low levels of activation products due to their exposure to neutrons. These lubricants become waste as a result of regular equipment maintenance, or when an item of equipment is discarded [2]. The removal of tritium from heavy water in the heat transport system of pressurized heavy water reactors can produce intermediate level tritiated oil waste through contamination of vacuum pump oil by gaseous tritium, which then becomes organically bound through isotopic exchange. This oil waste may contain up to 1.8 TBq/L of tritium and the estimated annual generation is about 75 L [3].

2.1.2 Organic solvents

A wide variety of organic solvents are used in research and medical facilities in the industry during the extraction of uranium (for the yellow cake production from the ores obtained during uranium mining) and in nuclear fuel reprocessing.

Tri-butyl phosphate (TBP) is the most used extraction solvent. For the extraction process the TBP is diluted, usually with a light saturated hydrocarbon, such as dodecane or a mixture of alkanes. Both TBP and its diluent are subject to degradation by hydrolysis and radiolysis. Eventually, the degradation significantly reduces the solvent’s performance, and it is declared RLOW. Depending on the origin of the solution on which the extraction solvent was used, the extraction solvents can be among the most highly contaminated organic waste, containing uranium, thorium (if uranium is extracted from uranium ore) and possibly plutonium and fission products (if generated from spent nuclear fuel reprocessing). Solvents can also be used for cleaning and degreasing. Chlorinated or fluorinated hydrocarbons have been used for this purpose, although this is no longer considered good practice. After use such solvents become RLOW. Perchloroethylene and similar solvents are used for dry-cleaning of contaminated clothes, with the resulting sludge being treated as an organic waste. Sometimes other organic compounds are used for the extraction of heavy metals, including tri- and tertiary amino-compounds, although the volumes are usually very small in comparison to TBP.

2.1.3 Scintillation cocktail

Scintillation liquids result from routine radiochemical analyses of radionuclides with low beta energy emissions both in research facilities and in NPPs (in the radioactive waste characterisation process). They consist of a mixture of a solvent (classical - toluene, xylene, safer – DIPN used in Ultima Gold scintillation cocktail), one or more scintillators and the sample under investigation. They may also contain a surfactant to be able to hold aqueous samples. Scintillation liquids are most used for measuring ^{3}H and ^{14}C, but also other long-lived beta emitting radionuclides such as ^{63}Ni, ^{99}Tc, ^{129}I, ^{36}Cl and less widely for ^{125}I, ^{32}P and ^{35}S.

2.1.4 Decontamination liquids

A wide variety of methodologies are used for decontamination of nuclear facilities to remove radionuclides and reduce doses to operators. One of them is the use of decontamination organic liquids that will be regarded as liquid organic waste after use. These liquids include toluene, carbon tetrachloride, acetone, alcohols and trichloroethane. Aqueous solutions of organic acids, such as citric acid, picolinic acid, ethylene-diamine tetra-acetic acid (EDTA) are also commonly used in the decontamination of equipment.

3 Experimental guidelines and protocols

In the beginning of Task T5.3, the experimental guidelines and protocols were defined (Sub-task T5.3.1) to ensure that partners applied consistent experimental procedures in the work performed under Sub-tasks T5.3.2-T5.3.5. These guidelines and protocols were developed based on partners' own experimental protocols and available standards for cement-based mortars. Additionally selecting criteria for the most promising formulations were defined and agreed in Sub-task T.5.3.1 based on a collection of general acceptance criteria for fresh and hardened cement-based mortars and reference WAC for cemented waste forms when available.

The experimental guidelines and protocols as well as the acceptance criteria are described below in further detail.

The guidelines are composed of two main sections:

1) Conditioning Materials Elaboration: Definition of the information and data to be collected: i.e. type of waste, type of conditioning option, waste loading, eventual pre-treatment, quantity and type of the row materials used, nr. and shape of the test specimens, etc.
2) Conditioning Materials Characterization: includes the reference protocols for each test.

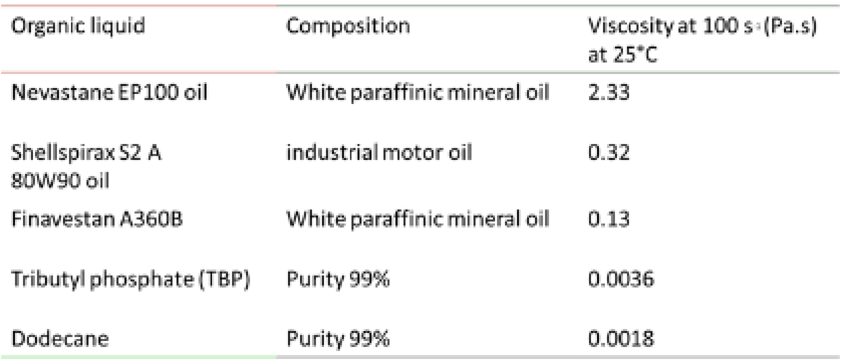
3.1 Conditioning Materials Elaboration

Defining all the materials involved in conditioning process is the starting point of performance evaluation in this scientific and technical work. It is necessary to describe the RLOWs and their corresponding surrogates and the characteristic of the conditioning materials used for the study. If a pre-treatment is foreseen before the conditioning step it is necessary to indicate the applied procedure.

During Task 5.2 a special questionnaire on a European scale was used to collect information on the types, amounts, characteristics of RLOWs stored in each country as well as the conditioning methods used (Sub-task T5.2.1). Additionally, an extensive scientific & technical review of available conditioning options was conducted (Sub-task T5.2.3). Based on this the Partners have decided on RLOWs and conditioning options to be studied in the scope of the PREDIS project, which are described below.

To allow conducting experiments without having to worry about radiation protection issues, the evaluation of the conditioning options was performed using non-radioactive representative samples (RLOW surrogates). The list of Reference Surrogates identified in Sub-task 5.2.1 is reported in Table 3 (MS30 [4]).

Table 3 *List of Reference Surrogates identified in Sub-task 5.2.1*



Organic liquid	Composition	Viscosity at 100 s^{-1} (Pa.s) at 25°C
Nevastane EP100 oil	White paraffinic mineral oil	2.33
Shellspirax S2 A 80W90 oil	industrial motor oil	0.32
Finavestan A360B	White paraffinic mineral oil	0.13
Tributyl phosphate (TBP)	Purity 99%	0.0036
Dodecane	Purity 99%	0.0018

Following some internal discussion, it was agreed among the Partners to replace Finavestan A360B oil with a scintillation cocktail surrogate. Thus, the final RLOW surrogates used in T5.3.2 laboratory activities were:

- Mechanical Oil (Nevastane EP100 and Shellspirax);
- Solvent (TBP);
- Dodecane (paraffinic oil – used as a solvent) or TBP diluent;
- Scintillation cocktails (Ultima Gold AB and INSTA GEL).

The importance of using locally sourced raw materials was stressed to secure supplies in the case of a future industrial use.

As a result of the review conducted in the scope of T5.2.3 the Partners decided to study two main conditioning options (MS31 [5]):

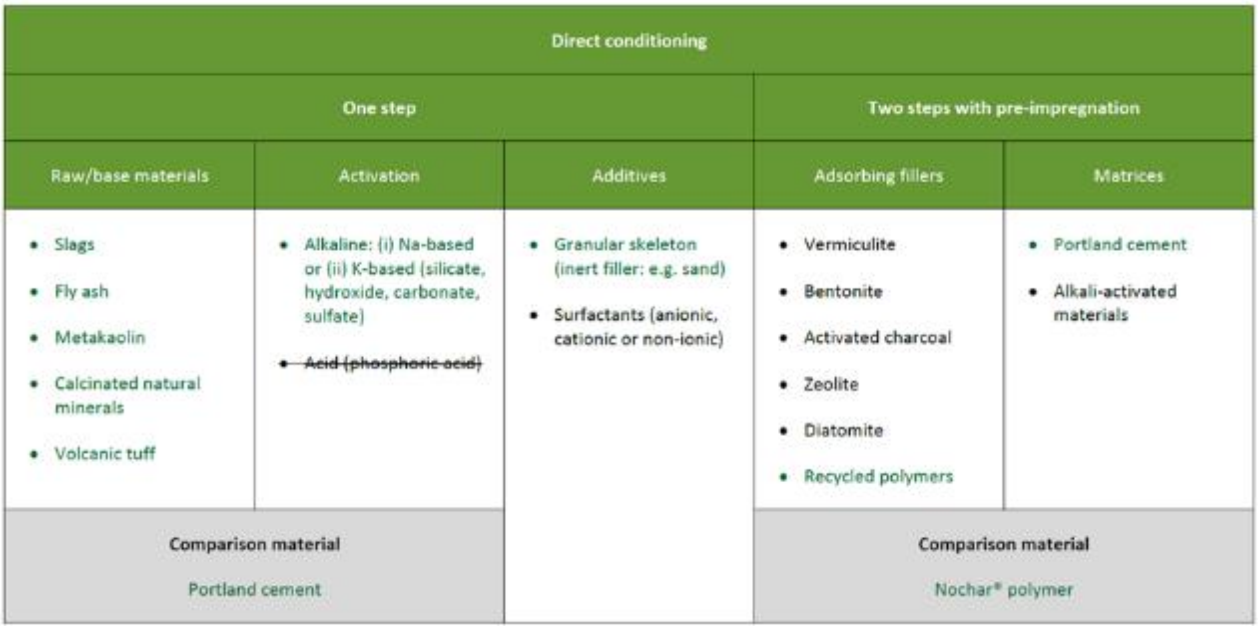
- Direct solidification ("one step")
- Two steps with pre-impregnation.

The guidelines for both options are detailed below.

Direct Solidification option:

The materials considered for the direct solidification option of RLOW are shown in Table 4. It was decided to rule out "acid activation" to keep the experimental approach simpler and focused on alkaline activation.

Table 4 *Summary of the different direct conditioning approaches of RLOW presented by Partners, together with reference comparison materials. In green font, the options that could be used for the experimental screening step (T5.3.2).*



Direct conditioning				
One step			Two steps with pre-impregnation	
Raw/base materials	Activation	Additives	Adsorbing fillers	Matrices
Slags Fly ash Metakaolin Calcinated natural minerals Volcanic tuff	Alkaline: (i) Na-based or (ii) K-based (silicate, hydroxide, carbonate, sulfate) ~~Acid (phosphoric acid)~~	Granular skeleton (inert filler: e.g. sand) Surfactants (anionic, cationic or non-ionic)	Vermiculite Bentonite Activated charcoal Zeolite Diatomite Recycled polymers	Portland cement Alkali-activated materials
Comparison material Portland cement			Comparison material Nochar® polymer	

During the experimental studies the description of the type of the raw material used in the solidification process could be performed according to the EN 197-1 classes.

Any pre-treatment of the raw materials (i.e. drying, homogenization, grinding, etc.) to produce the final solidification matrix should be properly described.

Portland cement is considered as a comparison material for few tests: i.e. bleeding, mechanical test, immersion test.

Two steps with pre-impregnation

The possible adsorbing fillers (i.e. polymer, vermiculite, bentonite, activated charcoal, zeolite, diatomite, etc.) should be described together with the conditioning material (i.e. Portland cement or alkali-activated materials).

In this case, Nochar polymer is used as comparison material for adsorbing filler tests.

For each test performed at least the following data should be collected:

- Test ID
- Waste loading (% in volume) related to the hardened samples
- N. of samples prepared
- Shape and dimensions of the samples

All the experimental data should be registered in a table as the following one:

***Table 5** Example of the experimental data input*

TEST	RLOW		Conditioning process					Waste Loading	SAMPLES	
			Direct solidification			Two steps with pre-impregnation				
ID	Type	Pre-treatment	raw/base materials	Activation	Additives	Adsorbing fillers	Matrices	vol.%	N.	Shape
1	*Oil*	*NO*	*Fly ash*	*Na-based*	*Surfactants*			*40*	*20*	*4x4x16 cm*

3.2 Conditioning Materials Characterization

This Chapter presents the tests performed both on the fresh paste and on the hardened matrix to investigate the performance of the waste form obtained from the direct conditioning of radioactive liquid organic waste. For each of them the reference standards and the possible methodologies/instrumentation to be used are indicated.

The Partners had the flexibility to perform the test according to their internal procedures.

A cross comparison among the Partners (performing the same test with the same formulation with different apparatus and protocols) is considered very useful to verify the robustness of the test results.

3.2.1 PHASE 1: Tests on Fresh Paste/Mortar

The tests performed on the fresh paste were, at least, the following:

- ✓ viscosity after mixing or workability
- ✓ heat reaction (using calorimetry methods)
- ✓ bleeding
- ✓ setting time.

Viscosity after mixing or Workability

This parameter was investigated in accordance with the following Reference Standards:

- **EN 1015-3:** Test methods for masonry mortars – Part 3: Determination of the consistency of fresh mortar
- **UNI 7044-72:** Determination of the consistency of cementitious mortars by using a shake board
- **ASTM C1437:** Standard Test Method for Flow of Hydraulic Cement Mortar
- **BS EN 13395-2:2002:** Test methods. Determination of workability. Test for flow of grout or mortar
- **ASTM D2196-99:** Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational Viscometer

The Rotational Viscosity after mixing was determined for paste after defined mixing period.

A recommended procedure consists in 120 s pre-shear at 262 s^{-1}, followed by a shear rate ramp from 0 s^{-1} to 262 s^{-1} over 150 s, and a return ramp back to 0 s^{-1} over 150 s. Apparent viscosity is taken at 106 s^{-1} on descending ramp. The paddle is an anchor design to provide data relevant to In Drum Mix techniques.

Heat reaction

The heat of reaction can be measured using calorimetry methods: solution calorimetry, semi-adiabatic calorimetry, adiabatic calorimetry, and isothermal (heat conduction) calorimetry.

Bleeding

The bleeding phenomenon can be investigated according to the following Reference Standards:

- **UNI 7122:** Test on fresh concrete. Determination of the amount of exuded water in the mixture
- **ASTM C940 – 16:** Standard Test Method for Expansion and Bleeding of Freshly Mixed Grouts for Preplaced-Aggregate Concrete in the Laboratory
- **EN 480-4:** Additives for concrete, mortar and grout - Test methods - Part 4: Determination of the amount of water exuded in concrete

It would be useful to consider both the water and organic component bleeding. A visual inspection (i.e. after 24 h) is possible.

As an example of possible procedure to be applied is: After mixing for defined period bleed could be measured as vol/vol% on surface of 100 cm^3 sealed sample after curing for 24 h at 20 °C and >90%RH

Setting time

This parameter can be evaluated in accordance with the following Reference Standard:

- **UNI EN 196-3:** Cement test methods - Part 3: Determination of setting time and stability

3.2.2 PHASE 2: Tests on Hardened Samples

The tests required on the hardened samples are, at least, the following:

- ✓ flexural and compressive strength
- ✓ water immersion tests
- ✓ thermal stability
- ✓ ability of polymer to retain liquid under compression (if a polymer is used to adsorb the liquid waste)

The samples curing conditions are:

Temperature: 20 +/- 1 °C

Relative Humidity: >90% (not underwater)

To prevent evaporation, mortar/paste samples can be tightly wrapped in polythene sheeting or sealed in polythene bags on demolding, secured with tape at both ends so just inserts protrude.

Compressive and flexural strength

The Compressive Strength can be evaluated in accordance with the following Reference standards:

- **UNI EN 12390-3:** Tests on hardened concrete. Compressive strength of the specimens
- **BS EN 12504-1:** Testing concrete in structures - Part 1: Cored specimens - Taking, examining and testing in compression
- **EN 196-1:** Methods of testing cement - Part 1: Determination of strength
- **ASTM C109 / C109M:** Standard Test Method for Compressive Strength of Hydraulic Cement Mortars

For the flexural strength evaluation, the reference standards are:

- **EN 12390-6:** Testing hardened concrete - Part 6: Tensile splitting strength of test specimens
- **EN 196-1:** Methods of testing cement - Part 1: Determination of strength

Water immersion tests

The water immersion test can be conducted according to a common procedure consisting in leaving the specimens immersed for 90 days in fresh water at room temperature.

As an example: the distance between the individual specimens and the distance of these from the walls of the tank must not be less than 5 cm. The immersion tank is filled with water until the level of water is 20 cm above the upper faces of the specimens.

The specimens are inspected before, during and after the immersion test. Mass variation is recorded. TOC in the water is measured at different time intervals, or just at the end of the immersion period. At the end of the immersion period the specimens are subjected to the compression test.

Also, the following Reference standard can be considered for the test:

- **BS 1881-122:** Testing concrete. Method for determination of water absorption.

Thermal stability

The thermal stability test will be performed for the “Two steps with pre-impregnation” option to check the polymeric material stability to thermal treatment.

Because the reference material (Nochar) has demonstrated high thermal stability with decomposition occurring at 300°C [6], the same Differential thermal analysis experiment will be performed during the study by measuring the weight loss (i.e. with a TGA-DSC analyzer) till a temperature of 400°C.

Ability of polymer to retain liquid under compression

This test should be carried out on samples consisting of liquids absorbed on a polymeric matrix. The test should be carried out by applying a known load on a defined quantity of sample and verifying the eventual release of liquid.

An example of a possible procedure to be applied is indicated in the following:

The load could be applied in a syringe by determining the surface area and attaching a weight at the top of the ‘plunger’ which then results in a load on the sample in the syringe of 5 psi. The moisture release is determined visually.

3.2.3 PHASE 3: Other Future Tests to be considered Relevant for the Scope

To further investigate the performance of cemented waste-forms deriving from the direct conditioning of radioactive liquid organic waste it should be very useful also to evaluate the RLOW distribution in the cement matrix via X-ray microtomography, SEM/EDS or similar techniques.

3.2.4 Reporting

Each Partner should collect the following main experimental data for the tests performed:

- Partner name
- Test ID
- Date of the test
- Waste type
- Matrix formulation (Conditioning option, type of conditioning material, additives, etc.)
- Waste loading (by volume, referred to the hardened sample)
- Reference standard (if available)
- Specimen description (number, shape, dimension, weight, etc.)
- Result of the test
- Acceptance criteria
- Comments

Periodically (i.e. quaternary) the Partners shared their results by using a common excel working file (see Annex 1) to produce a periodic report on the work done in T5.3.

3.2.5 Acceptance Criteria

In the following table the Acceptance Criteria for the experimental tests are summarized:

Table 6 *Acceptance Criteria range for the experimental tests*

	Test	**Acceptance Criteria (Range Values)**	**Note**
PHASE 1	**Viscosity after mixing or workability (fluidity)**	> 80 % (>200 mm at t=150 m mix time)	
	Rotational Viscosity after mixing	"Ideally < 1000 mPa.s for low viscous mix. Must be below 7 Pa.s for current In-Drum Mix processes"	
	Heat reaction	NA	
	Bleeding	< 2%	
	Setting Time	3 < t (h) < 48	
PHASE 2	**Compressive Strength**	Fc > 4 MPa at 7 d, Fc > 5 MPa at 28 d, Fc > 7 MPa at 90 d	The Fc evolution during curing time must be checked (7-28-90

			days) and no large decrease is accepted
	Flexural Strength	No specific value, generally 10% of Fc is considered acceptable	
	Water Immersion Test	no swelling or cracks after 90 days of immersion (Fc not less than the value measured after 28 days curing)	
	Thermal Stability	NA	
	Ability of polymer to retain liquid under compression	no visually detectable liquid under 5psi	
PHASE 3	**RLOW distribution in the cement matrix**	NA	

4 Reference formulations development

The objective of the Subtask (T5.3.2) was to evaluate and identify suitable conditioning options for RLOW encapsulation, allowing to achieve incorporation rates of at least 30 % by volume. Suitable conditioning options should lead to a sort of self-levelling, pourable grout with acceptable setting time, no or limited bleeding, and good flexural and compressive strengths.

To achieve this goal an experimental feasibility study and screening of the conditioning options identified in Sub-task T5.2.3 (see Table 4) was conducted by the partners. Five to ten conditioning options (1-2 option(s) studied by each partner) were tested for a RLOW incorporation rate of 30 % by volume.

Generally, the common approach used by all the Partners involved a first screening on the geopolymer formulation without the addition of RLOW surrogates, followed by a second stage done in inactive conditions, at laboratory scale, with RLOW surrogates. In this second stage, 5 reference surrogates (see Table 3) were added to the most suitable geopolymer formulations to test the waste loadings and to assess the effects of RLOW additions. Fresh and hardened mortars/pastes were characterized using the experimental guidelines previously agreed, the following parameters were measured: viscosity after mixing, heat reaction using calorimetry methods, bleeding, setting time, flexural and compressive strengths on bars cured in controlled conditions. Water immersion tests were also performed to evidence RLOW release and composite stability. Some partners assess the RLOW distribution in hardened waste forms by Scanning Electronic Microscopy or 3D X-ray microtomography.

The solidification process with Nochar polymer technology combined with Portland cementation also had to be evaluated for reference surrogates to compare the test results with geopolymers. Preliminary laboratory tests were conducted to verify the maximum waste loading to obtain a solid material and the process overall parameters (time, mixing sequence, volume variation after solidification, etc.). The Nochar polymer solidification was characterised by:

- ✓ measurement of the ability of the polymer to retain the liquid under compression
- ✓ thermal stability of the solidified product
- ✓ water immersion test to evidence RLOW release and composite stability

For the feasibility study, each partner tested specific conditioning options (see

Table **7**).

Table 7 *Proposed conditioning options for the feasibility study*

PARTNER	Conditioning option	RLOW surrogate
RATEN	1) BFS (alkaline activators) 2) Vulcanic Tuff	Pump oil (Shellspirax S2 A 80W90) Scintillation cocktail – Ultima Gold AB
KIPT	3) Metakaolin, fly ash, slag, sand (alkaline activators)	Pump oil
NUCLECO	4) BFS (alkaline activators)	TBP Dodecane TBP+Dodecane (70/30) Shellspirax S2 A 80W90 oil
POLIMI	5) Zeolitized volcanic tuff 6) pre-impregnation with recycled polymers	Vacuum pump oil Kerosene (+ TBP) Scintillation cocktails - Ultima Gold AB
USFD / NNL	7) Flash & Rotary Calcined MK with K Silicate/KOH activator	TBP TBP+Dodecane (70/30) Nevastane EP100 oil
CIEMAT	8) Metakaolin based	Oil Scintillation cocktails - INSTA GEL
SCK-CEN	9) Metakaolin based geopolymers 10) BFS based alkali activated materials	Liquid ionic Dodecane (75%), N,N dialklamides (DEHiBA,DEHBA, DEHDMPA) (0-20%), tributyl phosphate (TBP) (20%), Acetone (2%) Acetonitrile (70%), isopropanol (15%), water (15%) Other selection in progress

The outcome of this Task was the selection of 3 reference formulations to be further studied and developed (M32 [7]). The results obtained in the selection process (from M4 - Dec 2020 to M9 - May 2021) and the justification of the choice of these 3 reference formulations were summarised in an interim technical report (M33 [8]).

The laboratory tests performed by each Partner and the results obtained are summarized in the following paragraphs.

4.1 CIEMAT - Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Spain

4.1.1 Conditioning Options studied

The conditioning options studied by CIEMAT were based on:

- Raw materials: Metakaolin, Na-silicate/NaOH, Blast Furnace Slag (BSF);
- RLOW surrogates: Synthetic oil and Liquid scintillation cocktails.

The raw materials have been selected on the basis of some initial requisites: room-temperature curing and no additives. Interest on the role of BFS on the redox behaviour of the waste form is the immobilization of redox-sensitive RNs.

The raw materials tested are Spanish GP (AIMEN formulation), Czech commercial GP, French GP and German metakaolin.

The specific compositions of the raw materials are reported in the following Table 8, Table 9, Table 10 and Table 11:

Table 8 *Spanish GP AIMEN, %*

https://www.aimen.es/

SiO_2	Al_2O_3	Na_2O	K_2O	TiO_2	Fe_2O_3	CaO	MgO	P_2O_5	LOI
54.0	41.1	0.05	1.09	0.42	1.64	0.03	0.26	0.08	2.80

Table 9 C*zech commercial GP Ceske lupkove zavody a.s. (CLUZ)*

https://www.cluz.cz/

Metakaolin		Typical values					
Description according ČSN 721300	Trade mark	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	SiO_2 %	MgO %	Granulation
Mefisto L05	Mefisto L05	41.9	1.1	1.8	52.9	0.18	D50=3µm; D90=10µm

Table 10 *French MK&SL (supplied by CEA), %*

Metakaolin M1000	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	K_2O	MgO	SO_3	CaO	ZrO_2	Cl	
	53.44	40.71	1.78	1.50	1.06	1.00	0.16	0.11	0.08	0.05	
Slag Ecocem	CaO	SiO_2	MgO	Al_2O_3	SO_3	TiO_2	K_2O	Fe_2O_3	MnO	CuO	SrO
	43.77	33.13	10.60	8.66	1.95	0.67	0.42	0.35	0.14	0.08	0.06

Table 11 *German metakaolin, %*

SiO_2	Al_2O_3	Na_2O	K_2O	TiO_2	Fe_2O_3	CaO	MgO	P_2O_5	LOI
52.3	45.2	0.22	0.15	1.74	0.42	0.04	0.04	0.08	0.79

CIEMAT used in the experimental tests the following RLOW surrogates:

- Synthetic oil: REPSOL SUPER TAURO 100 SINTÉTICO, equivalent to NEVASTANE EP-100;
- Liquid scintillation cocktails: InstaGel Plus and Ultima Gold.

The proprieties of the synthetic oils are summarised in the following Table 12:

Table 12 *Proprieties of the synthetic oils*

PROPERTY	REPSOL SUPER TAURO 100 SINTÉTICO	NEVASTANE EP-100
Density a@ 15 ºC (kg/m^3)	853	850
Kinematic Viscosity at 40 ºC (cSt)	100	100
Kinematic Viscosity at 100 ºC (cSt)	14.5	11.13

InstaGel Plus is a classical cocktail widespread use, having the following observed proprieties:

- In the gel phase it has very high uptake capacity of up to 50%;
- Homogeneous phase sample volumes (0-2 ml water/10 ml);
- In the gel phase with larger volumes (4-10 ml water/10 ml);
- Between homogeneous and gel phase there is two heterogeneous phases, not useful;
- NaOH induce precipitation.

Ultima Gold is a safer cocktail with following proprieties:

- Based on Di isopropyl naphthalene (DIPN);
- Aqueous samples ≤56% of water;
- Very quench resistant;
- Flash point is 150 °C.

4.1.2 Tests and Results

The two alkaline activators were mixed at different ratios and when the mixtures reach the proper temperature, metakaolin powder was incorporated. Additional water was added if the geopolymer had not the adequate physical properties (Table 13).

The geopolymer samples obtained in the first stage (without RLOW incorporated) are shown in Figure 1.

The preliminary screening was based on visual inspection, to observe cracks, chipping, etc, while the second screening was related to compressive strength after 1 and 28 days.

The activities were continued as a part of Task 5.3.3 (see Chapter 5.1).

GPs has been produced by mechanical mixture of Metakaolin or Slags and an alkali activator, according to the standard procedure for mortars based on cement (UNE-EN 196-1-2005).

- Activator has been prepared before final mixture (2,5 h): SiO_2 was mixed with water and after that the NaOH pellets were added.

The RLOW surrogate with the surfactant can be added either to the Metakaolin + Activator mixture just before finishing the mixture process or dispersed in the alkali activator.

The fresh paste was shacked 3 minutes before pouring in the moulds.

***Table 13** Mixtures used for geopolymer preparation*

			ACTIVATOR				
NaOH (M)	**MK (% w)**	**Total Activator (% w)**	**NaOH (% w)**	**Sodium Silicate (% w) ($Na_2O \cdot nSiO_2$)**	**H_2O (% w)**	**$R_{Act/MK}$**	**$R_{L/S}$**
20	42	42	23	19	17	1,0	1,4
20	43	43	22	22	13	1,0	1,3
20	42	42	19	23	17	1,0	1,4
13,5	45	45	25	20	9	1,0	1,2
13,5	45	45	23	23	9	1,0	1,2
13,5	45	45	20	25	9	1,0	1,2
25	43	43	24	20	13	1,0	1,3
25	45	45	23	23	9	1,0	1,2
25	45	45	20	25	9	1,0	1,2
13,5	50	50	25	25	0	1,0	1,0
8	42	43	31	12	15	1,0	1,4
13,5	50	50	25	25	0	1,0	1,0
13,5	45	45	23	23	20	1,0	1,5
13,5	43	33	67	33	24	0,8	2,9

The Curing during 3 h has been carried out in following conditions:

- Room Temperature;
- Curing chamber at 65 ºC y HR > 90%.

The unmoulding has been done with a curing 48 h at room temperature.

***Figure 1** Geopolymer samples*

To homogenize the surrogate in the mixture, the curing options were:

- Temperature: 20º C, 40º C, 60º C, 80º C and 100º C;
- HR%: 50% 5% (first 12 h.);
- Time: 24 h, 48 h, 72 h 168 h.

Formulations started with 3 metakaolin-based geopolymers:

- Metakaolin and Sand from CEA (FR);
- Metakaolin from Check supplier (CZ);
- Metakaolin from AIMEN (SP).

For first trials with scintillation cocktail liquids, CIEMAT started with InstaGel+ and with a loading range between 10 – 40%wt.

4.2 KIPT - National Science Centre Kharkov Institute of Physics and Technology, Ukraine

Conditioning Options studied

The conditioning options studied by KIPT were based on:

- Raw materials: metakaolin, fly ash, slag, sand, alkaline activators (all raw materials sieved ≤500 µm)
- RLOW surrogate: Pump Oil (Shellspirax).

Metakaolin

Metakaolin was obtained by 800°C calcination of kaolin from the Zaporozhye region. The chemical composition of kaolin is shown in Table 14. The calcined kaolin was ground to a powder using an aluminium oxide pestle and mortar and particles passing through a 600 µm sieve.

Table 14 *Chemical composition of Kaolin (Ukr), wt.%*

SiO_2	Al_2O_3	CaO	MgO	Na_2O	Ka_2O	TiO_2	Fe_2O_3	Loss by ignition
51.00	35.50	0.25	0.16	0.15	0.27	0.78	1.05	10.84

Fly ash

The used FA was supplied by thermal power plant Burshtyn, Ivano Frankivsk region, and is classified as a class F fly ash. The fraction of the powder material obtained by sifting through a 600 µm sieve was used in the experiments. The chemical composition of FA is shown in Table 15.

Table 15 *Chemical composition of FA (Ukr), wt.%*

SiO_2	Al_2O_3	CaO	MgO	SO_3	Na_2O+ Ka_2O	TiO_2	MnO	Fe_2O_3	C	Loss by ignition
46.12	18.02	4.10	1.46	0.21	2.10	1.78	0.14	22.17	250	1.40

Blast furnace slag

The granulated BFS was supplied by CEMBUDSERVICE Co, Kam`yanske, Dnipro region. The fraction of granulated BFS with a particle size of less than 600 µm, as well as for FA, was used in the experiments. The chemical composition of BFS is shown in Table 16.

Table 16 *Chemical composition of BFS (Ukr), wt.%*

SiO_2	Al_2O_3	CaO	MgO	SO_3	Na_2O	Ka_2O	TiO_2	P_2O_5	MnO	Fe_2O_3	Loss by ignition
40.64	6.02	45.10	3.61	1.74	0.42	0.40	0.30	0.01	0.17	0.62	0.97

Quartz sand

The quartz sand was supplied by JSC "Novoselivskyi GZK", Kharkiv region. The fraction of the powder material obtained by sifting through a 600 μm sieve was used in the experiments. The chemical composition of sand is shown in Table 17.

Table 17 *Chemical composition of quartz sand (Ukr), wt.%*

SiO_2	Al_2O_3	CaO	MgO	Na_2O	Ka_2O	TiO_2	Fe_2O_3	Loss by ignition
98.50	0.50	0.10	0.02	0.05	0.05	0.08	0.05	0.65

Surfactant Castament FW-10

Castament FW-10 was supplied by BASF company. It is free-flowing, spray dried powder based on polyethylene glycol.

Activating solution

Preparation of activating solution was performed by dissolution of KOH/NaOH in distilled water and uniform stirring inside of stainless steel (SS) container with the use of planetary mill to obtain alkaline solution, adding potassium/sodium liquid glass into alkaline solution and final stirring to obtain a homogeneous solution. As the reagents were used: potassium/sodium hydroxide (Novohim, Kharkiv region), potassium liquid glass - UKRSIL 32 (UKRSILICATE LLc, Zaporozhye region) with SiO2/K2O molar ratio 3,1-3,3; density 1,4 g/cm3 and sodium liquid glass (Zaporizhskloflus, Zaporozhye region) with SiO2/Na2O molar ratio 3,0-3,3; density 1,5 g/cm3.

To perform the laboratory activities, different equipments such as furnace (Nabertherm 1200°C), planetary mill (grinding and mixing power components), vibrating table for casting the mould and plastic mould have been used.

Following parameters of the samples were studied:

- Rheology

Rheology measurement was performed using the rotational viscometer Brookfield LVDV-II+ Pro. Rheological behaviour of geopolymer pastes (slurries) was evaluated according to the ASTM D 2196 Standard test methods for rheological properties of Non-Newtonian materials by rotational viscometers. Rheograms were obtained at shear rate – 0,1-22 s-1.

- Setting time

The setting time values of the prepared fresh geopolymer pastes was determined by a Vicat apparatus. To determine the measurement uncertainty, the setting time test for every mixing proportion was conducted twice.

- Study of samples morphology

After setting of samples for 24 h at room temperature, the shrinkage cracking morphologies were observed and counted. The drying shrinkage was controlled by measuring three samples to obtain an average value. Also, the proportions of the raw materials for mixing were considered, as their values affect the behaviour of the geopolymer paste during the curing of the samples. In particularly, any excess alkaline solution is more likely to induce crystallization on the surface in the form of white salt deposits (efflorescence).

- Mechanical testing

For compressive strength testing, the fresh geopolymer slurry was filled into 40x40x40 mm cubes, as well as cylinders with a diameter of 20 mm and a height of 30 mm for the destruction of cured samples and the study of the structure homogeneity. Geopolymer samples have been characterized after 7, 14 and 28 days of curing time. Three different cubes of one sample were used to gain a dependable average value. Testing was conducted according to DIN EN 196-1.

- Acceptance criteria

The acceptance criteria were predefined for the optimization of geopolymer production parameters: setting time ≤ 48 hours, compressive strength ≥ 5 MPa and absence of significant defects.

The optimization of the formulation started from the definition of the best composition for the geopolymer matrix without waste surrogate. Selected compositions of geopolymer are presented in Table 18.

Table 18 *Mixing proportions*

Component	Content, wt.%				
	Composition No				
	1	2	3	4	5
FA (Ukr)				34	34
BFS (Ukr)				20	20
MK (Ukr)	36	36	26,5	14	14
Sand			26,5		
Na_2SiO_3	46			11	
K_2SiO_3		46	33		11
NaOH	6			9	
KOH		6	6		9
H_2O	12	12	8	12	12

It has been determined that the samples of compositions No. 1 and 2 have cracks and deformations (*Figure 2*). The samples of compositions No. 3, 4 and 5 didn't have significant defects, they are dense and homogeneous.


MK based (comp. No 1, 2)
MK-sand based (comp. No 3)
FA-BFS-MK based (comp. No 4, 5)

Figure 2 *Geopolymer samples after 28 days of curing*

Characteristics of geopolymers (Compositions No 3-5) are presented in Table 19.

Table 19 *Characteristics of geopolymers*

Parameter	Composition No		
	3	4	5
Setting time, h Start/finish	8/48	4/24	4/20
Density, g/cm^3	1,75	1,83	2,15
Compressive strength, MPa (7/14/28 d)	12/15/22	13/20/25	22/28/32

The composition No. 3 has the lowest mechanical strength in solid samples. But, in compositions No. 4 and No. 5, instead of sand, the FA and BFS participates in the reaction, resulting in a denser structure and higher compressive strength. It should be noted that the use of KOH in the activating solution leads to an increase in compressive strength compared to NaOH, 32MPa (28 d) as opposed to 25 MPa (28 d). Considering that the composition No 5 is characterized with best properties, that formulation (named as MIX) is the optimized geopolymer matrix for further study with the RLOW simulant (surrogate).

To develop the most optimised geopolymer formulation, the different geopolymer formulations with various Al-Si raw materials and different type of alkaline activators were investigated. The optimal MIX-formulation based on Ukrainian raw materials was developed and proposed for further studying (see Table 20).

Table 20 *Geopolymer optimized matrix composition*

Raw Material	**Percentage (w/w)**
Fly ash	34 %
Slag	20 %
Metakaolin	14 %
K_2SiO_3	11 %
KOH	9 %
H_2O	12 %

The properties of the above formulation are the following:

Table 21 *Optimized formulation properties*

Property	**Value**
Setting time - start/finish (h)	4/20
Density (g/cm^3)	2,15
7 -day Compressive strength (MPa)	22
14-day Compressive strength (MPa)	28
28-day Compressive strength (MPa)	31

In this preliminary phase the pseudoplastic behavior of the matrix and the effect of the shear rate on viscosity of geopolymer were also investigated:

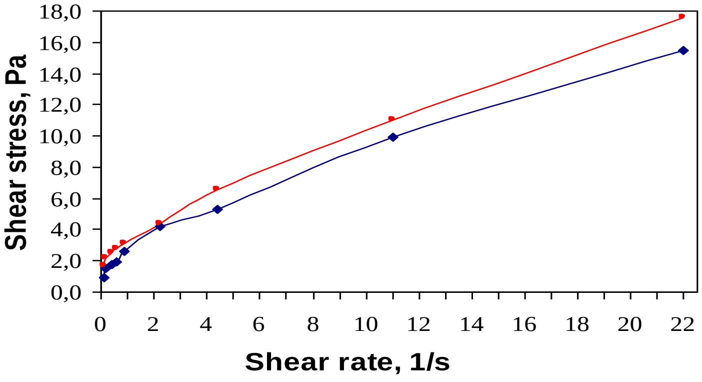


Figure 3 *Pseudoplastic behavior and rheopexy model*

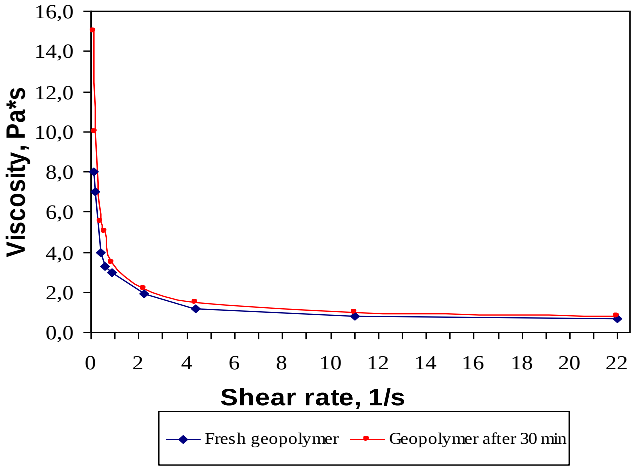


Figure 4 *Effect of shear rate on viscosity of geopolymer*

4.2.1 Tests and Results

An increasing amount (10, 20, 30 and 40 % volume) of RLOW surrogate (Shellspirax) Pump Oil has been introduced in the optimized geopolymer matrix. Both the fresh paste and the solidified samples have been characterized and the results are shown below.

Table 22 *Setting time at different Pump Oil percentage*

Setting time (start/finish)	Value
0-30% Oil	4/24
40% Oil	5/36
40% Oil + 0,5 % Castament FW 10 (BASF)[1]	3/24

In the case of 40% of Pump Oil in the geopolymer matrix a little fluidity has been observed. So the addition of Castament FW 10 (BASF) has been tested to improve homogeneity of the samples, increase compressive strength and reduce setting time.

The preparation of the samples has been performed as following:

- Without surfactant: preparation of alkaline silicate aqueous solution and then the simulated RLOW has been added to the solution. Finally, the sieved raw materials (MK+BFS+FA) have been added to the solution under mixing (60 minutes mixing in planetary mill, volume of container 250 ml) and forming (casting) of samples into plastic moulds.
- With surfactant: surfactant has been dispersed in water and added to prepare the alkaline silicate aqueous solution, then the simulated wastes have been added to that solution. Sieved raw materials (MK+BFS+FA) have been added to the solution under mixing (60 minutes mixing in planetary mill, volume of container 250 ml) and forming of samples into plastic moulds.

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[1] Castament is a good additive available in Ukraine (KIPT has a large experience with it). It is a solid Polyethylene glycol-based additive who increases fluidity.

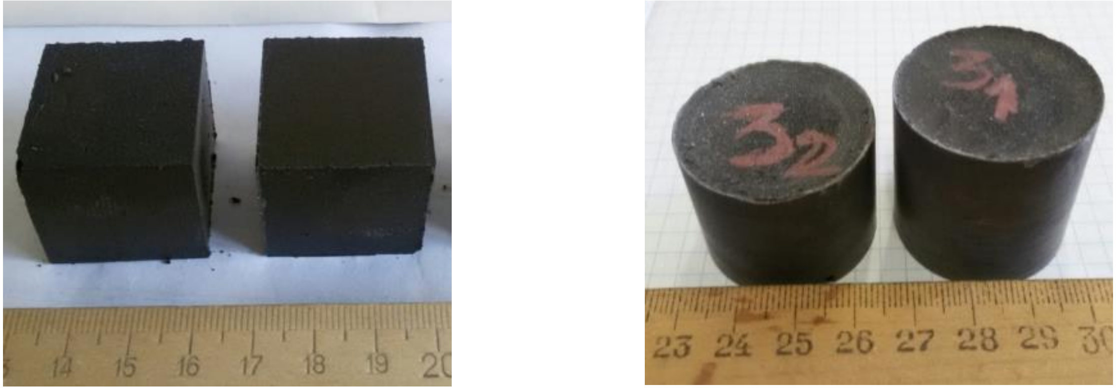

Figure 5 *Geopolymer samples (curing 24h)*

Figure 6 *Geopolymer samples with 30% of Shellspirax oil*

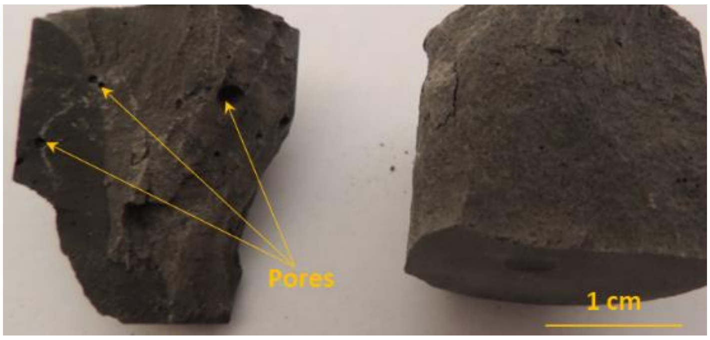

Figure 7 *Samples (40% oil - 7 days of curing) after strength testing - Castament influence on homogeneity of the samples: left – without FW-10, right – with 0,5% FW-10*

Compressive strength tests have been performed on the different formulations and results are reported in Table 23 and showed in Figure 8.

Table 23 *Compressive strength at different Pump Oil percentage*

Pump Oil (%)	**R_{c7} (MPa)**	**R_{c14} (MPa)**	**R_{c28} (MPa)**
0	22	28	30
10	12	14	16
20	9	10	12
30	5	7	8
40	6	8	

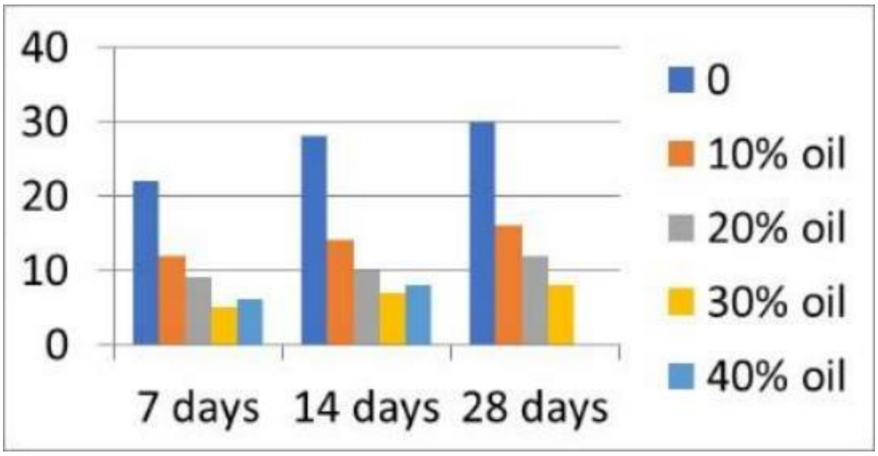

Figure 8 *Compressive strength at different Pump Oil incorporation rates*

4.3 NUCLECO

4.3.1 Conditioning Options studied

The conditioning options studied by NUCLELO are characterized by the following formulation:

- Raw materials: Blast Furnace Slag (BFS)[2] and alkaline activators;
- RLOW surrogate: Pump Oil (Shellspirax), Tributyl phosphate (TBP), Dodecane and TBP/Dodecane 70%/30% mixture.

The optimization of the formulation started from the definition of the best composition for the geopolymer matrix without waste surrogate. Both the fresh paste and the hardened mortar have been characterized in terms of:

- Workability
- Setting time
- Bleeding
- Compressive strength (on cylindrical specimens).

The observations registered are the following:

- The mixture based only on water and slag does not harden in a short time;
- The alkaline activation with NaOH or KOH allows the mixture to harden in a short time;
- The alkali-activated hardening leads to a green coloration of the specimens;
- The increase in the percentage of NaOH or KOH in the mixture improves hardening and compressive strength, up to a maximum value of 4% (for NaOH) or 5% (for KOH). Over these percentages there are no effects;
- If the quantity of water in the mixture is reduced, an increase in compressive strength is obtained;
- The addition of silica fume to the mixture, up to a maximum percentage of 15%, leads to an increase in compressive strength, proportional to the amount of additive. A further addition of this additive, up to 20%, does not produce further improvements in terms of compressive strength. With even higher percentages, a decrease in compressive strength is observed.
- $Ca(OH)_2$ (lime) does not work as an alkaline activator like NaOH and KOH;
- The addition of lime to the Na/K-activated mixture does not lead to any improvement.

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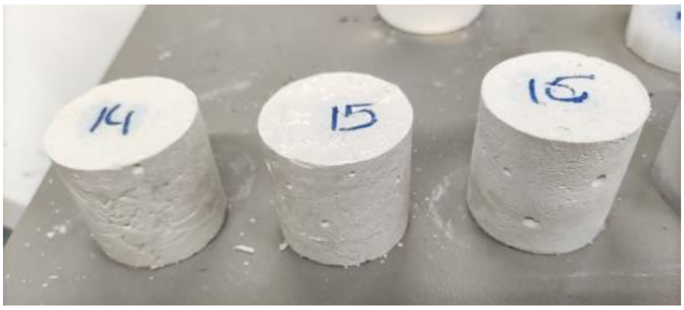
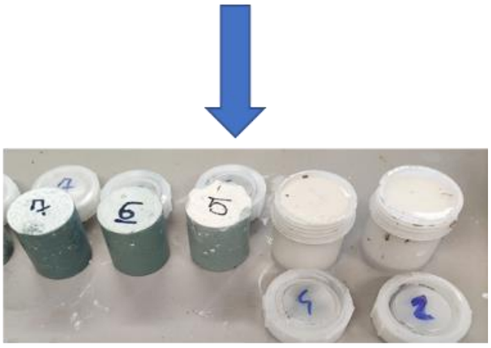
[2] Fos-sur-Mer (France) blast furnaces, Specific Surface Blaine: 4450±250 cm^2, average diameter: 11 µm.

Fresh mortar;



Water + slag + lime: the matrix does not turn green



After 2 days;

Figure 9 *Nucleco specimens without RLOW*

4.3.2 Tests and Results

After this first step the experimentation activities have considered the introduction in the matrix of the RLOW surrogate Pump Oil.

Alkaline activator has been added to the water under mixing and then the solution was added to the BFS powder (+ additives in some cases) under mixing (10 minutes mixing) and the preparation of the geopolymeric matrix with RLOW surrogates has been performed as following:

- Without emulsifier (surfactant): alkaline activator is added to the water under mixing and then the organic liquid is added to the solution. Finally, the BFS powder (+ additives in some cases) is added under mixing (10 minutes mixing).
- With emulsifier (surfactant): surfactant is dispersed in water and then organic liquid is added to obtain the emulsion under mixing. Alkaline activator is added and finally the BFS powder is added under mixing (10 minutes mixing).

The observations detected are the following ones:

<u>Addition of Shellspirax oil</u>

- Oil increased workability therefore W/B ratio was reduced to 0.15;
- The use of KOH as activator led to higher compressive strength than NaOH;
- About 60% (vol.) was loaded without bleeding but no hardening was checked even after one week
- Bleeding was observed only with the addition of silica fume
- With about 30% (vol.) it was possible to obtain formulations that allow hardening of the specimens, up to compressive strength values of about 8 MPa (after 28 days);

60% (vol.) Oil

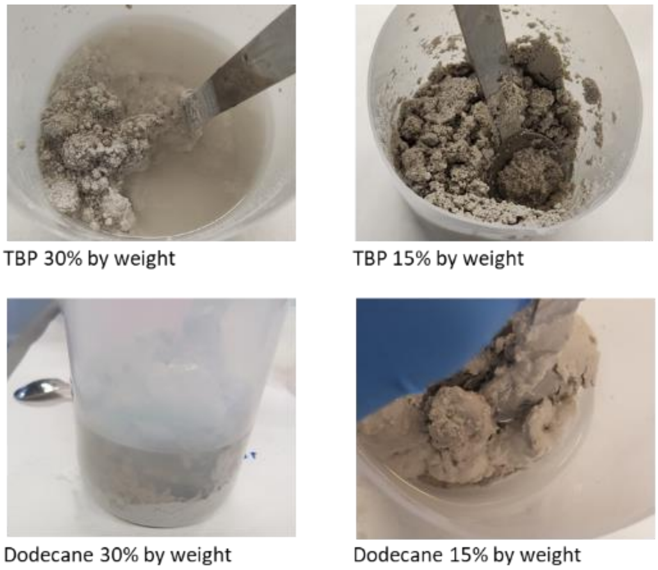
Oil bleeding with silica fume

30% (vol.) Oil with KOH as activator

Figure 10 *Geopolymer formulations with Shellspirax oil*

Addition of TBP and/or Dodecane

The fist tests with TBP and Dodecane showed that they are not incorporated into the mixture, even at low percentages. For this reason, it has been introduced an emulsifier (surfactant). A soap powder, a liquid soap and TRITON X were used for the scope.



TBP 30% by weight

TBP 15% by weight

Dodecane 30% by weight

Dodecane 15% by weight

Figure 11 *Tests on TBP and Dodecane*

The evidence registered during this step are the following:

- No results were obtained with soap powder and with TRITON X;
- TRITON X allows the liquid to be partially emulsified, but this is not sufficient to incorporate the waste into the geopolymer matrix;
- With liquid soap a good result is obtained in terms of liquid emulsion and incorporation;
- With some formulations based on Dodecane, it was obtained the complete hardening of the specimens (it was possible to carry out compression tests)

Since liquid soap contains anionic surfactants, it was decided to test one of the most common of these: sodium lauryl sulphate (SLS). Various SLS-based formulations have been tested, keeping the waste loading fixed at 15% by weight and varying:

- **Reference Surrogates:**
    - TBP
    - Dodecane
    - TBP/Dodecane 70/30
    - Shellspirax oil

- **Conditioning recipe parameters:**
    - Type of alkaline compound (KOH/NaOH)
    - Na or K-Activator/Mixture
    - Slag/Mixture
    - Water/Mixture
- **Sequence of adding components:**
    - Water+Activator+SLS+Waste+Slag
    - Water+SLS+Waste+Activator+Slag

For Shellspirax Pump Oil the results of the experimentation activities can be summarized as follows:

- The use of surfactant completely eliminates the bleeding of the mixtures, even if it is subjected to vibration;
- With the surfactant the workability of the mixture decreases but the mixture is much more homogeneous;
- The compressive strength values obtained so far (after one week of maturation) are similar to those determined without SLS.

For TBP, Dodecane and TBP/Dodecane 70/30 mixture:

- With the use of SLS, in all cases it was possible to obtain formulations capable of incorporating the waste, with a waste loading of 15% by weight;
- With dodecane have been found formulations with a good degree of hardening (compressive strength of about 5 MPa after one week);
- The compressive strength values obtained so far (after one week of maturation) are similar to those determined without SLS;
- With TBP have been obtained homogeneous and non-bleeding mixtures. One week after casting the mixtures, the specimens still have compressive strengths of about 2 MPa

Specimen with oil without SLS

Specimen with oil with SLS

Figure 12 *Experimentation with SLS*

4.4 POLIMI

POLIMI developed research concerning geopolymers for two different encapsulation approaches: the single step with a direct encapsulation and the two-step with a pre-impregnation on polymers. After the optimization of polymeric formulation, POLIMI started the experimentation on attempt of encapsulation into stable monolith.

POLIMI has collaborated with NUCLECO to exchange experimental data, materials, and laboratory tests to direct the research and to share achievements with all Partners.

4.4.1 Conditioning Options studied

The conditioning options studied by POLIMI are based on:

- Raw materials: novel tuff-based geopolymer for RLOW direct encapsulation and recycled polymer for RLOW pre-impregnation;
- RLOW surrogates: kerosene and TBP, scintillation cocktail (UG-AB) and vacuum pump oil (A120).

For the direct encapsulation of RLOW, POLIMI used novel tuff-based geopolymer. The choice of such a raw material is related to its worldwide availability, low costs and satisfactory reactivity. Besides, it contains zeolites for radionuclide trapping, and it has a high durability as proved by Roman concrete. The applied approach was:

- Preliminary study of Pozzolanic Reactivity of volcanic Tuff;
- Optimization of Tuff-based GP formulation;
- Direct encapsulation of RLOW in optimized Tuff-based GP.

Concerning the two-step conditioning of the RLOW involving pre-impregnation, POLIMI started from the understanding of the NOCHAR-N910 binding mechanism and proposed a recycled polymer as an alternative. It is a valid candidate because it has a low environmental footprint, low costs and a better RLOW impregnation.

4.4.2 Tests and Results

4.4.2.1 Single-Step Direct Encapsulation

POLIMI started from the comparison between Volcanic Tuff (VT) and Metakaolin pozzolanic reactivity. Both thermal and mechanical pre-treatments were considered to enhance VT pozzolanic reactivity: calcination up to 800 °C and grinding. The pozzolanic reactivity of both treated and untreated VT in alkaline solutions has been determined by two different methods:

- Chemical method, by quantifying the amount of dissolved Al and Si by ICP-OES and estimating the reacted fraction by gravimetry [11].
- Conductivity method, by estimating the pozzolanic reactivity by monitoring conductivity change in time [12].

In both cases 3.4 M and 8 M NaOH solutions were employed.

These experiments showed that VT is less reactive than MK in the same conditions. It was shown that at the same reference conditions (*i.e.,* in 3.4 M NaOH solution, room temperature), the reacted fraction of VT is far below that of MK, regardless of any thermal and mechanical pre-treatment. If NaOH concentration is increased, the VT reacted fraction increases as well. When the temperature is increased above 50 °C, the VT reacted fraction reaches about 37%w, approaching 42%w of MK at reference conditions. These results were confirmed by measurements of dissolved Si and Al and of conductivity changes in the filtered solutions.

The improved VT reactivity at higher NaOH concentration and temperature suggests some more suitable experimental conditions for VT-GP preparation, such as: optimal composition of the activation solution and curing temperature. Nevertheless, the lower reactivity of VT may encourage the addition of other raw materials (BFS and/or fly ashes) together with VT to improve the final mechanical properties of the manufacts.

After the preliminary studies, POLIMI worked on the optimization of Tuff-based geopolymer formulation with similar formulation of the mix-based reference, where metakaolin has been replaced by tuff, while BFS and fly ash have been kept in the formulation. First, the VT-based GP was prepared without surrogate waste. In this case, the alkaline activator is added to water under mixing some hours before GP preparation. Then the solution is added to the VT powder (10 minutes mixing). The GP grout (see Figure 12) is cured for 2 days at different temperatures between room temperature (20 °C) and 70 °C.

Figure 13 *Fresh geopolymeric grout*

Different types of alkaline activators (NaOH, KOH, Na-silicate) have been tested. The optimal amounts of water, activator, Volcanic Tuff have been determined based on literature [13] and experimentally verified:

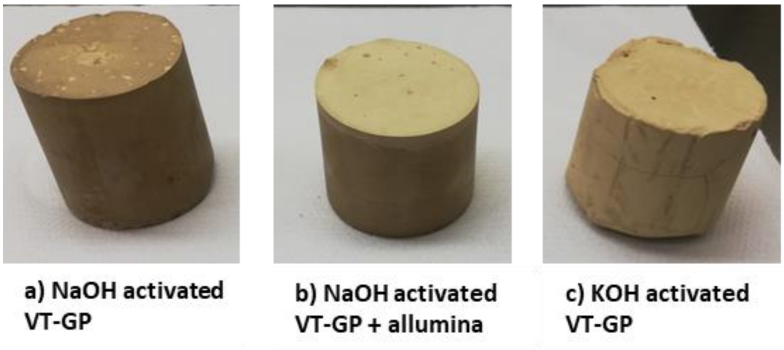
Table 24 *Alkaline activators tested by POLIMI*

Sample	Tuff-GP	Tuff-GP + Al_2O_3	Tuff-GP + mullite
NaOH solution	40%w	40%w	40%w
Tuff	60%w	52%w	47%w
Al_2O_3	0	8%w	0
Mullite	0	0	13%w

Both NaOH and KOH activation solutions allowed the geopolymer grout to harden at curing temperature above 50 °C, while the NaOH and Na-silicate mixture did not at all. The hardened specimen activated by KOH exhibited some cracks, so the NaOH solution was identified as the optimal activator (see Figure 14). Attempts to improve mechanical resistance were done by partially replacing Volcanic Tuff with amounts of alumina or mullite. In all cases, the workability was very high. The composition of the final optimized formulation is:

$$3\ SiO_2 + 1\ Na_2O + 0{,}6\ Al_2O_3\ (\text{or } 1.1\ Al_2O_3 \text{ if alumina is used}) + 12{,}5\ H_2O$$

Some preliminary compression tests proved that the addition of alumina is ineffective. Moreover, unsatisfactory compressive strength values of 1 MPa were registered on specimens cured for 28 days.



a) NaOH activated VT-GP

b) NaOH activated VT-GP + allumina

c) KOH activated VT-GP

Figure 14 *VT-GP activated with NaOH (a) and KOH (c), VT-GP + alumina activated with NaOH (b).*

Some preliminary tests were performed by adding RLOW surrogates.

The samples of Figure 14 are Tuff-GP loaded with RLOW and respectively: Kerosene and TBP 20%v; Ultima Gold 20%v and Vacuum pump oil 30%v.

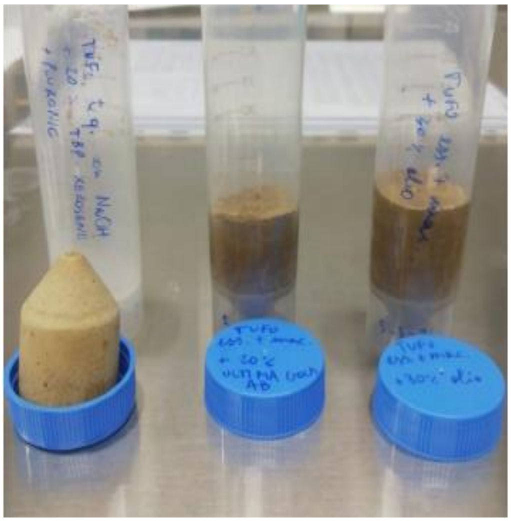


Figure 15 *Tuff-GP + loaded with RLOW Kerosene and TBP - 20 %v; Ultima Gold - 20 %v and Vacuum pump oil - 30 %v*

Pluronic surfactant was added to the first sample of Figure 15 in amount to be optimised but allowing satisfactory mixing with the geopolymer grout without subsequent bleeding. Anyhow, it would be preferable to use a cheaper surfactant. No surfactants were added to the other samples of Figure 14. The mixing of these surrogate RLOW with the fresh grout was efficient and no bleeding occurred. But the scintillation cocktail sample did not harden as other samples.

The optimization of direct encapsulation of RLOW by specific surfactants is reached with next formulations, corresponding to the samples in figure below:

1. 20%v Vacuum pump oil + Triton-X
2. 20%v Ultima Gold AB + Triton-X
3. 20%v Kerosene + TBP (30%v) + Pluronic

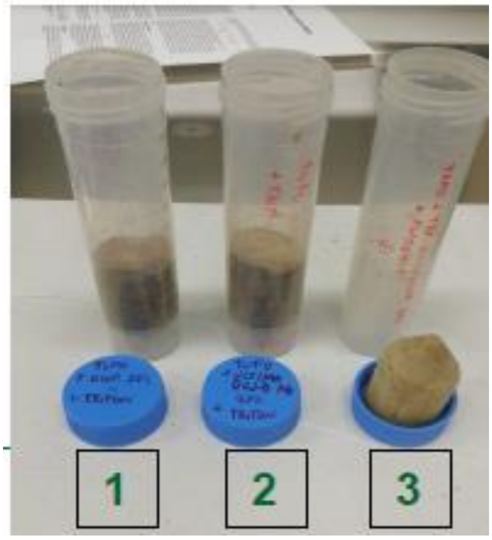


***Figure 16** Samples with optimized direct encapsulation of RLOW by specific surfactants.*

Following the preliminary results, new RLOW surrogate additions were tested:

- Vacuum Pump Oil (Alcatel120): 40%v loading can be achieved without employing any surfactant.
- Scintillation cocktail (Ultima Gold, UG-AB): at least 30%v loading can be achieved using a surfactant.
- 30%v TBP in kerosene (TBP/K): about 25%v loading can be achieved thanks to a surfactant.

Without surfactant: the surrogate RLOW was directly added to the geopolymer grout (10 minutes mixing).

With surfactant: the geopolymer grout was prepared with 70% of the total amount of water. The surfactant was dissolved in the remaining 30% of water (10 minutes mixing) and was then poured into the GP grout. Finally, the surrogate RLOW has been added to the mixture (10 minutes mixing).

In all cases, the addition of surrogate RLOW to VT-GP further improved workability. No bleeding was observed, and the specimens hardened within few days (see Figure 17).

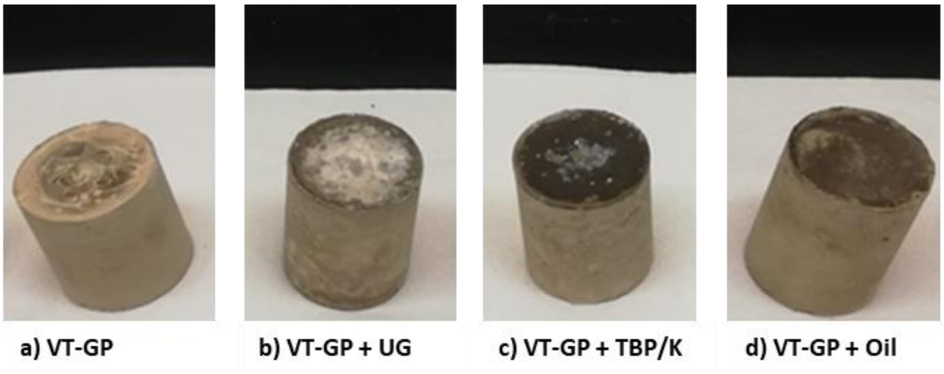

a) VT-GP
b) VT-GP + UG
c) VT-GP + TBP/K
d) VT-GP + Oil

***Figure 17** VT-GP without waste (a) and with scintillation cocktail (b), TBP/K (c), and Vacuum Pump Oil (d) surrogate waste.*

In the case of UG-AB and TBP/K the use of a surfactant was necessary to optimize or allow mixing with the GP grout respectively. Some surfactants were tested, but non-ionic Poloxamer copolymers resulted the more effective. About 2%w of Pluronic F-127 allowed UG-AB and TBP/K to be mixed with the GP grout enabling the specimens to harden without any bleeding.

Preliminary compression tests proved that the addition of surrogate RLOW worsens compressive strength values from 1 MPa to about 0.6 MPa (at 28 days of curing). Immersion tests following ANSI-ANS 16.1 leaching protocol are on-going on VT-geopolymer specimens with/without oil, UG-AB, and

TBP/K surrogate waste to determine stability and retention capability of the geopolymer towards RLOW surrogate and contaminants.

Concerning RLOW direct encapsulation in VT-geopolymer, preliminary results confirm that modifications of geopolymer formulation are necessary to improve mechanical properties. Further studies are needed to identify cheaper and more effective surfactants for the emulsification of surrogate RLOW in the geopolymer grout.

4.4.2.2 Two-Step approach With Pre-Impregnation

About the two steps conditioning with pre-impregnation, POLIMI started with characterisation of NOCHAR-N910 (see Figure 18). Preliminary XRD, ATR-IR, FT-Raman, CHNS, DSC, and TGA analyses on N910 polymer without surrogate waste were conducted to characterize the material. In particular, the XRD analysis showed that N910 is amorphous without any crystalline phase. ATR-IR and FT-Raman analyses allowed to identify the main functional groups of the polymer that may participate in the RLOW binding. TGA and DSC analyses were performed to further characterize the material and evaluate its thermal stability.

Furthermore, ATR-IR, FT-Raman, and TGA analyses were performed on N910 polymer loaded with some surrogate RLOW, such as Vacuum Pump Oil (A120), kerosene and the TBP/K mixture. Both ATR-IR and FT-Raman analyses suggested that no chemical bonds occur between polymer and waste, but the interaction is just due to physical absorption in the polymer cavities. This is in agreement with the partial RLOW release that can be observed once the loaded material is slightly compressed. A further confirmation of this hypothesis comes from the TGA experiments. These showed that a first weight reduction stage could be related to surrogate RLOW loss from the material, followed by the weight losses attributed to complete degradation of the N910 polymer.

Figure 18 *NOCHAR-N910 polymer*

From preliminary results, the interaction between NOCHAR-N910 and RLOW seems to be absorption by physical interaction, and a slight compression during analysis seems to be enough to cause RLOW release.

POLIMI has selected and characterised a valid alternative (cheaper and more sustainable) to NOCHAR-N910, i.e. a recycled polyurethane foam (see Figure 19).

Figure 19 *Recycled polymer*

The absorption mechanism is similar to the one hypothesized for N910 polymer, excluding the formation of chemical bonds between RLOW and polymer.

The capability of recycled PU of absorbing different types of surrogate RLOW (vacuum pump oil, scintillation cocktail, TBP/K) were studied. The surrogate RLOW has been added to the polymer (same procedure for NOCHAR N910 and recycled PU) under vigorous mixing before FT-IR, Raman, TGA, and DSC (just for PU polymer) analyses.

Absorbent capacity of up to 15:1 (RLOW to polymer ratio by weight) was obtained. The composite material (PU polymer and RLOW) was then cemented, similarly as already reported in the literature for N910 [14] .

The activities were continued as a part of Task 5.3.3 (see Chapter 5.6).

4.5 RATEN - Regia Autonoma Tehnologii pentru Energia Nucleara, Romania

The RATEN work in the frame of PREDIS T5.3 was performed by the Institute for Nuclear Research Pitesti (RATEN ICN).

4.5.1 Conditioning Options studied

RATEN contributed to the development RLOW conditioning in geopolymer matrix using industrial and natural sources of aluminosilicates. The conditioning options studied by RATEN are based on:

- Raw materials: granulated blast furnace slag (BFS) - indigenous BFS from Galati, volcanic tuff (from Barsana), standardized sand (certified CEN, EN 196-1), alkaline activator;
- RLOW surrogate: Pump Oil (Shellspirax S2A80W90); Scintillation Cocktail (Ultima Gold AB).

The BFS from Galati has a hydraulic activity (K_b) of 1.07 and consequently it has a basic character. To be used in GP formulation the BFS was dried, grounded and sieved to fineness up to 75 µm and the volcanic tuff was calcined at 800°C to increase its reactivity. Albite, anorthite and dolomite are the frequently phases identified in the volcanic tuff (Figure 20).

As alkaline activator a mixture of commercial sodium silicate solution (water glass) and 8 M NaOH solution was used. The sodium silicate solution used is produced by Merk and contains: 25.5% SiO_2, 7.5% Na_2O and 66% H_2O.

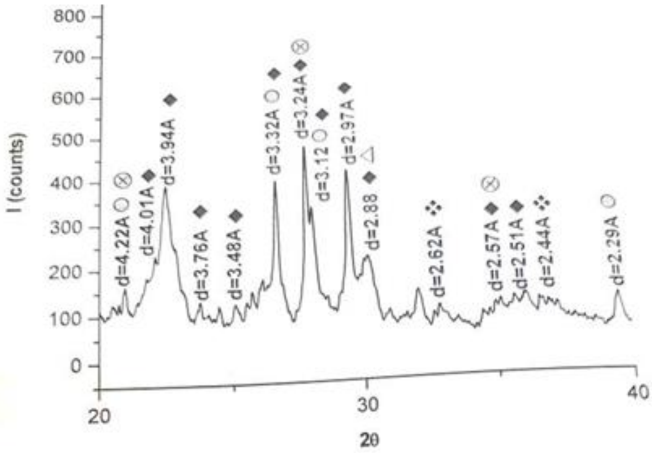


Figure 20 *Diffractogram for volcanic tuff used by RATEN*

The BFS produced by Liberty Steel Galati is not commercially available and three different batches were used in the RATEN ICN experimental program, only one of them (batch #3) being directly provided by the steel company. The chemical composition of the BFS (batch#1 – used for the first set of tests) and of the volcanic tuff is presented in (*Table 25*).

Table 25 *Chemical composition of Romanian Blast Furnace Slag (RO BFS (#1)) and Volcanic Tuff (VT), wt.%*

wt.%	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	TiO_2	MnO	Na_2O	K_2O
VT	55.45	9.83	1.18	10.97	2.55	0.13	-	1.67	1.55
RO BFS (#1)	34.72	44.56	4.47	11	0.8	0.48	0.66	0.7	0.65

To prepare the geopolymer mortars, the following mixing protocol was applied:

- Homogenization of the aluminates precursors (BFS and VT)
- Add activating solution to the mixture of aluminates and mix in a planetary mixer for 2 minutes (hand mixer for low scale formulations)
- Add sand and mix for 2 more minutes

- Cast the mortar into moulds, at room temperature

Before introducing the RLOW surrogate in the matrix, the GP formulation has been tested and optimized. The formulations tested are presented in the following table, where GP is the indicative for geopolymer mortars and CEM is the indicative for a cement-based mortar:

Table 26 *RATEN GP formulations tested*

composition, wt.%	**GP1**	**GP2**	**GP3**	**CEM II**
cement, CEM II	-	-	-	22.22
RO BFS (# 1)	20.45	15.91	14.32	-
VT	-	4.55	6.14	-
sand	61.36	61.36	61.36	66.67
8M NaOH	9.09	9.09	9.09	-
water glass	4.55	9.09	9.09	-
additional H_2O	4.55	-	-	11.11

For initial testing (setting time and bleeding) all mortar specimens were prepared at low scale, using hand mixer (~700 rpm) and small cylindrical moulds for curing. For mechanical strength measurements, the mortar specimens were mixed in a standard planetary mixer used to prepare cement-based mortars according to EN 196 part 1 and 3 standard (see *Figure 21)* and casted at room temperature in standardized prismatic moulds (40x40x80 mm or 40x40x160 mm).

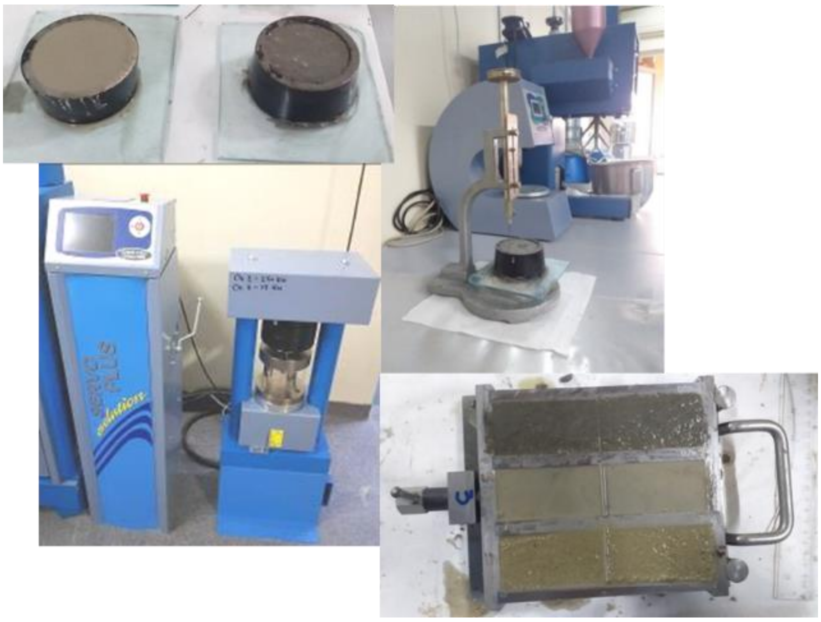


Figure 21 *Some pictures of RATEN laboratory activities*

4.5.2 Tests and Results

The fresh and cured mortar specimens were characterized according to SR EN 196-3 in terms of:

- setting time and soundness: using VICAT equipment
- compression strength: using MATEST equipment

Characteristics of the mortar specimens are reported in Table 27.

Table 27 *GP formulations characteristics*

		GP1	**GP2**	**GP3**	**CEM II**
setting time	initial	45 min	2h 40 min	2h 20min	4h 30min
	final	2h 15 min	4h 15 min	6h 20min	> 8 h
Mechanical strength, MPa		19.34	34.97	< 5	54.614
Density, g/cm3		2.113	2.107	1.974	2.214

For the GP1 and GP2 formulations good workability and setting times were obtained and after 28 days of curing. Since these two formulations had mechanical strength above the acceptance criteria, they were further tested for RLOW incorporation.

The tests done for RLOW surrogate incorporation in GP1 and GP2 matrices have shown that for both types of RLOW, without any additive, surfactant, or emulsifier it was not possible to obtain a matrix with good workability for waste loading higher than 10wt.%.

To avoid adding organic additives, sodium phosphate was tested (5%, 7.5%, 10% and 20% - reported to the volume of the waste), the resulted emulsions were not stable for more than 15 minutes and regardless the order of addition, the GP matrix with oil/scintillator did not appear homogeneous and after short time the waste was separated (see Figure 22).

Figure 22 *Pictures during oil incorporation and from the emulsification step*

A second set of tests to incorporate RLOW was carried out using a new batch of Blast Furnace Slag (RO BFS (#2)) whose composition is described in Table 28.

Table 28 *Composition of RO BFS (#2) used during second set of tests to incorporate RLOW*

wt.%	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	MnO	K_2O	LoI
RO BFS (#2)	25.29	37.61	3.85	5.22	3.08	0.62	0.52	21.73

To increase the waste loading the following surfactants were tested: sodium dodecyl sulphate, Hexadecyltrimethylammonium bromide (CTAB), polysorbate 80 (TWEEN® 80), tricosaethylene glycol dodecyl ether (Brij®L23) and alkyl-polyglucoside solution (Glucopone 600 CS UP).

Following the partners recommendations, in this second set of tests performed by RATEN ICN, the amount of sand was decreased to 20-30 wt.% and, to bring more Al2O3 in the binder, the amount of volcanic tuff was increased. Also, the concentration of NaOH solution was increased to 10M. Different formulations (see Table 29 were tested to select those that allow higher waste incorporation rates (the target value 20 wt%).

For incorporation of RLOW surrogates in geopolymer, the following mixing sequence was applied:

RLOW surrogate was mixed for 5 minutes on a stirring plate with adequate amount of surfactant and the emulsion was continuously stirred until it was added over the geopolymer.

- the two components of the activating solution were mixed together and added to the BFS (< 50 µm) and mixed for 2 minutes in a small scale planetary mixer
- the adequate amount of sand was added and mixed for 2 more minutes
- the emulsified RLOW surrogate was added and mixed for 5 more minutes

The resulted mortars were cured at room temperature into small moulds.

Table 29 *Range of mortar composition tested*

Mortar component	wt.%
RO BFS (#2)	20 - 55
VT	10 - 20
sand	20 - 30
10 M NaOH	5 - 10
water glass	4 - 10
w/b	0.3 - 0.6
waste loading	10 - 20

In the water to binder ratio (w/b) the additional water and the water content in the alkaline solution is considered and the binder includes precursors (BFS and VT) and the solid part of the alkaline activators. Good workability and insignificant bleeding were observed for geopolymer specimens containing:

- 20 wt.% of VT
- wt.% of 10M NaOH
- 10 wt.% of water glass
- W/B = 0.4
- oil incorporation up to 15 wt.%
- scintillator incorporation up to 10 wt.%

Mortars prepared with the oil emulsified using TWEEN® 80 and CTAB surfactants had good rheological properties but none of the surfactants tested had any effect on the rate of scintillation liquid incorporation.

After 28 days of curing, the mortars with mechanical strengths higher than 5 MPa were those with oil incorporation up to 10 wt.% and liquid scintillator incorporation up to 8 wt.%.

4.6 SCK-CEN

The SCK-CEN approach for laboratory activities is summarized in the following scheme:

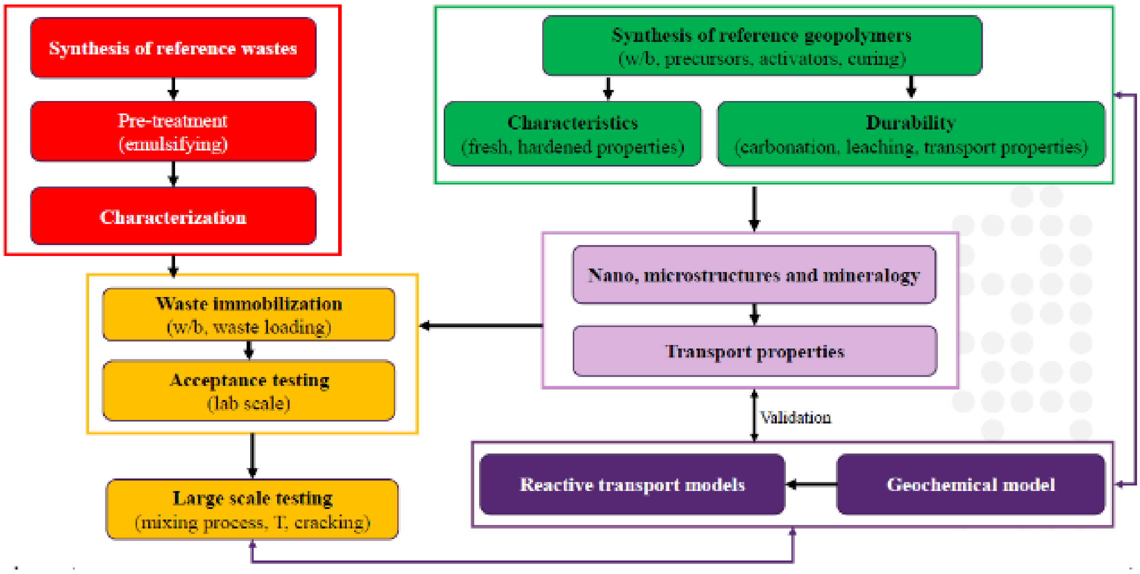


Figure 23 *Methodology and Planning of SCK-CEN*

4.6.1 Conditioning Options studied

The conditioning options studied by SCKCEN are based on:

- Raw materials: Ground Granulated Blast Furnace Slag (GGBFS, from Ecocem) and Metakaolin (MK, from Metamax),
- RLOW surrogates: TBP and Ionic liquid (Sigma-Aldrich), lubricating oil (Nevastane EP100 and Shellspirax 80W90, from UK lubricant supplies)

GGBFS and MK were activated by a mixture of sodium disilicate and NaOH (10 M). Extra water was used to adjust the water/binder ratio, which is an important parameter potentially affecting the liquid waste loading of the materials. The alkali activated mortars with a fixed 20 vol.% of aggregate (fine river sand) were selected to study in SCK CEN, aiming to create more space in the mortar matrices for future waste immobilization.

With the aim to comply the final waste form with ACRIA, the testing properties for the alkali activated materials (AAMs) are:

- Setting time, viscosity, heat release
- Mechanical strength
- Microstructure: SEM, MIP, nitrogen adsorption
- Mineralogy: XRD, FTIR, TGA/DSC, NMR
- Transport properties: water permeability, gas diffusivity
- Durability (alkali silica reaction, accelerated carbonation, and leaching)

The precursors composition (wt.%) is summarized in Table 30 below:

Table 30 *Precursor composition (wt.%)*

Oxides	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**TiO_2**	**SO_3**	**LOI***
GGBFS	32.4	11.1	0.60	43.40	7.77	0.53	0.27	1.01	2.41	0.51
MK	52.08	44.27	0.45	0.03	0.08	0.17	0.26	1.68	0.03	0.83

*Loss in ignition at 1000 °C

The mortar formulations are follows:

Table 31 *Mortar formulations*

Mortars	w/b*	NaOH$^{\#}$ (NH), wt.%	Na-disilicate$^{\#}$ (SS), wt.%	SiO_2/Al_2O_3	SiO_2/Na_2O	H_2O/Na_2O
AAS 0.35	0.35	4	2.69	5.22	7.87	29.15
AAS 0.45	0.45	4	2.69	5.22	7.87	37.35
AAS 0.55	0.55	4	2.69	5.22	7.87	45.55
MK 0.75	0.75	4	71.06	3.82	3.74	16.54
MK 0.85	0.85	4	71.06	3.82	3.74	18.75
MK 0.95	0.95	4	71.06	3.82	3.74	20.95

*Water in w/b ratio also includes water in activators, and binder includes precursors and the solid part of activators.

$^{\#}$ wt.% w.r.t. precursors

SiO_2, Al_2O_3, Na_2O, H_2O contents (mole) are the total amount of the mixture.

With the aim of obtaining reference AAMs with good performance and appropriate matrices for immobilizing the organic liquid waste, both GGBFS and MK precursors were used to investigate whether C-A-S-H or N-A-S-H network is more beneficial for waste encapsulation. The water to binder ratios (w/b) were also examined, and the results showed that the w/b ratios of 0.35, 0.45 and 0.55 were suitable for activated GGBFS mortars, while the higher w/b ratios of 0.75, 0.85 and 0.95 provided good MK-based polymers.

4.6.2 Tests and Results

To understand the underlying activation processes, the early-stage heat evolution of reference AAMs were determined at 20 ℃ within 7 days. A sharp exothermic peak (Figure 26-left) appeared immediately after mixing the solid precursors with activators, attributing to the wetting and dissolution of the raw materials. Following the initial peak was a broader exothermic peak, which was assigned to the geopolymerization to form C-A-S-H or N-A-S-H gels. It is clear that the higher the w/b ratio, the more delayed the geopolymerization and the lower the heat release.

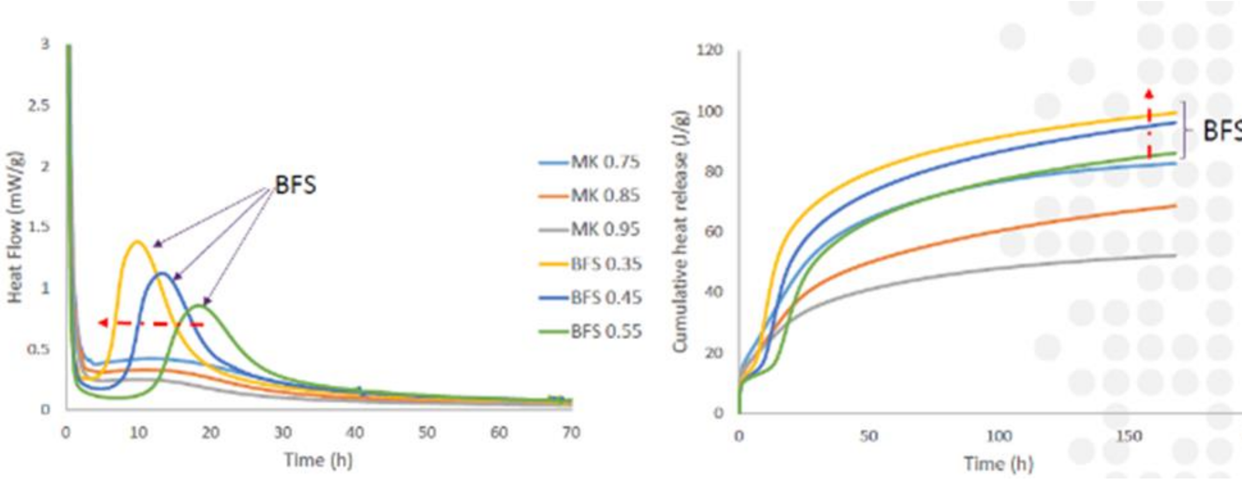


Figure 24 *Heat Flow and the Cumulative heat release of alkali activated slag (BFS) and MK-based geopolymers (MK****)***

Both compressive and flexural strengths of reference geopolymers consistently decreased with the increase in w/b ratio, i.e., the compressive strength reduced from 38 to 19 MPa, while the flexural strength decreased from 4.8 to 2.4 MPa when the w/b ratio increased from 0.75 to 0.95, respectively. For the reference AASs, the w/b ratio also affected remarkably the mechanical strength. The compressive strength increased from ~30 to 66 MPa, and the flexural strength increased from ~4 to 11 MPa when the w/b ratio decreased from 0.55 to 0.35, respectively.

To understand the durability of geopolymers, ASR, carbonation and leaching tests have been carried out. The ASR test followed the standard procedure ASTM C1260 (immersion of samples in 1M NaOH at 80 °C within 14 days). The carbonation conditions were 1% CO_2, 20 ℃, and 60% relative humidity for up to 28 days of exposure. The leaching test was done on saturated samples under immersion in 6M NH_4NO_3 for up to 28 days duration. MK-based geopolymers witnessed an excellent ASR resistance with a low expansion of about maximum 0,08% after 14 days immersion in 1M NaOH. Although AASs were more vulnerable to ASR than MK-based geopolymers, their expansion was still acceptable as around the standard threshold (ASTM 1260) of 0,1% expansion. AASs were also susceptible to carbonation, even rather than OPC system with the same w/b ratio, whereas MK-based geopolymers showed a better carbonation resistance. Leaching test was performed as a part of T5.4, the general results showed the preliminary leaching of Na and Ca from AAM matrix under exposure to 6M NH_4NO_3 solution.

Figure 25 *ASR test (left) and carbonation test (right)*

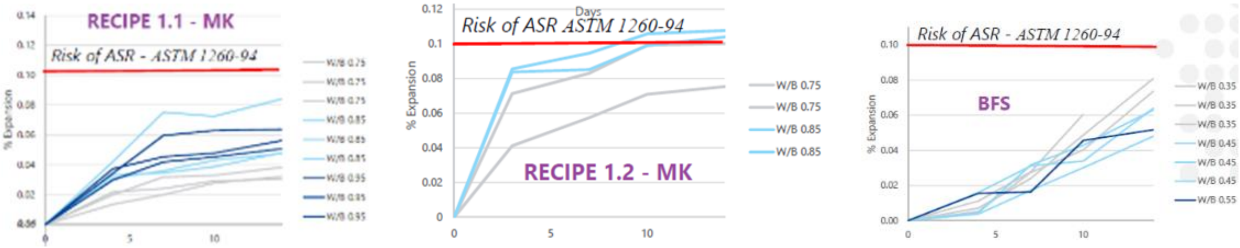


Figure 26 *Results of ASR tests*

SCKCEN has tested the accelerated leaching using saturated samples exposed to NH_4NO_3 6M; the testing system was examined after 7 days, at 14 days and at 28 days of immersion.

The leachate solution was tested by pH and inductively coupled plasma optical emission spectrometry (ICP-OES) for Ca, Na, K, Fe, Mg, Si, Al, SO_4 and Cl. After leaching tests were finished, the following investigations were performed for the solid samples: the leaching depth, mass changes, mineralogical changes, microstructural changes, and the alteration in transport properties (water permeability and gas diffusivity).

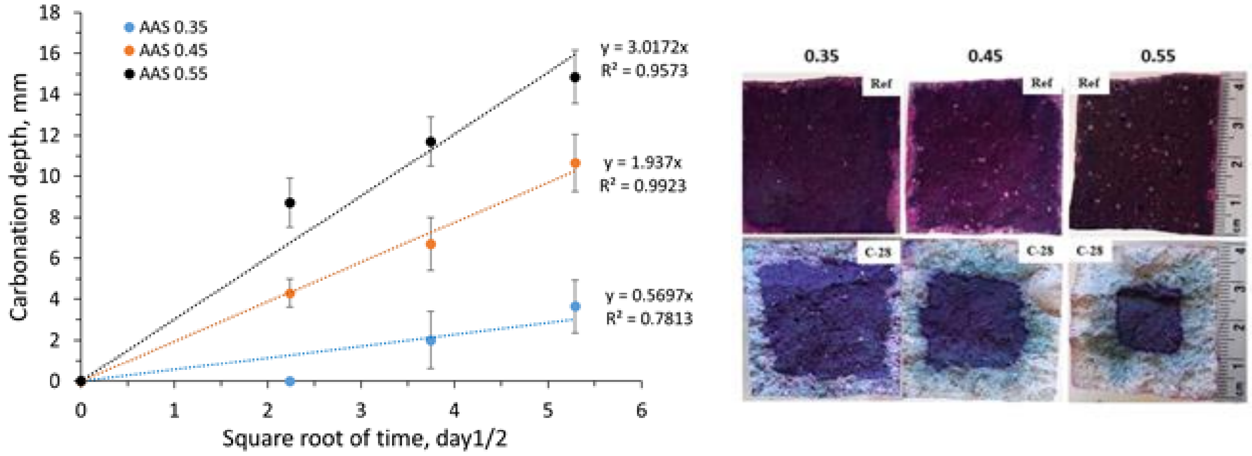


Figure 27 *Carbonation depth of AASs determined by phenolphthalein spraying*

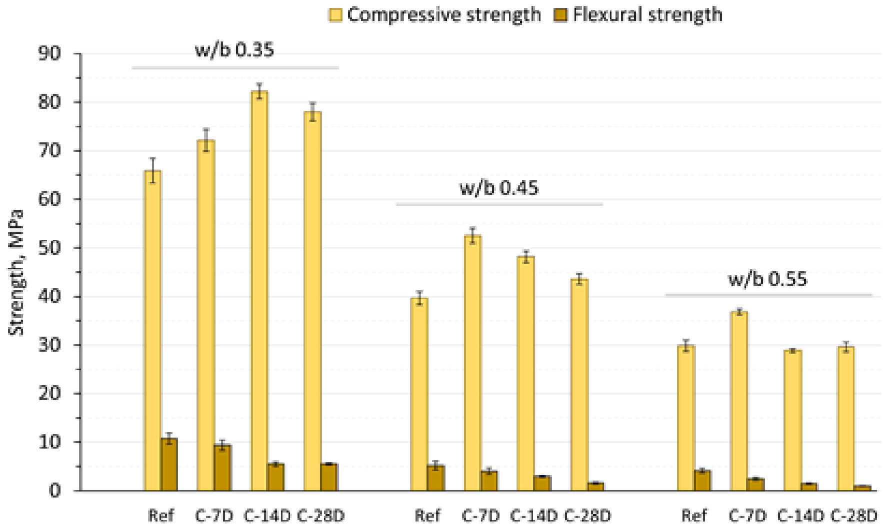


Figure 28 *Compressive Strength and Flexural Strength of AASs during carbonation*

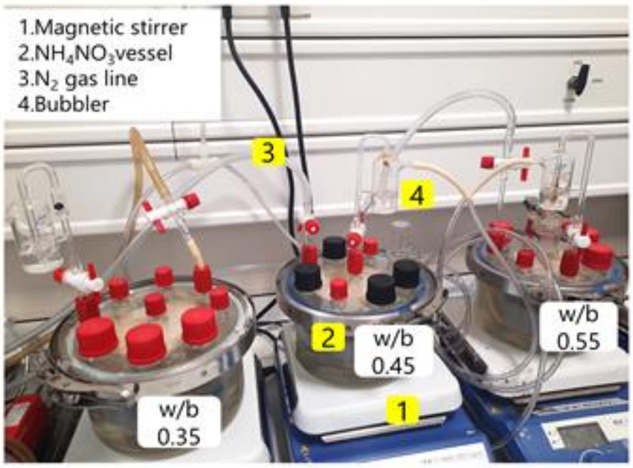


Figure 29 *Accelerated leaching test*

Leaching was studied in the scope of T5.4. In general, the leaching of alkali (Na, K) and alkaline earth elements has driven the leaching of both AASs and MK-based geopolymers. The increase in the w/b ratios significantly increased the leaching depth of mortars and leaching rates of the elements, i.e., 30% increase of leaching depth and twice increase of Ca-leaching rate when the w/b ratio increased from 0.35 to 0.55.

SCK CEN has tested the transport properties of the AAMs, the water permeability results are shown below:

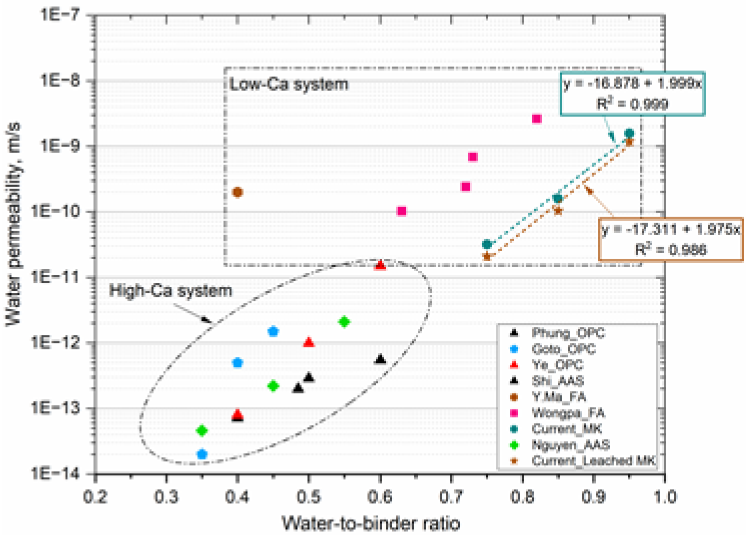


Figure 30 *Graph of Permeability coefficient in water/binder ratio*

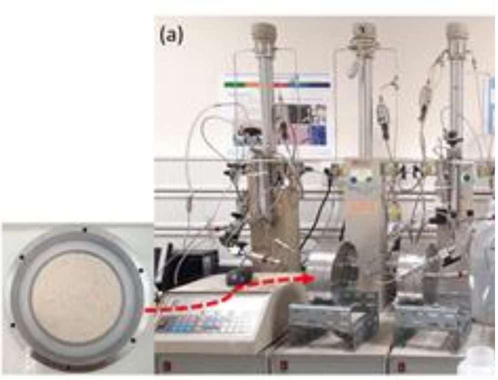


Figure 31 *Instrumentation used for mensuration of permeability*

The w/b ratio significantly influence the permeability coefficient of AAMs. With a similar w/b ratio, the water permeability coefficients of AASs (high-calcium systems) were similar to the values obtained for OPC (~1E-12 m/s to 1E-14 m/s), while the MK-based geopolymers (low-calcium systems) showed a higher permeability (~1E-8 m/s to 1E-11 m/s).

Trial tests on the miscibility of AAMs with different liquid wastes:

After testing the properties of the reference AAM mortars, the miscibility of the AAMs with wastes was tested. The results of trial testing on the MK-based geopolymers and AASs with liquid wastes, including TBP, Ionic (Trifluor and Aliquat 336), and lubricating oils (Nevastane and Shellspirax), were showed as follows:

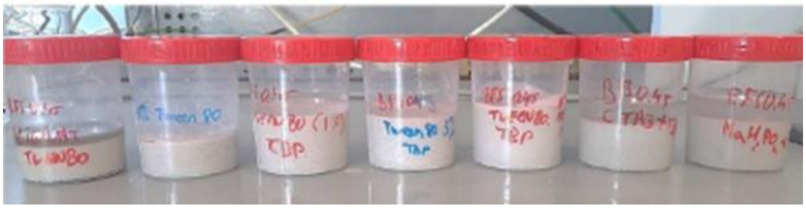


Figure 32 *Fresh mixtures containing AAS and wastes (TBP, ionic liquids), using different surfactants*

The mixtures after 7 days of seal curing are shown below, on left there are samples with TBP and on the right the samples with ionic wastes:

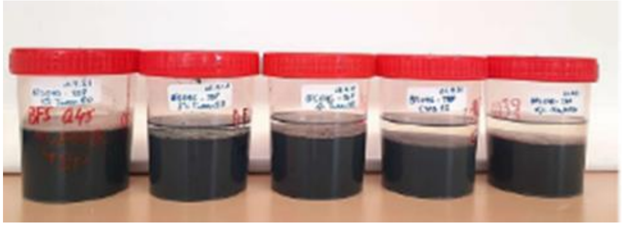


Figure 33 *AAS with TBP after 7 days of curing*

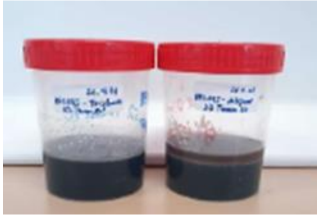


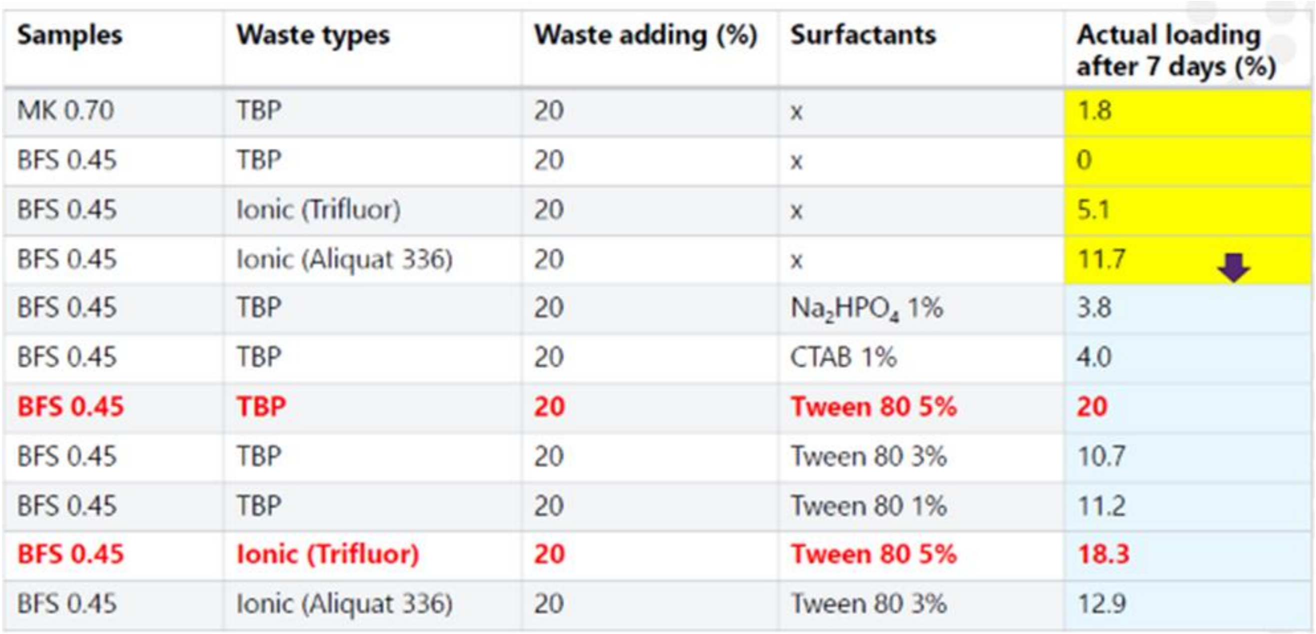
Figure 34 *AAS with ionic waste after 7 days of curing*

Observations from the trial tests showed that TBP and ionic liquids, including Aliquat 336 and Trifluor, were mostly not encapsulated in both MK-based geopolymers and AAS without using surfactants. A very limited amount of waste incorporated in the matrices was quantified as 11 wt.% as maximum percentage (with Aliquat 336). In general, the separation between waste and AAM binders was observed clearly. To deal with this issue, using surfactants was expected to improve the miscibility because the presence of surfactants can change the surface tension between geopolymer binder and waste. Amongst several surfactants examined, Tween 80 showed the best efficiency for both MK-based geopolymers and AASs. The results reveal that AASs can incorporate up to 20 wt.% (~36 vol.%) TBP and 25 vol.% Trifluor when using 5 wt.% (of waste) Tween 80, while MK -based geopolymers can encapsulate 32,5 vol.% all examined wastes by using only 1 wt.% Tween 80. In addition, the compressive strength of all waste-forms was determined. Results revealed that the waste-forms with MK-based geopolymers achieved a relatively high compressive strength (around 5 MPa after only 4 days of curing under ambient conditions), whereas the waste-form with the highest waste loading in AASs showed a lower strength of only 3 MPa after 19 days of curing. This implies that the MK-based geopolymers showed a higher potential immobilization of waste compared to AASs.

Figure 35 *State of waste-forms with AAS (left) and with MK-based geopolymer (right) when using Tween 80 as a surfactant after 7 days of curing*

The results of trial testing with wastes are followed:

Table 32 *Results of trial testing with wastes (TBP and ionic liquids)*



Samples	Waste types	Waste adding (%)	Surfactants	Actual loading after 7 days (%)
MK 0.70	TBP	20	x	1.8
BFS 0.45	TBP	20	x	0
BFS 0.45	Ionic (Trifluor)	20	x	5.1
BFS 0.45	Ionic (Aliquat 336)	20	x	11.7 ⬇
BFS 0.45	TBP	20	Na_2HPO_4 1%	3.8
BFS 0.45	TBP	20	CTAB 1%	4.0
BFS 0.45	**TBP**	**20**	**Tween 80 5%**	**20**
BFS 0.45	TBP	20	Tween 80 3%	10.7
BFS 0.45	TBP	20	Tween 80 1%	11.2
BFS 0.45	**Ionic (Trifluor)**	**20**	**Tween 80 5%**	**18.3**
BFS 0.45	Ionic (Aliquat 336)	20	Tween 80 3%	12.9

The results suggested to use surfactants. Surfactant has been dissolved in waste for around 5 minutes to obtain mixture 1. In the meantime, geopolymer (mixture 2) is prepared using the same procedure for the reference geopolymers preparation but reduce the mixing time with sand to 2 minutes. The mixture 1 is then poured into mixture 2 and mixed for 2+1 minutes more.

However, AAS demonstrated a good miscibility with lubricating oils (both Nevastane and Shellspirax), especially with use of Tween 80 (up to 40 vol.% oil loading). Due to the limited information on the performance of waste-forms containing AAS and lubricating oils, a comprehensive study via a robustness test was implemented on this kind of waste-form, which is showed in Section 5.2.

4.7 University of Sheffield (USFD) and National Nuclear Laboratory Limited (NNL), UK

4.7.1 Conditioning Options Studied (160 mL)

The conditioning options studied by USFD and NNL are characterized by the following formulation envelope:

- Raw materials: metakaolin powders (n°2) of varying chemical and physical properties. Flash & Rotary Calcined MK with K Silicate/KOH activator within the molar ratio range:
  - .0 - 1.4 SiO_2/K_2O molar ratio
  - 11 - 15 H_2O/K_2O molar ratio
- 1.0 - 1.5 K_2O/Al_2O_3 molar ratio RLOW surrogate:
  - Pump Oil (Nevastane EP100)
  - Tributyl phosphate (TBP)

Waste loading initially tested at 160 mL scale varied between 10 % to 50 % by volume of the total waste form, and changing the order of addition of mix components:

- RLOW to activator solution: Mix KOH, water and K silicate solution (K120) of appropriate molar ratios and allow to cool to 20 °C. Add appropriate vol% of RLOW (10-50 vol% of total wasteform mix volume) to activator solution and mix using Silverson high shear mixer at 2000 rpm for 1 min. Add the required quantity of metakaolin powder for the formulation under test and mix using a Kenwood HM220 hand mixer at ~700 rpm for 2 min.
- RLOW added to pre-formed GP: Mix KOH, water and K silicate solution (K120) of appropriate molar ratio and allow to cool to 20 °C. Add required quantity of metakaolin powder for the formulation under test and mix using a Kenwood HM220 hand mixer at ~700 rpm for 1 min. Add appropriate vol% of RLOW (10-50 vol% of total waste form mix volume) and mix using a Kenwood hand mixer at ~700 rpm for a further 1 min.

The fresh paste has been characterized in terms of:

- Viscosity after mixing according to ASTM C 1749, with values quoted at 100 s^{-1} on the descending ramp;
- Bleed (vol/vol%) on surface of 160 mL sealed polypot specimens after curing for 24 h at 20 °C and >90% RH ;
- Setting time based on EN 196-3. Samples were sealed and stored between measurements.
- Tests and Results

4.7.2 Tests and Results

Small-scale laboratory work (~160 mL) studies have been undertaken in which both Nevastane EP 100 paraffin oil and TBP have been incorporated in two different geopolymer systems using two different metakaolin powders pre-cursors over a range of formulations developed in previous UK studies. The aim of these trials was to assess likely RLOW loadings for both organics tested and if there is a preferred order of addition for incorporating the RLOW into the system for subsequent scale-up (4L) studies.

The GP systems used by NNL are Metamax® GP and Argicem® GP. For each geopolymer system the following molar ratio envelope was tested:

- Metamax® - Rotary Calcined (RC) metakaolin powder, SiO_2 = 51.48 wt%, Al_2O_3 = 43.99 wt%, D_{50}[3] = 3 µm, Fineness = 3843 m^2/kg
  - $SiO_2:K_2O$ molar ratio (1.0 – 1.4)
  - $K_2O:Al_2O_3$ molar ratio (1.0 – 1.5)
  - $H_2O:K_2O$ (11 – 15)

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[3] D_{50} represent the equivalent particle diameter at which 50% of the sample volume falls below.

- Argicem® - Flash Calcined (FC) metakaolin powder, SiO_2 = 73.79 wt%, Al_2O_3 = 19.97 wt%, D_{50} = 41 µm, Fineness = 670 m^2/kg
    - $SiO_2:K_2O$ molar ratio (1.0 – 1.4)
    - $K_2O:Al_2O_3$ molar ratio (1.0 – 1.35/1.5[4])
    - $H_2O:K_2O$ molar ratio (11 – 14/15)

Retardation and segregation of the Argicem® GP system at the combination of high H_2O/K_2O and high K_2O/Al_2O_3 molar ratios resulted in an adjustment of the design envelope studied for this GP system throughout this work as shown by the modified green lines in Figure 36.

Promising results have been obtained for Nevastane EP 100, in that up to 50 vol% loading has been incorporated into both geopolymer systems to give acceptable processing and setting characteristics and therefore loadings up to this vol% will be assessed in the next phase of scale-up studies at 4 L scale to measure product properties & visually assess retention characteristics. Trials with TBP have been less successful, in that above 20 vol% loading significant segregation and bleed was observed, producing a porous product, and in common with other partners, the incorporation of surfactants appears to be required to obtain a stable product. Scoping trials were carried out during next task T5.3.3 to identify a suitable surfactant and level and order of addition, prior to scale-up to obtaining product evolution data.

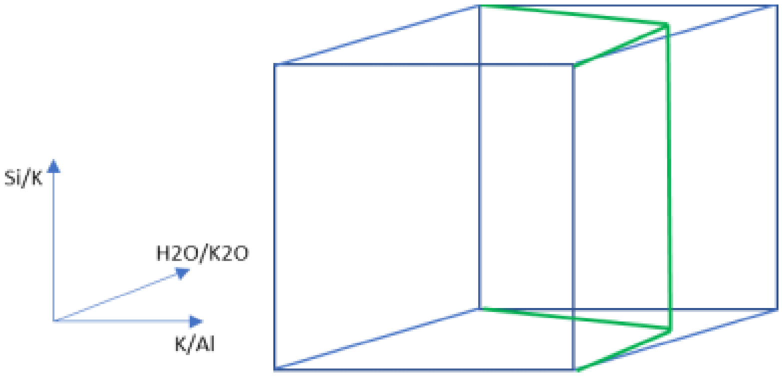

Figure 36 *Proposed Formulation Range for each Geopolymer System*

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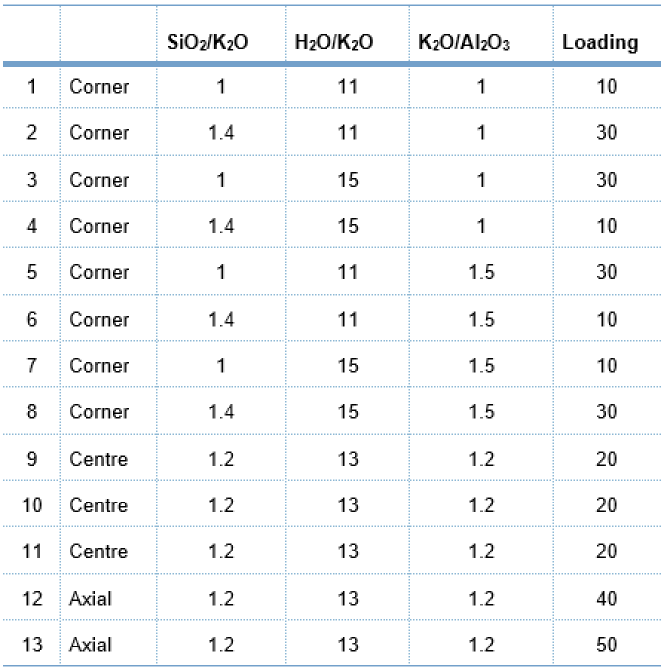
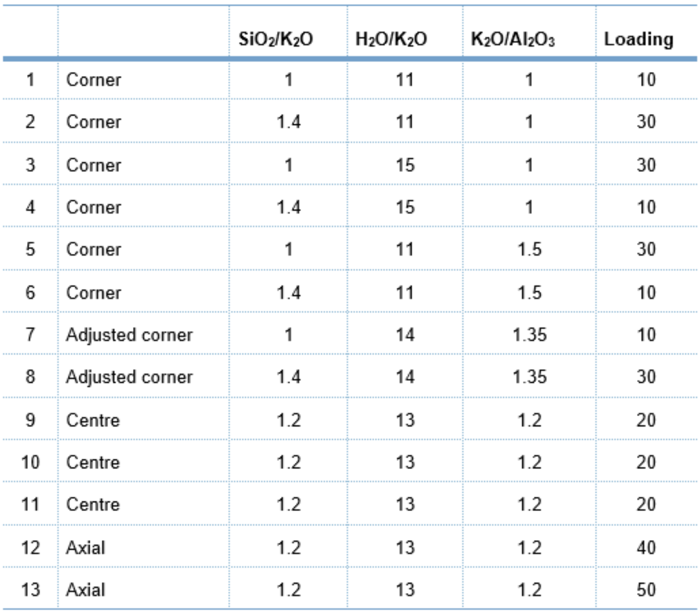
[4] Due to segregation and set time issues observed with Argicem® mixes the formulation range was restricted to avoid the combination of high H_2O/K_2O molar ratio = 15 and high K_2O/Al_2O_3 molar ratio = 1.5, whilst keeping the remainder of the formulation envelope intact, shown in green in Figure 36. The adjusted formulation tested had a high molar ratio combination of H_2O/K_2O = 14 and K_2O/Al_2O_3 = 1.35.

Table 33 *Metamax® mixes*



		SiO_2/K_2O	H_2O/K_2O	K_2O/Al_2O_3	Loading
1	Corner	1	11	1	10
2	Corner	1.4	11	1	30
3	Corner	1	15	1	30
4	Corner	1.4	15	1	10
5	Corner	1	11	1.5	30
6	Corner	1.4	11	1.5	10
7	Corner	1	15	1.5	10
8	Corner	1.4	15	1.5	30
9	Centre	1.2	13	1.2	20
10	Centre	1.2	13	1.2	20
11	Centre	1.2	13	1.2	20
12	Axial	1.2	13	1.2	40
13	Axial	1.2	13	1.2	50

Table 34 *Argicem® mixes*



		SiO_2/K_2O	H_2O/K_2O	K_2O/Al_2O_3	Loading
1	Corner	1	11	1	10
2	Corner	1.4	11	1	30
3	Corner	1	15	1	30
4	Corner	1.4	15	1	10
5	Corner	1	11	1.5	30
6	Corner	1.4	11	1.5	10
7	Adjusted corner	1	14	1.35	10
8	Adjusted corner	1.4	14	1.35	30
9	Centre	1.2	13	1.2	20
10	Centre	1.2	13	1.2	20
11	Centre	1.2	13	1.2	20
12	Axial	1.2	13	1.2	40
13	Axial	1.2	13	1.2	50

Each mix has been repeated for both RLOW and order of addition to give a total of 104 mixes.

The results concerning the experimentation on the Metamax® GP system with Pump Oil (Nevastane EP100) are the following:

- Waste loading up to 50 vol% Nevastane EP100 was successfully incorporated.
- Minimal – zero bleed (all mixes were <1 vol% bleed generally considered acceptable at this scale for typical PC blends used in UK encapsulation processes)
- Viscosity <1000 mPa·S at 100 s^{-1} for mid-point formulation ($SiO_2/K_2O = 1.2$, $H_2O/K_2O = 13$, K/Al = 1.2). Previous experience suggests viscosity <3000 mPa·S will mix acceptably via an In-Drum Mix (IDM) technique.
- Viscosity increased with Nevastane EP100 loading.
- Viscosity generally reduced on adding RLOW to pre-formed GP
- Set generally within 24 hrs.

- Similar observations were made for the Argicem® GP system. The mixes were more viscous than Metamax® GP mixes at equivalent formulations, with mixes still <1000 mPa·S at 100 s^{-1} for mid-point formulation (SiO_2/K_2O = 1.2, H_2O/K_2O = 13, K/Al = 1.2) at a 20 vol% RLOW loading and ~1000 mPa·S at 100 s^{-1} for the mid-point formulation at 50 vol% loading. All mixes had viscosity <3000 mPa·S at 100 s^{-1} with the exception of low water content mixes ($H_2O:K_2O$ = 11) and K/Al ratio = 1 at 10 & 30 vol% RLOW loading when Nevastane EP100 was added to activator solution prior to adding the MK component.

Figure 37 *50 vol% loading of Nevastane EP 100 in Metamax® geopolymer (left) and Argicem® geopolymer (right)*

The results concerning the trials on the Metamax® GP system with TBP alone found the following:

- Waste loadings up to 20 vol% could be achieved with only small amounts of residual bleed for the mid-point formulation (SiO_2/K_2O = 1.2, H_2O/K_2O = 13, K/Al = 1.2) of 0.1- 0.2 vol% at 24 h
- Viscosity < 300 mPa·S at 100 s^{-1} for mid-point formulation (SiO_2/K_2O = 1.2, H_2O/K_2O = 13, K/Al = 1.2) at 20 vol% RLOW loading
- Set in 24 hrs
- No significant difference in order of addition
- At TBP loadings of ≥30 vol% set product had a porous structure with poor RLOW incorporation.
- After some time, the samples have shown signs of a substantial increase in the measured bleed volume, suggesting that longer term retention has not been achieved.

In the case of Argicem® GP system, at TBP incorporation rates >10 vol% produced a porous paste with poor incorporation of TBP, and for all levels of incorporation rates studied for the Argicem® GP system, the TBP sat on top of the geopolymer mixture suggesting little to no incorporation of the oil (Figure 38). In addition, the top of the geopolymer product produced using Argicem® appeared more porous with the addition of TBP and this became more prominent with increased TBP addition (Figure 38). Therefore, these scoping trials showed a clear issue regarding incorporation of TBP without any addition of surfactant for Argicem® and Metamax® formulations, with the resulting bleed giving rise to structural issues within the GP products.

Figure 38 *20 vol% loading of TBP in Metamax® geopolymer (left), 10 vol% loading of TBP in Argicem® geopolymer (centre) and 20 vol% loading of TBP in Argicem® geopolymer (right).*

As mixes incorporating TBP were deemed unsuccessful, the addition of surfactants into the mix design (non-ionic surfactants (Tween 80 and Triton CG 110) and a cationic surfactant (CTAB)) was investigated in the scope of task 5.3.3 to assess if a stable emulsion with the geopolymer activator solution can be attained, thereby increasing the probability of producing a stable waste form with higher incorporation rates than those achieved thus far. In addition, and following discussions with EU partners further investigations of this solvent type were undertaken using a TBP/Dodecane mixture at 70/30 vol/vol%, rather than TBP alone.

4.8 CONCLUSIONS

At the end of all the activities described in this chapter it was agreed not to define three specific formulations to be further studied, but rather to consider 3 families of formulations, based on the different raw materials included in the conditioning options studied. These families of formulations are based on Metakaolin, Blast Furnace Slag and mixture of different raw materials.

For each family, 2-3 Partners were involved in the Optimisation and Robustness testing activities in the scope of the sub-task 5.3.3 (see §5).

5 Optimisation and robustness study

Sub-task T5.3.3 was focused on the optimization of the three reference formulation families selected in Sub-task 3.2 to maximize incorporation rates while fulfilling required material performances. An additional challenge was to ensure the robustness of conditioning materials concerning waste, raw materials, and process variability. A critical technical hurdle relates to the properties and stability of RLOW emulsion, particularly in activation solutions or fresh grout, possibly involving surfactants. A critical technical hurdle relates to the properties and stability of RLOW emulsion, particularly in activation solutions or fresh grout, possibly involving surfactants.

It was agreed to split the activities related to sub-task 5.3.3 (M10 (June 2021) - M27 (November 2022)) into two main parts:

1) Optimisation study: 7 months (from June 2021 to December 2021)
2) Robustness study: 10 months (from January 2022 to October 2022).

It was agreed to consider as reference surrogates for the study:

- TBP/Dodecane (30%) – to be closer to the real case
- Simple high viscosity oil (Nevastane)
- Complex low viscosity oil (Shellspirax)
- Scintillation liquids (Ultima Gold AB or INSTA GEL)

For each family, 2-3 Partners have been involved in the Optimisation and Robustness testing activities in the scope of the sub-task 5.3.3.

Optimization of reference formulations

The three reference formulation families were tested for RLOW incorporation rates ranging from 10 to 50 % volume and possibly more whenever possible (i.e. if homogeneous incorporation can be achieved with satisfactory materials performances). Samples of RLOW encapsulated in conditioning materials as paste or mortar were produced and characterised as part of Sub-task 3.3 but also with deeper examination in task 5.4. The formulations were tested at an about 3-L scale. Mixing was performed with a standardized mortar mixer and the resulting materials were characterised by measuring various parameters, typically:

- ✓ viscosity after mixing,
- ✓ flowability,
- ✓ heat reaction using calorimetry methods,
- ✓ bleeding,
- ✓ setting time,
- ✓ flexural and compressive strengths on bars cured at ambient temperature in sealed bag for 28 days and 90 days,
- ✓ potential for RLOW release and composite stability, by water immersion tests
- ✓ RLOW distribution by Scanning Electronic Microscopy or 3D X-ray microtomography.

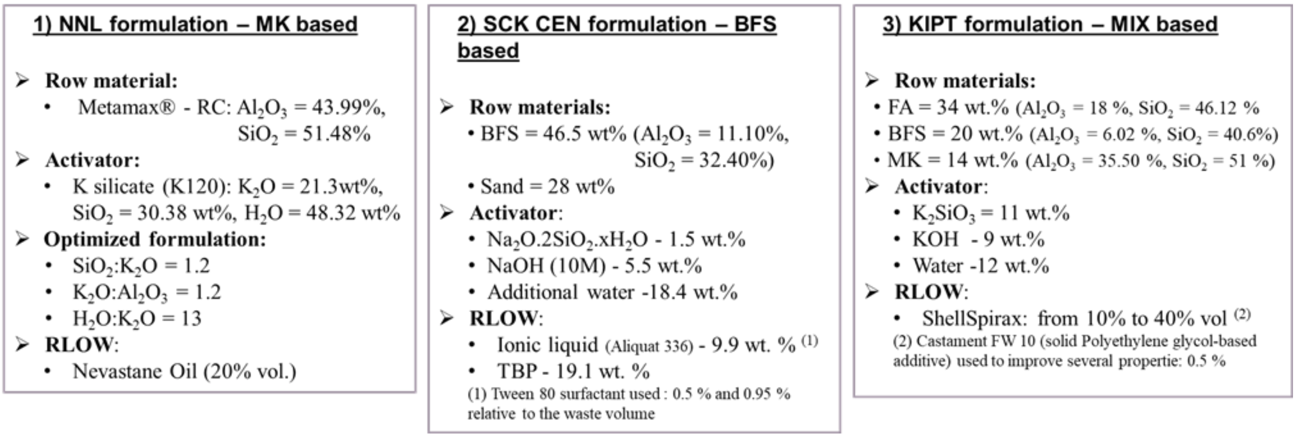
The following parameters had to be optimized to select the three most promising reference formulations:

- aluminosilicate precursor(s) content (including impact of Ca content),
- alkaline activator content,
- water content,
- filler nature and content,
- surfactant nature and content (if any),

- nature and contents of other additives such as superplasticizer… (if any).

At the end of the Optimisation phase (December 2021) a review of the Milestone (MS32 [7]) was performed to identify 3 specific reference formulations among the reference families (Table 35).

Table 35 *Reference formulations selected after the Optimisation phase*



1) NNL formulation – MK based

- **Row material:**
  - Metamax® - RC: $Al_2O_3 = 43.99\%$, $SiO_2 = 51.48\%$
- **Activator:**
  - K silicate (K120): $K_2O = 21.3$wt%, $SiO_2 = 30.38$ wt%, $H_2O = 48.32$ wt%
- **Optimized formulation:**
  - $SiO_2:K_2O = 1.2$
  - $K_2O:Al_2O_3 = 1.2$
  - $H_2O:K_2O = 13$
- **RLOW**:
  - Nevastane Oil (20% vol.)

2) SCK CEN formulation – BFS based

- **Row materials:**
  - BFS = 46.5 wt% ($Al_2O_3 = 11.10\%$, $SiO_2 = 32.40\%$)
  - Sand = 28 wt%
- **Activator**:
  - $Na_2O.2SiO_2.xH_2O$ - 1.5 wt.%
  - NaOH (10M) - 5.5 wt.%
  - Additional water -18.4 wt.%
- **RLOW**:
  - Ionic liquid (Aliquat 336) - 9.9 wt. % (1)
  - TBP - 19.1 wt. %

(1) Tween 80 surfactant used : 0.5 % and 0.95 % relative to the waste volume

3) KIPT formulation – MIX based

- **Row materials:**
  - FA = 34 wt.% (Al_2O_3 = 18 %, SiO_2 = 46.12 %
  - BFS = 20 wt.% (Al_2O_3 = 6.02 %, SiO_2 = 40.6%)
  - MK = 14 wt.% (Al_2O_3 = 35.50 %, SiO_2 = 51 %)
- **Activator**:
  - K_2SiO_3 = 11 wt.%
  - KOH - 9 wt.%
  - Water -12 wt.%
- **RLOW**:
  - ShellSpirax: from 10% to 40% vol (2)

(2) Castament FW 10 (solid Polyethylene glycol-based additive) used to improve several propertie: 0.5 %

✓ Robustness of optimized reference formulations

Robustness of optimized reference formulations was assessed following similar experimental procedures as in the previous step ("Optimization of reference formulations"). The impact of RLOW, raw materials and process variability have been studied, according to the following guidelines:

- RLOW variability

With fixed incorporation rate (for example 30 % volume - depending on the RLOW type) and fixed raw materials, different RLOW were tested

- Raw materials variability

With fixed incorporation rate (for example 30 % volume - depending on the RLOW type) and fixed RLOW, different raw materials depending on local availability were tested

- Process variability

With fixed incorporation rate (for example 30 % volume- depending on the RLOW type), fixed raw materials and fixed RLOW the following were tested:

- Variability of aluminosilicate source-to-activation source ratio (for example ± 2 %)
- Variability of RLOW composition (TBP-dodecane ratio: 70/30; 50/50; 30/70)
- Variability of water-to-binders ratio (for example ± 2 %)
- Variability of sand-to-water ratio (for example ± 2 %) (at fixed incorporation rate)
- Variability of emulsifier, if needed (for example ± 2 %) (at fixed incorporation rate)

Two partners have been identified to work on each formulation, considering the previous experiences of the different partners and the need for a complete evaluation of the robustness of the three reference formulations:

1) Metakaolin based Formulation: NNL/USFD + CIEMAT
2) Blast Furnace Slag based Formulation: SCK-CEN + RATEN
3) Mix based Formulation: NUCLECO/SOGIN + KIPT

It was agreed to leave POLIMI outside the selected formulations in order to continue with the study of an alternative solution (pre-impregnation) based on sustainable principles (see §5.6).

CEA (in close collaboration with all the other partners) worked to improve the understanding of the emulsification process, the influence on hardened materials properties and the identification of the most suitable emulsifier (if needed) for each formulation.

The three reference formulations were tested in the Robustness phase till November 2022 when it was possible to define the optimised formulations for reference formulations (MS34 [9]) as reported in §5.5.

- The studies conducted by all partners as well as the most promising formulations selection process with the results are presented below.

5.1 Metakaolin based formulations

The studies on Metakaolin (MK) based formulations were carried out by NNL, USFD and CIEMAT. The systems studied, as well as the studies performed including results are described in the following Sub-chapters.

5.1.1 Systems studied

The NNL and USFD have continued their studies of two systems with Flash & Rotary Calcined MK with K Silicate/KOH activator (described in Chapter 4.7):

- Metamax® - RC, SiO_2 = 51.48%, Al_2O_3 = 43.99%, D_{50} = 3 µm, Fineness = 3843 m^2/kg
- Argicem® - FC, SiO_2 = 73.79%, Al_2O_3 = 19.97%, D_{50} = 41 µm, Fineness = 670 m^2/kg
- K Silicate/KOH activator
  - K Silicate – K120, K_2O = 21.3 wt%, SiO_2 = 30.38 wt%, H_2O = 48.32 wt% (SiO_2:K_2O = molar ratio 2.23)
  - KOH – Pure flakes supplied by Fisher Scientific

Following RLOW Surrogates and organic surfactants were used:

- Nevastane EP 100 oil – Viscosity at 25ºC - 2.33 Pa·s
- TBP – subsequently TBP/Dodecane (70/30 vol/vol) –
  - Viscosity at 25ºC – Dodecane = 0.0018 Pa·s,
  - Viscosity at 25ºC – TBP = 0.0036 Pa·s
  - Tween 80 surfactant viscosity = 0.4 Pa·s
  - **CIEMAT** has studied metakaolin (Metamax®®), also with a potassium activator, with following composition:
- Metamax® - RC, SiO_2 = 51%, Al_2O_3 = 45%
- K-Betol activator: SiO_2=31,5%. K_2O=20,5%, H_20=48%

Activator has been prepared 24h before final mixture from KOH pellets.

RLOW surrogates (described in detail in Chapter 4.1.1):

- Synthetic oil - Repsol Super Tauro 100 Sintético, equivalent to Nevastane EP-100
- Liquid scintillation cocktails - InstaGel Plus

SiO_2:K_2O=1,2

K_2O:Al_2O_3=1,2

H_2O:K_2O=13

***Figure 39** Ratios of geopolymer components*

The optimal mixing time at a low speed for the final mixture (see *Figure 39*) has been tested to be 15 minutes.

To harden, the mixture was poured into 4x4x16 cm silicone moulds.

Hardening of the samples was carried out by 4 different methods.

- In air at room temperature
- In air at room temperature for 1 hour and climatic chamber
- In climatic chamber
- In refrigerator at 9-10 ºC

Following observations were made during the hardening of samples:

- Geopolymerization with this activator was highly exothermic
- The temperature reached was 46 ºC at 4 h
- Very fast setting
- No significant changes are seen with the introduction of RLOW surrogates, similar times and T of setting
- Density 1,62 g/cm^3

After examining the hardening options, it was decided to carry out the hardening in an air-conditioned laboratory, with a controlled temperature, as high temperatures facilitate rapid evaporation of water from the samples and formation of cracks in samples (see Figure 40).

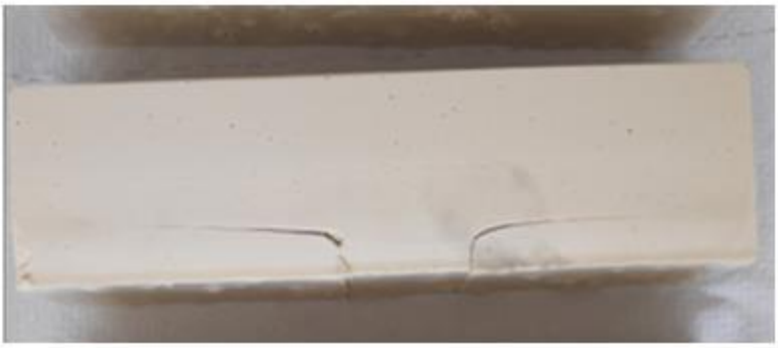


Figure 40 *Cracks in the surface of the geopolymer samples*

5.1.2 Optimisation and robustness studies and results

5.1.2.1 Studies with scintillation cocktail (Instagel Plus) and Repsol Super Tauro

The aim was to immobilise at least 30 %vol. of the waste.

Preparation of samples:

- RLOW surrogate was added in small amounts throughout 20 minutes of mixing
- Total time of mixing was 1 h

Figure 41 *Hardened samples of Geopolymer without RLOW surrogate (left), with 30% vol. of oil surrogate (middle) and 10-30% vol. of scintillation cocktail surrogate (right)*

The scintillation cocktail mixture was very liquid and the hardening time was similar as without waste, 4 h. All the waste was immobilized. No phase differences were observed even without surfactant.

After, mechanical strength tests have been carried out. The goal was to achieve a mechanical strength of at least <10 MPa after 28 days of curing (mechanical strength limit required by Enresa).

The samples were cured in a climatic chamber at 20°C and 90 % humidity, wrapped in film (endogenous condition).

The results of the tests can be seen in Figure 42 and Figure 43. At least 6 prismatic samples were prepared and broken in half to obtain 6 data. The data with the largest deviation were discarded, but the average data obtained were at least 4 measurements.

Samples with higher waste loading were not tested because 30% scintillation liquid and 40% oil were already at the mechanical strength limit of <10 MPa after 28 days. The samples containing scintillation liquid gave off a strong smell of Instagel Plus and were suspected of leaching.

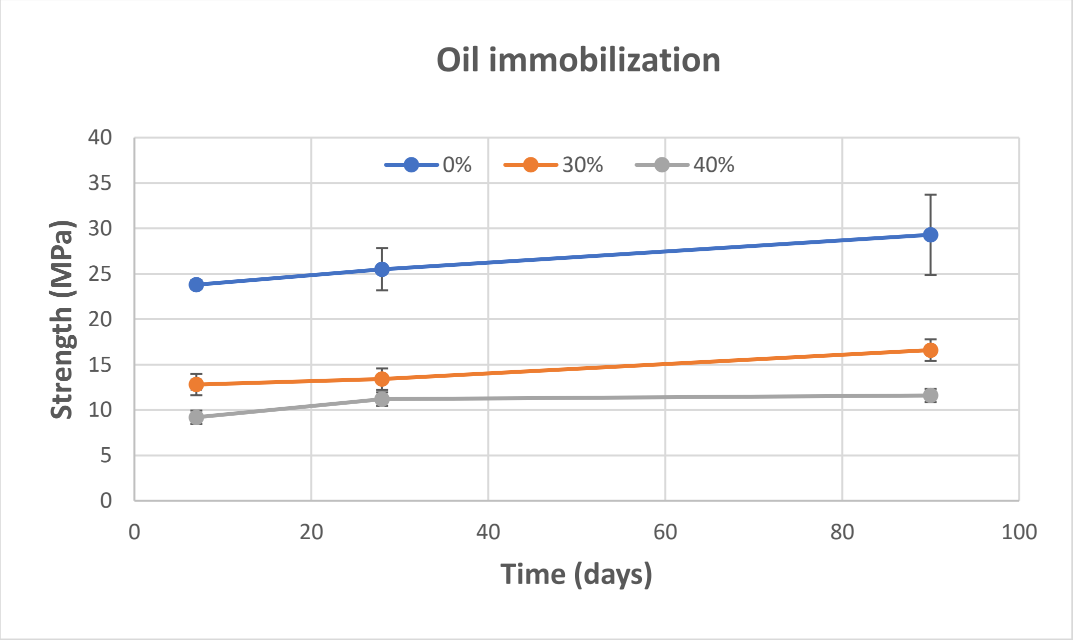


***Figure 42** Mechanical results in geopolymer samples with Repsol Super Tauro*

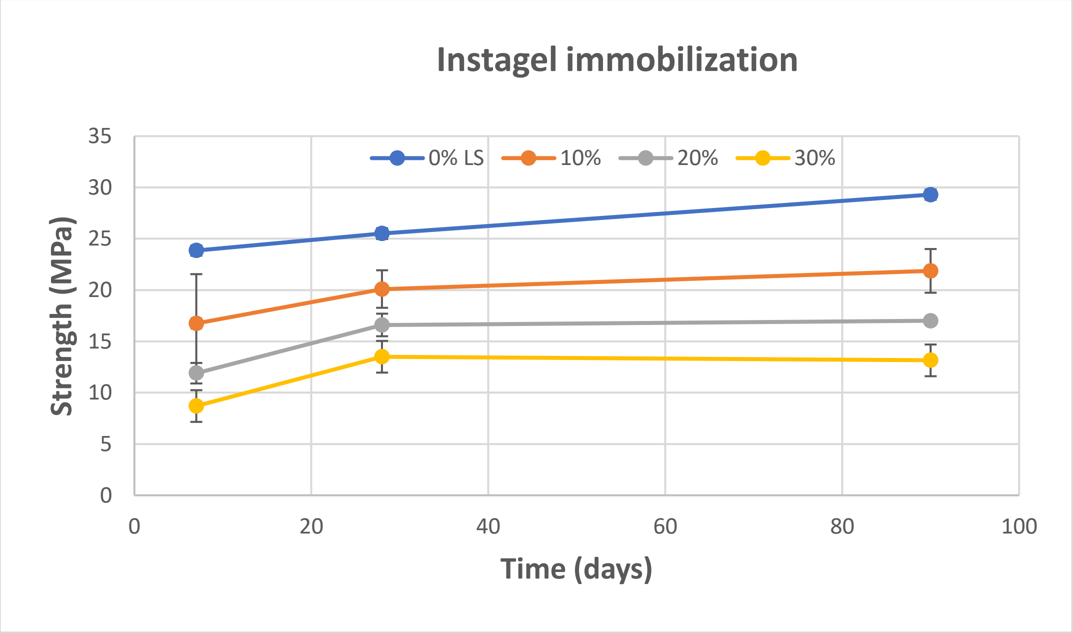


***Figure 43** Mechanical results in geopolymer samples with InstaGel Plus*

All samples hardened in less than 12h and bleeding was found to be negligible (< 1% by weight after drying the sample with absorbent paper and calculating the weight of the absorbed liquid).

Structural characterization has been carried out using XRD and infrared spectroscopy.

XRD studies of the geopolymer with and without surrogate waste have been carried out after curing for 28 days at 20ºC and are shown in Figure 44. These figures show X-ray- amorphous aluminosilicate phases. The peak at 2θ=25°could be for the presence of crystalline TiO_2.

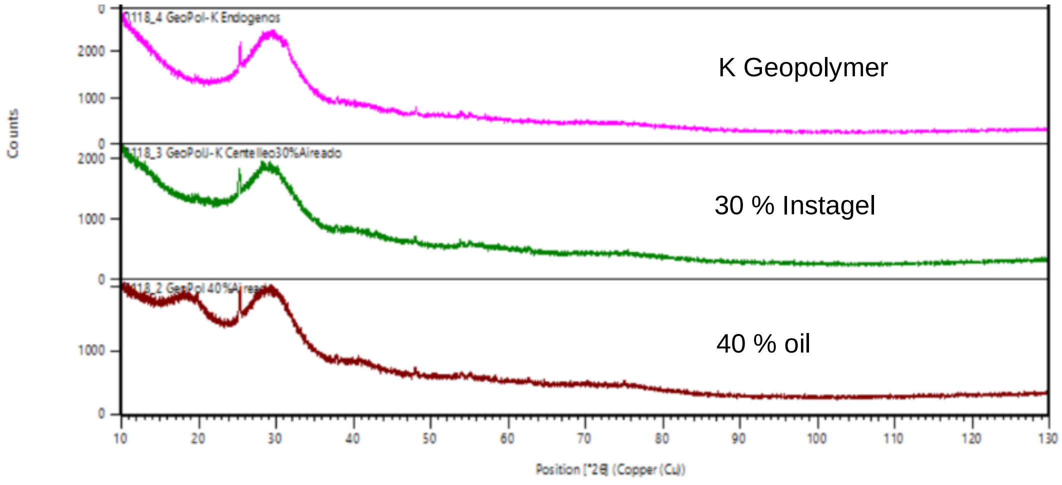


Figure 44 *XRD of K-based geopolymers*

Figure 45 compares the infrared spectra of the potassium geopolymer and the oil surrogate immobilised with the geopolymer. In both spectra, two bands are present at 950 and 650 cm^{-1} corresponding to the Si-O vibration and the Si-O-Si or Al-O-Si vibration. In the spectrum of the oil-containing sample, bands are observed between 3000 and 2800 cm^{-1} corresponding to C-H stretching and above 1300 cm^{-1} C-C stretching.

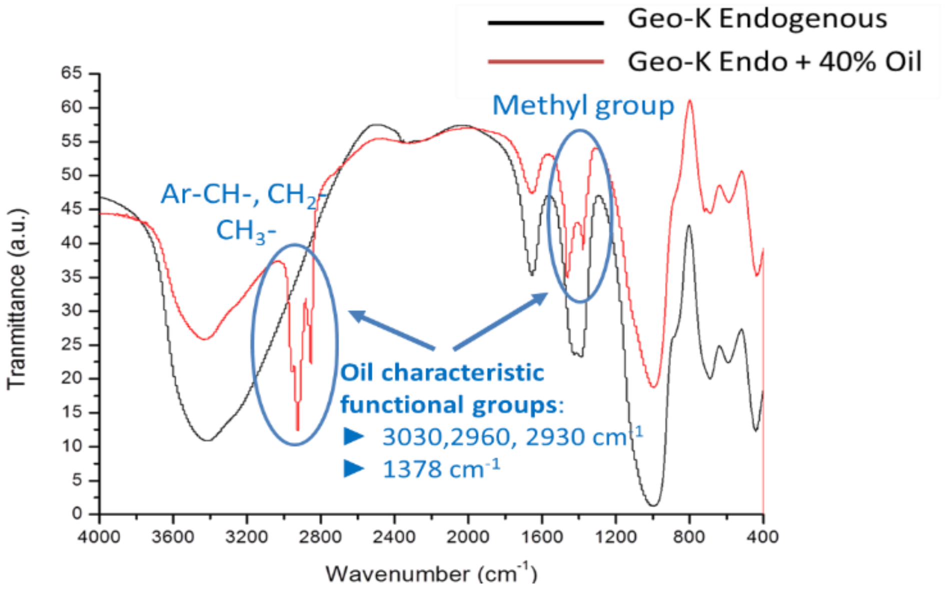


Figure 45 *Infrared spectra of the K-based geopolymer without waste (blue) and with oil surrogate waste (red)*

Incorporation of scintillation cocktail and mineral oil (Figure 46) leads to the modification of geopolymer absorption bands between 1700 and 400 cm^{-1} (aluminosilicate skeleton).

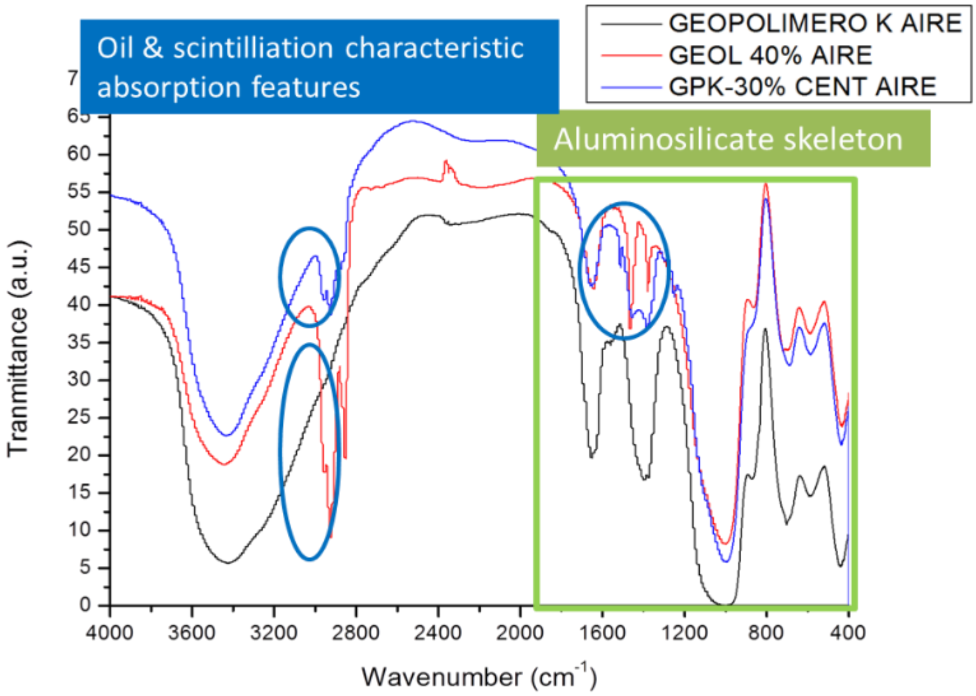


__Figure 46__ Infrared spectra of the potassium geopolymer, the Instagel and oil immobilised with the geopolymer

Leaching test in milliQ water have been carried out to analyse the stability of the samples.

Sample preparation:

- Cylindrical samples prepared using plastic PVC mould - height 4 cm, diameter 2 cm
- At least 2 specimens per leaching to be tested
- After preparation, the specimens were submerged in water to clean them

__Figure 47__ Samples submerged in leachant solution (left) were kept in gloveboxes (right)

Leaching test:

- The samples were suspended by a nylon wire in the middle of the leachant present in the container
- The layer of leachant surrounding the specimen was at least 2 cm thick
- The leachant had to be swapped after 1, 3, 7, 10, 14, 21, 28, 35, 42, 72, 98, 126, 156, 182, 210, 238…375 days from the start of the test and the old leachant had to be studied (pH, electrical conductivity and carbon content)
- The leachant remains in static form (no mixing)
- The ratio between the volume of leachant and exposed area of specimen ranges from 10-20 cm. The specimen has to be totally- submerged in the leachant.
- At the end of the leaching test the specimens were checked for cracks, crumbles or colour changes, weighed and measured again

The Geopolymer samples without surrogate RLOW and with oil surrogate waste were stable when immersed in water. Samples containing scintillation liquid surrogate were not very stable and breakage and cracks could be observed (see Figure 48). This could indicate the presence of leaching.

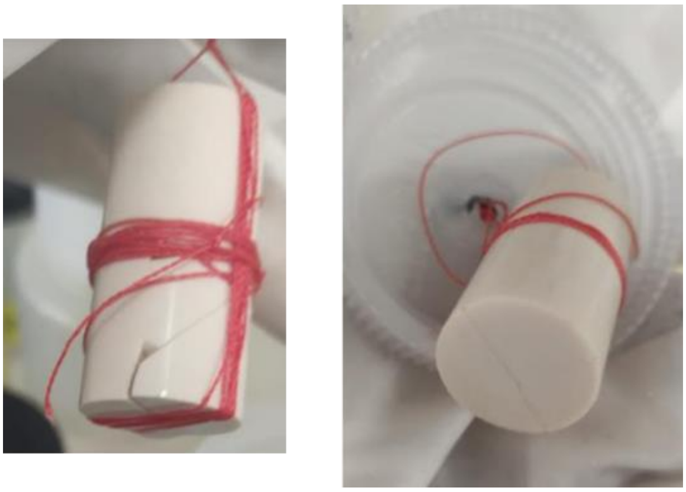


Figure 48 *Samples of geopolymers with InstaGel Plus after leaching test*

The results obtained during pH measurements in used leachant are shown in Figure 49 and Figure 50.

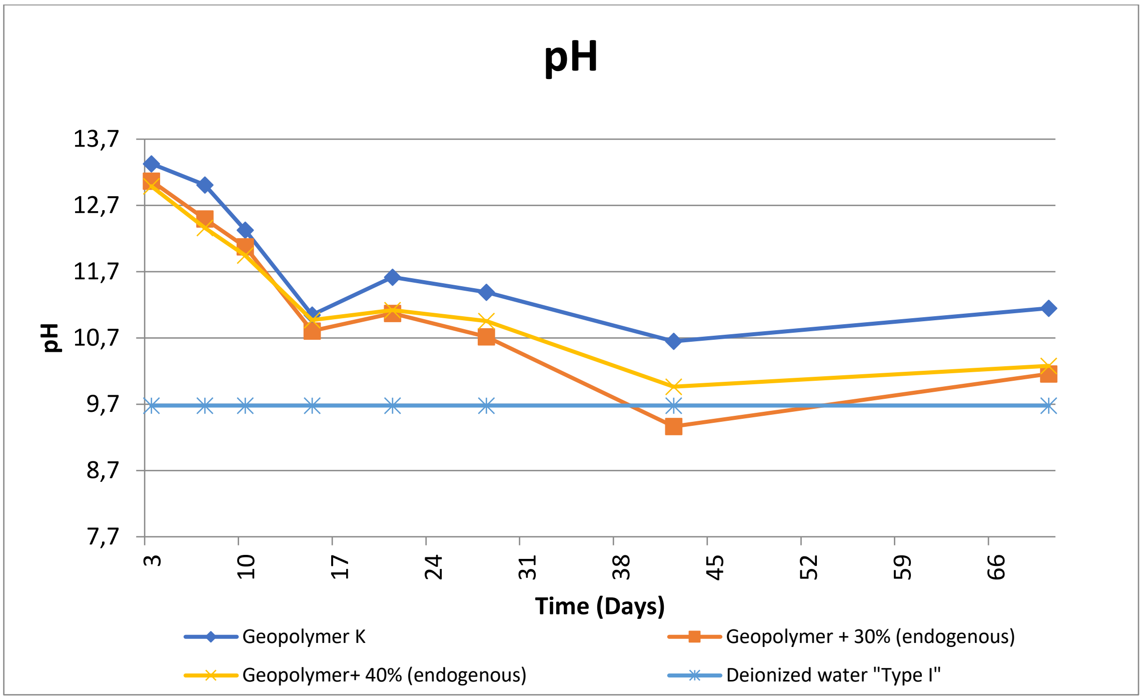


Figure 49 *pH variation in used leachant for Geopolymer without RLOW surrogate and with oil surrogate.*

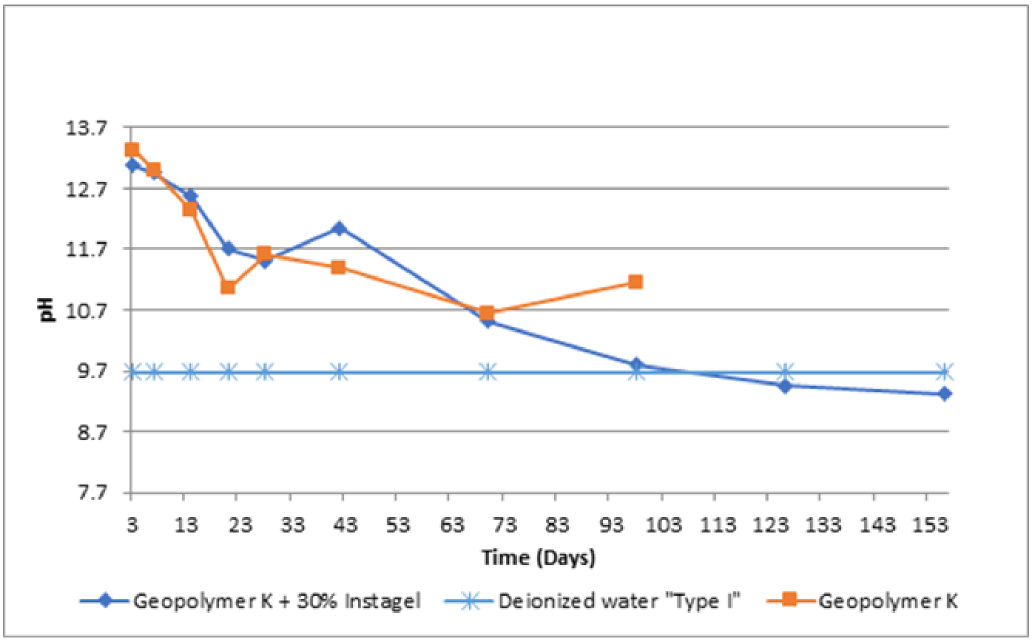


Figure 50 *pH variation in used leachant for Geopolymer without RLOW surrogate and with Instagel*

As can be seen in both figures, the pH values measured for leachant surrounding the waste samples decreased with time. In case of Instagel samples, the pH value drops lower than the pH of milliQ water after 100 days. This fact could indicate that the samples are prone to leaching.

The results of electrical conductivity measurements are presented in

Figure **51** and Figure 52. The results obtained for both waste surrogates were compared with results for Geopolymer without waste. The conductivity measured for Geopolymer without surrogates was higher than the conductivity of samples containing both oil and scintillation cocktail surrogates due to the lower content of activator (responsible for ion supply) in these samples. In case of the leachant used for sample containing InstaGel Plus, the conductivity was significantly lower, as the conductivity of Instagel itself is very low (0.040 µS/cm). Additionally, low conductivity of the leachant can also be a sign of leaching. The conductivity of the leachant used for oil surrogate samples was 0.123 µS/cm.

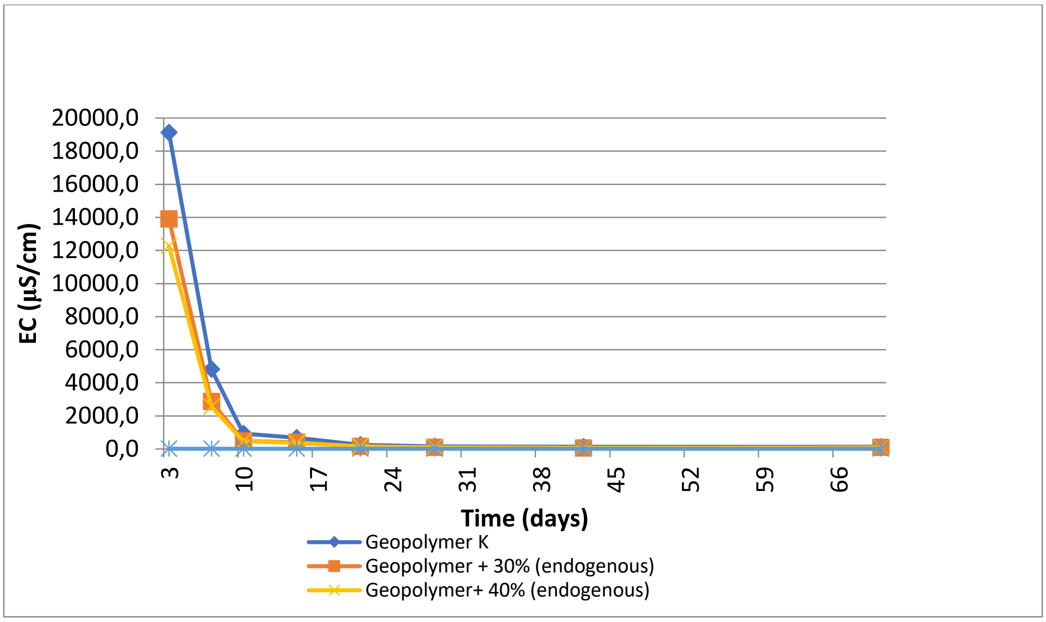


Figure 51 *Conductivity of leachant used to study leaching in Geopolymer and Geopolymer + oil waste samples.*

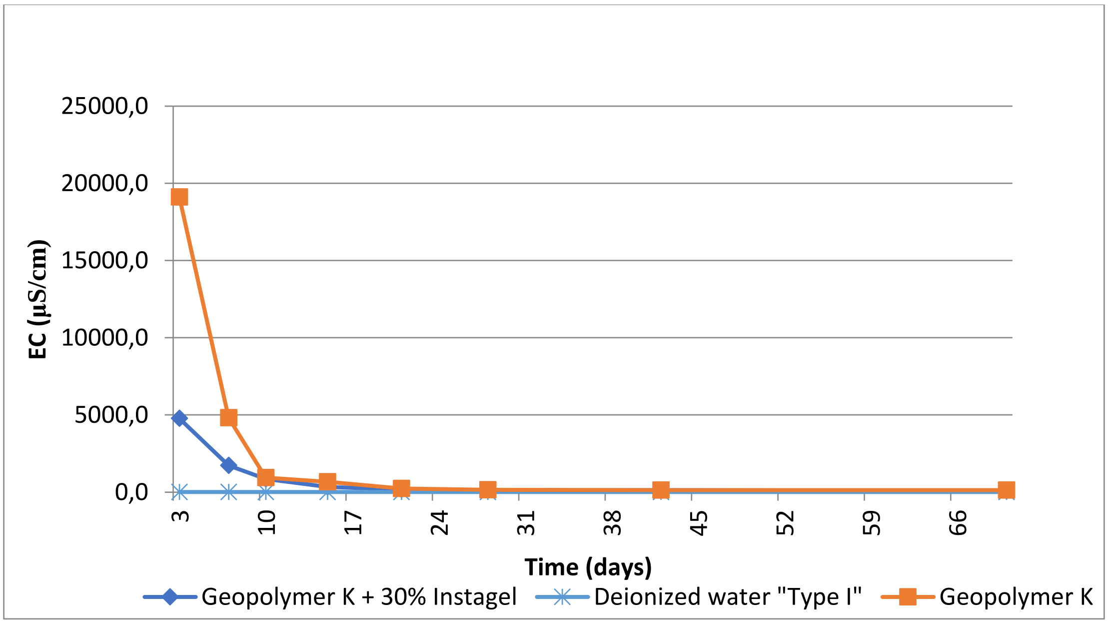


Figure 52 *Conductivity of leachant used to study leaching in Geopolymer and Geopolymer + scintillation (Instagel) waste samples.*

Carbon leaching was studied in leachant for samples with RLOW surrogates. The results obtained for oils samples (see Figure 53), specifically the TOC value, indicate that the waste remains encapsulated in the geopolymer. In case of the scintillation cocktail samples (see Figure 54), the observed TOC is high and thus leaching is suspected.

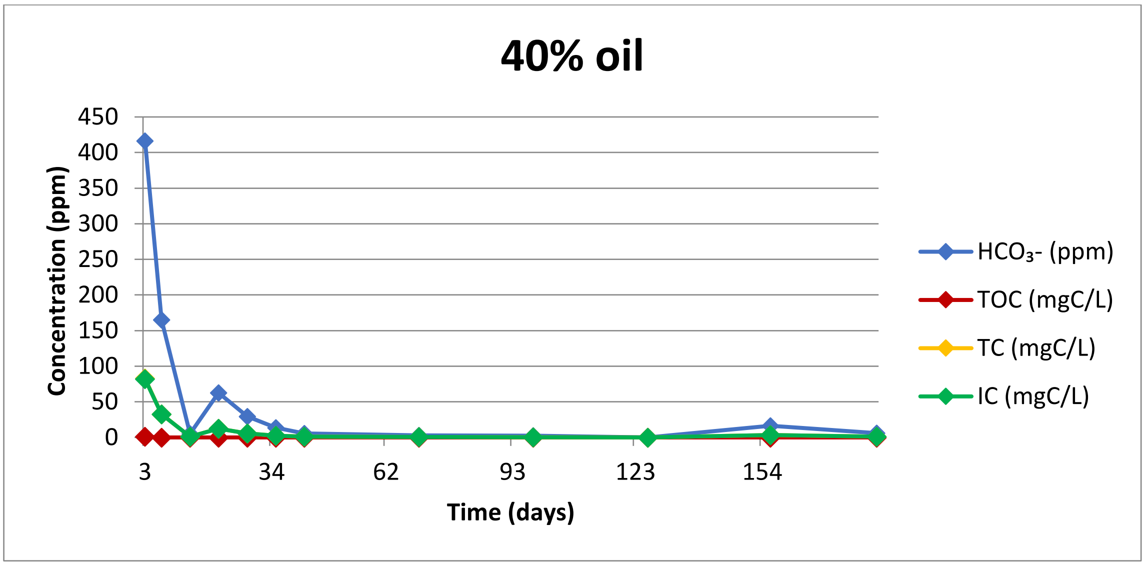


Figure 53 *Results of EC in leachants for 40% oil samples*

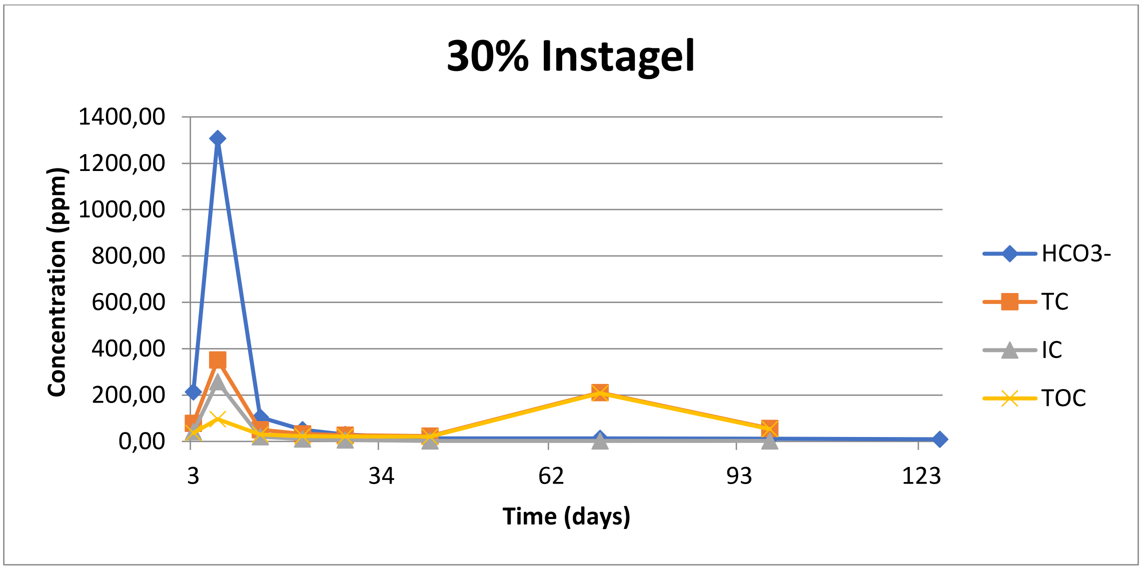


Figure 54 *Results of EC in 30% liquid scintillation samples*

Figure 55 *Foam formed after stirring the solution following leaching of samples containing scintillation liquid*

Additionally, to the observation of leaching signs during pH, conductivity and carbon measurement tests of leachate used for geopolymer samples containing InstaGel Plus, foaming was noticed during stirring of the leachant solution (see Figure 55). This foaming most likely occurred due to the surfactant contained in the scintillation liquid passing into the leach solution.

5.1.2.2 Studies with Nevastane EP 100

Following the first screening stage performed at small scale in ~160mL cylinders (see Chapter □), scale up tests (4L) were carried out to study the Metamax® and Argicem® GP formulations further.

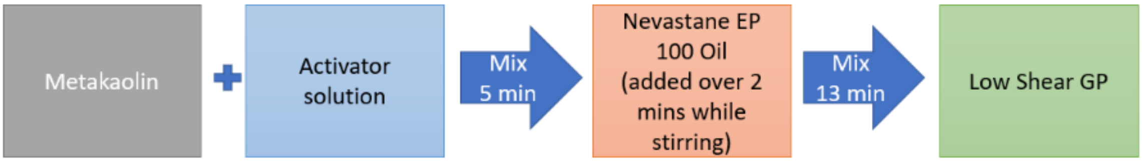
37 mixes were undertaken with waste loading of 10-50% vol based on total wasteform volume (based on formulations ranges from first screening stage).

These samples were studied following testing procedure described below:

- Mix for standard time (20 min) with limited consideration of shear conditions and mixes then tested as follows:
    - Rotational Viscosity test after mixing to ASTM C 1749 at 100 s^{-1} on the descending ramp, cf. Standard viscosity test undertaken by UK nuclear industry at 106 s^{-1} on the descending ramp
    - Fluidity after mixing based on BS EN 13395-2:2002
    - Heat of reaction via Isothermal Conduction Calorimetry at end of mixing – 25 °C
    - Bleed on sealed 100mL specimens measured as vol/vol% of total grout volume after curing for 24 h and 48 h at 20 °C and >90% RH
    - Set time based on EN 196-3
- Physical Properties:
    - Compressive strength at 2, 7, 28 and 90 days curing to EN 196-1 – samples cured in sealed polythene bags at 20 °C and >90% RH prior to testing and had moist tissue placed in bag but not in contact with the sample to prevent drying.
    - Flexural strength at 2, 7, 28 and 90 days to EN 196-1 – samples cured as above at 20 °C and >90% RH
    - Dimensional stability measurements on up to two prisms from each mix at 2, 7, 28, 56, 70 and 90 days curing to ASTM C490. Prisms were wrapped in polythene to prevent drying and cured at 20 °C and >90% RH

Two mixing methods were studied – low shear method with Hobart planetary mixer and high shear method also incorporating a Silverson high shear overhead mixer. Both methods are schematically represented in Figure 56. The high shear method formed the majority of mixes (30) with low shear tests (7 in total) undertaken at mid-point formulations at 20 vol% RLOW loading for both GP systems at the highest RLOW loading of 50 vol% for the Metamax® GP system for purpose of comparison

Low shear method (Hobart Only):



High shear method:

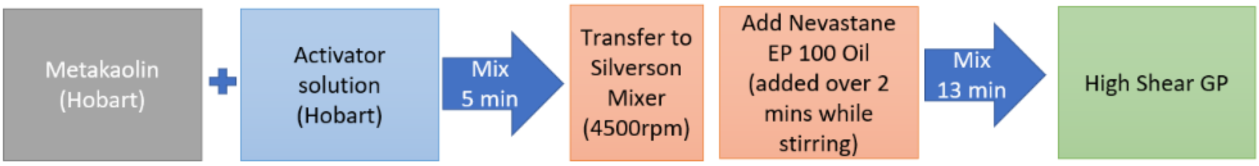


Figure 56 *Mixing methods used to prepare samples containing Nevastane oil*

The processing results for Metamax® and Argicem® GP are presented in Table 36 and Table 37 respectively. Formulations which were dismissed as RLOW could not be incorporated into the GP system are shown in red.

Following conclusions can be made:

- Encapsulation of up to 50 vol% was achieved for mid-point formulations (SiO_2/K_2O = 1.2, H_2O/K_2O = 13, K/Al = 1.2) for both Metamax® and Argicem® GP systems producing fluid, low viscosity mixes of <1000 mPa·s which achieved final set in 24 h
- In both GP samples the bleed values are below the acceptable bleed levels for Portland cement (<2%) although bleed volumes rose between 24 h and 48 h and prisms produced for product quality testing showed evidence of liquor on surface up to 90 d curing.
- Increase in RLOW loading has little effect on bleeding
- Increase in RLOW increases viscosity in samples
- GP formulations containing a H_2O/K_2O molar ratio = 11 and K/Al molar ratio = 1 could not incorporate Nevastane oil into the mix design
- In Metamax® GP samples no significant difference in viscosity can be observed between low and high shear samples at 20 vol% loading. However, at 50 vol% loading Nevastane could be incorporated into the mix under low shear but not at high shear. Hence shear/mix geometry appears important as RLOW loading increases.
- In Argicem® GP samples higher viscosities were generally obtained than for the Metamax® GP system at equivalent formulation ratios and can be observed to show a slight increase in samples prepared by the low shear method

Table 36 *Processing results for Metamax® GP with Nevastane EP 100*

SiO_2/K_2O ratio	H_2O/K_2O ratio	K_2O/Al_2O_3 ratio	Shear type	Oil loading (vol%)	Mass oil (g)	Colflow Fluidity at t=0 (mm)	Viscosity (mPa·s)		Bleed at 48 h (ml)	Final set (h)
							ASTM C1749 at 100 s^{-1}	UK at 106 s^{-1}		
1.4	11	1.5	High	10	348.4	>1020	217.2	287.9	0.5	21.5
1.4	15	1	High	10	348.4	>1020	151.3	230.5	1	21.75
1	15	1.5	High	10	348.4	>1020	50	94.3	1	24
1	11	1	High	10	348.4	740.0	1225	1137	1.25	23
1.2	13	1.2	High	20	696.8	>1020	260.8	303.7	1.25	22.75
1.2	13	1.2	High	20	696.9	960.0	404.8	313.8	1	22
1.2	13	1.2	High	20	696.8	1020.0	246.4	271	0.75	22.25
1.2	13	1.2	Low	20	696.8	990.0	256.8	285.5	1	20.75
1.2	13	1.2	Low	20	696.8	>1020	206.9	279.3	1	23
1.2	13	1.2	Low	20	696.8	>1020	203.6	279.7	0.5	21.75
1	11	1.5	High	30	1045.2	720.0	429	396.3	0.75	20.75
1.4	15	1.5	High	30	1045.2	>1020	152	192.9	0.25	23.75
1.4	11	1	High	30	1045.2					
1	15	1	High	30	1045.2	750.0	413.8	378.2	0.75	22
1.4	11	1	High	40	1393.6	660.0	2031	2061	-	24
1.2	13	1.2	High	40	1393.6	540.0	614.9	576.1	0.75	22.75
1.4	15	1.5	High	40	1393.6	930.0	231.7	243.6	<0.25	23.75
1.2	13	1.2	High	50	1741.9					
1.2	13	1.2	Low	50	1742.0	380.0	918.7	998.8	0.25	22

Table 37 *Processing results for Argicem® GP with Nevastane EP 100*

SiO_2/K_2O ratio	H_2O/K_2O ratio	K_2O/Al_2O_3 ratio	Shear type	Oil loading (vol%)	Mass oil (g)	Colflow Fluidity at t=0 (mm)	Viscosity (mPa·s)		Bleed at 48 h (ml)	Final set (h)
							ASTM C1749 at 100 s^{-1}	UK at 106 s^{-1}		
1	14	1.35	High	10	348.4	>1020	166.9	238.7	0.5	27.5
1.4	11	1.5	High	10	348.4	>1020	498.4	608.3	0	44.25
1.4	15	1	High	10	348.4	>1020	365.6	449.7	0.5	22.5
1	11	1	High	10	348.4					
1.2	13	1.2	High	20	696.8	800.0	472.4	504.1	0.5	22.5
1.2	13	1.2	High	20	696.9	920.0	445.6	488.7	0.25	21.25
1.2	13	1.2	High	20	696.8	870.0	434.9	486.9	0.25	23.5
1.2	13	1.2	Low	20	696.8	700.0	635.9	611.4	0.25	23.5
1.2	13	1.2	Low	20	696.8	820.0	981.1	594	0.5	22.75
1.2	13	1.2	Low	20	696.9	770.0	596.4	594.8	0.25	20
1.4	11	1	High	30	1045.2	NA	2022	1932		
1	11	1.5	High	30	1045.2	630.0	568.2	556.2	0.25	22.5
1.4	14	1.35	High	30	1045.2	760.0	445.8	435.9	0.25	24
1	15	1	High	30	1045.2	630.0	444.1	488.9	0.5	23
1.4	14	1.35	High	40	1393.6	560.0	499.5	508.3	0.25	23
1.2	13	1.2	High	40	1393.6	540.0	616.4	667.1	0.25	22.25
1.4	11	1	High	40	1393.6					
1.2	13	1.2	High	50	1742.0	470.0	735	723	0	23.75

The results of heat of reaction studies of the Metamax® GP system at mid-point formulations (SiO2/K2O = 1.2, H2O/K2O = 13, K/Al = 1.2) and varying RLOW loadings are presented in Figure 57 Nevastane EP 100 – Metamax® mid-point formulations Heat of reaction. The following observations and conclusions can be made:

- Mid-point formulations are characterised by high heats of dissolution of the MK powder.
- Heat output at 24 h curing is > at 25 °C in comparison to typical UK PC formulations (~100 kJ/kg) tested at 35 °C.
- Small second polymerisation peak
- Effect of shear and oil loading on cumulative heat output at 24 h appear negligible which is expected in the latter case as heat outputs were normalised to the solids content of each mix.

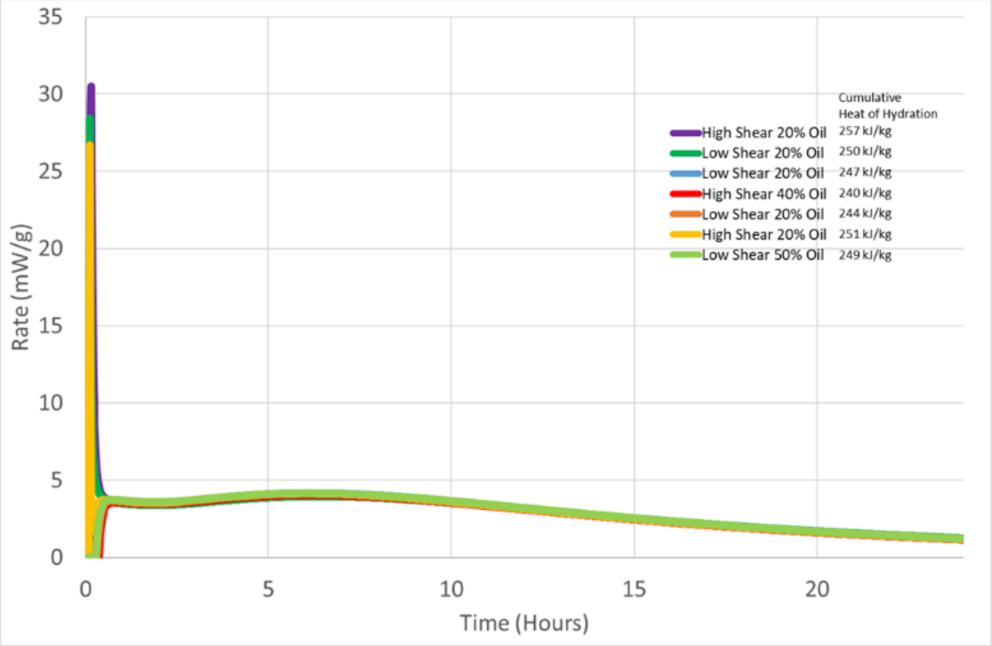


Figure 57 *Nevastane EP 100 – Metamax® mid-point formulations Heat of reaction*

Observations and conclusions made for Argicem® GP formulations (see Figure 58) are as follows:

- Mid-point formulations are characterised by a lower heat of dissolution than the Metamax® GP system
- Lower heat output over the first 24 h curing than Metamax® GP mixes (coarser MK powder, high SiO_2 filler content) consistent with the lower reactivity of Argicem® MK powder.
- Small second polymerisation peak
- Effect of shear and oil loading on cumulative heat output at 24 h appear negligible which is expected in the latter case as heat outputs were normalised to the solids content of each mix.

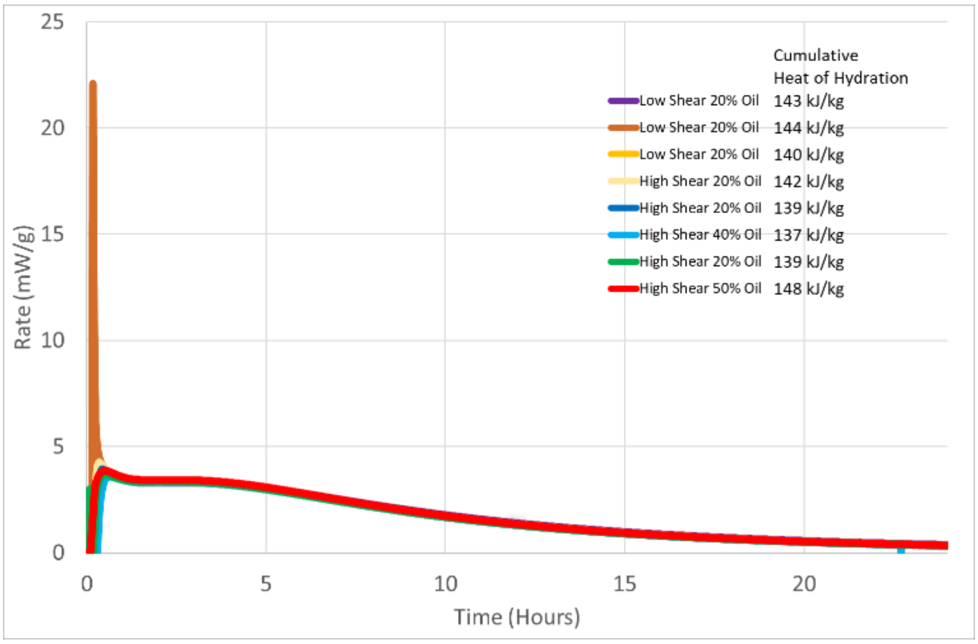


***Figure 58** Nevastane EP 100 – Argicem® mid-point formulations Heat of reaction*

The results of compressive strength tests for both Metamax® (Figure 59) and Argicem® (Figure 60) samples were based on an average of up to 6 tests from 3 beams for compressive strength. These results show:

- GP strength development characterised by relatively rapid strength development up to 7 days curing with strengths plateauing from this point to 90 days curing.
- Strengths considered acceptable over 90 days curing.
- Decrease in strength when oil loading increased.
- Slight increase in strength at 90 days for equivalent Metamax® formulations at equivalent RLOW loadings in comparison to Argicem® GP system

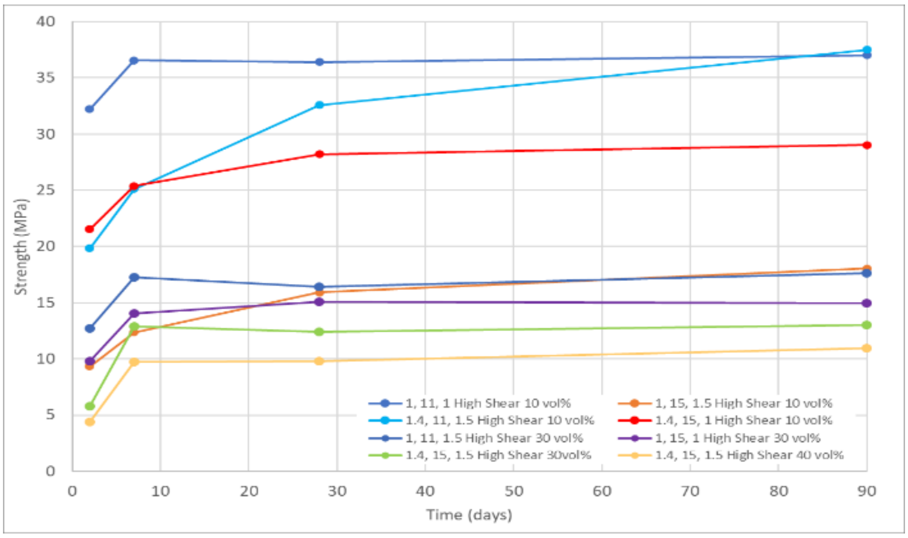


Figure 59 Compressive Strength results of Nevastane EP 100 – Metamax® samples

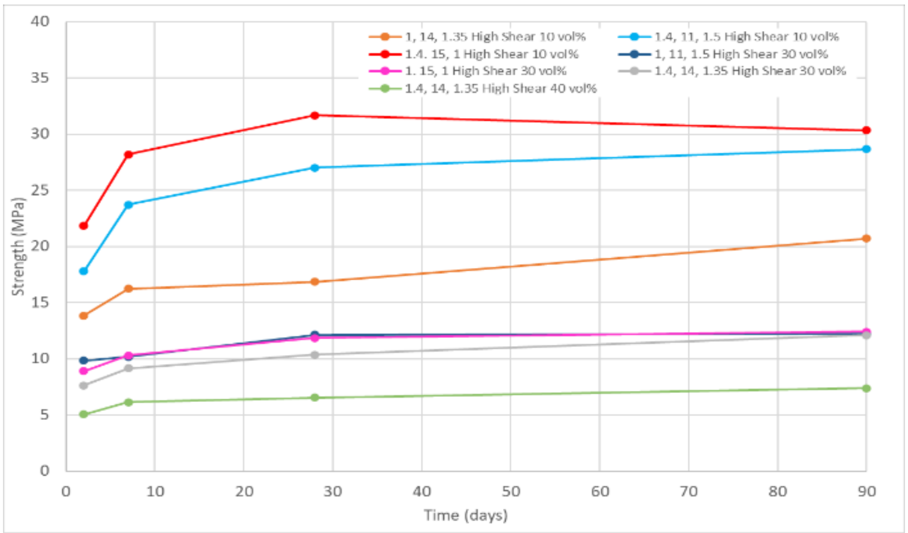


***Figure 60** Compressive Strength results of Nevastane EP 100 – Argicem® samples*

The shearing effect for mid point samples (RLOW loading of 20% vol.) was minimal (see Figure 61).

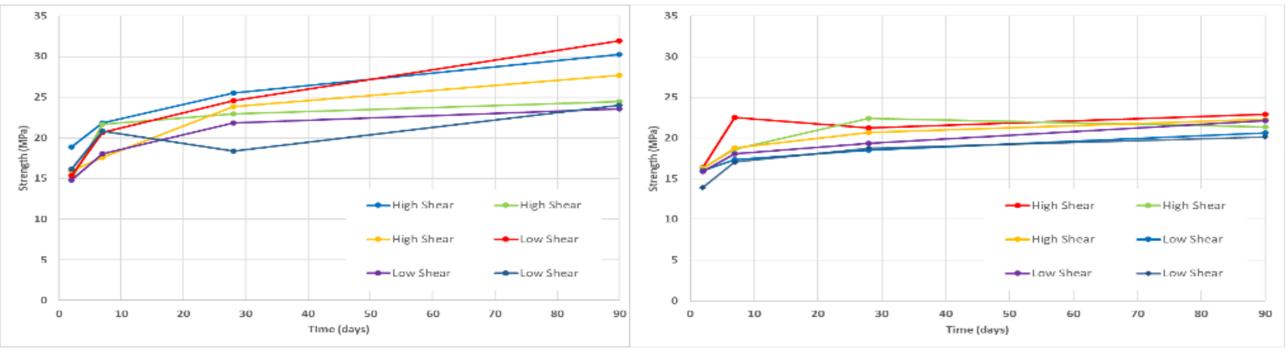


***Figure 61** Compressive Strength results for Metamax® (left) and Argicem® (right) mid point samples (RLOW loading of 20% vol.)*

Flexural strength was measured for Argicem® and Metamax® GP mid-point mixes (Figure 62 and Figure 63). Several observations have been made:

- Flexural strength values were >2 MPa for all samples at 90 days of curing, ranging from 8% - 28.5% of the compressive strength for Metamax® GP formulations and 16% - 68% of the compressive strength for Argicem® GP formulations at 90 days curing. Hence considered in acceptable range.
- Flexural strength data tended to fluctuate with curing time and oil loadings, possibly due to proliferation of micro cracks in the samples in their hardened state.
- Higher oil loadings may reduce flexural strength for both Argicem® and Metamax® GP systems up to 90 d curing

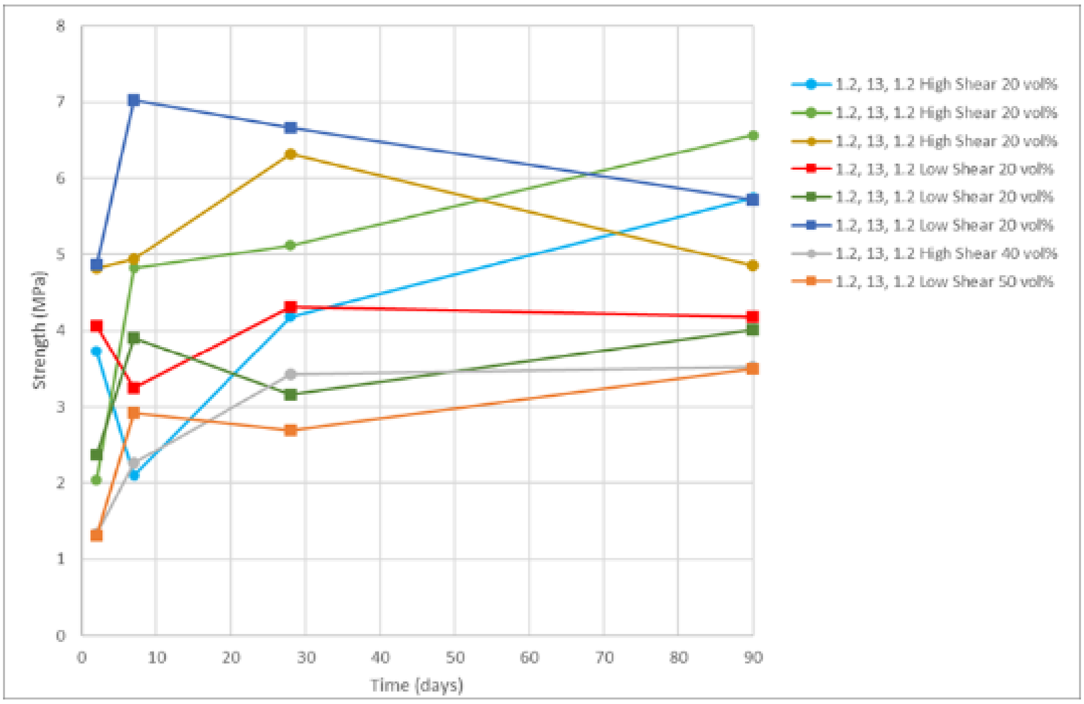


***Figure 62** Flexural strength for mid-point Metamax® formulations incorporating Nevastane EP 100*

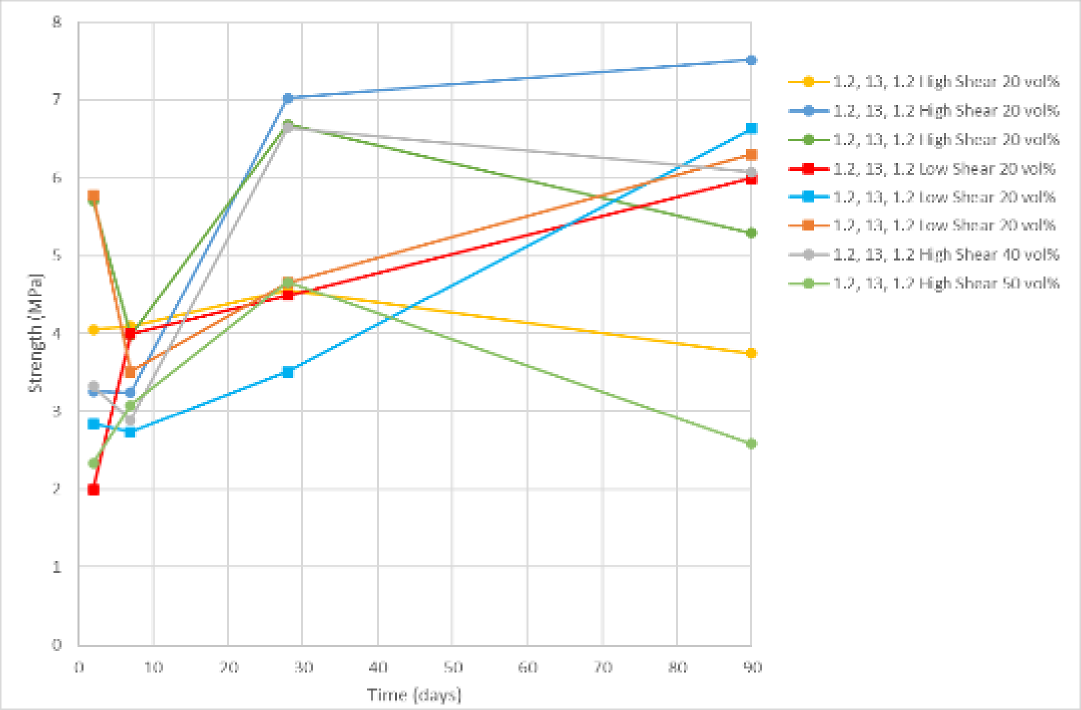


***Figure 63** Flexural strength for mid-point Argicem® formulations incorporating Nevastane EP 100*

Dimensional stability of Metamax® GP and Argicem® GP mid-point formulations is shown in Figure 64 and Figure 65 respectively. Small changes through time can be observed in both GP types, namely:

- Metamax® formulations show small 0.03 - 0.11% shrinkage at 90 d curing with negligible effect of shear for mid-point formulations.
- Argicem® formulations also shows small dimensional changes ranging from 0.003% expansion to 0.06% shrinkage at 90 d curing with shear having a negligible effect on shrinkage for mid-point formulations.

- Small number of formulations not stabilised at 90 d curing – longer monitoring recommended for these formulations in future work studies.

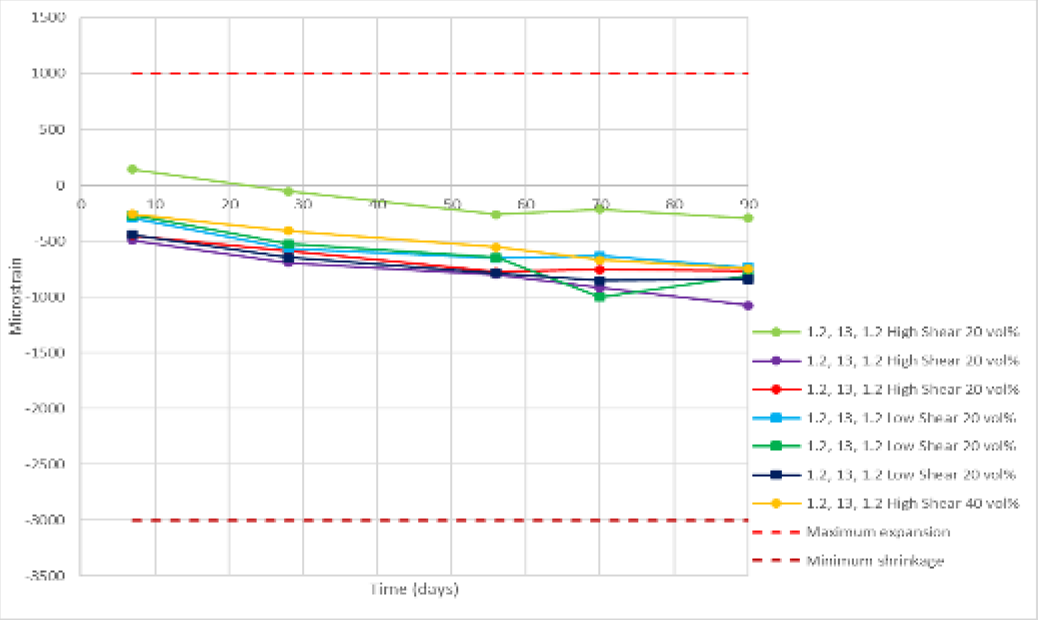


Figure 64 *Dimensional stability of Metamax® mid-point formulations incorporating Nevastane EP100*

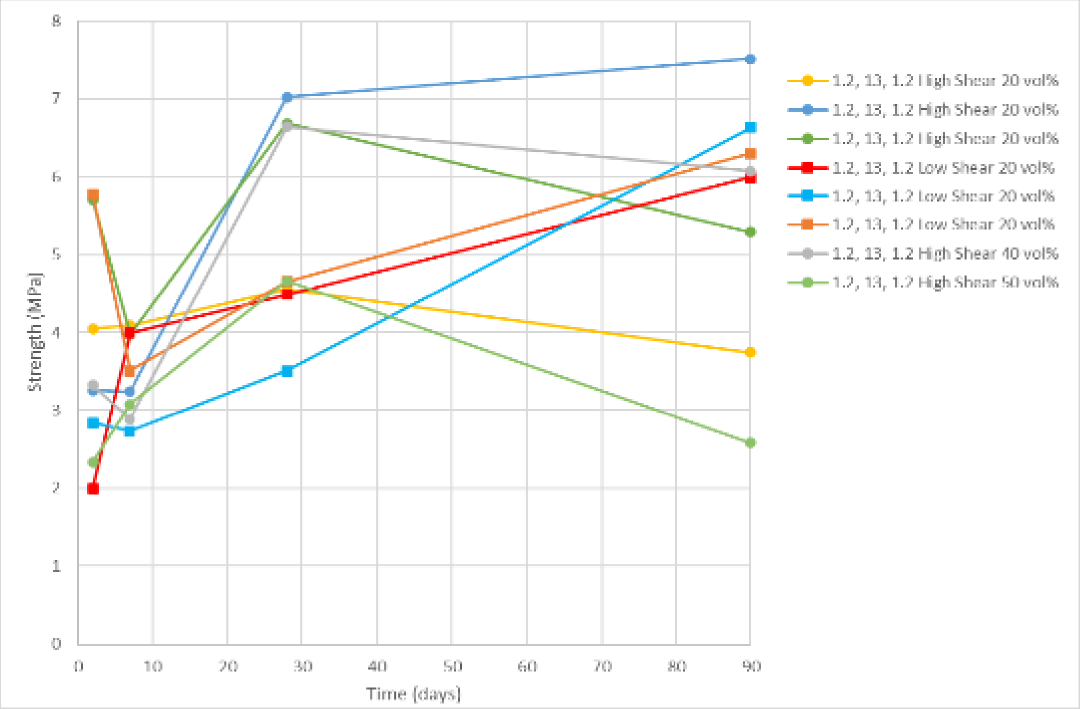


Figure 65 *Dimensional stability of Argicem® mid-point formulations incorporating Nevastane EP100*

5.1.2.3 Studies with TBP/Dodecane mix

Following the first screening stage and, as described in Section 4.7, due to the lack of success in incorporating TBP into the GP systems the addition of surfactants into the mix design (non-ionic surfactants (Tween 80 and Triton CG 110) and a cationic surfactant (CTAB)) was investigate to assess if a stable emulsion with the geopolymer activator solution can be attained, thereby increasing the probability of producing a stable waste form with higher incorporation rates than those achieved thus far.

In this study TBP/Dodecane (70/30 vol/vol%)[5] was investigated as a more realistic extractant solvent used in reprocessing operations rather than TBP alone and scoping studies with the three different surfactant types with Metamax® GP mid-point formulations at 20 vol% RLOW loading were undertaken at 160 – 240 mL scale, testing various order of addition of mix components. The surfactant loading was based on the RLOW volume in the mix. The focus of these studies was based on the Metamax® GP system as this produced less bleed when compared to the Argicem® GP system in trials with TBP alone. All formulations studied and the results are presented in Table 38.

Table 38 *Metamax® GP mid-point formulation - TBP/Dodecane (70/30) Scoping Studies with different Surfactant types at 20 vol% RLOW loading*

Surfactant type	Surfactant volume (%)	Order of Addition	Viscosity (mPas) Descending at 100 s^{-1}	Bleed at 24 h (vol%)	Bleed at 48 h (vol%)
CTAB	1	TBP/Dod + Surfactant, Add activator, Add MK	Not recorded	0.3	0.2
	1	TBP/Dod + activator, Add surfactant, Add MK	Not recorded	0.4	0.3
	1	TBP/ Dod + Surfactant, Add to PF GP	Not recorded	0.2	0.4
	2	TBP/Dod + Surfactant, Add activator, Add MK	Not recorded	0.2	0.4
	2	TBP/Dod + activator, Add surfactant, Add MK	Not recorded	0.1	0.3
	2	TBP/ Dod + Surfactant, Add to PF GP	Not recorded	0.1	0.1
Triton CG 110	1	TBP/Dod + Surfactant, Add activator, Add MK	223.9	0.7	1.1
	1	TBP/Dod + activator, Add surfactant, Add MK	221.2	0.6	1
	1	TBP/ Dod + Surfactant, Add to PF GP	154.5	17	17
	2	TBP/Dod + Surfactant, Add activator, Add MK	163.3	0.2	0.5
	2	TBP/Dod + activator, Add surfactant, Add MK	214.9	0.9	1.1
	2	TBP/ Dod + Surfactant, Add to PF GP	168.9	15.5	15.8
	3	TBP/Dod + Surfactant, Add activator, Add MK	122.7	1.1	1.5
	5	TBP/Dod + Surfactant, Add activator, Add MK	117.1	9.2	9.4
Tween 80	1	TBP/Dod + Surfactant, Add activator, Add MK	474.9	0.1	0.4
	1	TBP/Dod + activator, Add surfactant, Add MK	461.2	0.1	0.5
	1	TBP/ Dod + Surfactant, Add to PF GP	432	0.1	0.7
	2	TBP/Dod + Surfactant, Add activator, Add MK	534.9	0.1	0.5
	2	TBP/Dod + activator, Add surfactant, Add MK	515.4	0.1	0.3
	2	TBP/ Dod + Surfactant, Add to PF GP	500.4	0.1	0.7
	3	TBP/Dod + Surfactant, Add activator, Add MK	556.6	0	0.1
	5	TBP/Dod + Surfactant, Add activator, Add MK	589.9	0.1	0.4

Several observations were made:

- CTAB mixes were too viscous to get a measurement
- CTAB not incorporated efficiently into mix
- Triton CG 110 – low viscosity mixes but significant segregation occurred when mix components were added to pre-formed (PF) GP and when loading of Triton CG 110 increased to 5 vol%
- Triton CG 110 mixes produced set products with a ‘Crusty Porous’ top surface which may compromise integrity of the GP waste form
- Tween 80 – Slightly higher viscosity than Triton CG 110 mixes but still acceptable and generally lower bleed volume than obtained for Triton CG 110 mixes
- Tween 80 mixes set in 24 h and produced homogeneous products without the ‘crusty’ upper surface observed in Triton CG 110 mixes
- Little benefit of increase Tween 80 surfactant volume to 5 vol%.
- Tween 80 – Little effect in order of addition, with slightly elevated bleed at 48 h for mixes in which RLOW added to PF GP

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[5] Most of the tests have been performed on TBP/Dodecane (70/30) and very small study on (30/70) suggesting little difference in behaviour but needs testing further.

Taking these observations into account it was decided that surfactant Tween 80 will be investigated further with both Metamax® and Argicem® GP systems. Results of comparison studies at 160 – 240 mL scale with the Argicem® GP system at mid-point formulations and 20 vol% RLOW loading are presented in Table 39.

Table 39 *Results of studies on TBP/Dodecane mix with Metamax® and Argicem® mid-point formulations with Tween 80 surfactant at 20 vol% RLOW loading*

Metakaolin	Surfactant volume (%)	Order of Addition	Viscosity (mPas) Descending 100s-1	Bleed at 24 h (vol%)	Bleed at 48 h (vol%)
MetaMax	1	TBP/Dod + Surfactant, Add activator, Add MK	474.9	0.1	0.4
	1	TBP/Dod + activator, Add surfactant, Add MK	461.2	0.1	0.5
	1	TBP/ Dod + Surfactant, Add to PF GP	432.0	0.1	0.7
	2	TBP/Dod + Surfactant, Add activator, Add MK	534.9	0.1	0.5
	2	TBP/Dod + activator, Add surfactant, Add MK	515.4	0.1	0.3
	2	TBP/ Dod + Surfactant, Add to PF GP	500.4	0.1	0.7
	3	TBP/Dod + Surfactant, Add activator, add MK	556.6	0	0.1
	5	TBP/Dod + Surfactant, Add activator, add MK	589.9	0.1	0.4
Argicem	1	TBP/Dod + Surfactant, Add activator, Add MK	491.1	0.5	0.6
	1	TBP/Dod + activator, Add surfactant, Add MK	490.9	0.4	0.5
	1	TBP/ Dod + Surfactant, Add to PF GP	548.9	0.4	0.4
	2	TBP/Dod + Surfactant, Add activator, Add MK	497.2	0.4	0.5
	2	TBP/Dod + activator, Add surfactant, Add MK	564.7	0.4	0.5
	2	TBP/ Dod + Surfactant, Add to PF GP	517.5	0.3	0.5
	3	TBP/Dod + Surfactant, Add activator, Add MK	549.4	0.4	0.5
	5	TBP/Dod + Surfactant, Add activator, Add MK	491.9	0.3	0.4

Both GP systems produced a small volume of bleed up to 48 h and similar values of viscosity could be observed for both systems, with again little effect in changing the order of addition of mix components. However, over time (after 7 days) it was noted that the bleed on the Argicem® GP samples produced a 'gel' layer on the surface, which was not noted for Metamax® (GP) formulations. Hence, the Metamax® GP system was chosen as the primary GP system to take forward to 4L studies, with the Argicem® GP system only studied at the mid-point ($SiO_2/K_2O = 1.2$, $H_2O/K_2O = 13$, $K/Al = 1.2$) formulation.

Following these studies and considering their results further optimisation and robustness tests were carried out, studying the mix of TBP/Dodecane (70/30 vol/vol%), both GP types and Tween 80 surfactant at a 4L scale.

24 Mixes have been prepared and tested, out of which:

- 19 contained Metamax® GP – Covering the full formulation envelope: $SiO_2/K_2O = 1\text{-}1.4$, $H_2O/K_2O = 11\text{-}15$, $K/Al = 1\text{-}1.5$
- 5 contained Argicem® GP system: - Mid-point formulation only: $SiO_2/K_2O = 1.2$, $H_2O/K_2O = 13$, $K/Al_l = 1.2$

These mixes were prepared with:

- Surfactant (Tween 80) loading 1-3 vol% based on RLOW volume in the mix
- Waste Loading 10-30 vol% based on total mix volume
- 70:30 vol/vol% TBP/Dodecane

As little effect was observed regarding the order of addition of mix components in the scoping studies, one order of addition & shear regime was used to prepare the samples. First the surfactant and RLOW were mixed for 10 min using a Silverson L5 high shear overhead mixer with emulsifying head attachment at 3500 rpm, creating an emulsified solution. Then the activator solution was added and mixed in the Hobart mixer at 62 rpm for 2 min. Finally, the Metakaolin powder to give the correct formulation was added to the mixer over a 5 minutes period with continued stirring and the whole system was then transferred to Silverson L5 mixer with standard mixing head for a further 13 minutes at 4500 rpm to give a total mix time of 20 minutes from addition of activator solution to the mix. The flowchart of the process is presented in Figure 66.

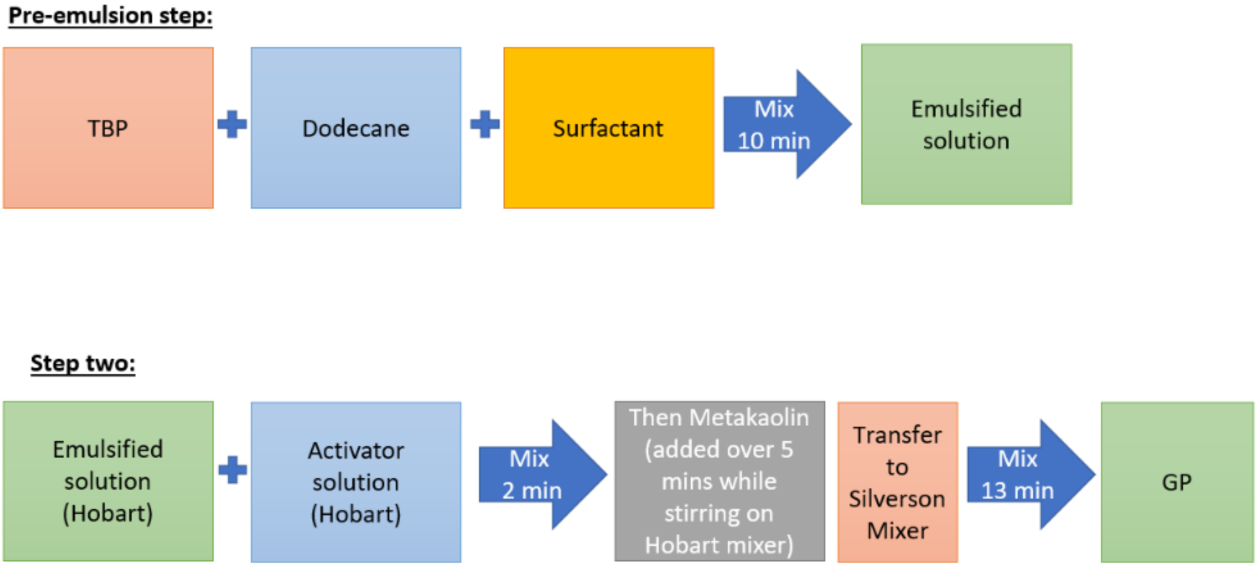


***Figure 66** Flowchart of addition & shear regime used to prepare samples for 4L studies with TBP/Dodecane*

To test these samples the same Testing protocol as per Nevastane EP 100 Oil 4 L mixes was used. The processing results for Metamax® and Argicem® GP are presented in Table 40 and Table 41 respectively. Formulations which were dismissed are shown in red.

To test these formulations the same testing protocol as per Nevastane EP 100 Oil 4 L mixes was used. The processing results for Metamax® GP and Argicem® GP are presented in Table 40 and Table 41 respectively. Formulations in which TBP/Dodecane could not be incorporated are shown in red.

Following observations were made for Metamax® GP formulations:

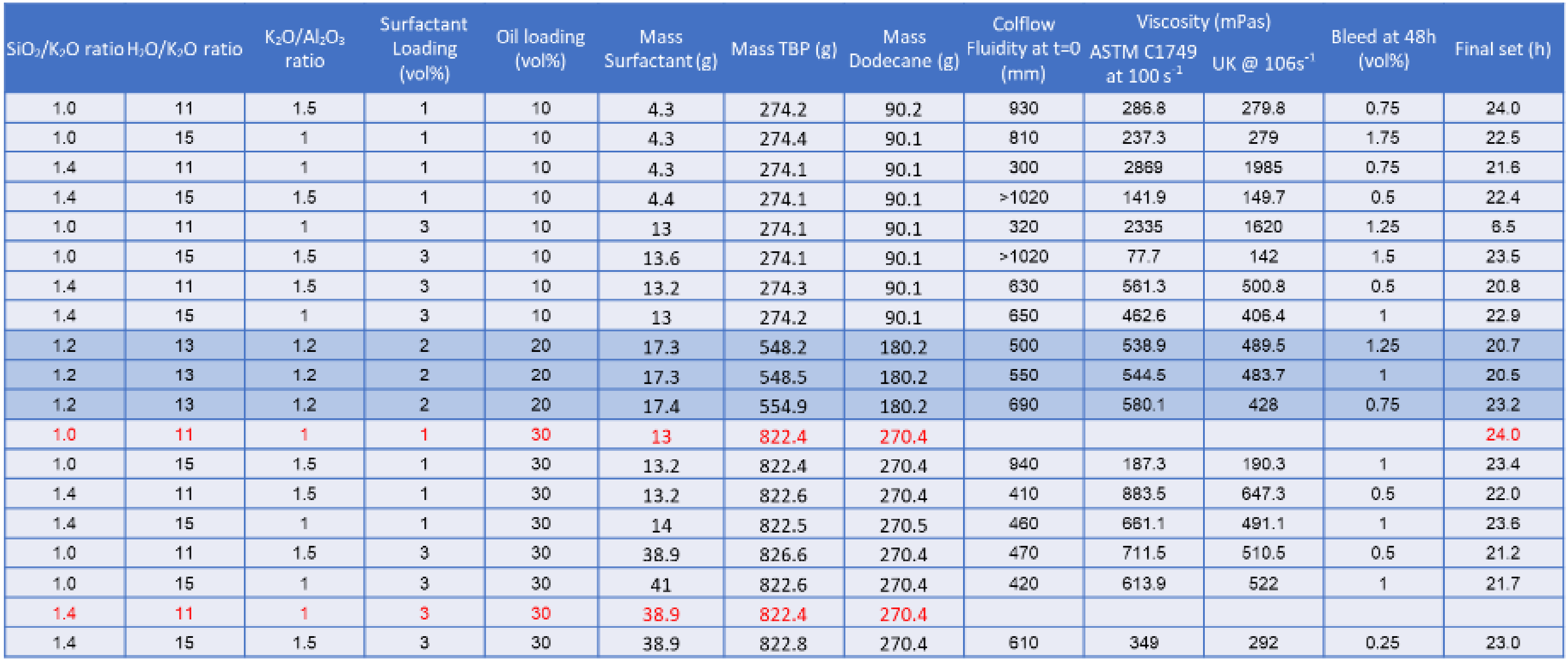
- Encapsulation of up to 30 vol% TBP/Dodecane was achieved across a range of formulations producing low viscosity mixes that achieved final set within 24 h
- Formulations at the low $H_2O/K_2O = 11$ and $K/Al = 1$ point of the envelope RLOW could not be incorporated into the GP system at 30 vol% loading
- In all samples the bleed values are below the acceptable bleed level for Portland cement (<2%) however bleed volumes generally rose between 24 h and 48 h with some evidence of surface sheen on product quality samples at 2 d curing which had disappeared by 90 d curing
- Increase in RLOW loading has little effect on bleed volumes produced over 48 h curing period
- Increase in RLOW generally increases the viscosity of the mixes although all mixes in which TBP/Dodecane could be incorporated are considered acceptable for mixing via an IDM process
- Viscosity of most formulations was < 1000 mPa·s

For Argicem® mid-point formulations similar observations were made:

- Encapsulation of up to 30 vol% TBP/Dodecane was achieved producing low viscosity mixes that achieved final set in 24 h
- Increase in RLOW loading showed a small increase in mix viscosity
- Viscosity of all samples < 1000 mPa·s
- Increase in surfactant loading showed a slight decrease in mix viscosity

- In all samples bleed values are below the acceptable bleed for Portland cement (<2%) however bleed volumes generally rose between 24 h and 48 h and with the exception of one mix some evidence of surface sheen on product quality samples at 2 d curing which had disappeared by 90 d curing
- Increase in surfactant loading may serve to slightly reduce bleed levels
- Increase in RLOW loading has little effect on bleed levels.

Table 40 *Processing results for Metamax® GP with TBP/Dodecane and surfactant*



SiO_2/K_2O ratio	H_2O/K_2O ratio	K_2O/Al_2O_3 ratio	Surfactant Loading (vol%)	Oil loading (vol%)	Mass Surfactant (g)	Mass TBP (g)	Mass Dodecane (g)	Colflow Fluidity at t=0 (mm)	Viscosity (mPas)		Bleed at 48h (vol%)	Final set (h)
									ASTM C1749 at 100 s^{-1}	UK @ 106s^{-1}		
1.0	11	1.5	1	10	4.3	274.2	90.2	930	286.8	279.8	0.75	24.0
1.0	15	1	1	10	4.3	274.4	90.1	810	237.3	279	1.75	22.5
1.4	11	1	1	10	4.3	274.1	90.1	300	2869	1985	0.75	21.6
1.4	15	1.5	1	10	4.4	274.1	90.1	>1020	141.9	149.7	0.5	22.4
1.0	11	1	3	10	13	274.1	90.1	320	2335	1620	1.25	6.5
1.0	15	1.5	3	10	13.6	274.1	90.1	>1020	77.7	142	1.5	23.5
1.4	11	1.5	3	10	13.2	274.3	90.1	630	561.3	500.8	0.5	20.8
1.4	15	1	3	10	13	274.2	90.1	650	462.6	406.4	1	22.9
1.2	13	1.2	2	20	17.3	548.2	180.2	500	538.9	489.5	1.25	20.7
1.2	13	1.2	2	20	17.3	548.5	180.2	550	544.5	483.7	1	20.5
1.2	13	1.2	2	20	17.4	554.9	180.2	690	580.1	428	0.75	23.2
1.0	11	1	1	30	13	822.4	270.4					24.0
1.0	15	1.5	1	30	13.2	822.4	270.4	940	187.3	190.3	1	23.4
1.4	11	1.5	1	30	13.2	822.6	270.4	410	883.5	647.3	0.5	22.0
1.4	15	1	1	30	14	822.5	270.5	460	661.1	491.1	1	23.6
1.0	11	1.5	3	30	38.9	826.6	270.4	470	711.5	510.5	0.5	21.2
1.0	15	1	3	30	41	822.6	270.4	420	613.9	522	1	21.7
1.4	11	1	3	30	38.9	822.4	270.4					
1.4	15	1.5	3	30	38.9	822.8	270.4	610	349	292	0.25	23.0

Table 41 *Processing results for Argicem® GP with TBP/Dodecane and surfactant*

SiO_2/K_2O ratio	H_2O/K_2O ratio	K_2O/Al_2O_3 ratio	Surfactant Loading (vol%)	Oil loading (vol%)	Mass Surfactant (g)	Mass TBP (g)	Mass Dodecane (g)	Colflow Fluidity at t=0 (mm)	Viscosity (mPa·s)		Bleed at 48h (vol%)	Final set (h)
									ASTM C1749 at 100 s^{-1}	UK @ 106s^{-1} (mPas)		
1.2	13	1.2	1	10	4.32	274.12	90.12	610	430.8	479.3	0.75	6.1
1.2	13	1.2	3	10	12.96	274.12	90.12	660	434.7	458	0.5	5.5
1.2	13	1.2	2	20	17.28	548.24	180.24	540	526.2	508.8	1	22.5
1.2	13	1.2	1	30	12.96	822.36	270.36	460	683.2	615	0.5	21.7
1.2	13	1.2	3	30	38.88	822.36	270.36	400	635.3	570.9	0.25	22.4

The results of heat of reaction studies for the Metamax® GP formulations with varying RLOW loadings are presented in Figure 67. The following observations and conclusions can be made:

- Formulations characterised by high heat output at 24 h curing is > at 25 °C in comparison to typical UK PC formulations (~100 kJ/kg) tested at 35 °C
- Increasing the SiO_2/K_2O ratio causes elongation and reduction in intensity in polymerisation peak and lower cumulative heat output at 24 h likely due to lower alkali content of the formulation
- Effect of RLOW loading has a negligible effect on cumulative heat output at 24 h which is expected in the latter case as heat outputs were normalised to the solids content of each mix
- Initial heat of MK dissolution likely missed in these trials hence polymerisation peak tended to form the peak rate observed

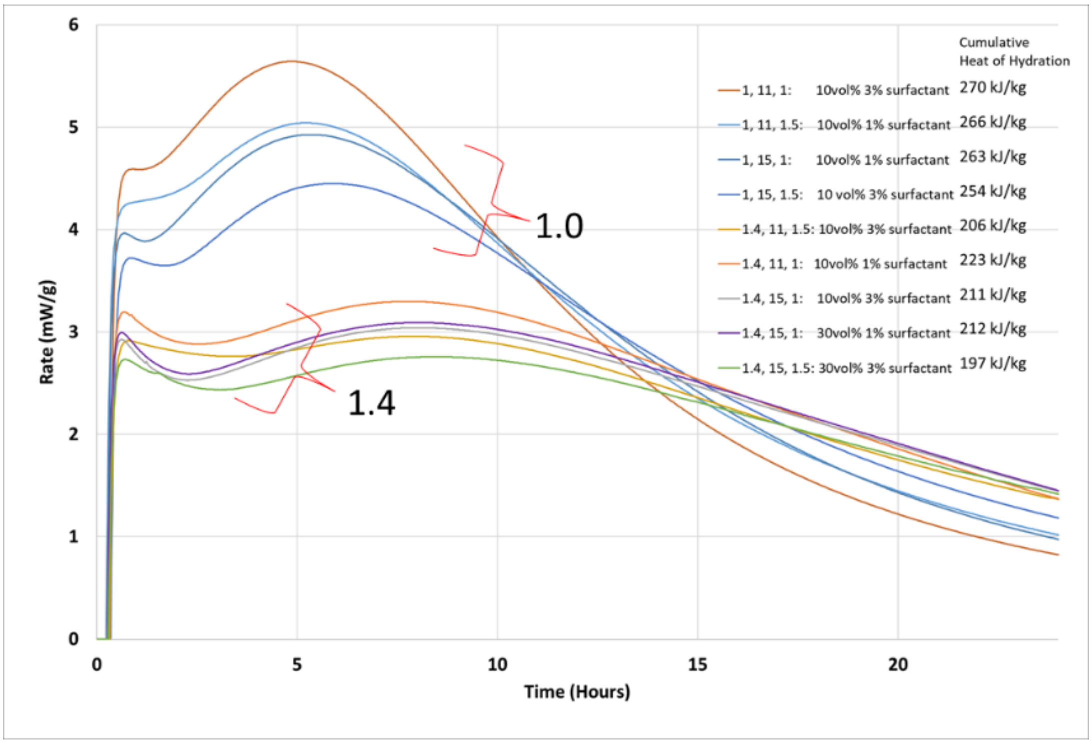


Figure 67 *TBP/Dodecane– Metamax® GP formulation ranges plus surfactant Heat of reaction with varying SiO_2/K_2O ratios*

Observations and conclusions made for Argicem® GP mid-point formulations (see Figure 68) are as follows:

- Lower heat output over the first 24 h curing than Metamax® GP mixes (coarser MK powder, high SiO_2 filler content) consistent with the lower reactivity of Argicem® MK powder, although these mixes still produce higher heat output at 25 °C in comparison to typical UK PC formulations (~100 kJ/kg) tested at 35 °C
- High heat of dissolution of MK powder captured in these trials followed by small polymerisation feature
- Results highly reproducible
- Effect of Surfactant and RLOW loading on cumulative heat output at 24 h appear negligible at formulation range tested which is expected as heat outputs were normalised to the solids content of each mix.

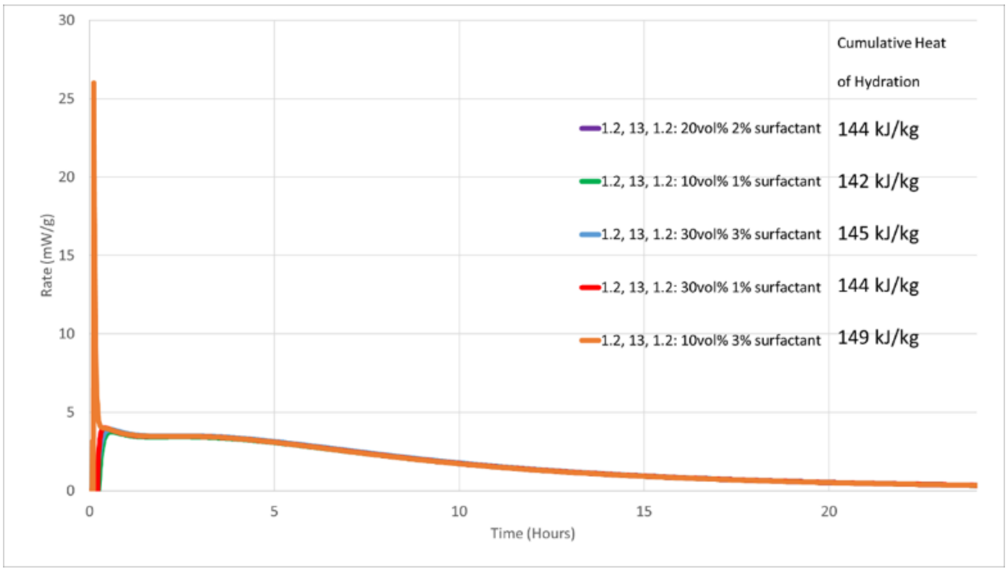


Figure 68 *TBP/Dodecane– Argicem® GP formulation plus surfactant Heat of reaction*

The compressive strength of mid-point Metamax® and Argicem® formulations (20 vol% RLOW) with 2% surfactant are presented in Figure 69.

The results show:

- Rapid strength gain up to 7 days curing with strengths plateauing from this point to 90 days curing
- Strengths are considered acceptable over 90 days curing
- Metamax® mid-point formulations have increased strength over Argicem® formulations (Figure 69)
- Mid- point Metamax® formulations exhibit similar 90 d strength showing good reproducibility

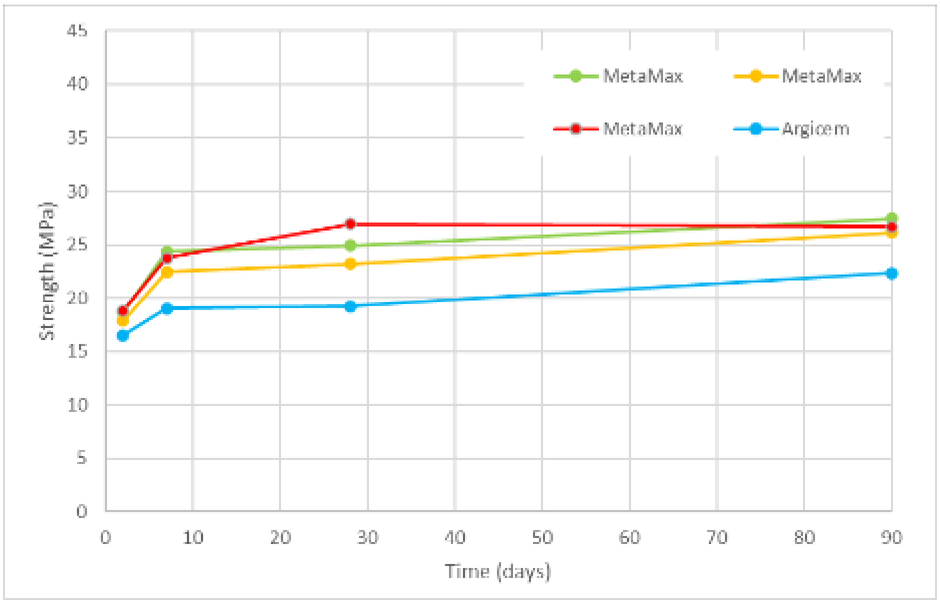


Figure 69 *Compression strength of mid-point (RLOW 20 vol%) TBP/Dodecane - Metamax® and Argicem® GP formulations, 2% surfactant*

The compressive strength results for all Argicem® samples (Figure 70) show, as expected, a decrease in strength when RLOW loading increased up to 90 curing, although still considered acceptable, while the effect of surfactant loading is less obvious, but given the small difference in volume of surfactant added over the loadings tested (a maximum difference of 32 mL in a 4 L mix) is anticipated to make little difference to resultant GP strengths.

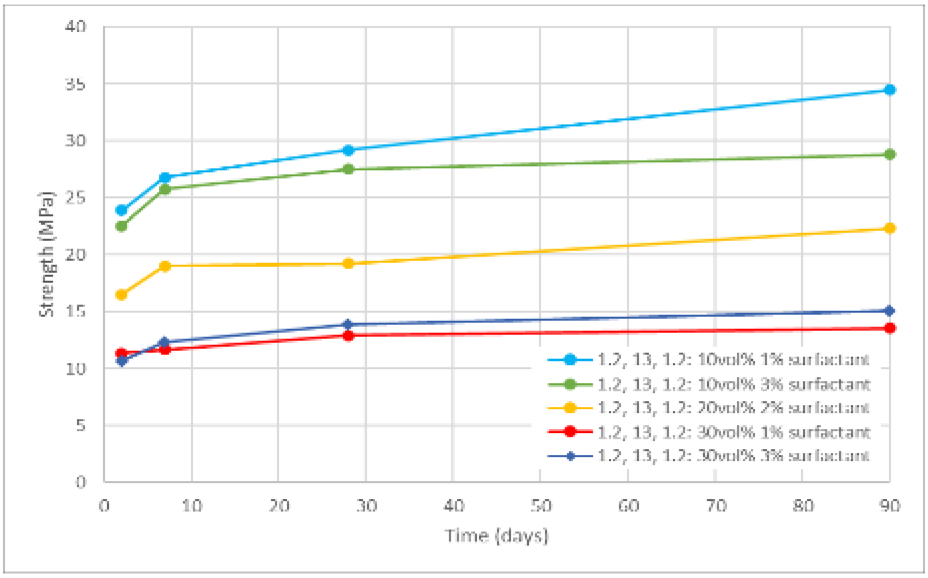


Figure 70 *Compressive strength of TBP/Dodecane – Argicem® formulations with varying RLOW and surfactant loading*

The following Figures show the compressive strength results for Metamax® formulations at 10 vol% (Figure 71), 20 vol% (Figure 72) and 30 vol% (Figure 73) RLOW loading. A reduced compressive strength can also be observed for this GP system as RLOW loading increased, although again are considered acceptable up to 90 days curing.

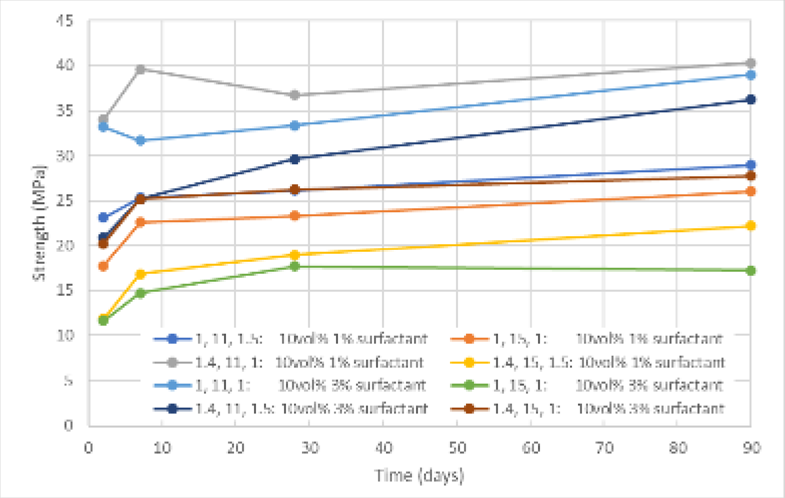


Figure 71 *Compressive strength of TBP/Dodecane – Metamax® formulations at 10 vol% RLOW and varying surfactant loading*

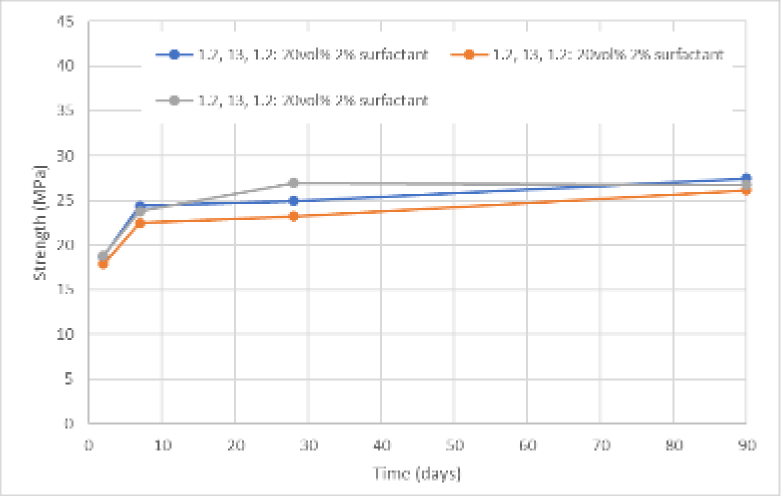


Figure 72 *Compressive strength of TBP/Dodecane – Metamax® mid-point formulations at 20 vol% RLOW and 2 vol% surfactant loading*

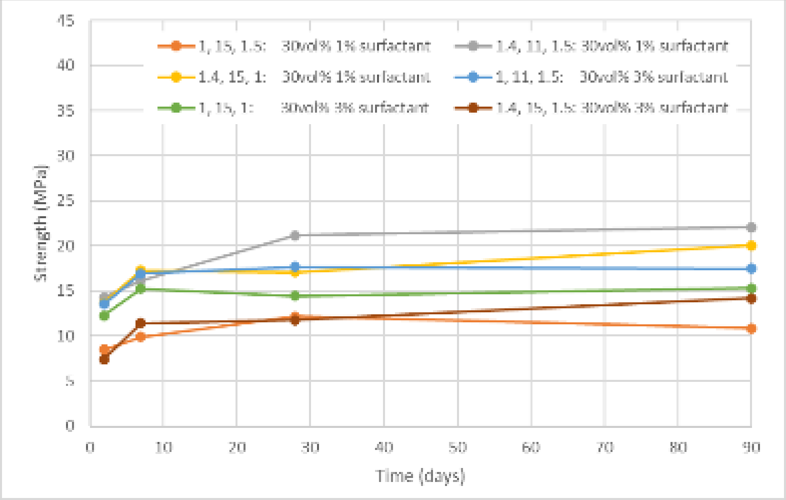


Figure 73 *Compressive strength of TBP/Dodecane – Metamax® formulations at 30 vol% RLOW loading and varying surfactant loading*

Flexural strength results for Metamax® formulations covering the 10 – 30 vol% RLOW loading tested are shown in Figure 74, Figure 75 and Figure 76 below.

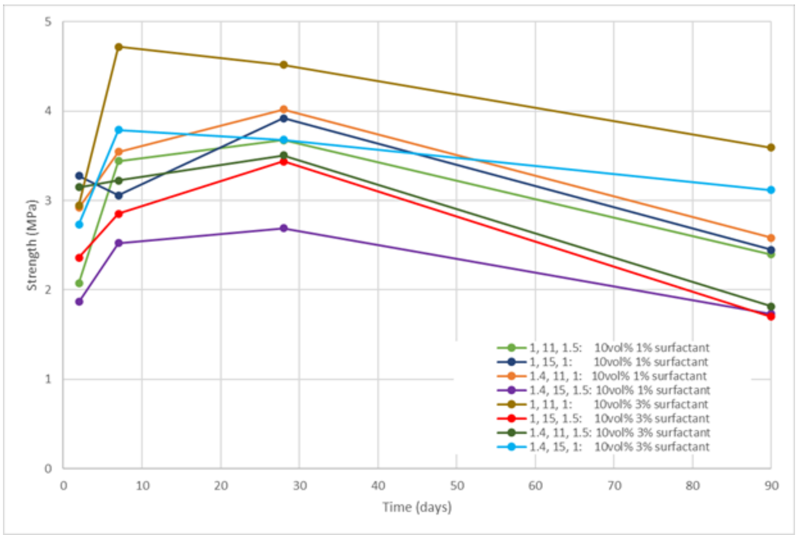


Figure 74 *Flexural strength of TBP/Dodecane – Metamax® formulations at 10 vol% RLOW loading*

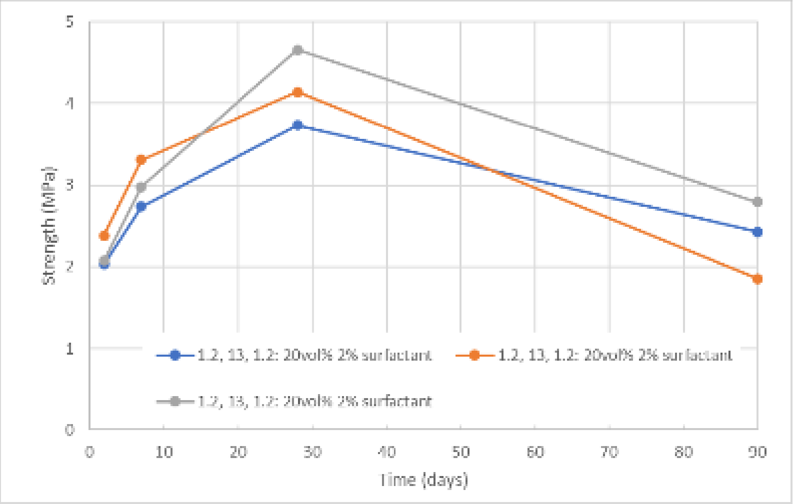


Figure 75 *Flexural strength of TBP/Dodecane – Metamax® mid-point formulations at 20 vol% RLOW loading*

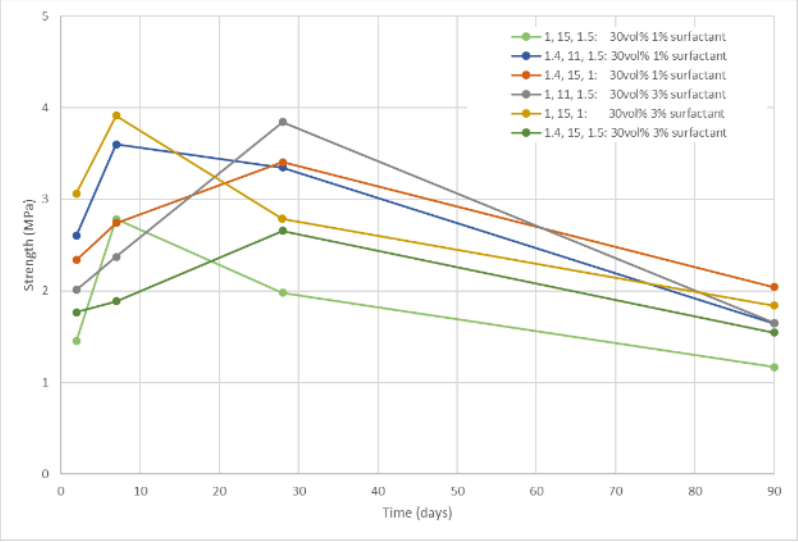


Figure 76 *Flexural strength of TBP/Dodecane – Metamax® formulations at 30 vol% RLOW loading*

The values of flexural strength for Metamax® formulations vary between 1.2 - 3.6 MPa at 90 days curing. These values generally ranged from 5% to 11.8% of the compressive strength value at 90 days curing and are considered within an acceptable range. However, a drop of flexural strength can be observed from 28 days to 90 days curing which was not observed in compressive strength results, discussed above, and are possibly arising from the presence of micro cracks within specimens due to drying with ongoing curing, despite best efforts to prevent this occurring by curing at >90% RH. Furthermore, there may be a possible drop in flexural strength at 90 days curing with increased RLOW loading given by the number of formulations with strengths <2 MPa at 90 days curing at 30 vol% RLOW loading.

The flexural strength results for Argicem® formulations is presented in Figure 77. Strength values vary between 2.0 - 3.5 MPa at 90 days, ranging from 9% and 17.3% of the compressive strength for Argicem® formulations at 90 days curing, which again are considered acceptable. As in the case of Metamax® mixes, a drop in strength is again observed between 28 days curing and 90 days which was not observed in compressive strength results, possibly for the same reason given above. Like Metamax® formulations, there is also a possible drop in flexural strength at 90 days curing with increased RLOW loading.

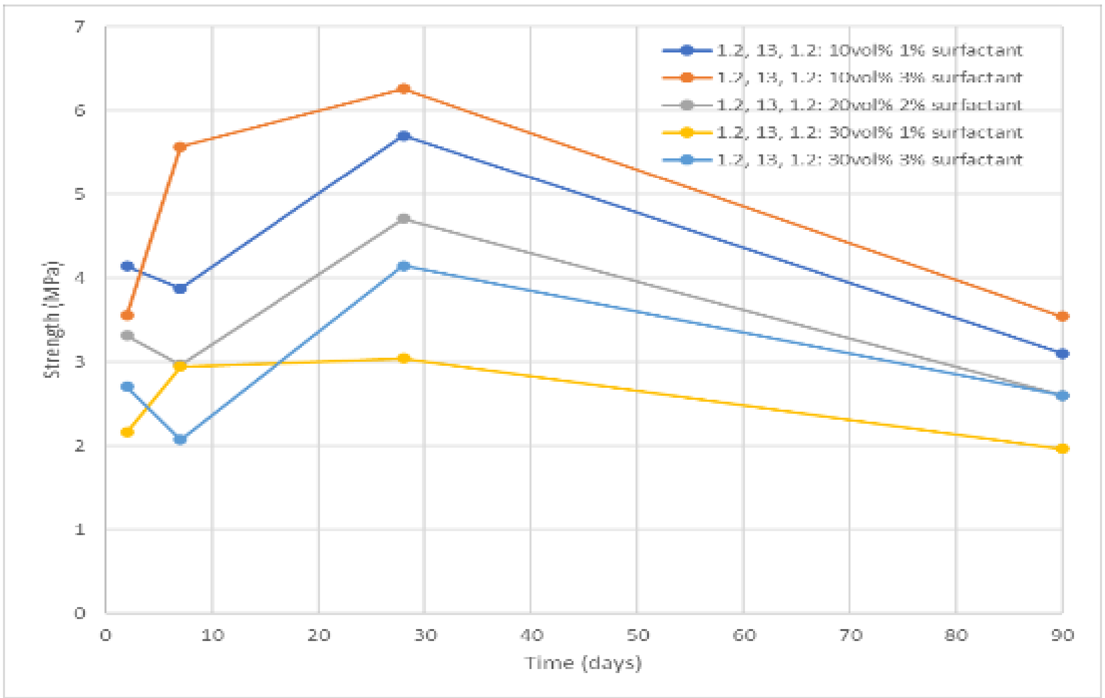


Figure 77 *Flexural strength of TBP/Dodecane – Argicem® mid-point formulations with varying RLOW and surfactant loadings*

Dimensional stability of Metamax® and Argicem® mid-point formulations is shown in Figure 78 and Figure 79 respectively and indicate general shrinkage up to 90 days curing for both GP systems that are within historic acceptable UK guideline values for grouted ILW products (shown by dashed horizontal lines in both Figures). In addition, a relatively large number of prism samples broke on demoulding, despite the rapid gain in compressive strength for the GP system. This is attributed to the relatively low flexural strength of GP samples in combination with the relatively long and thin geometry of prism samples, and the apparent brittle nature of GP wasteforms which will need to be considered further in assessing the disposability of GP wasteforms. The following observations for mid-point formulations are made:

- Metamax® GP system:
    - show shrinkage 0.05% - 0.15% at 90 days curing
    - Some samples had not reached stability over 90 d although there were no obvious signs of loss of integrity of these samples
    - There was no evidence of RLOW expulsion on the surface of prisms at 90 d curing
- Argicem® GP system:
    - Shows changes in dimensions from modest 0.06 % expansion - 0.12 % shrinkage – again within historic UK guideline values for grouted ILW products
    - Two formulations at 10 vol% and 30 vol% RLOW loading had not reached stability over 90 d although there were no obvious signs of loss of integrity of these samples
    - There was no evidence of RLOW expulsion on the surface of prisms at 90 d curing
    - No data was obtained for the mid-point 20 vol% RLOW, 2 vol% surfactant formulation due to breakage of prisms attributed to the relatively low flexural strength of GP wasteforms in combination with the geometry of prism samples

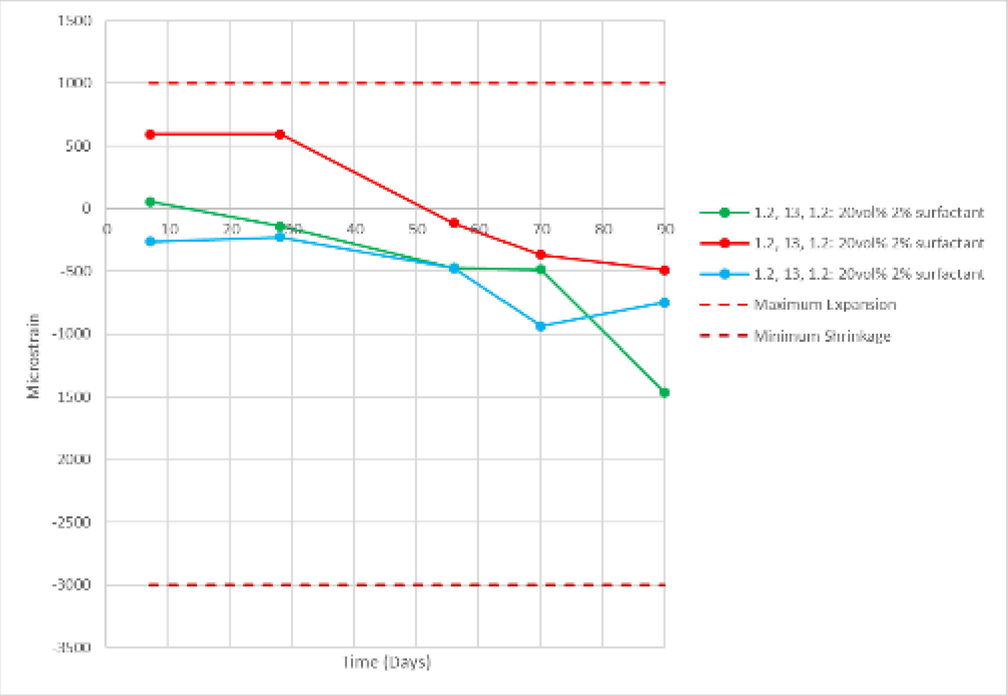


Figure 78 *Dimensional stability of Metamax® mid point formulations incorporating 20 vol% RLOW loading*

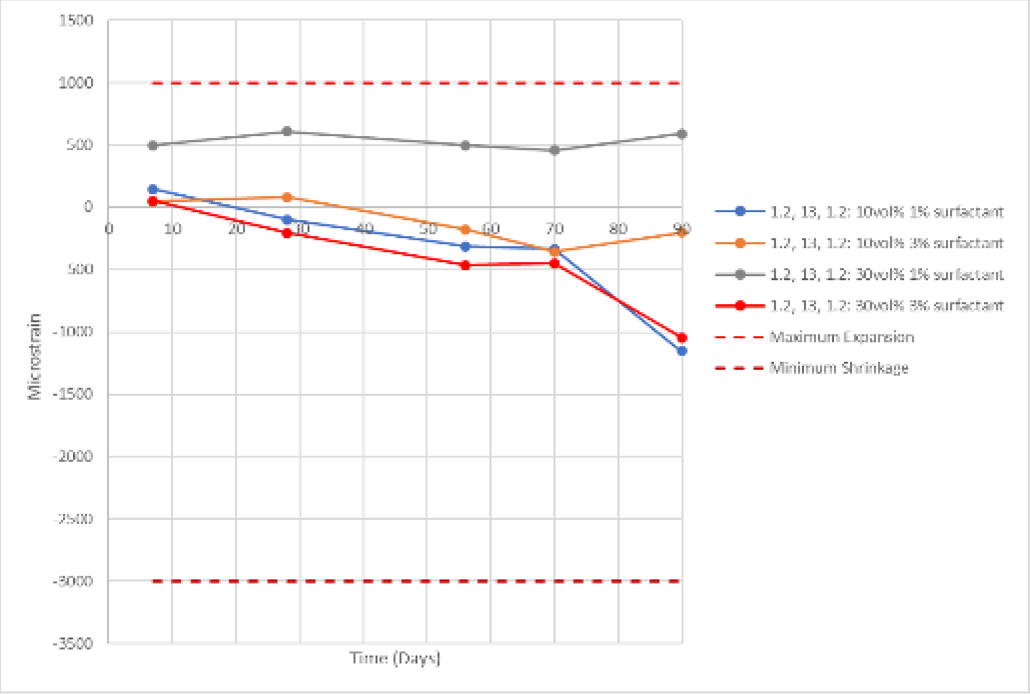


Figure 79 *Dimensional stability of Argicem® mid-point formulations with varying RLOW and surfactant loadings*

5.1.3 Conclusions

The conclusions for the NNL samples with Nevastane EP100 and TBP/Dodecane can be found below.

Nevastane Oil:

- Encapsulation of up to 50 vol% loading can be achieved for mid-point formulations (SiO_2/K_2O =1.2, H_2O/K_2O = 13, K/Al = 1.2) for both GP systems producing low viscosity grouts with high fluidity which achieved final set within 24 h
- Viscosity increased/fluidity decreased with increased RLOW loading
- Mixes at H_2O/K_2O ratio of 11 and K/Al ratio 1 could not incorporate Nevastane into GP formulations. At higher RLOW loadings (50 vol%) the effect of shear may become important in incorporating RLOW into the GP formulation and hence mixing methodology may be important
- Bleed volumes were low with <1.25 vol% bleed at 48 h on mixes in which Nevastane could be incorporated
- Relatively high heats of reaction were obtained for Metamax® GP mixes which will require further assessment on scale-up. The effect of shear appeared negligible on heat outputs at 24 h
- Compressive strengths developed rapidly by 7d which are reduced by RLOW loading – strengths were considered acceptable up to 90 days curing
- Products showed moderate shrinkage at 90 d for both GP systems within historic UK guidelines for grouted products. However, a small number of mixes had not stabilised by 90 days curing although no loss of integrity was evident
- Some formulations showed a surface sheen on product quality samples up to 90 d, indicating a small amount of liquor expulsion up to 90 days curing. Hence further optimisation of mix designs or mixing methodologies should be undertaken in order to further reduce or eliminate bleed liquor and improve retention of Nevastane in future GP mix designs.
- Longer term monitoring of samples required to ensure long term RLOW retention and product stability attained

TBP/Dodecane (70/30 vol/vol%):

- Scoping studies indicated surfactant required to incorporate TBP/Dodecane into either GP system due to segregation & forming porous products at ≥ 20 vol% RLOW loading
- Tween 80 preferred surfactant of those trialled
- Encapsulation of up to 30 vol% RLOW loadings achieved with 1-3 vol% surfactant – this was achieved across a range of formulations for Metamax® GP system and at mid-point formulation for Argicem® GP system producing low viscosity mixes of <1000 mPa s which achieved final set in 24 h.
- RLOW not incorporated in mixes at H_2O/K_2O ratio of 11 and K/Al ratio 1 at a 30 vol% loading
- Viscosity increased/fluidity decreased with increased RLOW loading but not considered significant for IDM encapsulation processes
- Bleed volumes were low with <1.75 vol% bleed at 48 h on mixes in which TBP/Dodecane could be incorporated
- In the case of Argicem® mixes – a 10 vol% RLOW loading produced a gel layer on the surface of the product at 1 vol% surfactant loading whilst at 3 vol% surfactant loading bleed was reabsorbed without gel production
- Relatively high heats of reaction were observed for Metamax® GP mixes which will require assessment on scale-up – increased SiO2/K2O ratio in the mix formulation reduced heat output due to the lower alkali content of the mix

- Compressive strengths developed rapidly by 7d which are reduced by RLOW loading although considered acceptable
- Samples showed general shrinkage up to 90 d which were within historic UK guidelines for grouted products, although several samples not stabilised by 90 days curing but no loss of integrity was observed
- A relatively large number of dimensional stability prisms broke on demoulding attributed to the relatively low flexural strength and geometry of prism samples. Hence the brittle nature of GP wasteforms will need to be considered further in assessing the disposability of GP wasteforms
- Formulations for product quality testing showed some evidence of ‘sweating’ after 2 d curing, however by 90 d curing there were no signs of surface liquor observed
- Further optimisation of mix design, including addition of surfactant levels and types, and mixing methods may further improve product performance regarding elimination of bleed and improving long-term retention of RLOW in GP systems
- Longer term monitoring of formulations is required to ensure long term RLOW retention and product stability attained

Several conclusions can be made from results obtained by CIEMAT:

- A very workable mixture was obtained. Homogeneous mixtures were obtained which hardened in a short time. The use of surfactant was not necessary to obtain homogeneous mixtures.
- It has been possible to immobilise 40% oil and 30% scintillation liquid, obtaining more than 10 MPa after 28 days of curing.
- Leaching tests indicate that samples containing oil do not leach but samples containing scintillation liquid do, giving positive TOC values.
- Samples with scintillation liquid are not stable in water and appear crack.

5.2 Blast Furnace Slag based formulations

The studies on Blast Furnace Slag (BFS) based alkali activated materials were carried out by RATEN and SCK-CEN. The systems studied, as well as the studies performed including results are described in the following Sub-chapters.

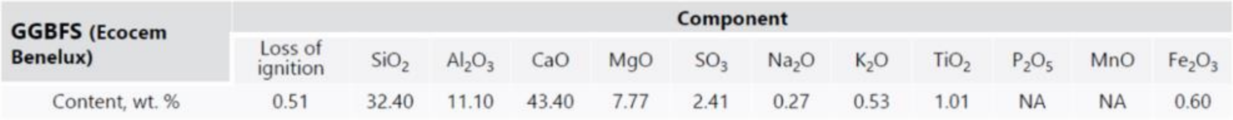
5.2.1 Systems studied

Both Partners focused on developing the best mortar formulation in terms of workability, waste loading, setting time and mechanical strength and other. RATEN used different BFS (Romanian BFS and Ecocem BFS) and SCK-CEN used the Ecocem BFS.

Reference recipes and raw materials and mixing methodology used during the optimisation and robustness studies by SCK-CEN were the same as during Task T5.3.2:

1) BFS - Ecocem (1):

Table 42 *Composition of GGBFS (Ecocem Benelux)*



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

2) Alkaline activator - $Na_2O.SiO_2$ in powder form + 10M NaOH

Table 43 *Composition of alkaline activator used by SCK-CEN*

$Na_2O.2SiO_2{\cdot}xH_2O$ (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)

3) River sand <2 mm and density of 2.67 g/cm^3
4) Waste forms – Nevastane 100 (density 850 g/l) and Shellspirax oils (density 885 g/l)
5) Surfactant – Tween 80 (density 1060 g/l)

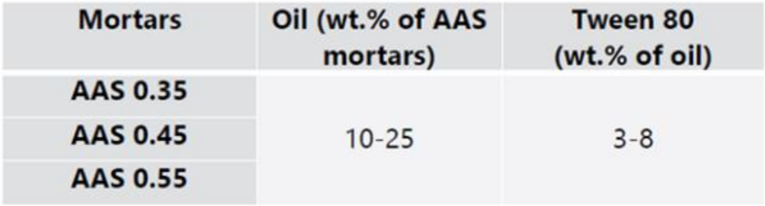
Reference mortars used by SCK-CEN are listed below. All these formulations were fixed with ~ 25wt.% of river sand.

Table 44 *Reference mortars used by SCK-CEN*

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

The formulations tested by SCK-CEN had waste loading and surfactant ranges as shown below:

Table 45 *Waste loading and surfactant ranges tested by SCK-CEN*



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

Additionally, the sensitivity with the variation of Sodium silicate content (SS) and NaOH (NH) was also studied.

To prepare the samples the following mixing procedure was used:

- A - Activating solution (Na-silicate + NaOH 10M + extra H_2O) - Prepared ~24h before casting
- B - Oil + Tween 80 - Mixed in ~5 min before mixing with mortar
- Procedure of reference mortars
    - Mix A with BFS in the mixing bowl for 3 minutes low speed
    - Pour sand into the mixing bowl and mix for 2 minutes low speed
    - Mix further for 2 min High speed
- Procedure of waste-forms
    - Start preparing B: mix in a beaker using a magnetic stirrer
    - 2 minutes after mixing B --> mix A with BFS in the mixing bowl for 3 minutes low speed
    - Pour B into the mixing bowl and mix for 8 minutes high speed
    - Pour sand into the mixing bowl and mix for 2 minutes high speed

RATEN tested the variability of raw materials and RLOW for the reference formulation developed by SCK-CEN. Regarding the raw materials, RATEN used in their tests two batches of Romanian BFS (not commercially available) and two batches of Ecocem BSF (commercially available) received from SCK-CEN and from CEA:

1) BFS (#2), the same Romanian BFS used for the studies performed by RATEN under T5.3.2 (see composition in Table 28)
2) BFS (#3), a new batch of Romanian BFS, supplied directly by Liberty Steel Galati (see composition in Table 39)

Table 46 *Composition of Romanian BFS (#3)*

wt.%	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	TiO_2	MnO	Na_2O	K_2O
RO BFS (#3)	38.20	41.60	7.50	9.20	0.55	0.48	0.54	0.30	0.72

3) Ecocem (1) received from SCK-CEN, from the same batch used in their own studies (see Table 42)
4) Ecocem (2) received from CEA (see Table 47for its composition)

Table 47 *Composition of Ecocem (#2)*

wt.%	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	Na_2O
Ecocem (2)	36.7	42.7	7	11.3	0.6	0.7

The alkaline activator consists of mixtures of 10M NaOH and commercial sodium silicate (water glass) solution (produced by Merk), whose composition is given in Table 48

Table 48 *Composition of sodium silicate solution (water glass) used by RATEN*

	SiO_2	Na_2O	H_2O
wt.%	25.50	7.50	66.00

Regarding the RLOW surrogates, RATEN used Shellspirax S2A80W90 and liquid scintillator - UltimaGold AB. Tween 80 was used as a surfactant for oil incorporation while for the liquid scintillator incorporation no surfactant was used.

The GP mortars were prepared using standardized sand and following the same mixing procedure as the one used during Task T5.3.2 (see section 4.5).

5.2.2 Optimisation and robustness studies and results

All formulations studied by SCK-CEN are presented in Table 49. The workability, setting time, heat release, mechanical strengths, porosity and microstructure were studied.

During the preparation of these samples (Figure 80) the oil mixed very well with AAS due to:

- very high viscosity of the mix (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)

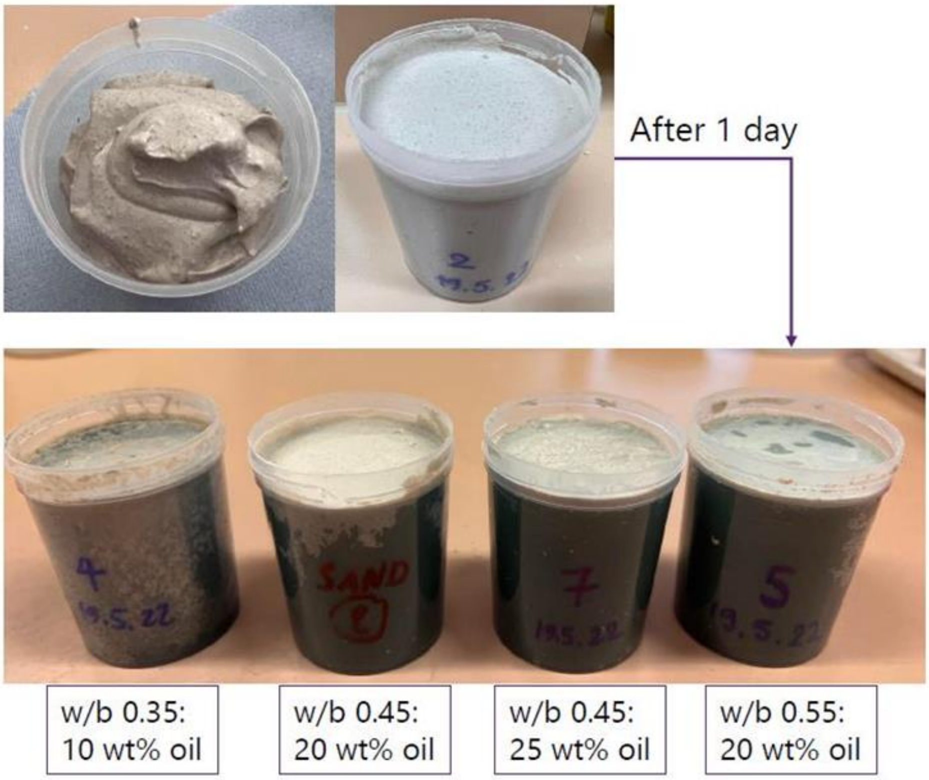


Figure 80 *Pictures from SCK-CEN sample preparation process*

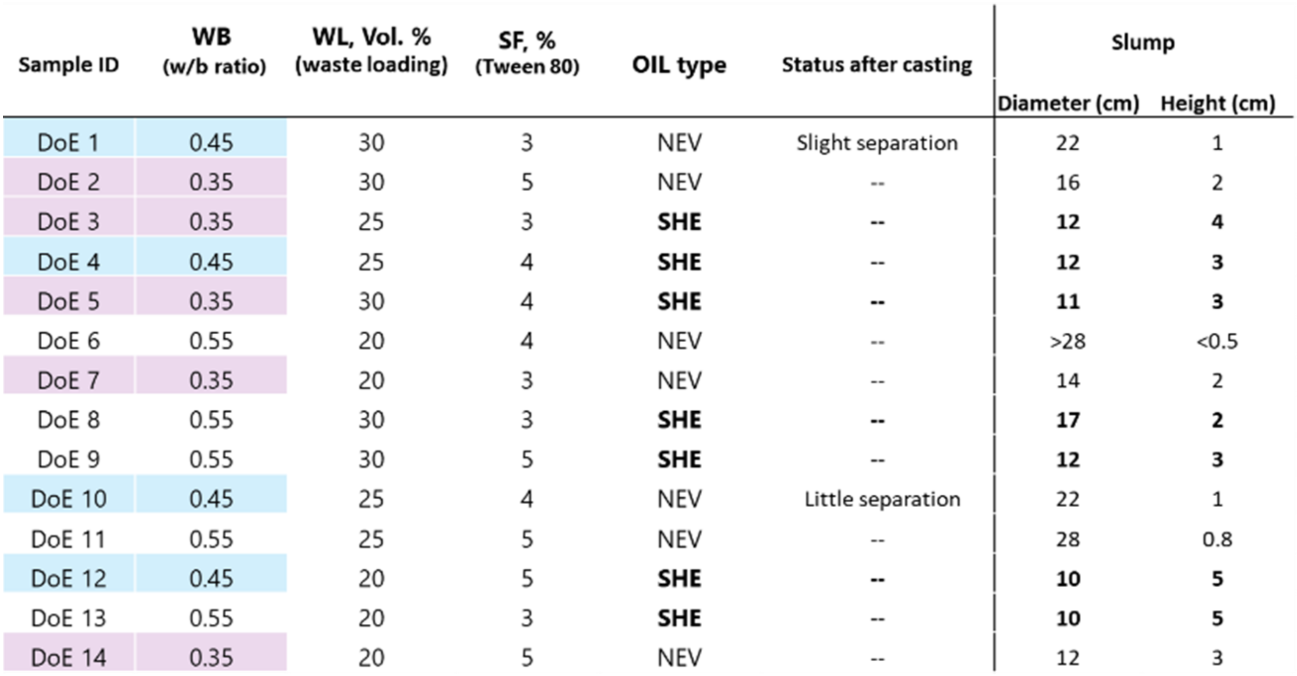
Slump test was performed to look at the workability of the samples. AAS samples with Shellspirax oil had better workability than the samples with Nevastane oil due to higher viscosity of the Shellspirax oil compared to the Nevastane oil.

Table 49 *Robustness test of waste-forms containing AASs and lubricating oils, studied by SCK-CEN*

Sample ID	SS	NH	WB	WL, vol. %	SF, wt.%	Oil type
DoE 1	2.79	4.2	0.45	30	3	NEV
DoE 2	2.59	4	0.35	30	5	NEV
DoE 3	2.59	4.2	0.35	25	3	SHE
DoE 4	2.69	4	0.45	25	4	SHE
DoE 5	2.79	3.8	0.35	30	4	SHE
DoE 6	2.59	4.2	0.55	20	4	NEV
DoE 7	2.69	3.8	0.35	20	3	NEV
DoE 8	2.59	3.8	0.55	30	3	SHE
DoE 9	2.69	4.2	0.55	30	5	SHE
DoE 10	2.69	4	0.45	25	4	NEV
DoE 11	2.79	3.8	0.55	25	5	NEV
DoE 12	2.59	3.8	0.45	20	5	SHE
DoE 13	2.79	4	0.55	20	3	SHE
DoE 14	2.79	4.2	0.35	20	5	NEV

SS and NH: sodium silicate and NaOH (g per 100 g GGBFS), respectively
WB: w/b ratio
WL: waste loading (vol.%, volume of oil per total volume of waste-form)
SF: surfactant Tween 80, (wt.%, w.r.t. mass of oil)
DoE 4 and DoE 10: center points of the design

Table 50 *Slump test results, by SCK CEN*



Sample ID	WB (w/b ratio)	WL, Vol. % (waste loading)	SF, % (Tween 80)	OIL type	Status after casting	Slump	
						Diameter (cm)	Height (cm)
DoE 1	0.45	30	3	NEV	Slight separation	22	1
DoE 2	0.35	30	5	NEV	--	16	2
DoE 3	0.35	25	3	**SHE**	**--**	**12**	**4**
DoE 4	0.45	25	4	**SHE**	--	**12**	**3**
DoE 5	0.35	30	4	**SHE**	**--**	**11**	**3**
DoE 6	0.55	20	4	NEV	--	>28	<0.5
DoE 7	0.35	20	3	NEV	--	14	2
DoE 8	0.55	30	3	**SHE**	**--**	**17**	**2**
DoE 9	0.55	30	5	**SHE**	--	**12**	**3**
DoE 10	0.45	25	4	NEV	Little separation	22	1
DoE 11	0.55	25	5	NEV	--	28	0.8
DoE 12	0.45	20	5	**SHE**	**--**	**10**	**5**
DoE 13	0.55	20	3	**SHE**	--	**10**	**5**
DoE 14	0.35	20	5	NEV	--	12	3

Setting times for samples with w/b ratios of 0.35, 0.45, and 0.55 are shown in Figure 81, Figure 82 and Figure 83 respectively. As can be seen, the w/b ratio is the main factor affecting the setting time. Concentration of alkaline activating solution also affects the setting time significantly: high NaOH content shortens the setting while high content of Sodium Silicate extends the setting. The type of oil also has an effect on setting time – Nevastane oil (NEV) prolongs the setting time compared to setting time of Shellspirax oil (SHE). The effect of waste loading is not significant.

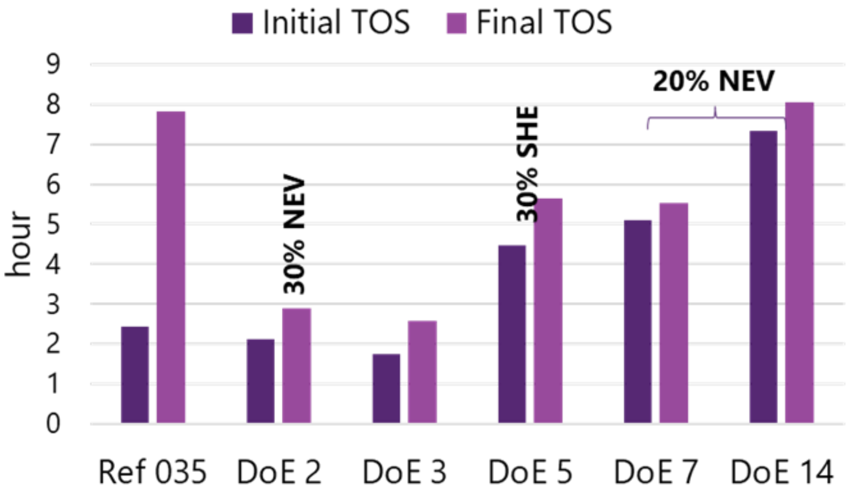


Figure 81 *Time of setting (TOS) for samples with w/b = 0.35*

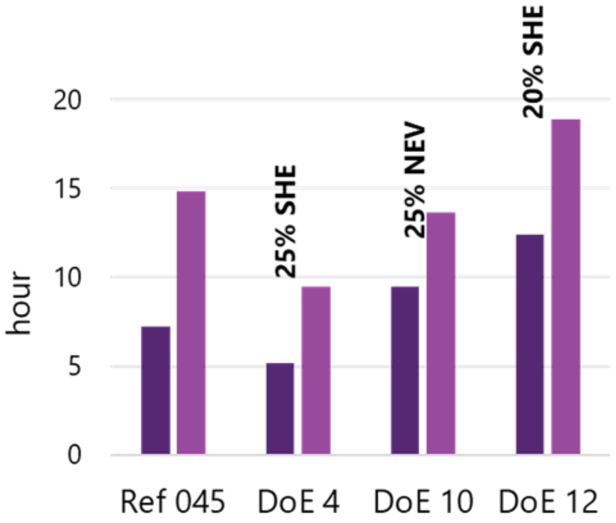


Figure 82 *Time of setting (TOS) for samples with w/b = 0.45*

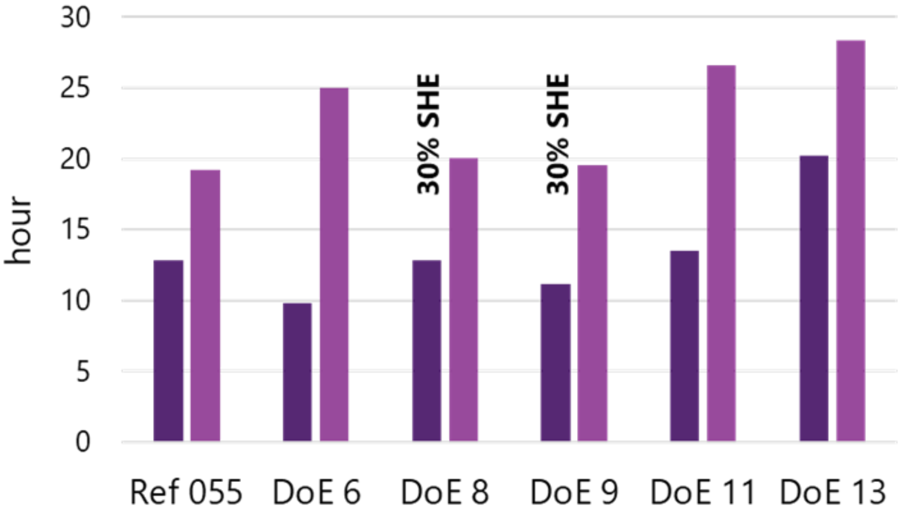


Figure 83 *Time of setting (TOS) for samples with w/b = 0.55*

The Heat Release of the samples has been studied by Isothermal calorimetry (see *Figure 84*, *Figure 85* and *Figure 86*). As seen in the Figures, the appearance of oil delayed the geopolymerization as it interrupted the interaction between the BFS and activating solution and thus the absorption/dissolution of BFS. However, after ~7 days oil seems not significantly affect the heat release and the geopolymerization degree.

High NaOH content and total alkaline content (NaOH + Sodium Silicate) tend to accelerate the geopolymerization and then heat release, while the high Sodium Silicate content delays the geopolymerization degree. Additionally, the total alkaline content controls the geopolymerization (heat release) after 7 days.

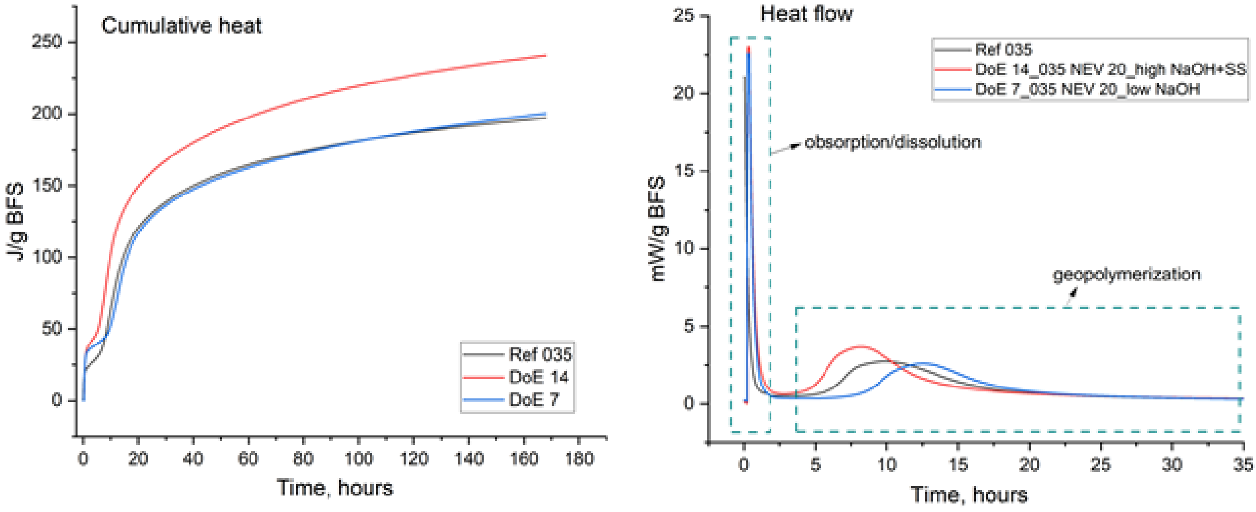


Figure 84 *Isothermal calorimetry results for samples with w/b = 0.35*

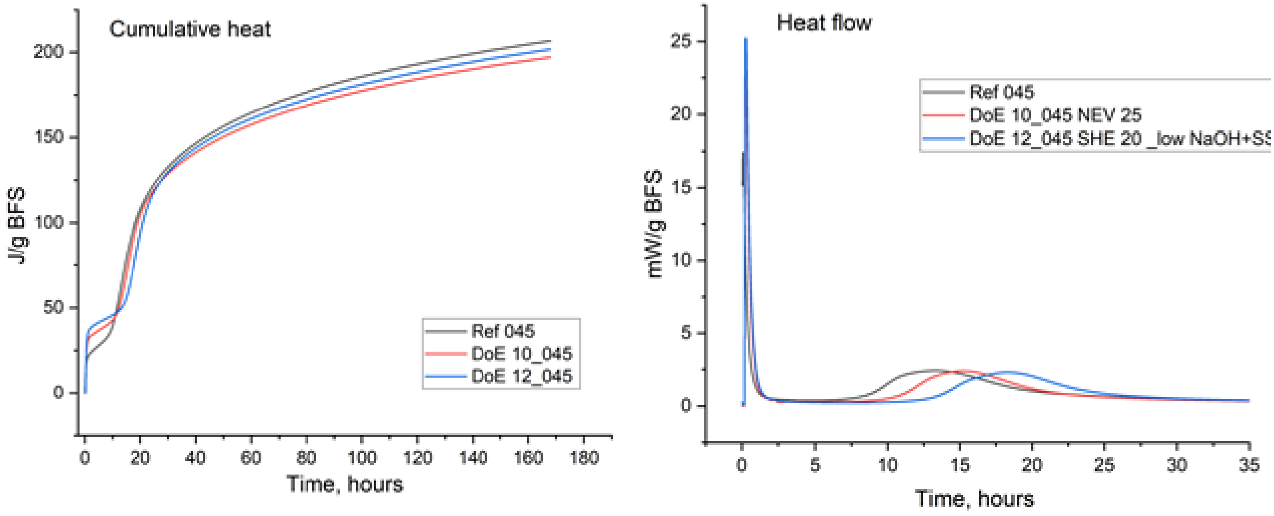


Figure 85 *Isothermal calorimetry results for samples with w/b = 0.45*

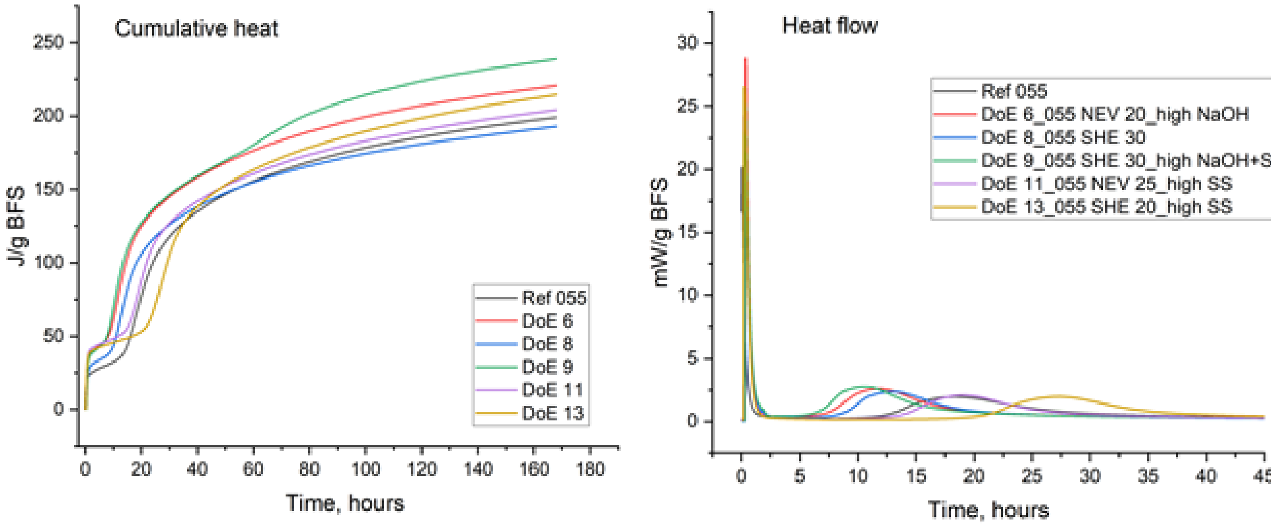
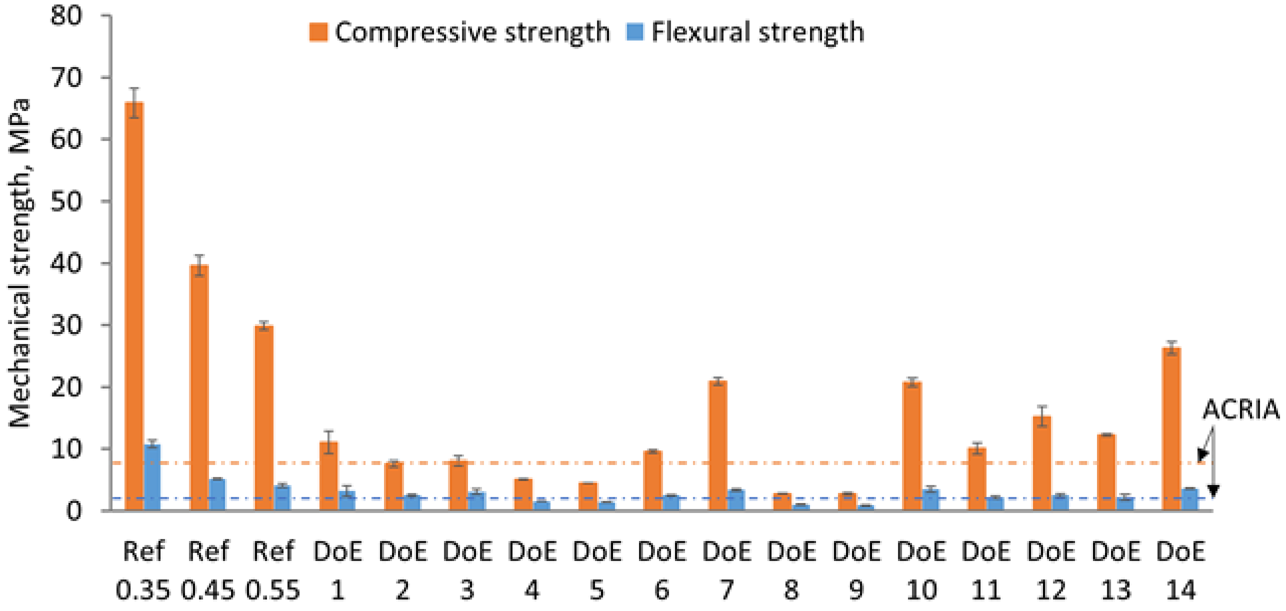


Figure 86 *Isothermal calorimetry results for samples with w/b = 0.55*

The presence of oils significantly reduced the mechanical strength of AASs (> 50% reduction). However, the flexural and compressive strength results of most samples meet ACRIA (2 MPa of flexural strength and 8 MPa of compressive strength) (see Figure 87



). The strengths of the samples were strongly affected by the w/b ratio and waste loading.

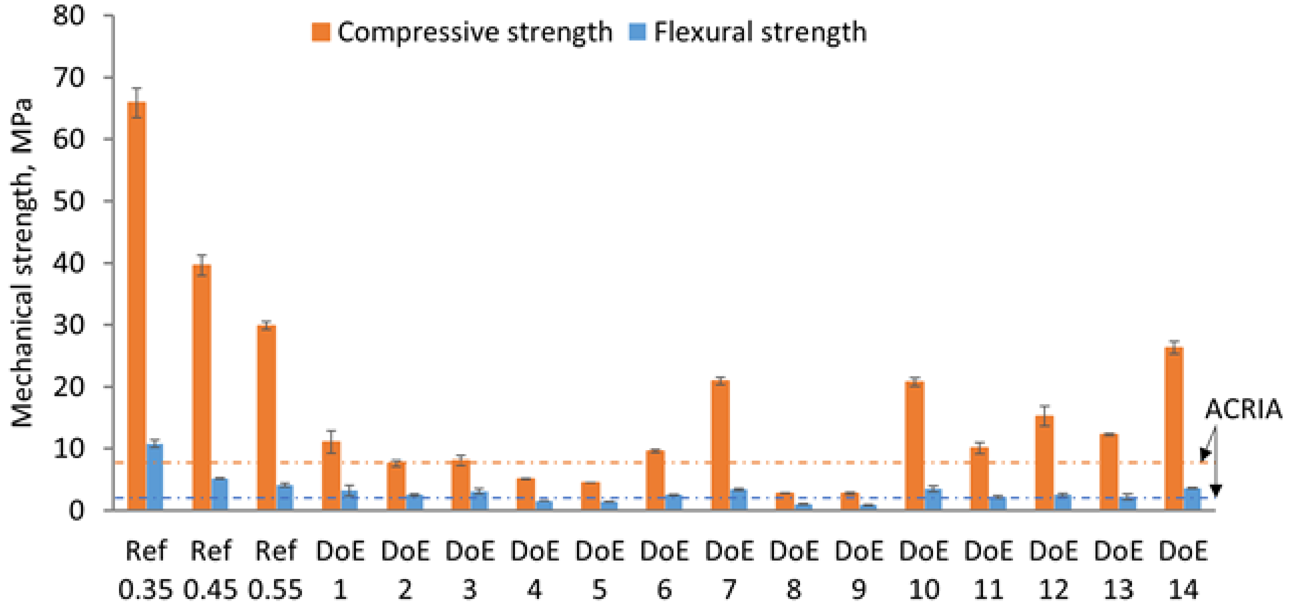


***Figure 87** Flexural and compressive strength of waste-forms in comparison with reference AASs*

The statistical analysis for the 14 robustness formulations was done (using Minitab software) in SCK CEN, and summary of the importance of variables with respect to the responses analyzed by the stepwise approach was shown in *Table 51*.

***Table 51** Summary of the importance of variables with respect to the responses: × = not important; ×× – relatively important; ××× – strongly important; CB, CD, etc. – interaction between factors; AA, BB, etc. – squared effect for each factor; “>” is used to compare the extent of interaction effects*

Response	SS (A)	NH (B)	WB (C)	WL (D)	SF (E)	OIL (F)	Interaction
Initial setting time	×	××	×××	×××	×	×	×
Final setting time	×	××	×××	×××	××	×	CC > CD

Heat release	×	×	×	××	×	×	×
Second peak of heat flow (S2)	××	××	×××	×××	×	×	×
Compressive strength	×	×	×	×××	×	××	CD
Flexural strength	×	×	××	××	×	×××	DF

SS, NH, WB, WL, SF, OIL: sodium silicate (wt.%), NaOH (wt.%), water/binder ratio, waste loading (vol.%), surfactant (wt.% of oil), types of oil, respectively.

×, ××, and ××× are qualitatively indicators, which are assessed based on Pareto charts of the standardized effect. The ×, ××, and ××× are linked to how much the main effects pass the reference line. The reference line in the Pareto chart refers to the statistical significance, which depends on the significance level, which is actually the alpha to enter/remove values.

In the first set of tests performed by RATEN the reference formulation developed by SCK-CEN in Task T5.3.2 was reproduced using the Romanian BFS (#2). Since the alkaline activator used by RATEN is based on sodium silicate solution (water glass) having different content of SiO_2 and Na_2O than sodium silicate powder used by SCK-CEN for the reference formulation development, the following molar ratios SiO_2/Al_2O_3, H_2O/Na_2O and Na_2O/Al_2O_3 of the SCK-CEN reference formulation were reproduced as much as possible. The composition of mortars prepared, and the value of the molar ratios of interest are presented in Table 52 and Table 53 respectively. The samples obtained during this testing set (Figure 88) show good workability and normal fluidity composition. For two oil loading rates (15 and 19%wt.), the fresh mortars were homogeneous with no oil separation, and with final setting times of less than 24 hours. However, after 5 and 10 days of curing at room temperature the hardened mortars had a brittle structure, and after 28 days of curing the mechanical strengths off al specimens were around 1MPa.

Table 52 *Composition of mortars studied in the first set of tests*

	Composition, wt.%				
	SCK ref. form.	with Ro BFS and activator	SCK_TBP	RO_oil 1	RO_oil2
BFS	46.5	47.1	37.2	46.6	46.6
Water glass	1.5	1.5	1.2	3.6	3.6
10M NaOH	5.5	6.2	4.4	5.8	5.8
Additional water	18.4	16.9	14.7	15.9	15.9
Sand	28	28.3	22.4	22.1	22.1
Waste	0	0	19.1	17.8	23.8
Tween 80 (5% of waste vol)	-	-	0.95	0.9	1.2

Table 53 *Molar ratios of certain components of studied mortars*

mol/mol	**SCK ref. form.**	**with Ro BFS and activator**
SiO_2 / Na_2O	9.67	8.12
SiO_2 /Al_2O_3	5.22	8.48
H_2O / Na_2O	45.73	49.02
Na_2O/Al_2O_3	0.54	1.05
w/b	0.45	0.45

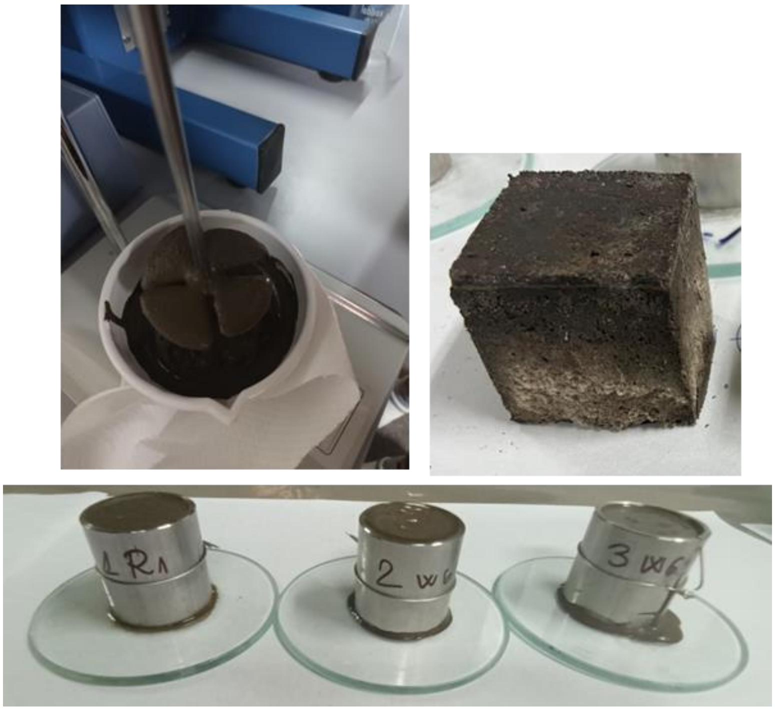


Figure 88 *Samples produced during first set of testing*

The influence of the proportion of Sodium Silicate and NaOH in the alkaline solution was studied using mortars described in Table 54. Results were similar to the previous set of tests, including the mechanical strength, that had values lower than the limit for WAC for disposal (5MPa).

Table 54 *Composition of mortars obtained using different ratios of sodium silicate solution and NaOH in the alkaline activator*

% wt.	**#1**	**#2**	**#3**
BFS	47.05	50.72	46.65
water glass	1.51	1.5 ÷1	1.5 ÷ 3.6
10M NaOH	6.21	6.21÷8.02	5.77÷6.21
sand	28.33	27.57	28.09
w/b	0.45	0.45	0.45

Second set of tests was performed with the same w/b ratio, and the same content (wt.%) of BFS and sand as in SCK-CEN DoE #7, while trying to fit the SiO_2 and Na_2O content in the activation solution as in the one used by SCK-CEN.

To obtain a mortar with good workability, a higher amount of water had to be added, equivalent to a W/B ratio of 4.0 (compared to 3.5 in SCK-CEN DoE#7). The setting time of the mix was ~24 h. A foam-like layer was formed on the surface of the mortar specimens during curing at room temperature (see Figure 89). This foam-like layer indicates a potential lime contamination of the BFS (#2) used in these tests. After 10 days of curing, the mechanical strength of this specimen was 4 MPa.

Table 55 *Compositions of the mortars studied*

SCK - DoE #7	**wt.%**	**RO**	**wt.%**
commercial BFS (Ecocem (1)	49	Ro BFS (#2)	49.1
Sodium silicate- powder	3.4	water glass	1.6
10M NAOH	7	10M NaOH	6.2
Additional water	11.1	Additional water	13.6
Sand	26.6	Sand	26.7
w/b	0.35	w/b	0.4
SiO2	0.9	SiO2	0.9
Na2O	1.9	Na2O	1.9
Total H2O	18.3	Total H2O	18.3

Figure 89 *A foam-like layer formed on the surface of samples during curing at room temperature in the mould*

The influence of Volcanic Tuff addition on the formulations was tested, using composition ranges presented in Table 56. After 5 days of curing, the mechanical strength of all formulations with no waste were higher than 5MPa. A white precipitate was observed on surfaces exposed to air on two of these formulations. All formulations reached oil loadings less than 10 wt%, in samples with higher waste loading swelling was observed after few days of curing at room temperature. Liquid scintillator samples observed a sligtly lower waste loadings of 8-9 wt.%.

Table 56 *Composition of mortars with Volcanic Tuff added*

	wt.%
BFS	34.5 - 44.4
VT	0 - 10
sand	21.4 - 23.7
10 M NaOH	4.9 -19.7
water glass	3.0 - 9.9
H_2O	0 - 13.4
w/b	0.3 - 0.45
Oil / scintilator	10 - 20
Tween 80	0.5 - 1

The Romanian BFS (#2) used for these studies (purchased from a Liberty Steel Galati subcontractor) seems to be very heterogeneous and has quite high LOI (21.73%) and it may be contaminated with lime. An attempt to improve the properties of this BFS was made by its calcination at 900°C, however the mechanical properties of GP mortars were not improved, and the waste incorporation rate was not increased.

To try to avoid these problems a new batch of Romanian BFS was purchased directly from Liberty Steel Galati (RO BFS(3) – see Table 46). To compare the test results an Ecocem BFS was received from CEA (see Table 47). The mortar composition studied with these Blast Furnace Slags is shown in Table 57.

Table 57 *Mortar composition studied with RO BFS (3) and Ecocem slag from CEA*

Mortar composition	wt.%
RO BFS (#3) / Ecocem (1) and Ecocem (2)	36.4 – 46.0
Water glass	1.2 - 4.7
10 M NaOH	5.2 - 10.1
Additional water	6.9 - 15.2
Sand	23.3 - 25.0
oil	10.0 - 13.5
Tween 80	5% of the waste volume
scintillator	8.6 - 11.0
w/b	0.35 - 0.45

Figure 90 *Samples containing RO BFS (#3) and Ecocem (1) BFS*

The mortar specimens prepared with Ecocem (1) and Ecocem (2) BFS had the following properties:

- Good workability and normal fluidity composition for all formulations tested
- Waste loading rates:
  - up to 19%wt. for oil waste
  - up to 15%wt. for liquid scintilator
- Setting times ~ 18 hours
- Mechanical strength: between 5 - 14 MPa

The mortar specimens prepared with RO BFS (#3) had the following properties:

- Good workability and normal fluidity composition for all formulations
- Waste loading rates:
  - up to 15%wt. for oil waste
  - up to 10%wt. for liquid scintilator
- Setting times < 24 hours
- Mechanical strength: 5 - 6 MPa

The formulation with best results is presented below:

Table 58 *Formulation with best results*

Mortar composition	
BFS (Ecocem (1) and (Ecocem (2) / Ro_BFS (#3)	42.9 wt.%
water glass	4.4 wt.%
NaOH 10M	8.6 wt.%
Additional water	7.5 wt.%
Sand	23.3 wt.%
oil	30 vol.%
Tween 80	5% of the oil volume
w/b	0.35

The Ecocem (1 and 2) and RO BFS (#3) have a similar oxide composition, and the only significant difference is the fineness of the powder: the Ecocem BFS is much finer than RO BFS (#3) (75µm). As the fineness of the BFS powder plays an important role in the geopolymerization process, the mortars obtained with Ecocem BFS have increased mechanical properties and allow waste incorporation to higher rates.

5.2.3 Conclusions

During the preparation of samples both with commercial Ecocem BFS and Romanian BFS a good workability was observed. The oil waste, especially Shellspirax oil, mixed very well with AAS due to high viscosity.

Setting time of samples containing both BFSs were <24 hours and w/b ratios had the main effect on setting time. Other factor significantly affecting the setting time was the concentration of alkaline activation solution, where high NaOH content shortens, and high content of Sodium Silicate extends the time of setting. Oil type also affects setting time – Nevastane oil samples had a prolonged setting time, however the waste loading itself does not seem to have any significant effect on setting.

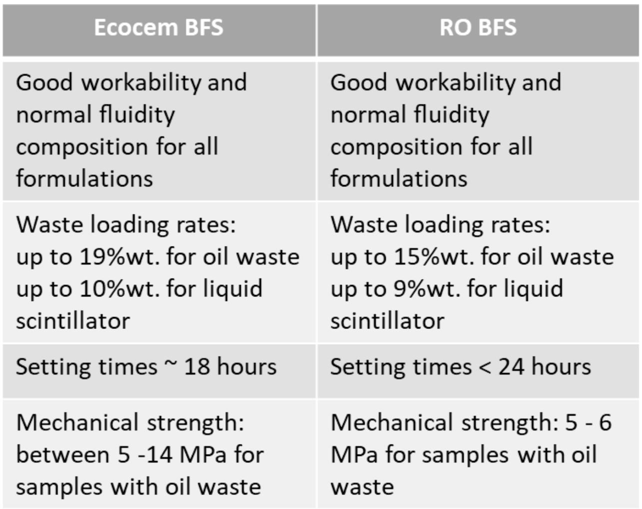
The presence of immobilised oil in samples delayed the geopolymerization up to 7 days, after which it did not have any additional recorded effect. Higher NaOH content accelerates geopolymerization, while high Sodium Silicate content seems to delay the process. The total alkaline content (both NaOH and Sodium Silicates) additionally controls the geopolymerization (heat release) after 7 days.

The experimental results obtained in reproducing the BFS reference formulation with Romanian slag (not commercially available) indicating the importance of both slag purity and fineness. Using one of the batches of Romanian slag (RO BFS (#2)) that proved to be very heterogeneous and potential contaminated with lime. Cured mortar samples obtained with this slag batch had mechanical strength above the minimum value imposed by the WAC for disposal (5MPa) only for the specimens containing no RLOW surrogate, while for those with oil or liquid scintillator the mechanical strength was lower than this this threshold value.

The geopolymer mortars prepared with the RO BSF (#3), directly provided by the steel producer, have good mechanical properties and it was possible to incorporate the two types of RLOW surrogate (oil and liquid scintillator) with higher rates compared to the previous ones.

Even though RO BSF (#3) has a similar oxide composition to Ecocem BFS, the same GP formulation prepared with the two types of slag resulted in mortars with different mechanical strengths (see Table 59).

Table 59 *Main properties of Ecocem and Romanian BFSs*



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

Both types of BFS display good waste loadings and mechanical strength. Using Ecocem BFS slightly higher RLOW surrogates' incorporation rates and with higher compression strengths due to its higher fineness.

5.3 Formulations based on mixture of different raw materials (MIX formulations)

During T5.2 KIPT proposed a new technique based on direct incorporation of organic liquids (various oils as simulants of RLOW) into a mix FA-BFS-MK based geopolymer matrix. This technique was studied during the sub-sequent T5.3.3 with the aim of analysing the possibility of using both Ukrainian (KIPT) and similar, non-Ukrainian raw materials (NUCLECO and CEA) to produce the optimal MIX formulation and in result to understand the performances of the MIX formulation geopolymer for oily liquids immobilization. The work was focused on the workability of said formulations, their mechanical properties, and the impact of variability of said raw materials and RLOW simulants.

5.3.1 Systems studied

Both KIPT and NUCLECO formulations developed under subtask 5.3.2 had proven suitable to be studied further during Task 5.3.3.

The KIPT MIX formulation is as following:

Table 60 *MIX formulation*

Precursors			Activating solution		
FA (Ukr)	BFS (Ukr)	Metakaolin (Ukr)	Water glass (UkRSILL)	KOH	H_2O
34 wt.%	20 wt.%	14 wt.%	11 wt.%	9 wt.%	12 wt.%

To study the robustness of this formulation KIPT used the same raw materials used for Task 5.3.2 (Chapter 4.2). Oils - Shellspirax and Nevastane EP 100 were used as simulants of RLOW. The sample preparation methodology used by KIPT is described below:

Geopolymer pastes preparation

Geopolymers were synthesized with a varying Si/Al ration. As Al-Si raw materials were used: MK, FA, BFS and quartz sand. Mixing of dry components was carried out in a planetary mill: container (200 ml) and balls of SS, rotation speed 200 rpm, time 30 minutes.

The final part of the geopolymerization included adding the Al-Si dry mixture to the SS container containing alkaline solution and planetary mill mixing for 15-20 minutes to prepare a fresh geopolymer paste. All samples were casted into plastic molds lubricated inside with Vaseline and the surface of the samples was covered with a polyethylene film. Then, the samples are stored under indoor ambient conditions until testing during 7, 14 and 28 days.

Geopolymers with oils

The synthesis of the geopolymers with addition of oils was slightly different. At the final stage, oils were added to freshly prepared geopolymer paste and mixing 30 min to obtain a homogeneous slurry which was used for casting into plastic molds. Oils - Shellspirax and Nevastane were used as simulants of liquid RAW. Geopolymer/oil composites have been made with various oil content (10, 20, 30 and 40 vol.%).

Since it was not possible for NUCLECO to find UKRSILL, the Ukrainian waterglass used by KIPT, an attempt was initially made to replicate the KIPT formulation using Betol 52 T, in an amount equal to the sum of the amounts of UKRSILL, KOH and water in the KIPT formulation. This recipe is called, for simplicity's sake, KIPT Betol (see Table 61).

Another attempt to replicate the KIPT formulation was made by replacing UKRSILL with potassium silicate (K2SiO3) in solid form. This recipe is called, for simplicity's sake, KIPT Silicate (see Table 62).

Table 61 *KIPT Betol formulation*

Precursors			Activating solution
FA	BFS	Metakaolin	Water glass (Betol 52 T)
34 wt.%	20 wt.%	14 wt.%	32 wt.%

Table 62 *KIPT Silicate formulation*

Precursors			Activating solution		
FA	BFS	Metakaolin	K2SiO3	KOH	H_2O
34 wt.%	20 wt.%	14 wt.%	11 wt.%	9 wt.%	12 wt.%

The formulation previously developed and studied by NUCLECO is shown below:

Table 63 *NUCLECO MIX formulation*

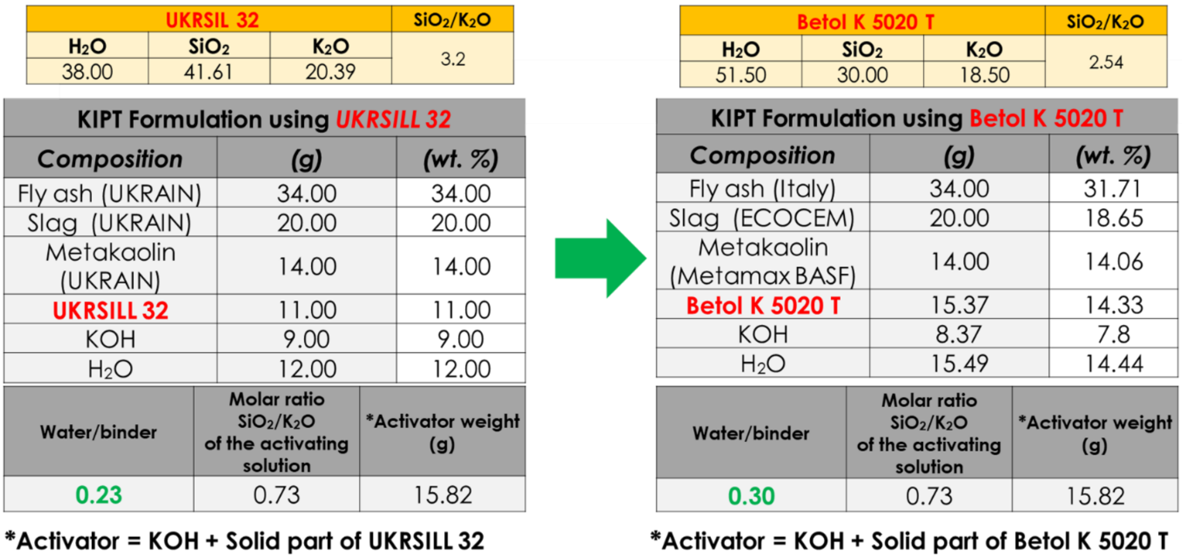
Precursors			Activating solution
FA	BFS	Metakaolin	Water glass (Betol 52 T)
31 wt.%	19 wt.%	13 wt.%	37 wt.%

Raw materials used to produce samples with these formulations are following:

- Metakaolin (MK) METAMAX®, from BASF
- Blast Furnace Slag (BFS), from ECOTRADE, France
- Fly Ash (FA), from Italy
- Waterglass Betol 52 T, from Wöllner
- Betol K 5020 T, from Wöllner
- Potassium hydroxide (KOH)

CEA has also adapted the KIPT formulation by using another combination of raw materials. The transposition of the KIPT formulation to the other one is presented in the

Table 64 *KIPT MIX formulation adapted by the CEA using other raw materials*



UKRSIL 32			SiO_2/K_2O
H_2O	SiO_2	K_2O	3.2
38.00	41.61	20.39	

KIPT Formulation using UKRSILL 32		
Composition	(g)	(wt. %)
Fly ash (UKRAIN)	34.00	34.00
Slag (UKRAIN)	20.00	20.00
Metakaolin (UKRAIN)	14.00	14.00
UKRSILL 32	11.00	11.00
KOH	9.00	9.00
H_2O	12.00	12.00

Water/binder	Molar ratio SiO_2/K_2O of the activating solution	*Activator weight (g)
0.23	0.73	15.82

*Activator = KOH + Solid part of UKRSILL 32

Betol K 5020 T			SiO_2/K_2O
H_2O	SiO_2	K_2O	2.54
51.50	30.00	18.50	

KIPT Formulation using Betol K 5020 T		
Composition	(g)	(wt. %)
Fly ash (Italy)	34.00	31.71
Slag (ECOCEM)	20.00	18.65
Metakaolin (Metamax BASF)	14.00	14.06
Betol K 5020 T	15.37	14.33
KOH	8.37	7.8
H_2O	15.49	14.44

Water/binder	Molar ratio SiO_2/K_2O of the activating solution	*Activator weight (g)
0.30	0.73	15.82

*Activator = KOH + Solid part of Betol K 5020 T

From this table, we can see that the proportion of raw materials is different and that the water to binder ratio is higher for the CEA adapted formulation.

To study the applicability for other types of waste, the KIPT and Nucleco formulations developed by for oil, were also tested for the following RLOW surrogates:

- Scintillation cocktail ULTIMA GOLD
- TBP/Dodecane (70/30) mix

To study the robustness of the formulation developed by KIPT oil waste was used as surrogate:

- Nevastane Oil
- Shellspirax Oil

5.3.2 Optimisation and robustness studies and results

5.3.2.1 Robustness tests of original KIPT MIX formulation

To study the robustness of the MIX formulation two sets of tests were performed:

- Robustness tests incorporating oils
  - Waste (Shellspirax and Nevastane) loading 10, 20 and 30 vol.% without surfactant
  - Waste loading > 30% vol with surfactant
- Robustness tests considering process variability (waste loading = 30 vol.%)
  - + 2% in amounts of raw materials for MIX formulation

Robustness tests incorporating oils

<u>Samples with oil waste with loading up to 30 vol.%</u>

An amount 10, 20, 30 vol.% of RLOW simulant (oils: Shellspirax and Nevastane) was introduced into the optimized (MIX formulation) geopolymer matrix. The fresh paste and the hardened samples have been characterized, and the results are shown in Table 65 and Figure 91.

Table 65 *Characteristics of geopolymers with Shellspirax/Nevastane*

Parameter		Shellspirax/Nevastane oils content, vol.%		
		10	20	30
Setting time, h	Start	3/3	4/3	4/4
	finish	22/20	22/20	24/24
Density, g/cm³		2,10/2,12	1,96/1,98	1,88/1,90

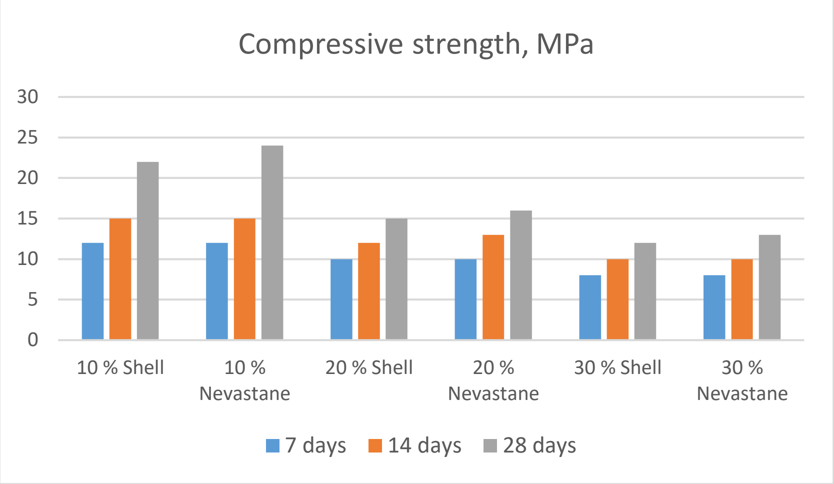


Figure 91 *Compressive strength of geopolymers with different content of Shelspiraxl and Nevastane*

Characteristics of MIX formulation based geopolymers with Shellspirax and Nevastane are similar with the content of oils from 10 till 30 %. Samples have accepted setting time and compressive strength, suitable density and don't have essential defects.

Samples with oil waste with loading > 30 vol.% and use of surfactant Castament FW 10

In case of waste=40 %, the samples with Nevastane are qualitive with accepted criteria (Table 66), but the samples with Shellspirax oil have decreased characteristics and a lot of pores due to very viscous paste (even impossible to evaluate the viscosity) in the molding process.

Table 66 *Characteristics of optimized geopolymers with Shellspirax/Nevastane*

Parameter		Shellspirax/Nevastane oils content, vol.%	
		40	40 + 0,5 % Castament FW 10
Setting time, h	Start	5/4	4/-
	finish	36/24	24/-
Density, g/cm³		1,65/1,8	1,82/-

Thus, the use of surfactant is the key to improve the fluidity (corresponding to the viscosity decreasing) of the geopolymer paste with 40 vol.% Shellspirax oil. The positive result of using the surfactant in the MIX formulation geopolymer paste with 40 vol.% Shellspirax oil is also presented in Table 66.

For the understanding the effect of surfactant Castament FW 10 on behavior of the geopolymeric pastes the rheology measurement was performed. Rheograms of optimal geopolymeric paste and the paste with different content of oil Shellspirax are presented in Figure 92.

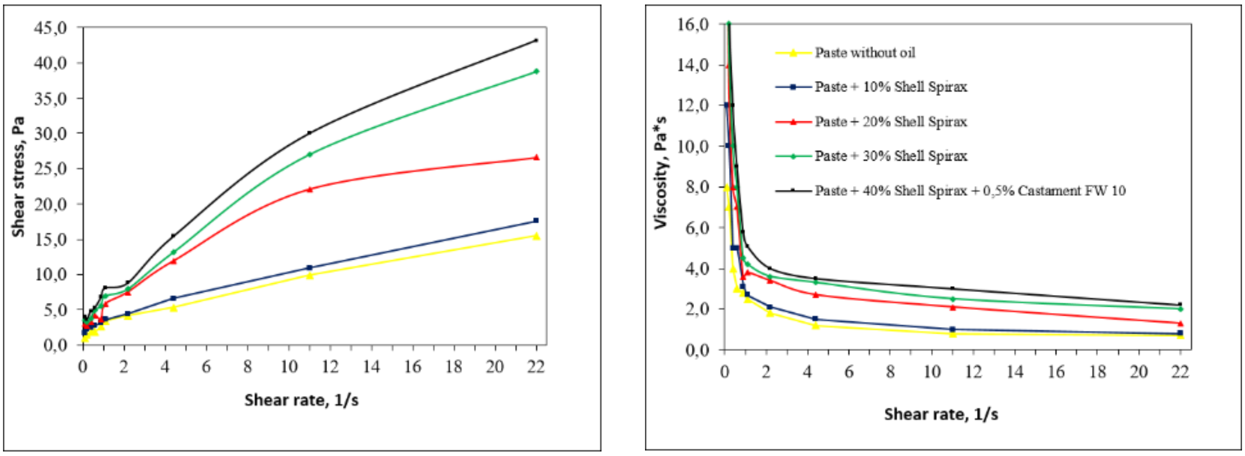
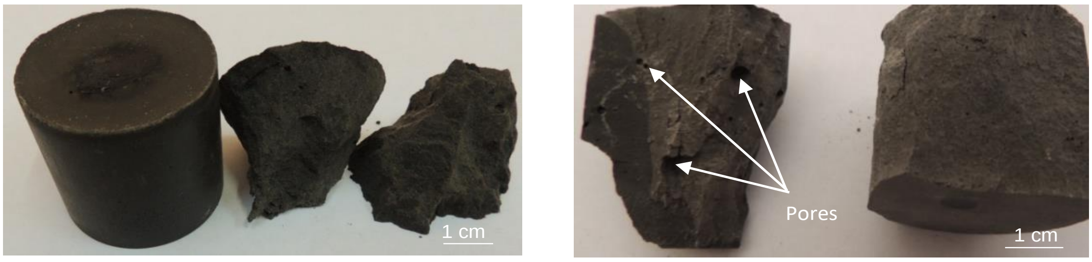


***Figure 92** Rheograms of optimal geopolymeric paste and the paste with different content of Shellspirax oil*

It is worth noting that the rheograms of the paste with different content of Shellspirax are analogous to rheograms of the paste with corresponding content of Nevastane. Therefore, the Figure 92 is presented only with the rheograms of the paste with different content of Shellspirax oil.

Analysing rheograms obtained at increasing shear rate it has been determined that pastes of all compositions are characterizing with decreasing of viscosity, which indicates the pseudoplastic behaviour of the tested materials. As the oils content increases from 10 till 40 %, the viscosity of paste and related shear stress increase at all researched shear rate. In this way, fresh paste with the content of oil 40 % is characterizing with the greatest tendency to the structuration.

The addition of the surfactant Castament (0,5 % wt) into the fresh paste initiates essential decreasing of viscosity and provides the quality samples obtaining with dense and homogeneous structure, and acceptance criteria, which had a greater effect on samples with Shellspirax (Figure 93).



Sample with 40 vol.% of Nevastane

After mechanical test of samples with 40 vol. % Shell: without (left) and with (right) Castament

***Figure 93** Geopolymer samples after 7 days of curing*

Positive influence of Castament addition on the fluidity and structure improvement of geopolymer is related with the typical effect of surfactant that causes a decrease in surface or interfacial tensions. In addition, Castament contains the lithium and calcium which accelerate the setting time of geopolymeric paste with 40 % of Shellspirax oil. The use of the surfactant led to an increase in the mechanical strength of the geopolymer material, which is shown in Figure 94.

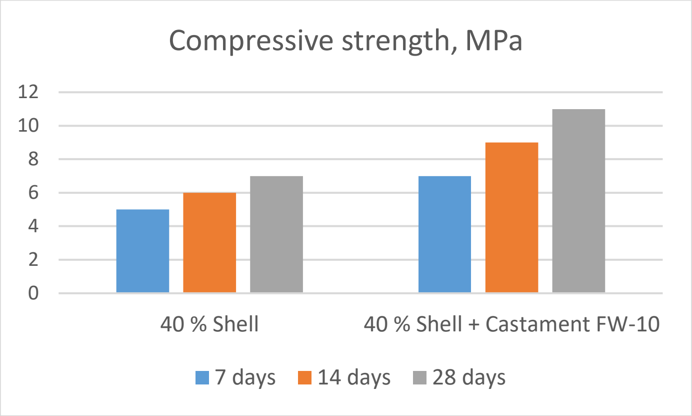


Figure 94 *Compressive strength of geopolymers after procedure of curing*

Robustness tests considering process variability

The process variability of aluminosilicate source-to-activation source ratio (±2 %) was studied. In study Ukrainian Al-Si raw materials and alkaline activators were used. Oil Shellspirax and oil Nevastane EP 100 were used as RLOW simulant with fixed incorporation rate - 30 vol.%. The compositions of the prepared samples are presented in the Table 67. These compositions were chosen by Definite Screening Design technique, which allows to study the effects of many factors in a relatively small number of experiments.

The hardened geopolymeric samples were characterized after 7 and 28 days of curing time with comparison of the optimal formulation of geopolymer (composition № 9).

Table 67 *Content of raw materials in MIX formulation based geopolymers, * - samples with 30 % of oil Shellspirax / ** - samples with 30 % of oil nevastane EP 100*

Component			**Composition number / Content, wt%**												
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9 Optimal**	**10**	**11**	**12**	**13**
Al-Si source	FA		32 (-2%)	36 (+2%)	36 +2%)	34	34	32 (-2%)	32 (-2%)	36 (+2%)	**34**	32 (-2%)	36 (+2%)	32 (-2%)	36 (+2%)
	Slag		18 (-2%)	22 (+2%)	18 (-2%)	18 (-2%)	22 (+2%)	20	18 (-2%)	22 (+2%)	**20**	22 (+2%)	18 (-2%)	22 (+2%)	20
	MK		14	12 (-2%)	12 (-2%)	12 (-2%)	16 (+2%)	12 (-2%)	16 (+2%)	14	**14**	12 (-2%)	16 (+2%)	16 (+2%)	16 (+2%)
Activator	K_2SiO_3		9 (-2%)	9 (-2%)	13(+2%)	9 (-2%)	13 (+2%)	13 (+2%)	13 (+2%)	13 (+2%)	**11**	11	11	9 (-2%)	9 (-2%)
	KOH		11 (+2%)	11 (+2%)	9	7 (-2%)	11 (+2%)	11 (+2%)	7 (-2%)	7 (-2%)	**9**	7 (-2%)	11 (+2%)	9	7 (-2%)
	H_2O		14 (+2%)	12	14(+2%)	10 (-2%)	14 (+2%)	10 (-2%)	12	10 (-2%)	**12**	14 (+2%)	10 (-2%)	10 (-2%)	14 (+2%)
Properties	Setting time, h		24* / 24**	24 / 24	32 / 32	**No fluidity**	32 / 32	24 / 24	24 / 24	**No fluidity**	**24 / 24**	24 / 24	24 /24	**No fluidity**	24 / 24
	Density, g/cm³		1,65/1,67	1,72/1,74	1,90/1,92		1,88/1,92	1,97/2,01	1,93/1,90		**2,03/2,08**	1,88/1,93	1,85/1,90		1,62/1,65
	Comp. strength, MPa	7 d	6 / 6	5 / 6	8 / 8		7 / 8	9 / 9	8 / 8		**10 / 10**	8 / 8	7 / 7		5 / 5
		28 d	8 / 9	9 / 9	11/11		10 /11	12/13	11 /11		**15 / 15**	12/ 12	10/ 10		7 / 7

It was found that the pastes of compositions No. 4, 8, 12 don’t flow due to reduced quantity of water and liquid glass (Figure 95 left).

No fluidity paste Low fluidity paste Normal fluidity paste

Figure 95 *No fluidity paste (left), low fluidity paste (middle) and normal fluidity paste (right)*

Low fluidity of compositions No. 11, 13 (Figure 95 middle) initiates large pores in structure of samples. As a result, the cured samples had an inhomogeneous structure with different defects.

Compositions No. 1, 2, 3, 5, 6, 7, 10 have quite normal fluidity of the paste (Figure 95 right), as well as dense homogeneous structure of hardened samples without large pores and acceptable compressive strength and can be used in future.

5.3.2.2 Optimisation of NUCLECO, KIPT Betol and KIPT Silicate

Tests without waste

The Nucleco, KIPT Betol and KIPT Silicate formulations were first tested without the use of waste.

The test planning included both rheological tests (workability and setting time) and tests on the hardened matrix (compressive strength).

The results of these tests on the three formulations without waste are shown below:

- Nucleco formulation
    - Workability: low
    - Setting time: about one day
    - Compressive strength (28 days): 25 MPa
- KIPT Betol
    - Mixture too dry. Tests not possible.
- KIPT Silicate
    - Mixture too dry. Tests not possible

It can be concluded that without waste, only the NUCLECO formulation results in a good mixture. Its mechanical strength is also good.

Tests with scintillation cocktail

Nucleco tested KIPT Betol and KIPT Silicate formulations with 25%, 20% and 15% by weight of ULTIMA GOLD.

The test plan included both rheological tests (workability, setting time, bleeding) and tests on the hardened matrix (compressive strength).

All mixes with 25% and 20% waste did not result in hardening and were therefore discarded.

The results of the tests with 15% waste (Waste/Mixture = 0,15) on the three formulations are shown below:

- Nucleco formulation (Waste/Mixture = 0,15)
    - Workability: good
    - Setting time: about one day
    - Bleeding: present after casting and on subsequent days
    - Compressive strength (28 days): 11 MPa
- KIPT Betol (Waste/Mixture = 0,15)
    - Workability: low
    - Setting time: about one day
    - Bleeding: present after casting and on subsequent days
    - Compressive strength (28 days): 8 MPa
- KIPT Silicate (Waste/Mixture = 0,15)
    - Workability: low
    - Setting time: about one day
    - Bleeding: no
    - Compressive strength (28 days): 1 MPa

Tests with scintillation cocktail + surfactant

KIPT Silicate and KIPT Betol formulations (Waste/Mixture = 0,15) were tested with ULTIMA GOLD, in presence of surfactant (1%).

The tests were carried out with three types of surfactants: sodium lauryl sulphate (SLS), sodium succinate (DSS) and Tween 80.

The results for KIPT Silicate are reported below:

- KIPT Silicate (Waste/Mixture = 0,15) + 1% SLS
    - Workability: low
    - Setting time: about one day
    - Bleeding: no
    - Compressive strength (28 days): 2 MPa
- KIPT Silicate (Waste/Mixture = 0,15) + 1% DSS
    - Workability: low
    - Setting time: about one day
    - Bleeding: no
    - Compressive strength (28 days): 2 MPa
- KIPT Silicate (Waste/Mixture = 0,15) + 1% Tween 80
    - Workability: low
    - Setting time: about one day
    - Bleeding: no
    - Compressive strength (28 days): 2 MPa

The results for KIPT Betol are as following:

- KIPT Betol (Waste/Mixture = 0,15) + 1% SLS
    - Workability: good
    - Setting time: low
    - Bleeding: no
    - Compressive strength (28 days): cannot be tested. Hardening only apparent
- KIPT Betol (Waste/Mixture = 0,15) + 1% DSS
    - Workability: low
    - Setting time: low
    - Bleeding: little
    - Compressive strength (28 days): 3 MPa
- KIPT Betol (Waste/Mixture = 0,15) + 1% Tween 80
    - Workability: low
    - Setting time: low
    - Bleeding: little
    - Compressive strength (28 days): 6 MPa

With scintillation cocktail, the Nucleco and KIPT Betol formulations present sufficient mechanical strength values but have the problem of bleeding; the KIPT Silicate formulation, on the other hand, does not present bleeding but has very low strengths; the use of surfactant, tested on the KIPT formulations, improves bleeding but significantly lowers mechanical strength.

Tests with TBP/Dodecane

KIPT Betol and KIPT Silicate formulations were tested with 25%, 20% and 15% by weight of TBP/Dodecane (70/30) mix.

The test plan included both rheological tests (workability, setting time, bleeding) and tests on the hardened matrix (compressive strength).

No mixture showed good liquid incorporation due to the very different viscosity of TBPO/Dodecane compared to that of the geopolymer matrix.

Tests with TBP/Dodecane + surfactant

KIPT Silicate and KIPT Betol formulations (Waste/Mixture = 0,15) were tested with TBP/Dodecane mix, in presence of surfactant (1%).

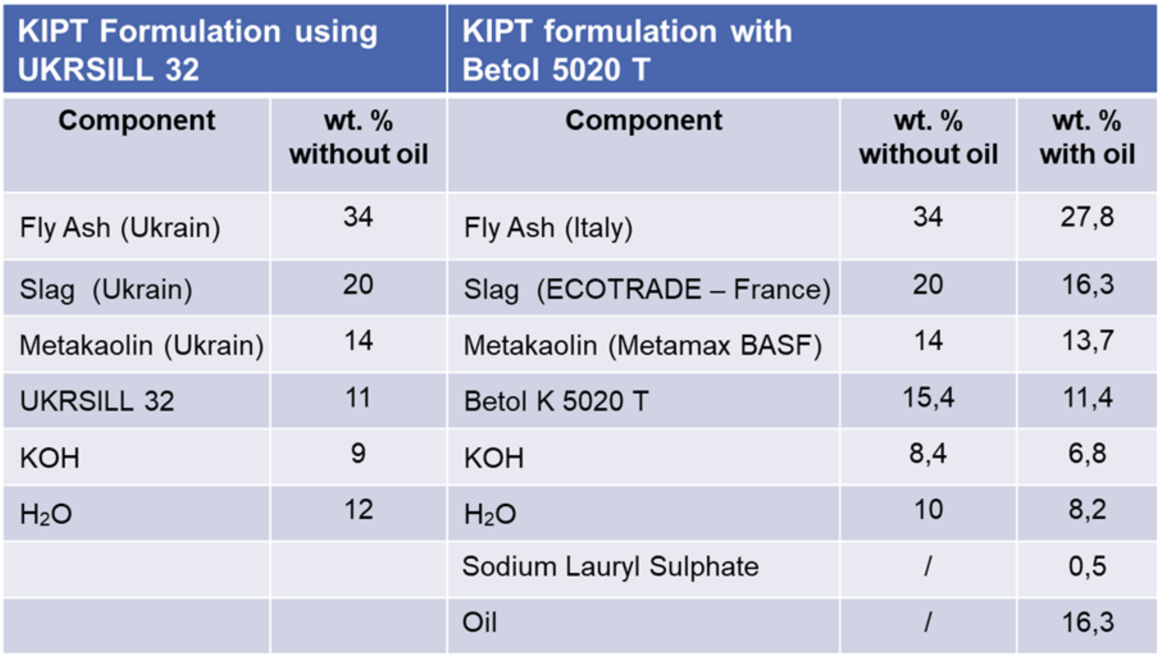
The tests were carried out with three types of surfactants: sodium lauryl sulphate (SLS), sodium succinate (DSS) and Tween 80.

No mixture showed good liquid incorporation. Despite the use of surfactant, the waste does not emulsify and is segregated from the matrix due to TBP preventing the formation of the emulsion.

Despite the improved results in terms of mechanical strength, the Nucleco formulation was abandoned as it was agreed with the other participants in Task 5.3 that Nucleco would continue with the KIPT formulation.

Based on the obtained results, the KIPT formulation was reworked, with the support of CEA, to replace UKRSILL waterglass with another waterglass, Betol K 5020 T, which is available in Europe. The next step, the study of the robustness of the KIPT formulation (using oil like waste), was therefore conducted using the revised formulation shown in the following table:

***Table 68** Reworked KIPT formulation, tested by NUCLECO and CEA*



KIPT Formulation using UKRSILL 32		KIPT formulation with Betol 5020 T		
Component	**wt. % without oil**	**Component**	**wt. % without oil**	**wt. % with oil**
Fly Ash (Ukrain)	34	Fly Ash (Italy)	34	27,8
Slag (Ukrain)	20	Slag (ECOTRADE – France)	20	16,3
Metakaolin (Ukrain)	14	Metakaolin (Metamax BASF)	14	13,7
UKRSILL 32	11	Betol K 5020 T	15,4	11,4
KOH	9	KOH	8,4	6,8
H_2O	12	H_2O	10	8,2
		Sodium Lauryl Sulphate	/	0,5
		Oil	/	16,3

5.3.2.3 Robustness tests on reworked KIPT formulation (NUCLECO, CEA)

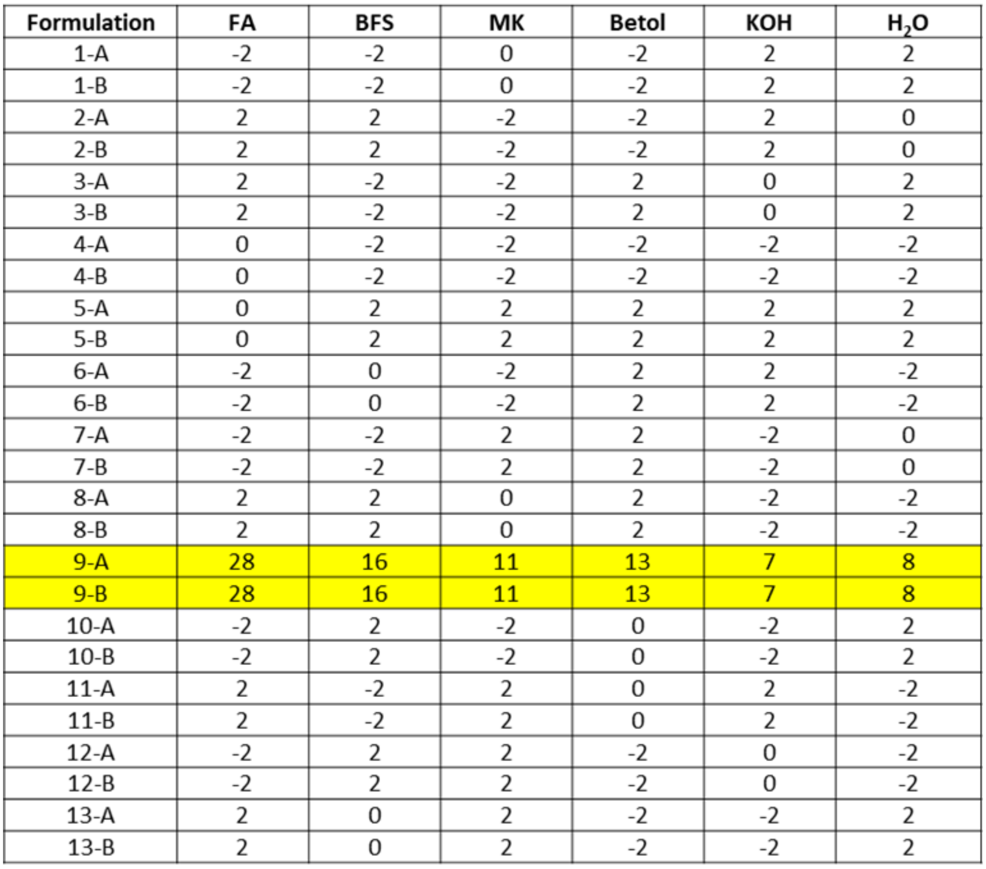
For the study of the KIPT formulation's robustness, the recipe shown in Table 68 was used. Passing from the recipe developed by KIPT to the revised one, changes were made to keep the SiO2/K2O molar ratio in the activation solution constant. In the last column of the table the percentages of the various components in the formulation containing the waste can be seen.

Initially it was planned to carry out the same test campaign using first Shellspirax and Nevastane oil and subsequently the TBP/Dodecane mix as waste.

In the case of 30 vol% of oil (Nevastane and Shellspirax), after some preliminary tests NUCLECO needed to add a small amount of surfactant (was sodium lauryl sulphate) to obtain the emulsion. As can be seen in the case of CEA, 30 vol.% of Nevastane oil could be easily incorporated without surfactant. This is most likely due to the fact that mixing system has a crucial role on the emulsification process.

The formulations studied by NUCLECO for robustness were obtained by varying by ±2%, the six parameters shown in the Table 69, from the reference formulation which is highlighted in yellow. The parameters varied are FA, BFS, MK, Betol, KOH and water. A total of 13 formulations were prepared for each of the two oils (A - Nevastane-based, B - Shellspirax-based). In all cases the percentage of oil (16% by weight, 30% by volume) and of surfactant (0.5% by weight) have been kept constant.

Table 69 *Formulations studied by NUCLECO during robustness trials*



Formulation	FA	BFS	MK	Betol	KOH	H_2O
1-A	-2	-2	0	-2	2	2
1-B	-2	-2	0	-2	2	2
2-A	2	2	-2	-2	2	0
2-B	2	2	-2	-2	2	0
3-A	2	-2	-2	2	0	2
3-B	2	-2	-2	2	0	2
4-A	0	-2	-2	-2	-2	-2
4-B	0	-2	-2	-2	-2	-2
5-A	0	2	2	2	2	2
5-B	0	2	2	2	2	2
6-A	-2	0	-2	2	2	-2
6-B	-2	0	-2	2	2	-2
7-A	-2	-2	2	2	-2	0
7-B	-2	-2	2	2	-2	0
8-A	2	2	0	2	-2	-2
8-B	2	2	0	2	-2	-2
9-A	28	16	11	13	7	8
9-B	28	16	11	13	7	8
10-A	-2	2	-2	0	-2	2
10-B	-2	2	-2	0	-2	2
11-A	2	-2	2	0	2	-2
11-B	2	-2	2	0	2	-2
12-A	-2	2	2	-2	0	-2
12-B	-2	2	2	-2	0	-2
13-A	2	0	2	-2	-2	2
13-B	2	0	2	-2	-2	2

The order of addition of the various components of each mix was as follows: water, surfactant, Betol, the geopolymer mix, and finally the oil. A planetary mixer was used as the mixing system. The curing of the specimens was done at room temperature, without humidity saturation.

The tests performed in this campaign were flowability, setting time and compressive strength.

The results of the tests for Nevastane (Figure 96) and Shellspirax (Figure 97) oil samples are summarized in the following graphs.

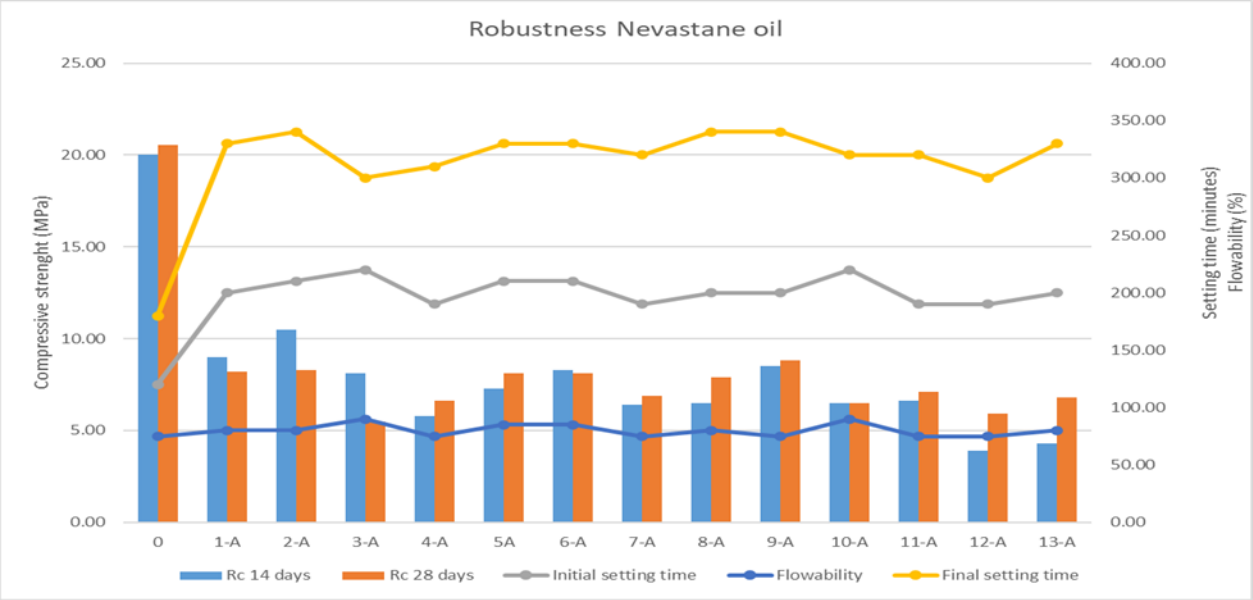


__Figure 96__ Results of robustness test for Nevastane oil samples

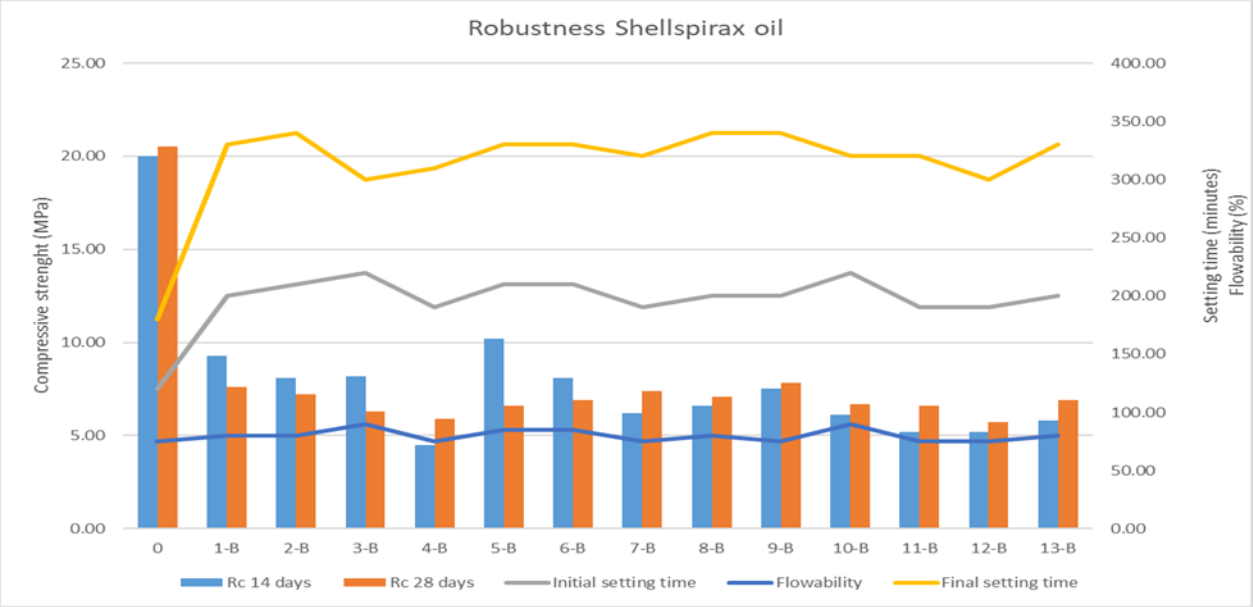


__Figure 97__ Results of robustness test for Shellspirax oil samples

The blue bars represent the compressive strength at 14 days. The orange bars represent the compressive strength at 28 days. The first bar on the left is the base recipe, without oil. The lines represent the other tests. The blue line represents workability while the gray and yellow lines represent initial setting time and final setting time. The recipes with the red mark are those that showed bleeding. From the graphs it's immediately visible that the trend of results is very similar for the two different oils and that Nevastane is a bit more problematic for bleeding.

Several observations can be made:

- Regarding oil:
    - From the point of view of bleeding, this is observed in 1A/B-2A-6A, so mainly with Nevastane.
    - The range of variability of flowability is 75%-90%.
    - The setting times vary as follows: without oil there is an initial setting time of 2 hours and a final setting time of 3 hours. With oil the initial setting time varies from 3 hours

    10 minutes to 3 hours 40 minutes while the final setting time varies from 5 hours to 5 hours 40 minutes.
  - The compressive strength is always higher than 5 MPa.
- Regarding TBP/Dodecane 70/30 mix:
  - There is no emulsion and the mixture does not incorporate waste.
  - Given the result obtained with the reference recipe, all tests for robustness determination were not performed (on the varied formulations).

In the case of CEA the heat flow evolution is presented in Figure 98. It can be seen that Nevastane EP100 does not affect the geopolymerization of KIPT geopolymers. The mechanical strengths measured after 28 days for samples without oil and with 30 vol.% of oil are 55±3 MPa and 23±2 MPa respectively. It can be highlighted that storage conditions (temperature & relative humidity) play a crucial role on the mechanical properties.

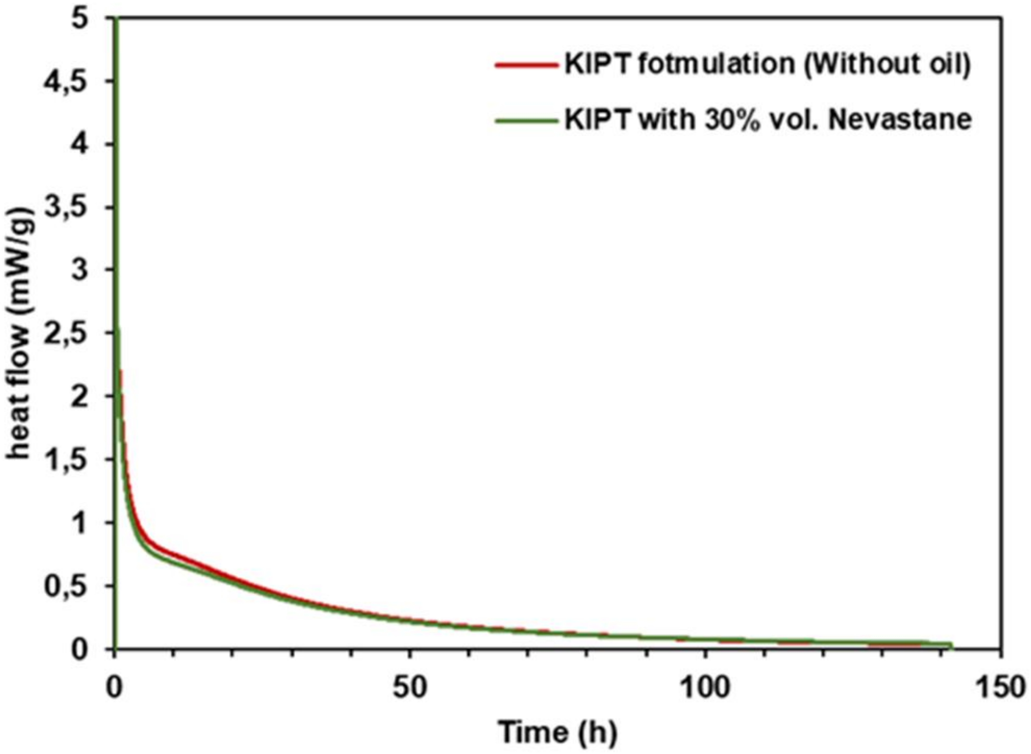


Figure 98 *Heat flow evolution of KIPT formulation samples studied by CEA*

A waste loading higher than 30 vol.% could not be achieved by CEA without the use of surfactant. Three different surfactants were studied in samples with 50 vol.% of waste loading (most unfavourable) with the same dosage (0.5 wt.%). The Surfactants studied are reported in the following Table 70.

Table 70 *Surfactants studied by CEA*

Commercial name	Chemical description	Category
SDS	**Sodium Dodecyl Sulfate**	**Anionic (-)**
Glucopon 225DK	**C8-C10-alkyl polyglucoside**	**Non-ionic (Ø)**
Brij O10	**Polyoxyethylene (10) oleyl ether**	**Non-ionic (Ø)**

As can be seen in Figure 99 the best emulsification and stability with 50% of Nevastane EP100 was obtained with Glucopon. This may be due to various reasons:

- The solubility of Glucopon is higher than that of Brij O10.
- The viscosity of the geopolymer grout seems to have a crucial role on the stabilization of the emulsion.
- The size of the surfactant molecules can partly explain the stabilization efficiency of the adopted surfactant.

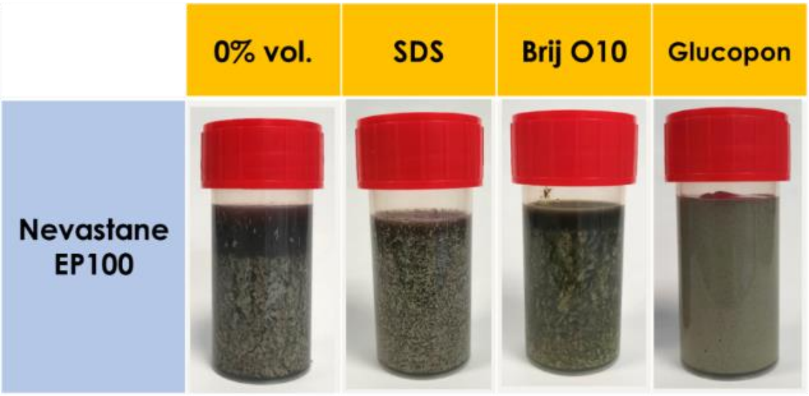


Figure 99 *Samples with 50 vol.% of Nevastane oil and different surfactants*

Regarding the TBP/Dodecane mix, using the same reference formulation (KIPT) tested by NUCLECO, there is no emulsion and the mixture does not incorporate waste. Given this result, all tests for robustness determination were not performed (on the varied recipes).

In the case of CEA TBP/Dodecane samples were tested with the same surfactants as in the case of Nevastane oil. Glucopon was also found to be the most efficient surfactant for the encapsulation of TBP/Dodecane mix.

5.3.3 Conclusions

For the original KIPT formulation with Ukrainian raw materials several conclusions can be made:

- The incorporation of Shellspirax and Nevastane EP 100 oils, used as RLOW simulants, into a MIX-based formulation geopolymer has been studied. The content of Shellspirax/Nevastane 10, 20, 30 vol.% provides both acceptable criteria, as well as a dense and uniform homogeneous structure of the cured geopolymer material.

- Based on rheology measurement of selected geopolymeric pastes, it has been shown the pseudoplastic behavior of the tested materials, that is corresponding to decreasing viscosity at all increasing shear rate.
- As the oils content increases from 10 till 40 vol.%, the viscosity of paste and corresponding shear stress increases at all researched shear rate. Therefore, a geopolymer paste with an oil content of 40 vol.% is the most structured, and the formation of pores in a solid product is possible.
- The use of the surfactant Castament FW-10 (0,5 wt. %) in the paste preparation process with 40 vol.% of Shellspirax oil improved material fluidity and provided the quality samples manufacturing without large pores.

The most important parameters that can influence the waste form properties are:

- Compliance with the modes of preparation of the dry mixture:
  - mechanical grinding and sifted through a sieve of 600 µm;
  - mechanical mixing of all dry ingredients.
- Thorough mixing of water with potassium water glass and KOH to prepare an activation solution.
- The obtaining of samples of MIX based formulation geopolymers containing RLOW simulants proceeded according to the diagram below:

Figure 100 *Sample production process by KIPT*

- Strict adherence to proportions for mixing components according to MIX formulation.
- Variations in the content of dry components are possible within + 2% according to Robustness tests considering process variability.
- An important parameter is the water content. Its content may be changed due to the presence of internal water in dry components other than Ukrainian.

NUCLECO tested the MIX formulations by using different RAW materials including the waterglass solution.

Additionally, NUCLECO studied a formulation that they previously developed. All those formulations were studied both without waste and with oil, scintillation cocktail and mix of TBP/Dodecane.

During testing without waste, the previously developed NUCLECO formulation presented a good mixture while for the KIPT formulation with different raw materials the results were not adequate due to a wrong replication of the correct molar ratio between the formulation components:

- The potassium silicate powder didn't easily dissolve in the activating solution;
- The first Betol waterglass solution tested (Betol 52 T) was based on Na and not on K.

When testing with waste the NUCLECO and Betol formulation presented good mechanical strength, however bleeding was present. During testing with TBP/Docecane mixture both KIPT Betol and Silicate formulation could not form a mixture, even when using a surfactant.

Due to this fact the KIPT formulation was reworked with the support of CEA and a new formulation using Betol K 5020 T as a replacement for Ukrainian waterglass UKRSILL was tested in robustness studies.

Despite the improved results, the NUCLECO formulation was abandoned after discussing with other T5.3 partners.

During the robustness studies an incorporation rate of Nevastane and Shellspirax oil up to 30 vol.% was achieved without a surfactant by the CEA and with sodium lauryl sulphate surfactant by NUCLECO. This may have been due to the mixing system having a crucial role during sample preparation. Bleeding has been observed in some of studied samples, mainly with Nevastane oil. The compressive strength of all samples was higher than 5 MPa.

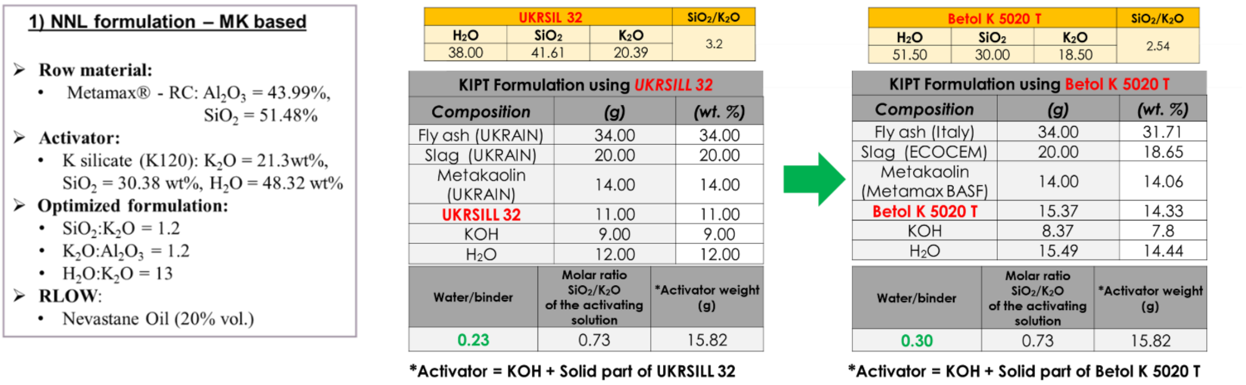
CEA has achieved a higher waste loading of 50 vol.% by using Glucopon 225DK as a surfactant. This surfactant can be also used in TBP/Dodecane samples.

5.4 Influence of the addition of surfactant on the geopolymer composite at fresh and solid state

CEA worked mainly on two formulations: those proposed by NNL and those adapted from the KIPT team formulation with the collaboration of Italan team, to condition reference surrogates such as Nevastane EP100 oil, Shellspirax oil and a mix of TBP/dodecane. The proportion of raw materials is given in the Table 71.

The preparation of the geopolymer emulsions was performed in 20 min, by: (1) Mixing the MK powder and the alkaline solution for 5 min at 600 rpm then 2 min at 2000 rpm; then (2) gradually adding the OL to the geopolymer paste and mixing for 13 min at 2000 rpm. It should be noted that when the surfactant was used, it was mixed with the solution before adding MK. The fresh composites were then used for rheological tests, and triplicate 40 mm cubic samples were prepared for compressive strength determination. For microstructural analysis, emulsion samples were cast into plastic cylinder molds of 2 cm diameter and 5 cm height. All specimens were kept in sealed molds for endogenous curing, at 20°C for 28 days before testing.

***Table 71** Formulation of alkali activated materials used at CEA*



1) NNL formulation – MK based

- **Row material:**
  - Metamax® - RC: $Al_2O_3 = 43.99\%$, $SiO_2 = 51.48\%$
- **Activator:**
  - K silicate (K120): $K_2O = 21.3wt\%$, $SiO_2 = 30.38$ wt%, $H_2O = 48.32$ wt%
- **Optimized formulation:**
  - $SiO_2:K_2O = 1.2$
  - $K_2O:Al_2O_3 = 1.2$
  - $H_2O:K_2O = 13$
- **RLOW**:
  - Nevastane Oil (20% vol.)

UKRSIL 32			SiO_2/K_2O
H_2O	SiO_2	K_2O	3.2
38.00	41.61	20.39	

KIPT Formulation using UKRSILL 32		
Composition	*(g)*	*(wt. %)*
Fly ash (UKRAIN)	34.00	34.00
Slag (UKRAIN)	20.00	20.00
Metakaolin (UKRAIN)	14.00	14.00
UKRSILL 32	11.00	11.00
KOH	9.00	9.00
H_2O	12.00	12.00

Water/binder	Molar ratio SiO_2/K_2O of the activating solution	*Activator weight (g)
0.23	0.73	15.82

***Activator = KOH + Solid part of UKRSILL 32**

Betol K 5020 T			SiO_2/K_2O
H_2O	SiO_2	K_2O	2.54
51.50	30.00	18.50	

KIPT Formulation using Betol K 5020 T		
Composition	*(g)*	*(wt. %)*
Fly ash (Italy)	34.00	31.71
Slag (ECOCEM)	20.00	18.65
Metakaolin (Metamax BASF)	14.00	14.06
Betol K 5020 T	15.37	14.33
KOH	8.37	7.8
H_2O	15.49	14.44

Water/binder	Molar ratio SiO_2/K_2O of the activating solution	*Activator weight (g)
0.30	0.73	15.82

***Activator = KOH + Solid part of Betol K 5020 T**

According to the nature of the oil we want to incorporate, and the nature of alkali activated materials (metakaolin based or Mix formulation), it could be necessary to use a surfactant to stabilize the emulsion in order to avoid at liquid state, the coalescence of bubbles and therefore the demixing.

Sometimes, the presence of surfactants is not necessary if some conditions are fulfilled between the nature of the AAM and the nature of the oil. Indeed, if the surface tension and the ratio of the viscosity between the suspending fluid and the organic liquid are in a good range, no surfactant is needed. We cannot exclude the physico-chemical nature of the organic liquid as we will see later.

The NNL formulation to condition organic liquids

Seven organic liquids (Nevastane EP100, Shellspirax, pure TPB, pure Dodecane (C12), 30/70 C12/TBP, 50/50 C12/TBP and 70/30 C12/TBP) at various volume fraction (from 20 to 50%) and three surfactants (when needed) were studied for a conditioning in a metakaolin based geopolymer. The protocol and the experimental plan are described in Figure 101

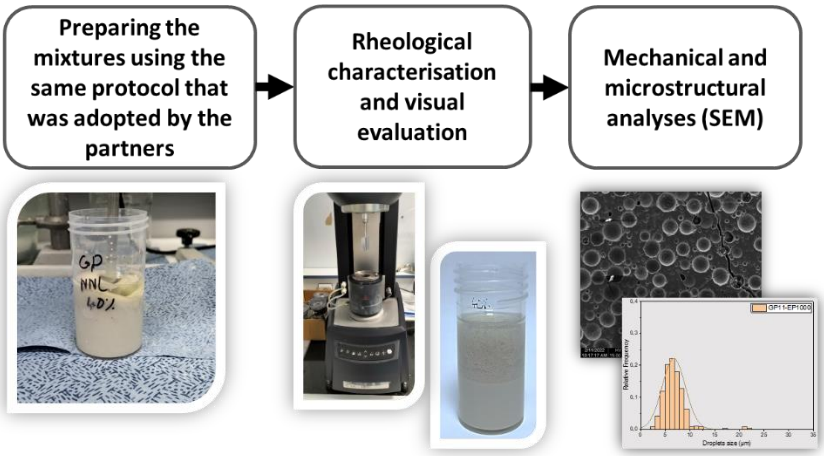


Figure 101 *Preparation of composite and characterisation at liquid and solid state*

For Nevastane EP100 and Shellspirax LOR, no problem was detected whatever the volume fraction of oil and without the use of surfactants as shown in Figure 102.

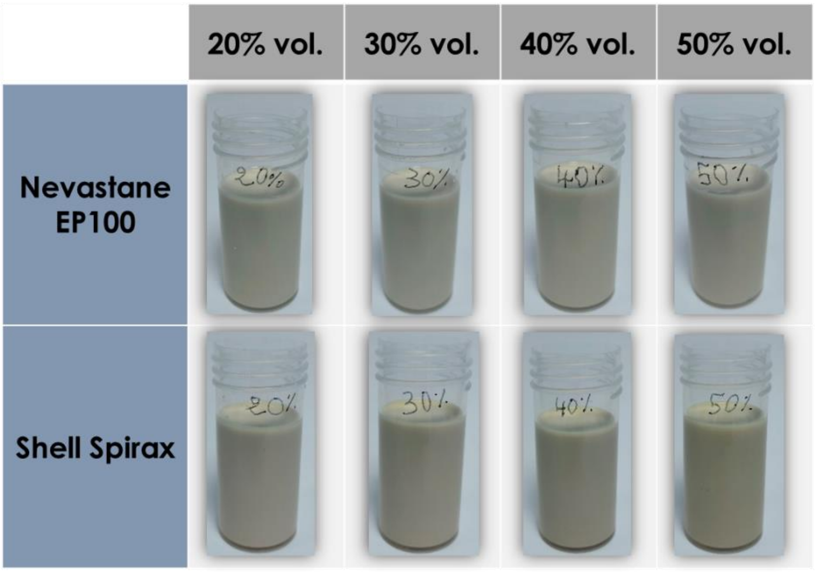
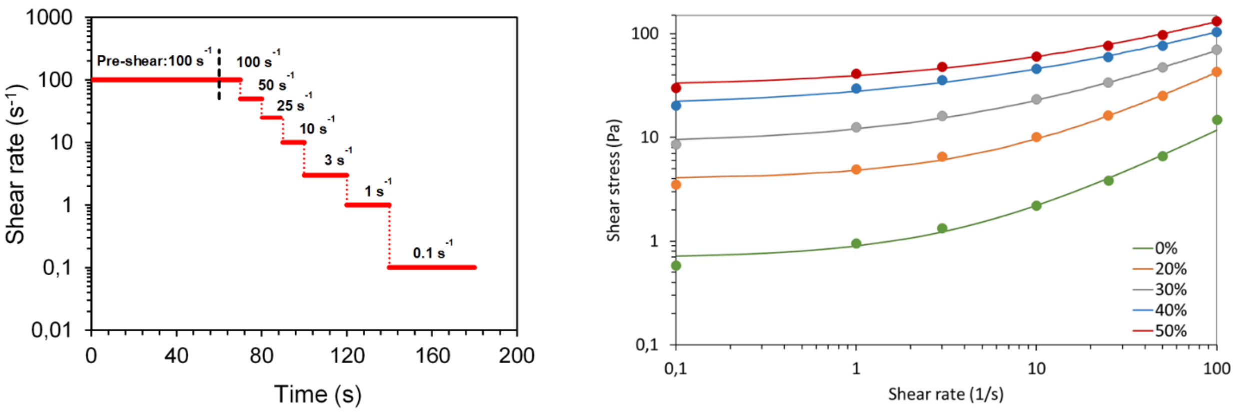


Figure 102 *Photos of the composites at liquid state, no bleeding observed*

The Figure 103 presents the flow curves for some Geoil composites with various volume fraction of Shellspirax oil. We show that the flow curves have the same shape, but the shear stress is higher for a higher volume fraction of oil resulting from the emulsification process. All mixtures display shear-thinning behavior with an apparent yield stress that is adequately fitted by the Herschel-Bulkley model given by:

$$\tau = \tau_0 + K\,\dot{\gamma}^n \tag{1}$$

Where τ is the shear stress (Pa), τ_0 is the yield stress, K is the consistency index (Pa.s^n), $\dot{\gamma}$ is the shear rate (s^{-1}) and n is the flow index. The rheological properties of each mixture are presented in Table 72**.**



(a) (b)

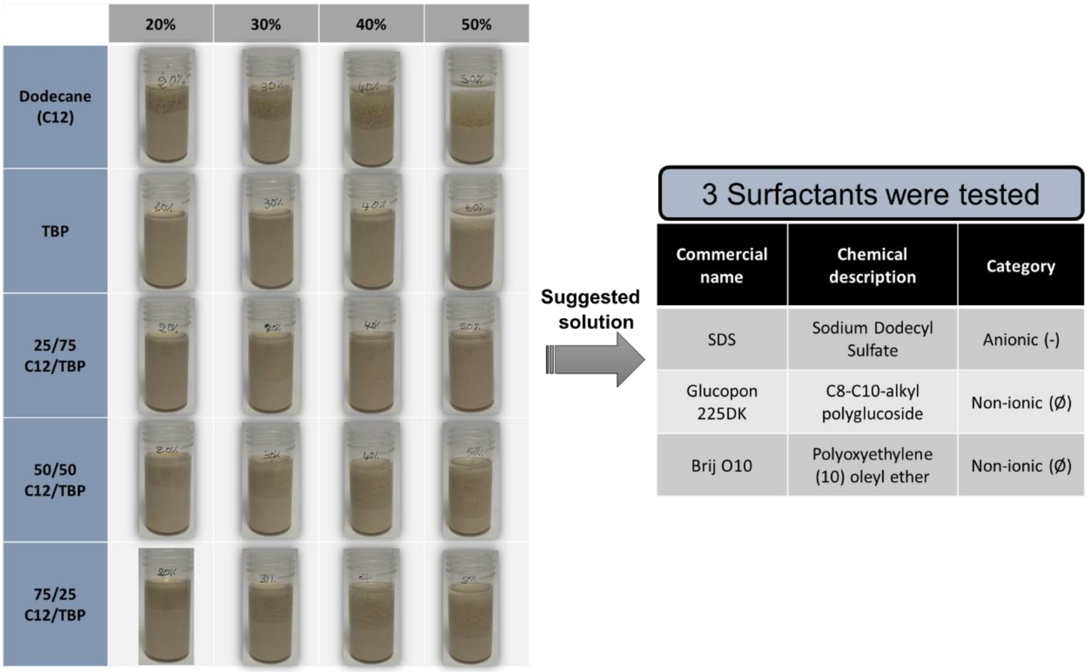
Figure 103 *(a) Protocole used for the acquisition of the shear stress for a step of shear rate and (b) Influence of the volume fraction of Shellspirax on the flow curve. The oil is embedded in a metakaolin geopolymer. The symbol represents the experimental data and the line the fit by a Herschel-Bulkley model*

The rheological behaviour for the composites with Nevastane oil is very similar to the Shellspirax one with a slight difference in the rheological parameters obtained from the fits, Table 72. The yield stress and the stress as a function of the shear rate remain reasonable and should not be a problem for the up-scaling process.

Table 72 *Rheological parameters determined from the Hershel Bulkley fits for the Nevastane EP 100 and Shellspirax oil at various volume fraction.*

	Liquide percentage	Rheological parameters		
		τ_0	k	n
Control	0%	0,69	0,21	0,86
Nevastane EP100	20%	3,67	0,69	0,85
	30%	8,54	2,79	0,66
	40%	19,02	7	0,52
	50%	31,3	10,42	0,48
Shell Spirax	20%	3,97	0,84	0,83
	30%	8,75	3,29	0,63
	40%	19,81	7,99	0,51
	50%	30,72	8,65	0,53

For the TBP, dodecane or a mix of both solvents, the stabilization of the emulsions needs to add a surfactant as suggested by the visual observation in Figure 104. Therefore, we have tested three kind of surfactant in order to improve the emulsion process.



3 Surfactants were tested

Commercial name	Chemical description	Category
SDS	Sodium Dodecyl Sulfate	Anionic (-)
Glucopon 225DK	C8-C10-alkyl polyglucoside	Non-ionic (Ø)
Brij O10	Polyoxyethylene (10) oleyl ether	Non-ionic (Ø)

Figure 104 *Photos of the composites at liquid state and the proposed solution by testing three surfactants in order to improve the stabilization of the emulsion*

First of all the use of surfactant at a concentration of 0.03 mol/l of the activating solution does not affect significatively the geopolymerization process and the setting time as shown in Figure 105.

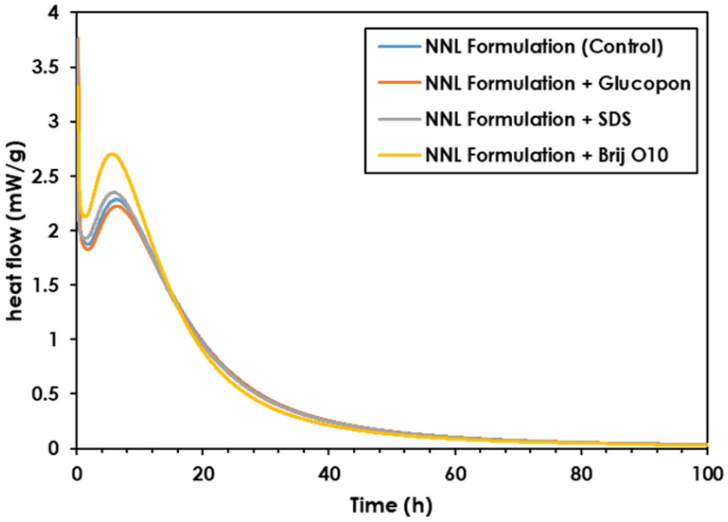


Figure 105 *Influence of the nature of the surfactants on the reactivity of the geopolymer for NNL formulation*

If now, we focus specifically on a 50/50 C12/TBP mix and we look at the influence of the surfactant, we show that Brij O10 is the most suitable surfactant to encapsulate this organic liquid from 30 to 50 % in volume, Figure 106. SDS surfactant for 30% in volume works quite well too but for upper volume fraction, the homogeneity of the emulsion is not guarantee. It is commonly known that SDS precipitates in alkaline environments, and especially in the presence of potassium salts [15]. This can partly explain the ineffectiveness of the SDS for the emulsification of the geopolymer/OL mix, particularly when using a potassium based activator solution.

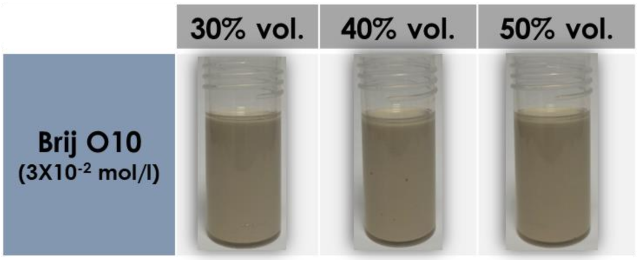


Figure 106 *Good encapsulation of the mix 50/50 C12/TBP for 3 volume fractions. A slight bleeding is observed at the top.*

From rheological point of view, the flow curves were also fitted by a HB model and the rheological parameters are given in the Table 73. The SDS sample shows a higher yield stress and consistency certainly due to its poor solubility in potassium alkaline solution. If now, we compare the results with the results of the Table 72, we can notice that even with the presence of surfactant such as Brij O10, the yield stress and the consistency are lower than for the composite geopolymer/Nevastane or Shellspirax. The viscosities of the suspending fluid and the organic liquid, combined with the level of surface tension and the nature of the surfactant as structuring or non structuring agent as defined in [16] are again intimately connected.

***Table 73** Rheological parameters determined from the Herschel Bulkley fits for the mix 50/50 C12/TBP and for 3 volume fractions and for SDS at 30 % in volume*

Formulation		Control	Brij O10			SDS			Glucopon		
Liquide %		0	30	40	50	30	40	50	30	40	50
Rheological parameters	τ_0	0.69	8.72	11.05	13.5	31,46	-	-	-	-	-
	k	0,21	3.01	3.11	3.34	6.67	-	-	-	-	-
	n	0,86	0.61	0.62	0.62	0.53	-	-	-	-	-

It is important to note that for all the proportion of C12/TBP mises, the Brij O10 surfactant works very well whatever the volume fractions of organic liquid.

Another important point concerns the influence of the concentration of surfactant in the flow properties but also on the solid network after curing the samples at room temperature at 100 % of relative humidity during 28 days.

At liquid state the increase of the concentration of Brij O10 results in an increase of the rheological parameters such as the yield stress as shown in the Figure 107 but in a limited manner. Of course, the slope is higher for the highest volume fraction of mix as suggested by the fits in Figure 107.

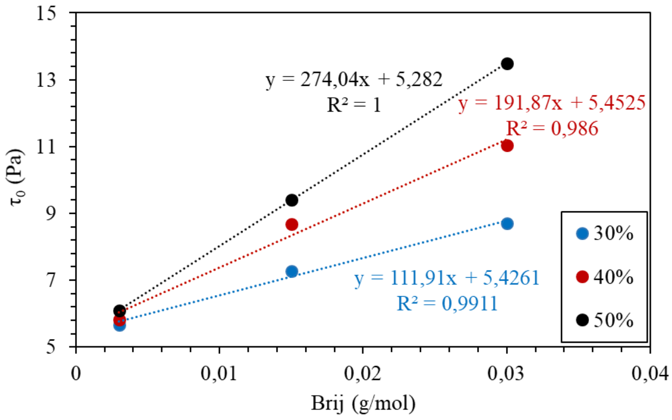
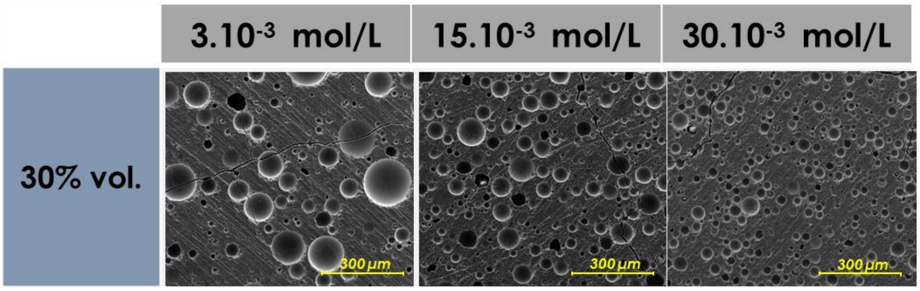
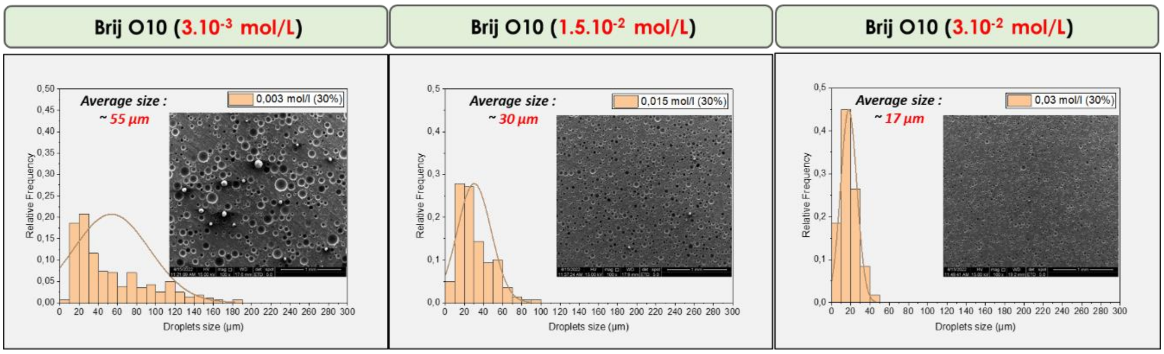


***Figure 107** Influence of the concentration of Brij O10 on the yield stress for the three volume fraction of 50/50 C12/TBP mix*

The surfactant concentration on the microstructure and especially on the droplet size distribution is also impactful. Visually and with a more detailed analysis, increasing the Brij O10 concentration leads to a significantly decrease of the droplet size and ensure a homogeneity in the composite, Figure 108a. The distribution of the droplet size in also narrower with increasing the concentration of surfactant, Figure 108b. The raise of the yield stress and the consistency is also a direct consequence of the droplet size distribution and especially the number of droplets that increase the surface contacts.



(a)



(b)

Figure 108 *(a) influence of the concentration of the surfactant on the bubbles size and (b) Evaluation of Brij O10 effectiveness for various concentration with 30% of 50/50 C12/TBP*

Finally, the compressive strength was measured for three volume fraction for the formulation 50/50 C12/TBP and 0.03 mol/L of Brij O10. Classically, the mechanic properties decrease as a function of the volume fraction and interestingly, follow a power law with a critical exponent of -0.9, Figure 109. Even for a volume fraction of 50% of organic liquid, the compressive strength remains higher than 10 MPa.

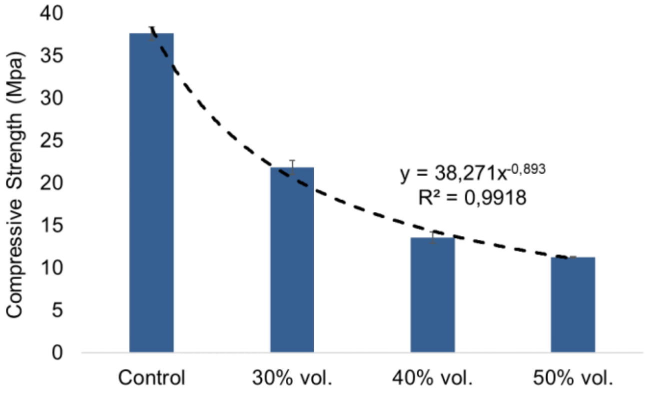


Figure 109 *Evolution of the compressive stress as a function of the volume fraction of 50/50 C12/TBP mix for 0.03 mol/L of Brij O10*

To sum up:

- In terms of initial stability and rheological properties, the use of surfactant is not necessary for NSFD/NNL formulation with high viscosity oils (Nevastane EP100 and Shellspirax).
- The use of surfactant is required for the encapsulation of low-viscosity liquid (TBP, Dodecane and the mix of both).
- the *Brij O10* surfactant seems to be very efficient in the case of K-Geoils with USFD/NNL formulation whatever the proportion of C12/TBP
- The reactivity of the geopolymer is not affected by the presence of organic liquid and surfactant
- The flow properties are impacted by the nature of the oil, the volume fraction and the concentration of surfactants. However, the rheological parameters remains sufficiently low to expect an easy scale-up
- The droplets size and distribution can be well controlled by the Brij O10 concentration that impact also the rheological properties
- The mechanical properties remains higher than 10 MPa even for 50% of volume fraction (accepted limit in France = 8 MPa)

The KIPT formulation modified by CEA to condition organic liquids

As discussed earlier, given that the Ukrainian raw materials were difficult to supply. Consequently, CEA has adapted the mix formulation with their raw materials and with a water to binder ratio = 0.3 as shown in Table 71.

First of all, before incorporate the different oil, we measured the apparent viscosity of the mix formulation and compared it with the apparent viscosity of NNL formulation. We notice that the mix formulation has a higher viscosity on all the range of shear rate, Figure 110.

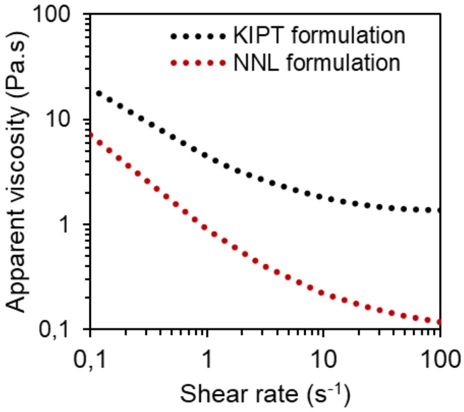


Figure 110 *Comparison of the flow curve for both formulations*

With this formulation, we did not perform as many experiments as for the metakaolin based geopolymer but some key results will be addressed. We studied:

- two types of oil, the high viscosity Nevastane EP100 and the low viscosity 70/30 C12/TBP
- 3 volume fractions, 30, 40 and 50%
- 3 surfactants, the SDS, the Glucopon and the Brij O10 at one concentration = 0.02 mol/L

As in the previous paragraph, we applied the same methodology as shown in Figure 101, and we first checked the absence of interaction between the oil and the alkali activated materials by using calorimetry (data not shown here).

In figure 11, we gathered some photos of emulsions for different conditions. All the samples encircled by a dash red line are stable and homogeneous. We can notice that it is not necessary to add a surfactant to encapsulate Nevastane oil up to 30% in volume but for higher volume fraction a surfactant is necessary. Contrary to the previous paragraph, Glucopon turns out to be the best surfactant for this composite KIPT/organic liquid whether for Nevastane oil or the C12/TBP mix whatever the volume fraction 30% or 50%

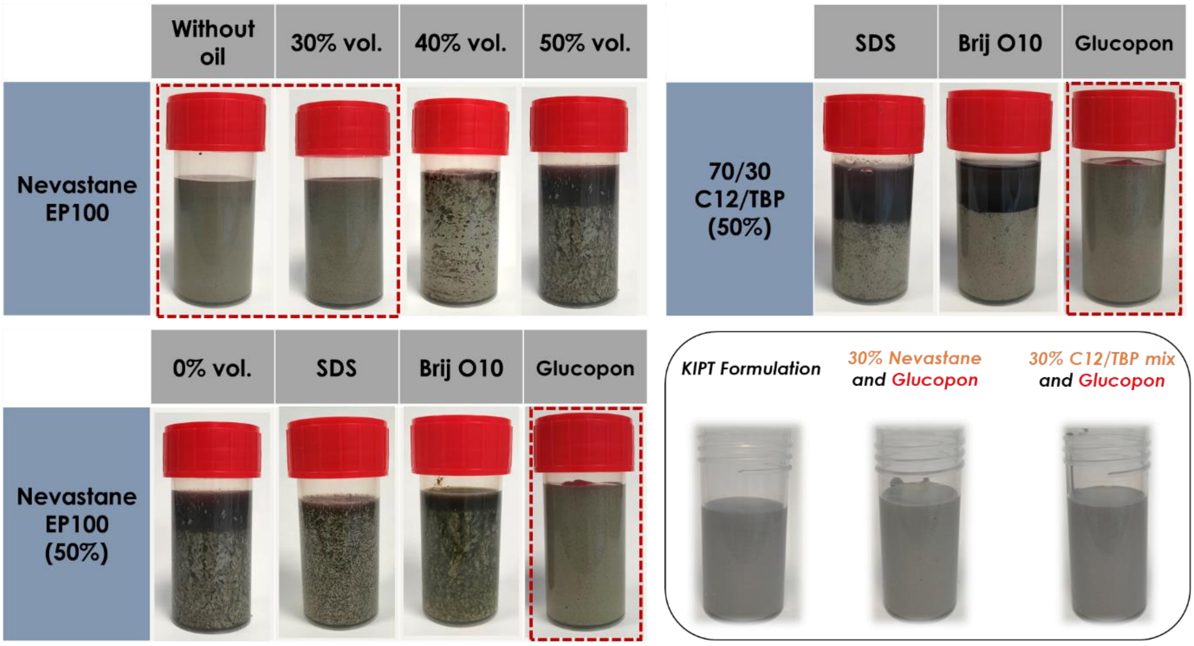


Figure 111 *Various combinations (oil/volume fraction/nature of surfactant) with the KIPT AAM to obtain a homogeneous stabilized emulsion*

The rheological behavior 10 minutes after the mixing of all the constituents show some difference between the different materials elaborated, Figure 112. Indeed, the composite with the more viscous oil (Nevastane) show the highest apparent viscosity

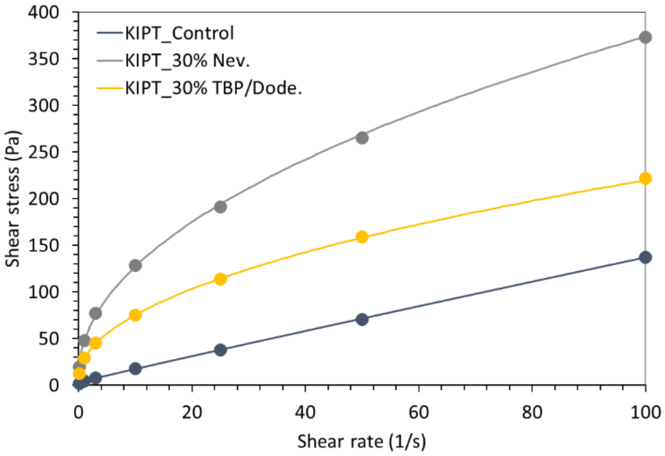


Figure 112 *rheological behaviour for three compositions of alkali activated materials with or without oil or solvent*

The experimental data are fitted by a Hershel Bulckley model and the fitting parameters are given in the Table 74.

Table 74 *rheological parameters for the 3 formulations.*

Rheological parameters			
Parameters	KIPT_Control	KIPT_30% Nev.	KIPT_30% TBP/Dode.
τ_0 (Pa)	2,9	9,3	6,21
K (Pa.s^n)	1,54	38,2	22,4
n	0,97	0,49	0,49

After few days of storage, SEM observations were conducted on the three samples. The KIPT formulation without oil show few air bubbles due to the mixing process. For the two other formulations with oil and solvent, the size of the bubbles is ranged between 30-150 µm. It is also important to note that the size of the bubbles is drastically control by the presence of glucopon.

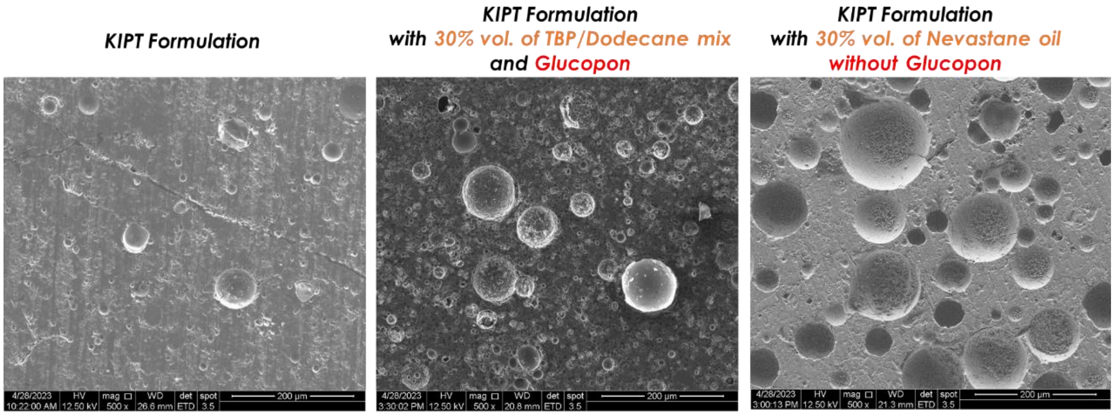


Figure 113 *SEM analysis for the consolidated materials.*

A decrease of the compressive strength is observed with the addition of surfactant and obviously with 30% in volume of oil. However, the KIPT 30% TBP/dodecane sample is around 18±2 MPa so largely higher than the French limit fixed at 8 MPa.

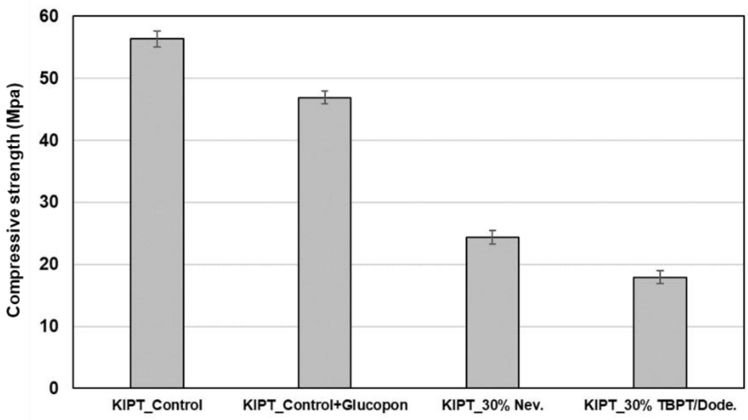


Figure 114 *Compressive strength for various formulation*

As a final summary

- In terms of emulsification and initial stability, the use of surfactant is not necessary for KIPT formulation up to 30% of Nevastane EP100. However, the use of surfactant is required for higher volume fraction and to decrease the size of the droplets
- The use of surfactant is also required for the encapsulation of low-viscosity liquid (TBP, Dodecane and the mix of both) in the KIPT formulation.
- the *Glucopon* surfactant is very efficient in the case of KIPT formulation

- The flow properties are impacted by the nature of the oil, the volume fraction and the concentration of surfactants. However, the rheological parameters remain sufficiently low and similar to the NNL composite BUT the setting time is very short (around 35 minutes). Consequently, it is difficult to envisage this formulation for the scaling up with respect to NNL formulation that sets around 4-5 hours. Moreover, the fact the setting time is very short allows also to limit the creaming and to encapsulate easily the oil droplets.
- In one case, Glucopon is used and in other case it is the Brij O10 surfactant that is very efficient. It is not completely understood but, there is a difference in the solubility and in the interaction with the solid particles in the mix. In [16], it is explained as structuring or non-structuring mechanisms that modify the range of interaction that implies a significant modification of the flow properties.
- Finally, something really essential concerns the storage of the samples before the mechanical tests but also before external aggression such as irradiation, leaching, gas adsorption etc. At CEA, the samples were demolded 24 hours after casting and are conditioned at 20°C and with a relative humidity higher than 90%. Some tests were performed at 50% RH and we can observe the appearance of cracks due to the evaporation of the free water entailing a drying shrinkage, Figure 115.

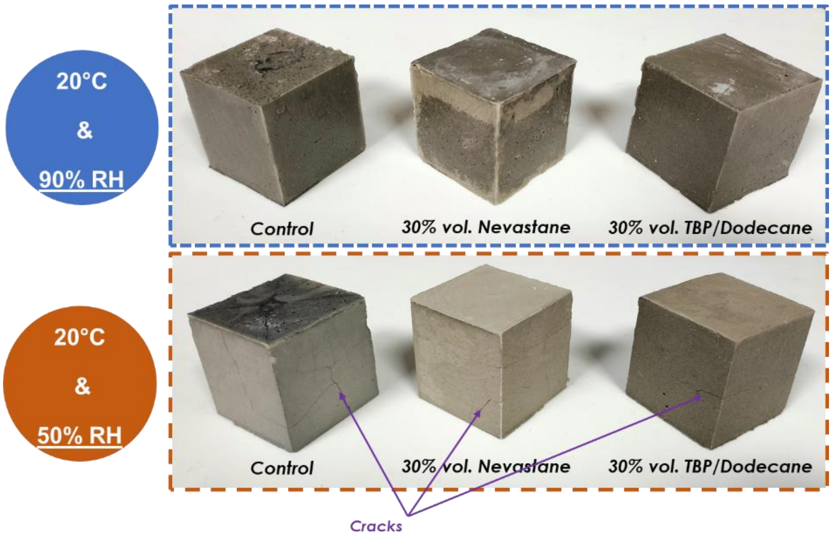


***Figure 115** Influence of storage conditions on the integrity of the solid samples*

5.5 Choice of optimised reference formulations

Following the tests performed by the partners a WP5 Task 5.3.3 progress on-line meeting was held on 21.11.2022 devoted to the achievement of Milestone 34 "Optimised formulations for reference formulations".

The goal of the milestone was the selection of a limited number of optimised formulations to be used in Subtasks T5.3.4 and T5.3.5 for the investigation of reference formulations with real RLOW and direct conditioning process scale-up.

A large number of formulations were developed and tested within Task 5.3.3 (see Table 75). Among such big variety, the selection of the most promising formulations was based on qualitative analysis of the available data.

Table 75 *List of considered Formulations*

	Option	**Formulation**	**Waste**
Oil	1	MK - Metamax®	Nevastane oil
	2	MK - Argicem®	Nevastane oil
	3	MK - Metamax®	Repsol supertauro 100 oil
	4	MK-BFS-FA (Ukr)	Shellspirax oil
	5	MK-BFS-FA (Ukr)	Nevastane oil
	6	MK-BFS-FA - Metamax®-Ecotrade-FA IT	Nevastane oil
	7	MK-BFS-FA - Metamax®-Ecotrade-FA IT	Shellspirax oil
	8	MK-BFS-FA - Metamax®-Ecocem-FA IT	Nevastane oil
	9	MK-BFS-FA - Metamax®-Ecocem-FA IT	Shellspirax oil
	10	BFS + Sand	Nevastane oil
	11	BFS + Sand	Shellspirax oil
TBP-dodecane	12	MK - Metamax®	TBP-Dodecane (70-30)[6]
	13	MK - Argicem®	TBP-Dodecane (70-30)[1]
	14	MK-BFS-FA - Metamax®-Ecocem-FA IT	TBP-Dodecane (30-70)
Scintill cocktails	15	MK-BFS-FA - italian MK-BFS IT-FA IT	scintill
	16	MK - Metamax®	scintill INSTAGEL plus
	17	BFS + Sand	scintillation cocktail (UG AB)

The set of criteria used for the evaluation, agreed between the T5.3 Partners, are described in the following Table 76.

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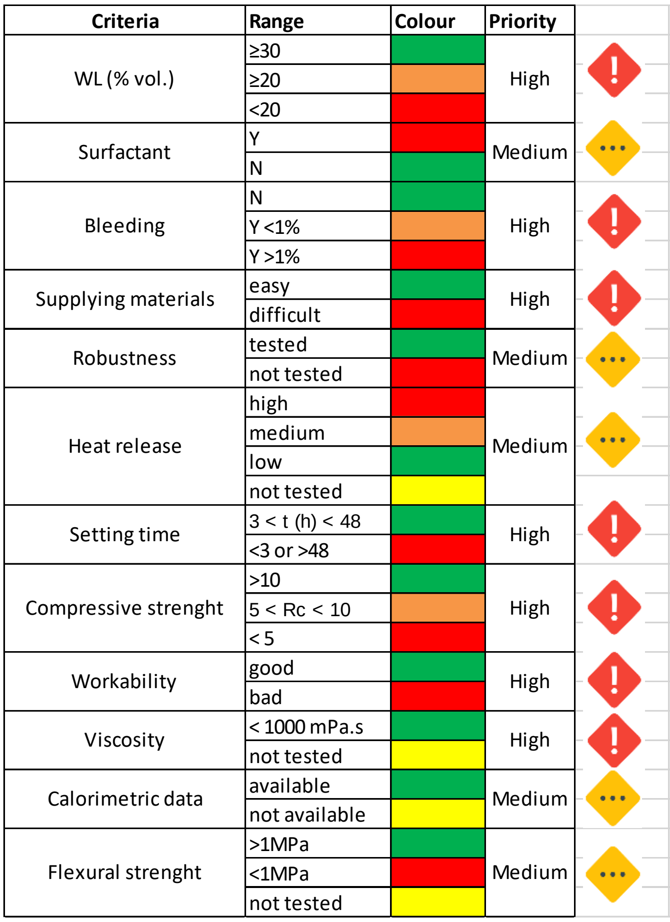
[6]. Additional studies with TBP-Dodecane (30-70) are still ongoing

Table 76 *List of Criteria for formulations selection*

Criteria	**Description**	**Criteria**	**Description**
WL (% vol.)	Percentage by volume of Waste Loading	Setting time	Time needed for the matrix to set
Surfactant	Presence of any surfactant in the formulation	Compressive strength	Measured after 28 days of curing
Bleeding	Percentage by volume of water or waste not incorporated in the matrix	Workability	Qualitative evaluation of the workability of the fresh paste
Supplying materials	Difficulty of supplying of raw materials	Viscosity	Of the fresh paste
Robustness	Availability of results on robustness tests for the reference formulation	Calorimetric data	Availability of calorimetric data
Heat release	Rough evaluation of the amount of heat released from the matrix during the hardening	Flexural strength	Measured after 28 days

For each criteria a specific range was established, and a colour-based scale was used for the qualitative analysis of proposed formulations. Additionally, different priorities (high and medium) were assigned to the defined criteria (see Table 77).

Table 77 *Criteria range and priority*



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

Prior to the meeting each partner was asked to fill the table with the properties referred to their own formulation. The collected data are reported in the following Table 78.

A matrix (see Table 79) was obtained using the colour-base evaluation of the criteria from Table 77.

The matrix was discussed and additional information was given by the partners during the meeting to focus the selection of the optimised formulations to a limited number of options.

For the oily waste it was agreed to move forward with the optimised formulation for each of the three reference formulations under study (MK based, MIX based, BFS based), leaving to T5.3.4 and T5.3.5 partners the possibility to choose one or more than one for the real waste testing and the process scale up.

For the MK based formulation, Metamax® system was selected due to its high reactivity compared to the Argicem® system

For the MIX based formulation: the French BFS (Ecocem) was selected due to the availability of raw materials, compare to the Ukrainian one.

For all three optimised formulations it was decided to use Nevastane oil as RLOW surrogate due to the better incorporation rate.

For the solvent waste and the scintillation cocktail the choice of the formulation was focused on the one with higher waste loading and who had the most complete set of data to date.

The selected formulations are highlighted in blue in the Table 79 and they are considered as the Milestone 34 “Optimised formulations for reference formulations”.

***Table 78** Data collected for the different Formulations*

				Criteria	**WL %, (vol%)**	**Surfactant**	**Bleeding %**	**Supplying materials**	**Robustness**	**Heat release**	**Setting time h**	**Compressive strenght MPa**	**Workability**	**Viscosity**	**Calorimetric data**	**Flexural strenght**
	Option	**Formulation**	**waste**	**Range**	***≥30; ≥20; <20***	***Y (xx%); N***	***Y >1%; Y<1%; N***	***easy; difficult***	***Y (tested); N (not tested)***	***high; medium; low; N (not tested)***	***3 < t (h) < 48; <3 or >48***	***>10; 5 < Rc < 10; < 5***	***good / bad***	***< 1000 mPa.s; N (not tested)***	***Y (available); N (not available)***	***> 1MPa; N (not tested)***
OIL	1	MK Metamax	Nevastane oil		≥30	N	y<1.25 vol%	easy	Y	high	24	>10	good	<1250	Y	> 1MPa
	2	MK Argicem	Nevastane oil		≥30	N	y<1 vol%	easy	Y	medium	24	>10	good	<1000	Y	> 1MPa
	3	MK Metamax	Repsol supertauro 100 oil		≥30	N	N	easy	Y	N	3-48 h	>10	good	not tested	N	N
	4	MK-BFS-FA (Ukr)	Shellspirax oil		≥30	Y (0,5% wt)	N	easy	Y	N	24	>10	good	At minimum speed (0,5-1 rpm) the viscosity is >1000 mPa•s, at higher speed (50-100 rpm) the viscosity is <1000 mPa•s.	N	N
	5	MK-BFS-FA (Ukr)	Nevastane oil		≥30	N	N	easy	Y	N	24	>10	good		N	N
	6	MK-BFS-FA metamax-Ecotrade-FA IT	Nevastane oil		≥30	Y (0,5% w/w)	N	difficult BFS and FA	Y	N	3-48 h	5 < Rc < 10	good	N	N	N
	7	MK-BFS-FA metamax-Ecotrade-FA IT	Shellspirax oil		≥30	Y (0,5% w/w)	N	difficult BFS and FA	Y	N	3-48 h	5 < Rc < 10	good	N	N	N
	8	MK-BFS-FA metamax-Ecocem-FA IT	Nevastane oil		≥30	N	N	easy	Y	n.a.	3-48 h	>10	good	n.a.	Y	N
	9	MK-BFS-FA metamax-Ecocem-FA IT	Shellspirax oil		≥30	N	N	easy	Y	n.a.	3-48 h	>10	good	n.a.	Y	N
	10	BFS + Sand	Nevastane oil		≥30	Y (0,5% w/w)	N	easy	Y	low heat release	3-48 h	>10	good	< 1000	Y	> 1MPa
	11	BFS + Sand	Shellspirax oil		≥30	Y (0,5% w/w)	N	easy	Y	low heat release	3-48 h	>10	good	< 1000	Y	> 1MPa
TBP-dodecane	12	MK Metamax	TBP-Dodecane (70-30)		≥30	Y (1-3vol%)	Y<2 vol%	easy	Y	high	24	>10	good	<2900	Y	> 1MPa
	13	MK Argicem	TBP-Dodecane (70-30)		≥30	Y (1-3vol%)	Y<1 vol%	easy	Y	medium	24	>10	good	<1000	Y	> 1MPa
	14	MK-BFS-FA metamax-Ecocem-FA IT	TBP-Dodecane (30-70)		≥30	Y	N	difficult FA	N	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
scintill cocktails	15	MK-BFS-FA italian MK-BFS IT-FA IT	scintillation cocktail		> 20	N	N	easy	N	N	3-48 h	5 < Rc < 10	good	not tested	N	N
	16	MK Metamax	scintill INSTAGEL plus		≥30	N	N	easy	N	N	3-48 h	>10	good	not tested	N	N
	17	BFS + Sand	scintillation cocktail (UG AB)		> 20	Y (0,5% w/w)	N	difficult	Y	N	3-48 h	>10	good	not tested	N	N

***Table 79** Matrix for qualitative evaluation of Formulations*

				Priority	H ❗	M ⋯	H ❗	H ❗	M ⋯	M ⋯	H ❗	H ❗	H ❗	H ❗	M ⋯	M ⋯
	Option	Formulation	Waste	Criteria	WL %, (vol%)	Surfactant	Bleeding %	Supplying materials	Robustness	Heat release	Setting time h	Compressive strenght MPa	Workability	Viscosity	Calorimetric data	Flexural strenght
OIL	**1**	**MK - Metamax**	**Nevastane oil**		🟩	🟩	🟥	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩
	2	MK - Argicem	Nevastane oil		🟩	🟩	🟧	🟩	🟩	🟧	🟩	🟩	🟩	🟩	🟩	🟩
	3	MK - Metamax	Repsol supertauro 100 oil		🟩	🟩	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟨	🟨	🟨
	4	MK-BFS-FA (Ukr)	Nevastane oil		🟩	🟩	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟨	🟨
	5	MK-BFS-FA (Ukr)	Shellspirax oil		🟩	🟥	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟨	🟨
	6	MK-BFS-FA (metamax-Ecotrade-FA IT)	Nevastane oil		🟩	🟥	🟩	🟥	🟩	🟨	🟩	🟧	🟩	🟨	🟨	🟨
	7	MK-BFS-FA (metamax-Ecotrade-FA IT)	Shellspirax oil		🟩	🟥	🟩	🟥	🟩	🟨	🟩	🟧	🟩	🟨	🟨	🟨
	8	**MK-BFS-FA (metamax-Ecocem-FA IT)**	**Nevastane oil**		🟩	🟩	🟩	🟩	🟩	⬜	🟩	🟩	🟩	⬜	🟩	🟨
	9	MK-BFS-FA (metamax-Ecocem-FA IT)	Shellspirax oil		🟩	🟩	🟩	🟩	🟩	⬜	🟩	🟩	🟩	⬜	🟩	🟨
	10	**BFS + Sand**	**Nevastane oil**		🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
	11	BFS + Sand	Shellspirax oil		🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
TBP-dodecane	**12**	**MK - Metamax**	**TBP-Dodecane (70-30)**		🟩	🟥	🟥	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩
	13	MK - Argicem	TBP-Dodecane (70-30)		🟩	🟥	🟧	🟩	🟩	🟧	🟩	🟩	🟩	🟩	🟩	🟩
	14	MK-BFS-FA (metamax-Ecocem-FA IT)	TBP-Dodecane (30-70)		🟩	🟥	🟩	🟥	🟥	⬜	⬜	⬜	⬜	⬜	⬜	⬜
scintill cocktails	15	MK-BFS-FA (MK-BFS-FA IT)	scintill		🟧	🟩	🟩	🟩	🟥	🟨	🟩	🟧	🟩	🟨	🟨	🟨
	16	**MK - Metamax**	**scintill INSTAGEL plus**		🟩	🟩	🟩	🟩	🟥	🟨	🟩	🟩	🟩	🟨	🟨	🟨
	17	BFS + Sand	scintillation cocktail (UG AB)		🟧	🟥	🟩	🟥	🟩	🟨	🟩	🟩	🟩	🟨	🟨	🟨

5.6 Pre-impregnation methodology

Besides the direct conditioning option studied by most of the partners, a two-step pre-impregnation methodology has also been investigated by POLIMI in the scope of T5.3.

This methodology is presented in flowchart in Figure 116. The first step consists of mixing the RLOW with the absorber. As mentioned in Chapter 4.4.2.2, an absorption of RLOW occurs in the polymer cavities with no chemical bonds between polymer and waste. Afterwards, the absorber impregnated with RLOW is encapsulated in a geopolymeric matrix resulting in a final waste form.

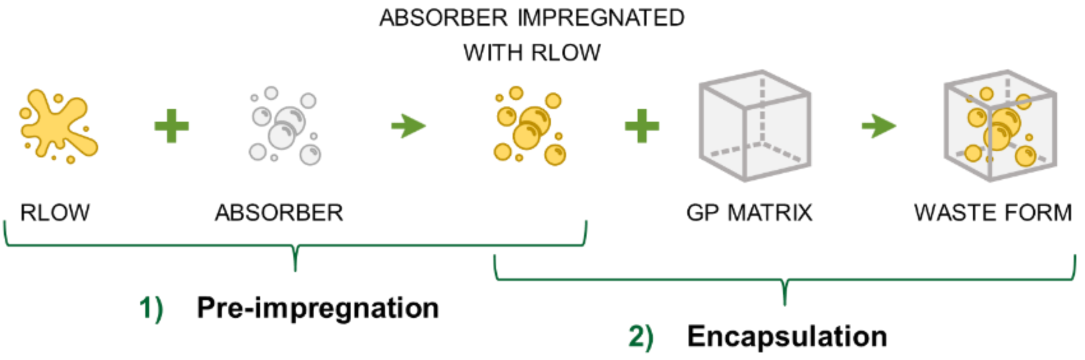


Figure 116 Flowchart of pre-impregnation methodology

The variables studied during both steps are given below:

- Pre-impregnation
    - RLOW (type, amount)
    - absorber (type, amount)
    - matrix (type, amount, rheology)
- Encapsulaton
    - RLOW/absorber ratio
    - RLOW loading factor
    - impregnation-encapsulation order

The following materials have been used during the testing:

- Waste: liquid scintillation cocktail (LSC) and tributyl-phosphate/kerosene (TPB-K) mixture
- Absorber: recycled polyurethane (rPU)
- Matrix: tuff-based geopolymer
    - precursors: BFS, Fly ash, Volcanic tuff

The operating conditions are listed below:

- Waste-to-absorber: 1:1 and 2:1 mass ratio
- Waste loading factor: 10 and 20% wt.
- Procedure: mixing of pre-impregnated waste in matrix fresh grout

First, the feasibility of pre-impregnation has been studied. The samples without waste with different rPu loading are shown in Figure 117.

As for the samples with waste, during the pre-impregnation step LSC and TBP-k were successfully absorbed on rPU. However, during the encapsulation rPU degradation has been observed which led to the formation of cavities and bleeding of RLOW (see Figure 118).

Figure 117 *Samples with different rPU loading (no RLOW): left – 0 wt.%, middle – 5 wt.%, right 10 wt.%*

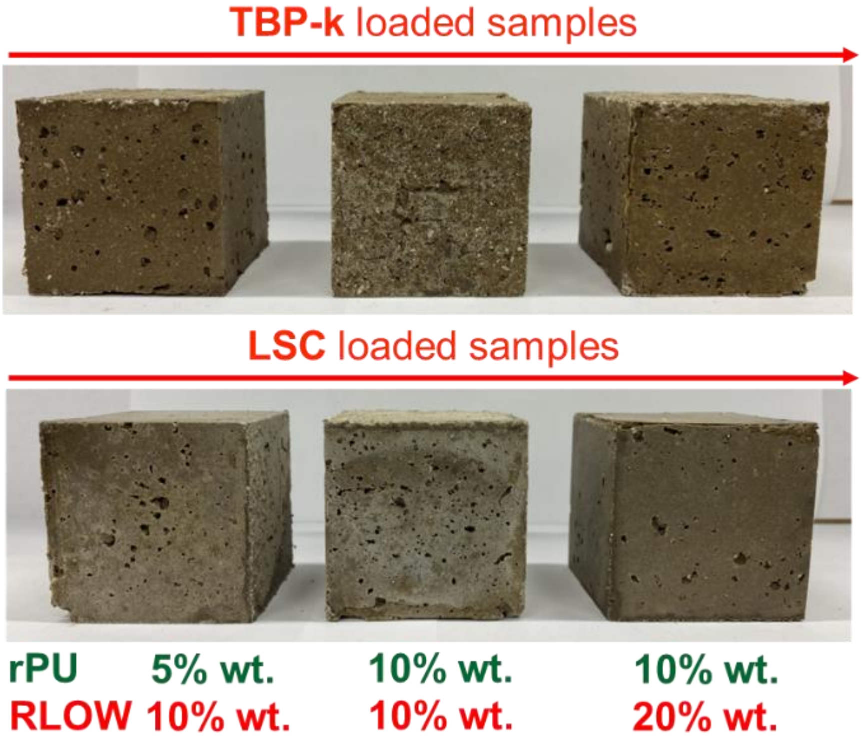


Figure 118 *Samples with different rPU and RLOW loading*

Effect of rPU and RLOW loading on mechanical strength has been studied (see Table 80). The samples showed a compressive strength degradation (Italian WAC = 10 MPa).

Table 80 *Mechanical strength results for rPU samples, *- samples with RLOW bleeding [10]*

Sample No.	GP [%wt.]	rPU [%wt.]	TBP-k [%wt.]	LSC-UG [%wt.]	R_c [MPa]
1	**100**	0	0	0	23.7 ± 1.9
2	**95**	5	0	0	7.7 ± 0.8
3	**90**	10	0	0	1.1 ± 0.2
4	**85**	5	10*	0	4.3 ± 0.5
5	**80**	10	10*	0	1.5 ± 0.2
6	**70**	10	20*	0	1.0 ± 0.2
7	**85**	5	0	10*	3.3 ± 0.5
8	**80**	10	0	10*	1.9 ± 0.3
9	**70**	10	0	20*	1.0 ± 0.2

The samples used to study the effect of rPU and RLOW loading on immersion stability (according to ANSI-ANS 16.1) are shown in Figure 119. Preservation of structural integrity but RLOW release upon water immersion can be observed. A slight TBP-k release can be observed for samples No.4-6 and high LSC release can be observed for samples No.7-9. The leachant around sample No.9 was of milky appearance, as can be seen in Figure 119, which can also indicate the presence of leaching.

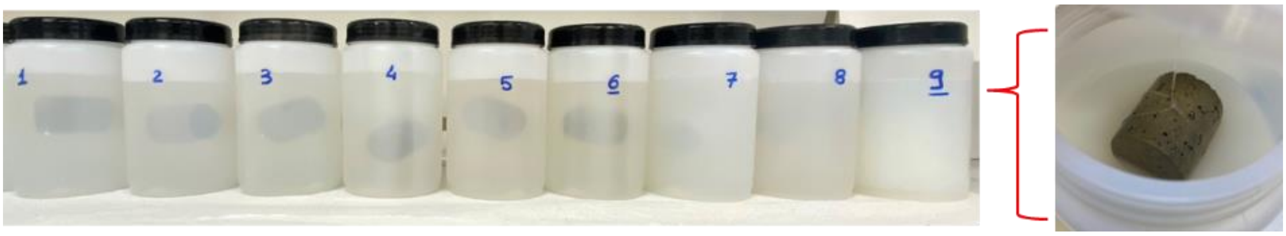


Figure 119 *On the left - samples used to study the effect of rPU and RLOW loading on immersion stability, on the right - a sample surrounded by leachant of a milky consistency.*

The rPU degradation was further studied. The X-ray diffractograms with different rPU and waste loading are shown in Figure 120. Preservation of the geopolymer mineralogic structure even in presence of rPU and RLOW as well as the preservation of parental chabazite zeolite (*) upon geopolymerisation can be observed.

There is an increase of carbonate peak (highlighted by a black frame in the figure) which is consistent with the rPU hydrolysis in alkaline media. This produces CO_2 which then undergoes carbonation, confirmed by TGA. This result is coherent with the observed rPU degradation.

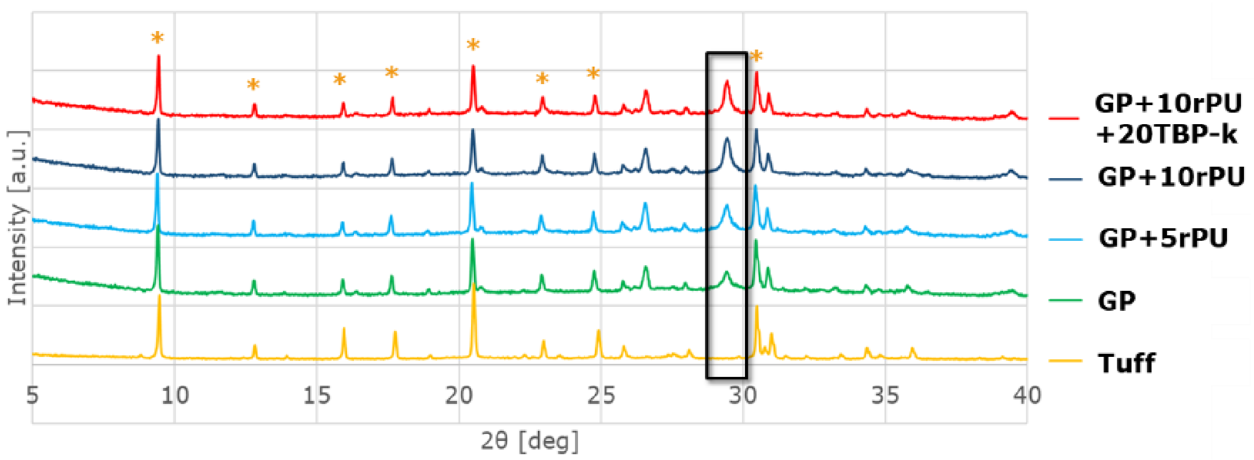


Figure 120 *X-ray diffractograms of samples with different rPU and waste loading, *- chabazite zeolite peaks*

As a result of this observations, it was decided that the matrix and absorber were incompatible. It was decided to test NOCHAR N910 as absorber.

The materials used for testing were similar materials used for rPU tests:

- Waste: liquid scintillation cocktail (LSC) and tributyl-phosphate/kerosene (TPB-K) mixture
- Absorber: NOCHAR N910
- Matrix: tuff-based vs BFS-based geopolymer

The operating conditions were slightly changed:

- Waste-to-absorber: up to 3:1 mass ratio
- Waste loading factor: 10 and 20% wt.
- Procedure: testing of different orders of addition

The RLOW was successfully absorbed during the pre-impregnation step on N910. After the encapsulation in geopolymer, no cavities nor RLOW bleeding were observed (see Figure 121).

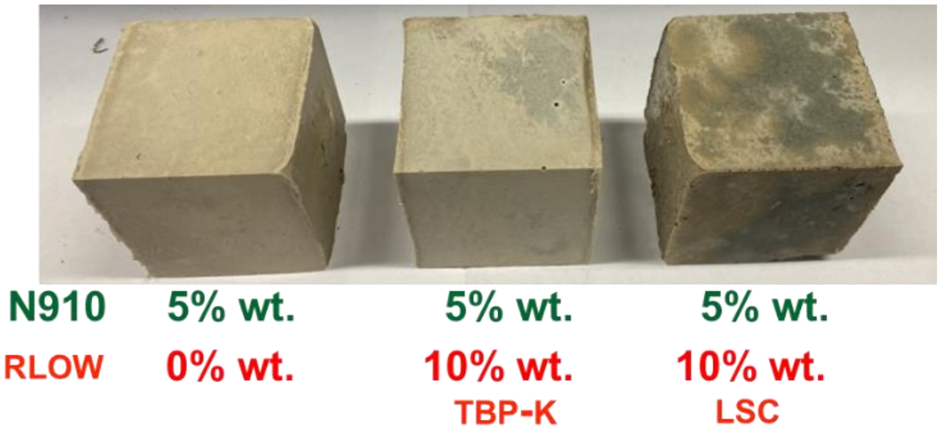


Figure 121 *Samples with NOCHAR N910 absorber and different RLOW*

The compressive strength of the samples with NOCHAR N910 was also higher that the compressive strength of rPU samples, as shown in Table 81 (Italian WAC = 10 MPa).

Table 81 *Compressive strength results with NOCHAR N910, *- RLOW bleeding*

GP [%wt.]	rPU [%wt.]	N910 [%wt.]	TBP-k [%wt.]	LSC-UG [%wt.]	R_c [MPa]
100	0	0	0	0	23.7 ± 1.9
95	5	0	0	0	7.7 ± 0.8
95	0	5	0	0	13.4 ± 1.4
85	5	0	10*	0	4.3 ± 0.5
85	0	5	10	0	5.9 ± 0.7
85	5	0	0	10*	3.3 ± 0.5
85	0	5	0	10	10.4 ± 1.1

However, upon mixing of the absorber with TBP-k swelling was observed due to enlargement of heterogeneities in the waste form (see Figure 122).

Figure 122 *Mixing of the NOCHAR N910 with TBP-k*

At higher RLOW/absorber ratios bleeding was observed:

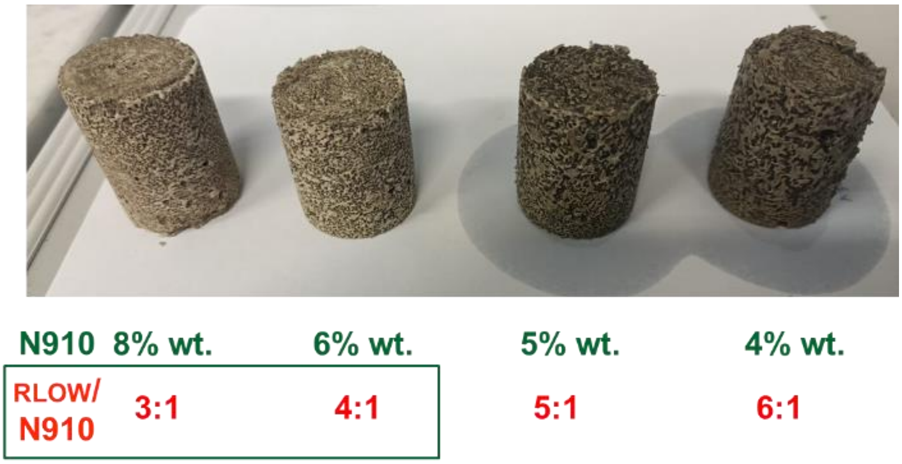


Figure 123 *Samples with different RLOW/absorber ratios*

To overcome this issue, N910 optimization was attempted. Different orders of addition have been tested to avoid heterogeneities in the final waste form. The most promising order of addition is shown below:

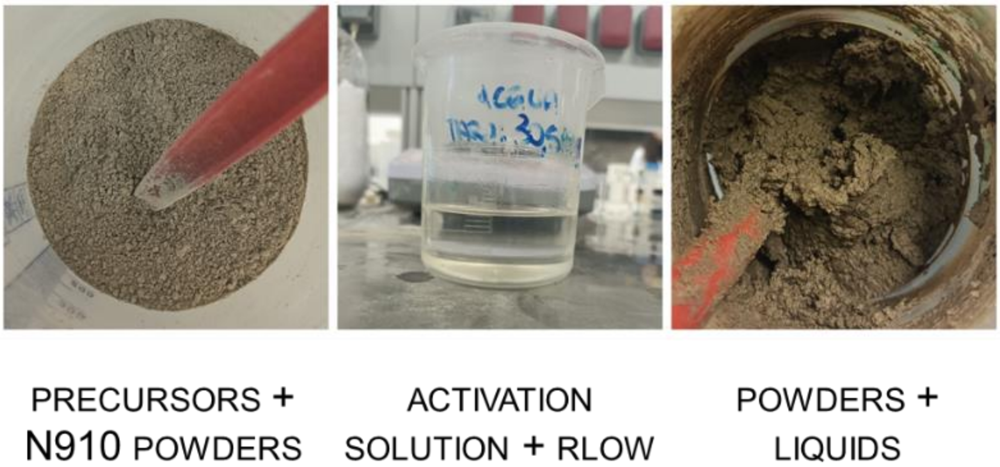


Figure 124 *Most promising order of addition*

Compressive strength of samples produced with old and new procedure and with different geopolymers (tuff and BFS-based formulations) is shown in Table 82. The new procedure (Figure 124) seems to result in better compressive strength. BFS-based formulations used during encapsulation seem to be also yield higher compressive strength compared to the ones using VT.

Table 82 *Tuff and BFS-based formulations*

	Tuff-GP [%wt.]	**BFS-GP [%wt.]**	**N910 [%wt.]**	**TBP-k [%wt.]**	**R_c [MPa]**
	100	0	0	0	23.7 ± 1.9
	0	100	0	0	55.0 ± 11
Old procedure	85	0	5	10	5.9 ± 0.7
New procedure	85	0	5	10	8.1 ± 1.4
New procedure	0	85	5	10	14.1 ± 1.9

Several conclusions can be made considering the obtained results:

- N910 is a better RLOW absorber as it is compatible with alkaline matrices
- The heterogeneity could reduce the waste form durability and mechanical strength
- BFS-based matrix could produce better results

Further experiments are required to identify the best conditions:

- Order of addition
- RLOW/absorber ratio
- Encapsulating matrix

6 Investigation of reference formulations with real RLOW

6.1 UJV Rez activities

The study of the binding and leaching of ^{63}Ni and ^{14}C radionuclides from real liquid organic waste (RLOW).

The following tests were performed:

- Compressive strength
- ^{63}Ni and ^{14}C radionuclide sorption tests
- ^{63}Ni and ^{14}C radionuclide leaching tests

6.1.1 The material used and the preparation of the mixtures

Blast furnace slag (***BFS***) and metakaolin based geopolymers (***GP***) were used by UJV to incorporate two RLOW prepared in their laboratory: a ***scintillation cocktail*** and an ***ionic solution***. As the real RLOWs available had low level of radioactivity (0.56 Bq/ml of ^{14}C and 0.84 Bq/ml of ^{63}Ni in the scintillation cocktail and 12.05 Bq/ml of ^{14}C and 11.04 Bq/ml of ^{63}Ni in the ionic solution), small amounts of radioactive solutions (1.5 ml of ^{63}Ni and 1.5 ml of ^{14}C solutions) were added to increase the activity concentrations of the monitored radionuclides.

The final radioactivity of RLOW used, expressed in „CPM“ (counts per minute), were:

- 37 380 597 CPM/100 ml: ^{63}Ni in the scintillation cocktail (~ 0.8 MBq/100 ml)
- 37 420 944 CPM/100 ml: ^{63}Ni in the ionic solution (~ 0.81 MBq/100 ml)
- 150 003 114 CPM/100 ml: ^{14}C in the scintillation cocktail (~ 2.5 MBq/100 ml)
- 150 069 489 CPM/100 ml: ^{14}C in the ionic solution (~ 2.56 MBq/100 ml)

Suitable components (alkali activators, sand, water) were added to obtain homogeneous mixtures.

Inactive BFS and GP mixtures were also prepared for compressive strength measurements and sorption testing.

UJV followed recipes recommended by CVR (Research Centre Rez) for the preparation of the inactive mixtures. The matrix materials (of Czech origin) were also provided by colleagues from CVR.

The following materials were used in the experiments

Matrix

- Blast furnace slag
- Geopolymer – metakaolin & activator

RLOW (with addition of ^{63}Ni and ^{14}C solutions)

- Scintillation cocktail
- Ionic solution

Activating solution: mixture of $Na_2O.3SiO_2$ and 10M NaOH

Aggregate: Sand

Details of the characteristics of the materials used are provided in the PREDIS 5.3 technical report. A summary of the materials and their weights is provided in Table 83.

Table 83 *Materials used for the BFS and GP mixtures*

Matrix		**MK**	**Activator**	**RLOW** *(addition of 1.5 ml $^{63}Ni/^{14}C$)*			**$Na_2O.3SiO_2$**	**10M NaOH**		**Sand**	**Add. water**	**wt% of RLOW fulfillment**
	g	g	g		ml	g	g	ml	g	g	g	
BFS	465.44			scintalliation cocktail	100.0	86.3	15.15	46.87	62.33	279.93	50.0	**9.9**
	465.44			ionic liquid	100.0	118.0	15.15	46.87	62.33	279.93	50.0	**13.5**
GP		600.0	400.0	scintillation cocktail	100.0	86.3						**8.6**
		600.0	400.0	ionic liquid	100.0	118.0						**11.8**

Mixing procedure (small scale using at laboratory mixer):

- Production of NaOH 10M solution from NaOH pellets and the cooling of the solution to room temperature
- Dissolution of sodium silicate in the NaOH solution
- Mixing the BFS + NaOH solution + RLOW + water for 10 minutes
- Addition of sand and mixing for a further 3 minutes
- Mixing the GP + RLOW for 10 minutes

The resulted mortars (cubes of 50 x 50 x 50 mm, 20 ml cylinders) were cured under controlled wet conditions in a closed box for 28 days (Figure 125), following which the samples were removed from the moulds and subjected to testing (Figure 126).

Figure 125 *Curing of the samples in a closed box with the addition of water*

Figure 126 *Matured samples*

6.1.2 Testing of the samples

6.1.2.1 Compressive strength tests

Compressive strength tests were performed by UJV for both inactive and radioactive mortars, using a „MEGA 11-300 DM1-S“ press (see Figure 127). 3 or 4 cubic samples were tested for each mixture.

Figure 127 *MEGA 11-300 DM-1-S Presser*

Table 84 *Results of the compressive strength tests*

Compressive Strength [MPa]			addition of ^{63}Ni	addition of ^{14}C
inactive BFS matrix	**20.64**	BFS + scintillation cocktail	**19.88**	**13.28**
		BFS + ionic liquid	**21.37**	**21.59**
inactive GP matrix	**21.11**	GP + scintillation cocktail	**25.71**	**18.6**
		GP + ionic liquid	**21.93**	**16.51**

As indicated by the results shown in Table 84, no significant differences were observed between the radioactive and inactive mixtures after 28 days of curing. The maximum strength was obtained for the „GP + scintillation cocktail with the addition of ^{63}Ni“ mixture: 25.71 MPa.

6.1.2.2 Sorption tests

^{63}Ni and ^{14}C sorption on the BFS and GP matrices was investigated. Matrices material was grinded and sieved to obtained material at mesh size < 0.5 mm. 1 g and 0.5 g of inactive samples were applied in sorption experiments and contacted with 5 ml of liquid phase with radioactive tracer (activity of ^{63}Ni: 26 000-30 000 CPM, activity of ^{14}C: 17 000-22 000 CPM).

„Hidex“ liquid scintillation spectrometer (which detects both α and ß radiation) was used for the measurement of the samples collected during the sorption tests (Figure 128). The measurement process involved the weekly sampling of the liquid phases (0.5 ml) over a period of 7 – 49 days with the addition of the scintillation cocktail (4 ml).

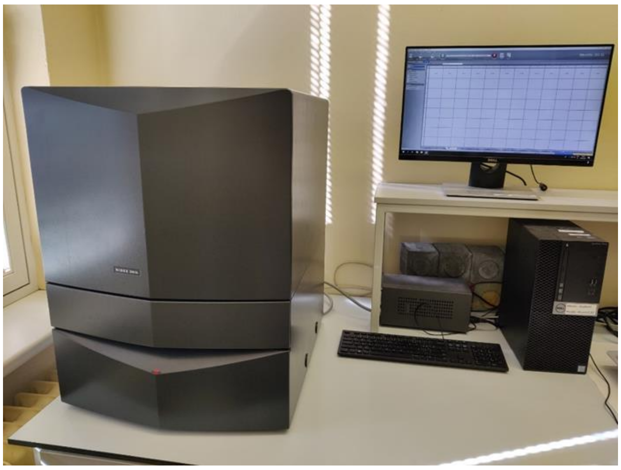


Figure 128 *The Hidex liquid scintillation spectrometer*

Two parameters – the distribution ratio „Rd“ and the sorption efficiency „ŋ“ – were subsequently calculated from the resulting data „CPM“.

The results of the ^{63}Ni sorption tests on the BFS and GP matrices are presented in Table 85 - Table 88 and the results of the ^{14}C sorption tests are presented in Table 89 - Table 92. The results are displayed in graph form for reasons of clarity, Figure 131 - Figure 136.

^{63}Ni sorption

Table 85 *The "Rd" distribution ratio values, ^{63}Ni sorption on the BFS matrix*

BFS / ^{63}Ni	1 g (< 0.5 mm), S/L=1/5	0.5 g (< 0.5 mm), S/L=1/10
day	Rd [ml/g]	Rd [ml/g]
7	154.7812655	388.053472
14	222.5568649	556.2222339
21	279.568759	577.832733
28	239.415398	710.602171
35	309.792831	575.9396675
42	283.128959	694.3427524
49	370.5722302	740.6010988

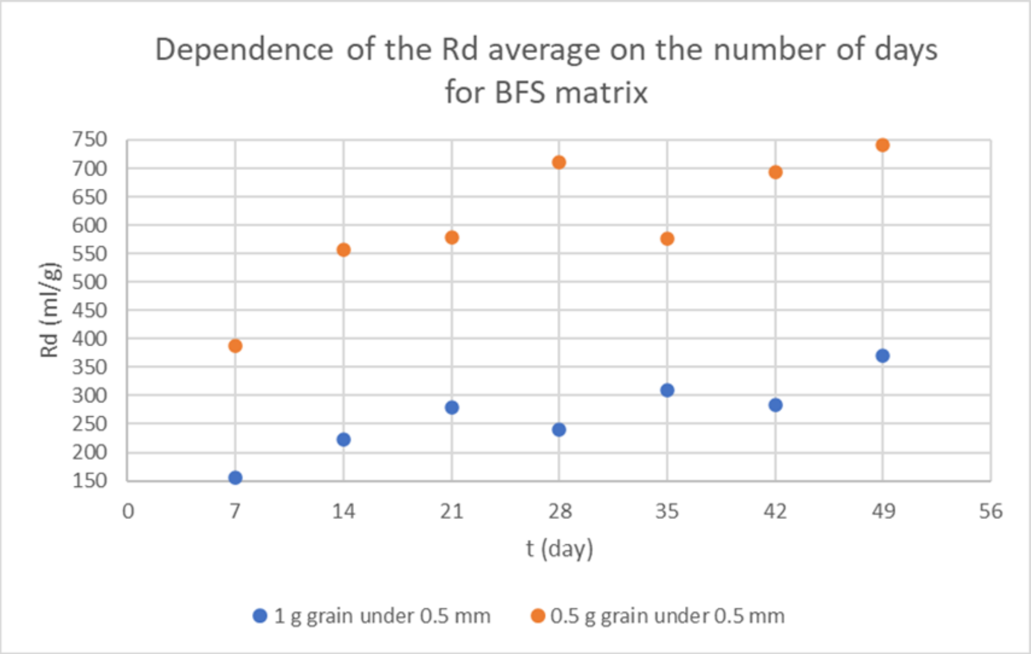


Figure 129 *Time dependence of the "Rd" (^{63}Ni sorption on the BFS matrix)*

Table 86 *The „η" sorption efficiency values, ^{63}Ni sorption on the BFS matrix*

BFS / ^{63}Ni	1 g grain under 0.5 mm	0.5 g grain under 0.5 mm
day	η	Ŋ
7	0.967197844	0.974465189
14	0.977499956	0.982404625
21	0.982448951	0.982821476
28	0.980281315	0.986204554
35	0.985251398	0.98286492
42	0.982490877	0.98561539
49	0.987348427	0.987474319

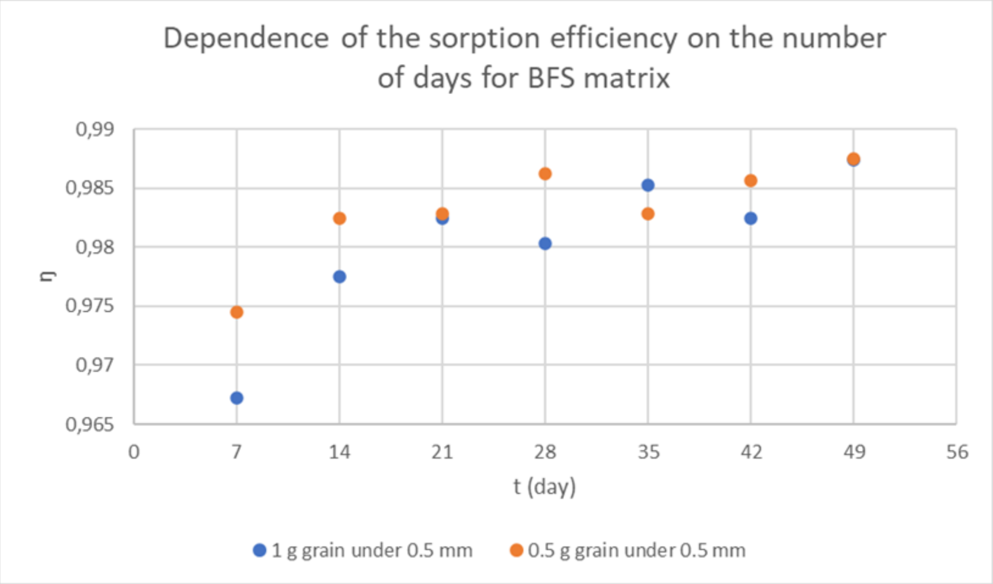


Figure 130 *Time dependence of the „η" (^{63}Ni sorption on the BFS matrix)*

Table 87 *The "Rd" distribution ratio values, ^{63}Ni sorption on the GP matrix*

GP / ^{63}Ni	1 g (< 0.5 mm), S/L=1/5	0.5 g (< 0.5 mm), S/L=1/10
day	Rd [ml/g]	Rd [ml/g]
7	327.4422	617.412533
14	549.334033	828.94163
21	529.4647	891.819067
28	508.669633	972.140533
35	559.7218	914.8396
42	512.1626	892.032633
49	422.096433	1016.860767

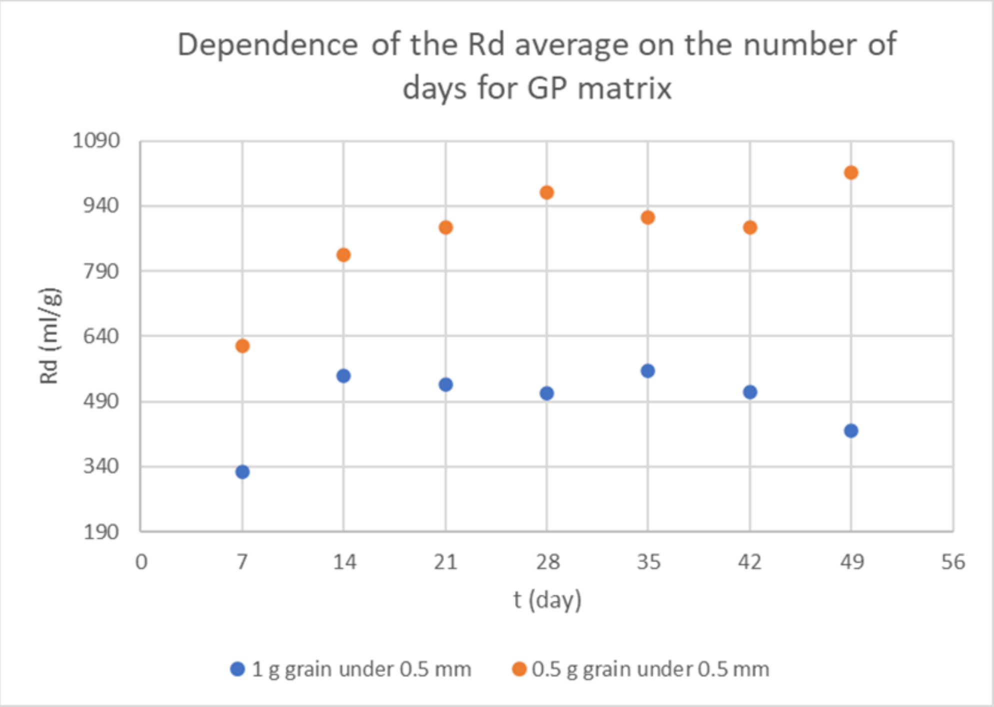


Figure 131 *Time dependence of the "Rd" (^{63}Ni sorption on the GP matrix)*

Table 88 *The „ŋ“ sorption efficiency values, ^{63}Ni sorption on the GP matrix*

GP / ^{63}Ni	1 g grain under 0.5 mm	0.5 g grain under 0.5 mm
day	ŋ	ŋ
7	0.984771607	0.983978806
14	0.991168184	0.98849785
21	0.990542243	0.98961787
28	0.990532387	0.989706924
35	0.990719423	0.989754432
42	0.990470766	0.989057747
49	0.988204249	0.990670428

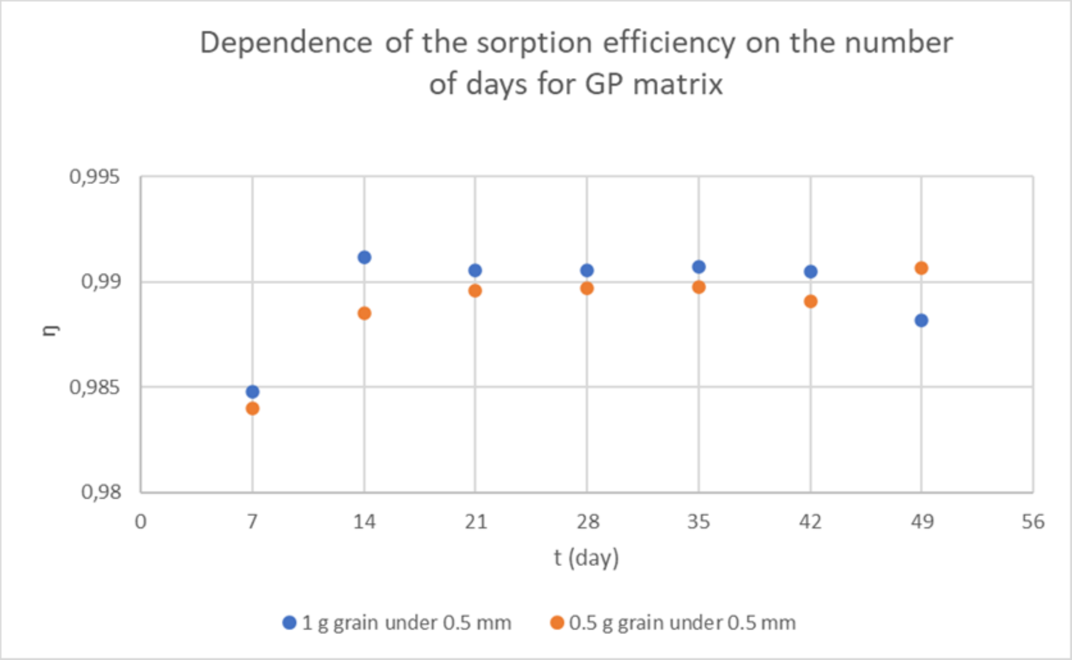


Figure 132 *Time dependence of „ŋ“ (^{63}Ni sorption on the GP matrix)*

6.1.2.2.1 Results of the ^{63}Ni sorption tests

Linear distribution coefficient **Rd**: The samples with lower weights (0.5 g) evinced higher Rd values in the case of both matrices, BFS and GP. The maximum values were recorded for the samples after 49 days of matrix solution interaction (Figure 129, Figure 131).

Sorption efficiency **ŋ**: Significant increases in the ŋ were evident for the initial sampling period (days 7 and 14) for both matrices, BFS and GP. The values were relatively stable from day 14 onwards (Figure 130, Figure 132).

^{14}C sorption

Table 89 *The "Rd" distribution ratio values, ^{14}C sorption on the BFS matrix*

BFS / ^{14}C	1 g (< 0.5 mm), S/L=1/5	0.5 g (< 0.5 mm), S/L=1/10
day	Rd (ml/g)	Rd (ml/g)
7	1,6652763	2,869172969
14	1,7296233	3,1338732
21	1,2267544	2,4578388
28	1,305079808	2,5183747
35	1,75158833	3,14056399
42	1,3406298	2,18649108
49	1,1806594	2,102916

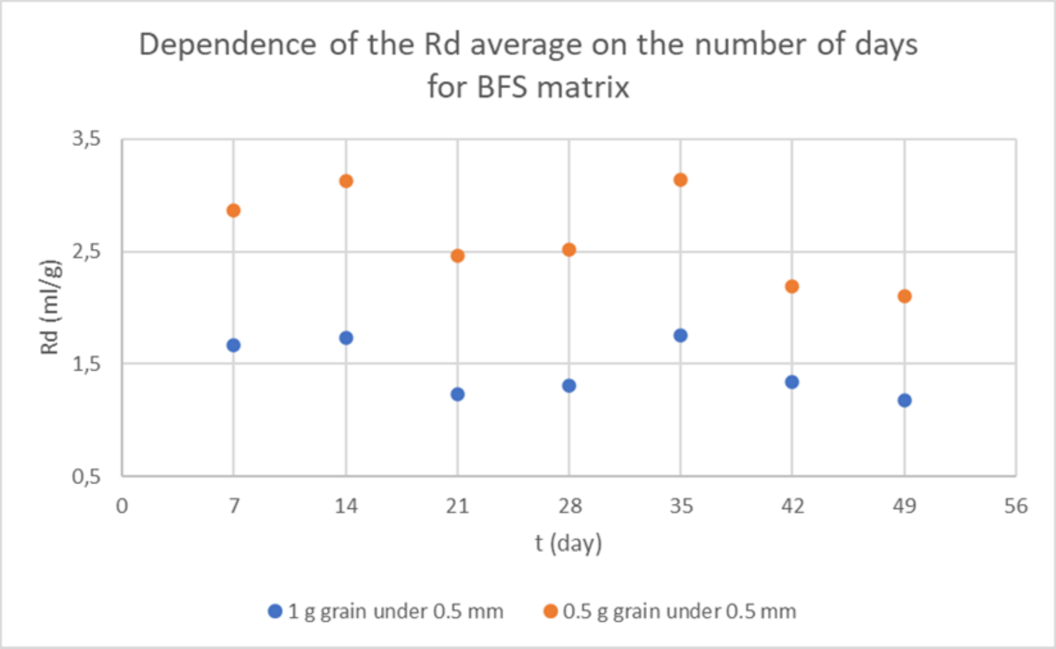


Figure 133 *Time dependence of the "Rd" (^{14}C sorption on the BFS matrix)*

***Table 90** The „ŋ“ sorption efficiency values, ^{14}C sorption on the BFS matrix*

BFS / ^{14}C	1 g grain under 0.5 mm	0.5 g grain under 0.5 mm
day	ŋ	ŋ
7	0,262180096	0,200224344
14	0,255623991	0,237963345
21	0,195822749	0,19161757
28	0,203768661	0,198755402
35	0,255681789	0,245349839
42	0,210612957	0,168597204
49	0,178983474	0,159766252

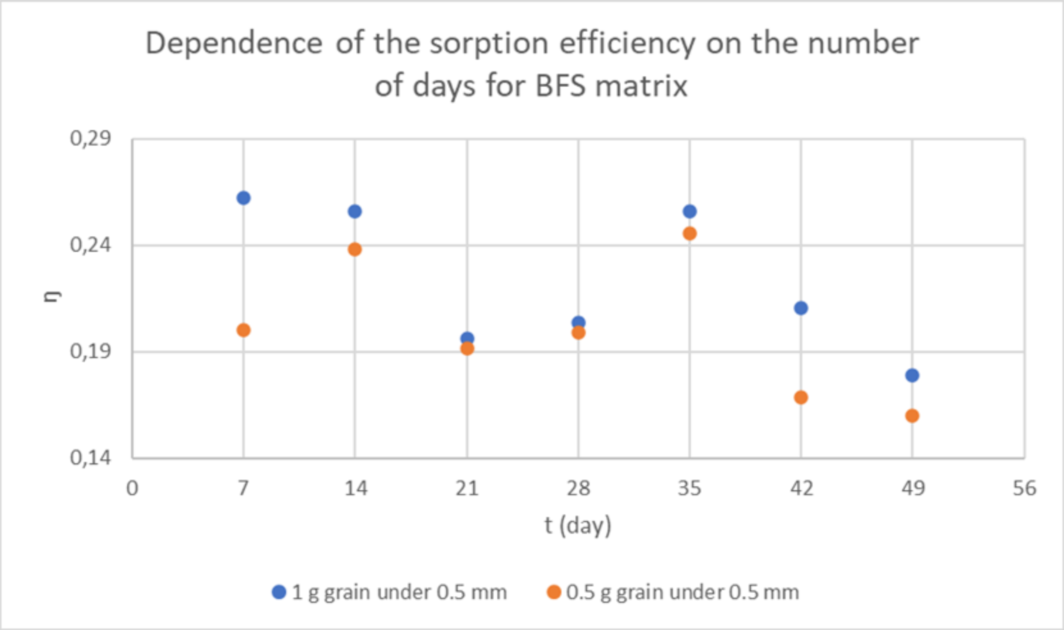


***Figure 134** Time dependence of the „ŋ“ (^{14}C sorption on the BFS matrix)*

Table 91 *The "Rd" distribution ratio values, ^{14}C sorption on the GP matrix*

GP / ^{14}C	1 g (< 0.5 mm), S/L=1/5	0.5 g (< 0.5 mm), S/L=1/10
den	Rd (ml/g)	Rd (ml/g)
7	0,890251	2,110596
14	0,7401833	1,03244133
21	0,3703533	0,59444033
28	0,49491667	0,32609333
35	0,42220367	0,86466
42	0,3350223	0,6423303
49	0,416183	0,47412233

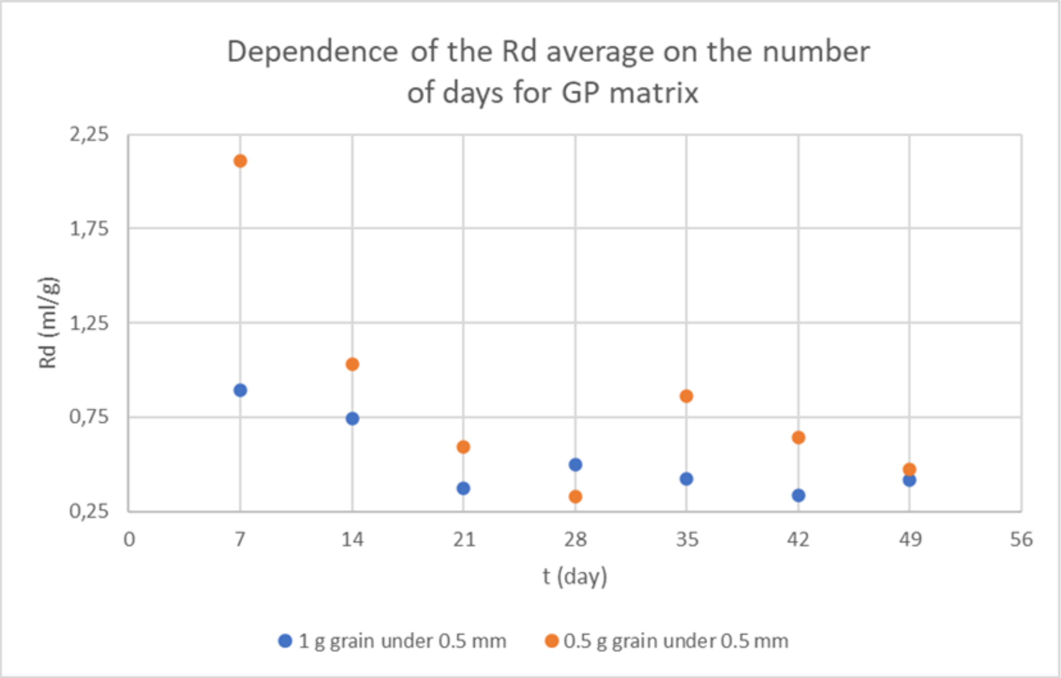


Figure 135 *Time dependence of the "Rd" (^{14}C sorption on the GP matrix)*

Table 92 *The „ŋ“ sorption efficiency values, ^{14}C sorption on the GP matrix*

GP / ^{14}C	1 g grain under 0.5 mm	0.5 g grain under 0.5 mm
den	ŋ	ŋ
7	0,144021335	0,159423554
14	0,130708491	0,098081834
21	0,073152917	0,049457838
28	0,087766379	0,035156209
35	0,083621928	0,079934185
42	0,053609877	0,03806383
49	0,084138863	0,038007137

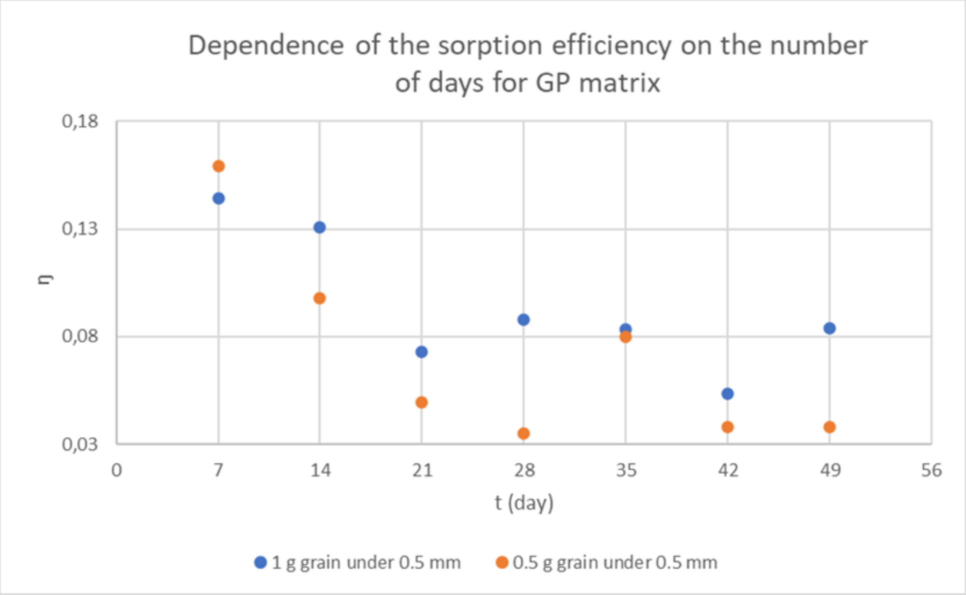


Figure 136 *Time dependence of the „ŋ“ (^{14}C sorption on the GP matrix)*

6.1.2.2.2 Results of the ^{14}C sorption tests

Linear distribution coefficient **Rd**: Samples with lower weights (0.5 g) evinced higher Rd values in the case of the BFS matrix. The values were relatively stable (Figure 133).

Higher values were also recorded for the lower loadings (0.5 g) in the case of the GP matrix. The difference compared to the BFS matrix concerned the attainment of the maximum value on sampling day 7, following the values were observed to be significantly lower (Figure 135).

Sorption efficiency **ŋ**: Only slight differences in the values were observed for the BFS matrix, with the exception of sampling day 28 on which the minimum value was attained (Figure 134).

Concerning the GP matrix, the maximum ŋ value was observed on the first sampling day and the values were significantly lower from the sampling day 21 onwards (Figure 136).

6.1.2.2.3 Results of the sorption tests

It can be stated that the samples with lower weights (0.5 g) evinced more efficient ^{63}Ni sorption on the BFS matrix and, conversely, the samples with higher weights (1 g) exhibited more efficient sorption on the matrix.

A higher ^{14}C sorption efficiency was evinced by the 1 g samples than the 0.5 g samples in the case of both, BFS and GP matrices.

6.1.2.3 Leaching tests

The approach to the leaching experiments followed the **ANSI method** „ANSI/ANS-16.1.1986“ (The measurement of the leachability of solidified low-level radioactive wastes by a short – term test procedure). The principle comprises the leaching of radionuclides from solidified waste as a function of time.

The test sample must be both representative and homogeneous. It must have a cylindrical shape with a length to diameter ratio of 0.2 – 5. The preparation approach is unique for each type of waste.

Leaching solution: DEMI water with the appropriate characteristics is used for determination purposes – conductivity < 5mmho/cm at 25°C.

A constant temperature within the range 17.5 – 27.5 °C must be maintained during the testing procedure.

The volume of the leaching solution is calculated as: V_L / S = 10 ± 0.2 cm

V_L = the volume of leaching solution [cm^3]

S = the sample surface [cm^2]

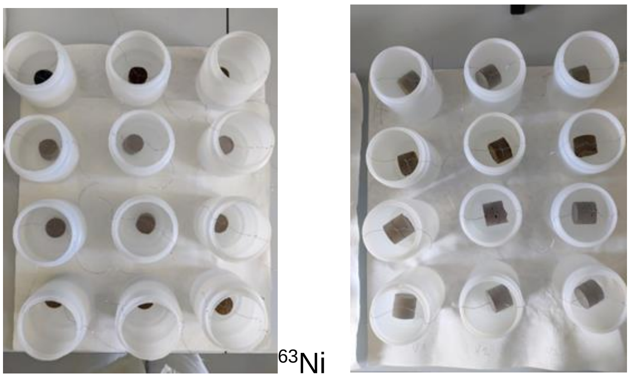
The method:

The prepared sample is placed in the specified volume of the leaching solution. Once the time interval has elapsed, the leaching solution is replaced with a clean solution and the activity of the solution is determined. The procedure is repeated at set intervals: 1d, 2d, 3d, 4d, 5d, 19d, 47d and 90d.

A „Hidex“ liquid scintillation spectrometer „Hidex“ (which detects sources of both α and ß radiation) was used to measure the samples (Figure 128). The measurement process involved the extraction of leachates (1 ml) at set intervals and the addition of 4 ml of scintillation cocktail.

The „CPM“ (the average values of 3 samples from each matrix) values are shown in Table 93 and Table 94, and graph form in Figure 138 and Figure 139.

Figure 137 provides images of the samples subjected to the leaching tests.



^{63}Ni ^{14}C

__Figure 137__ Leaching samples

__Table 93__ Results of the leaching of ^{63}Ni in CPM

^{63}Ni	**CPM**			
Days	**BFS - scintillation cocktail**	**BFS - ionic solution**	**GP - scintillation cocktail**	**GP - ionic solution**
1	71.57	58.39	56.84	55.57
2	61.4	52.47	50.9	49.44
3	60.39	56.92	52.37	49.58
4	54.59	51.19	50.84	49.56
5	52.93	49.9	45.63	43.94
19	59.37	58.38	74.1	63.14
47	75.5	87.68	76	68.61
90	70.54	55.7	58.94	55.07

__Table 94__ Results of the leaching of ^{14}C in CPM

^{14}C	**CPM**			
Days	**BFS - scintillation cocktail**	**BFS - ionic solution**	**GP - scintillation cocktail**	**GP - ionic solution**
1	57.17	55.3	64.35	76.62
2	72.17	59.69	68.75	75.95
3	62.23	58.19	66.89	62.9
4	62.12	61.63	72.37	84.13
5	64.69	67.2	62.57	74.5
19	65.64	65.08	65.8	71
47	59.7	65.6	58.56	59.77
90	60.09	67.09	59.64	61.58

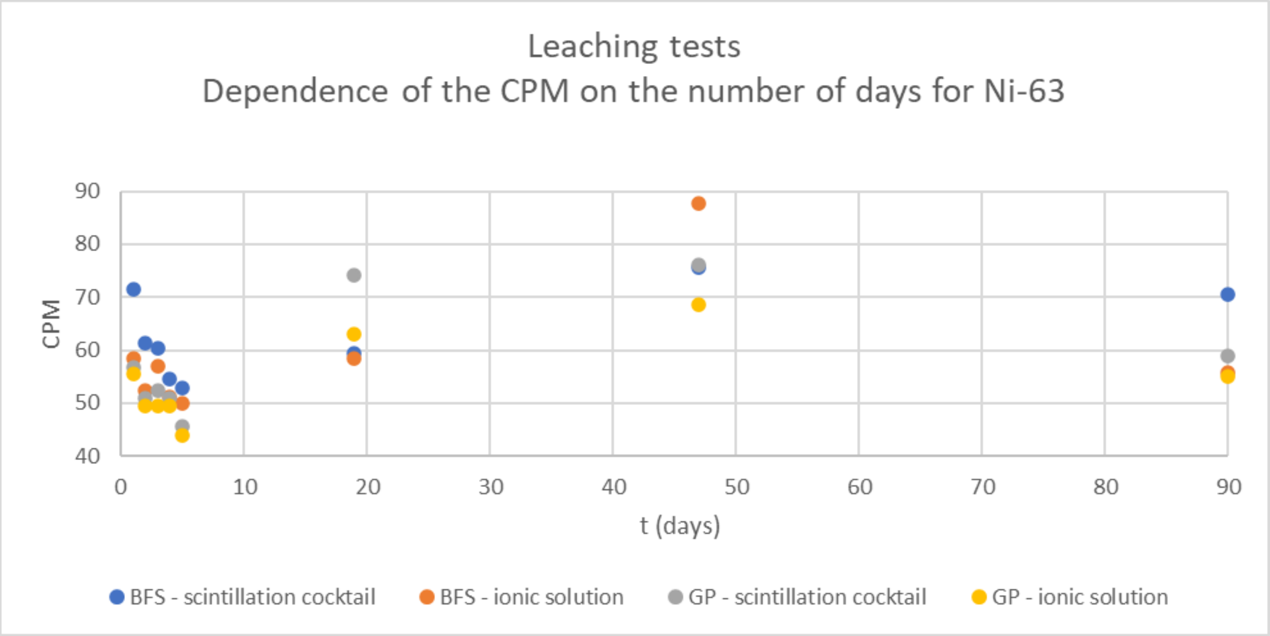


Figure 138 *Leaching tests - Dependence of the CPM on the time for* ^{63}*Ni*

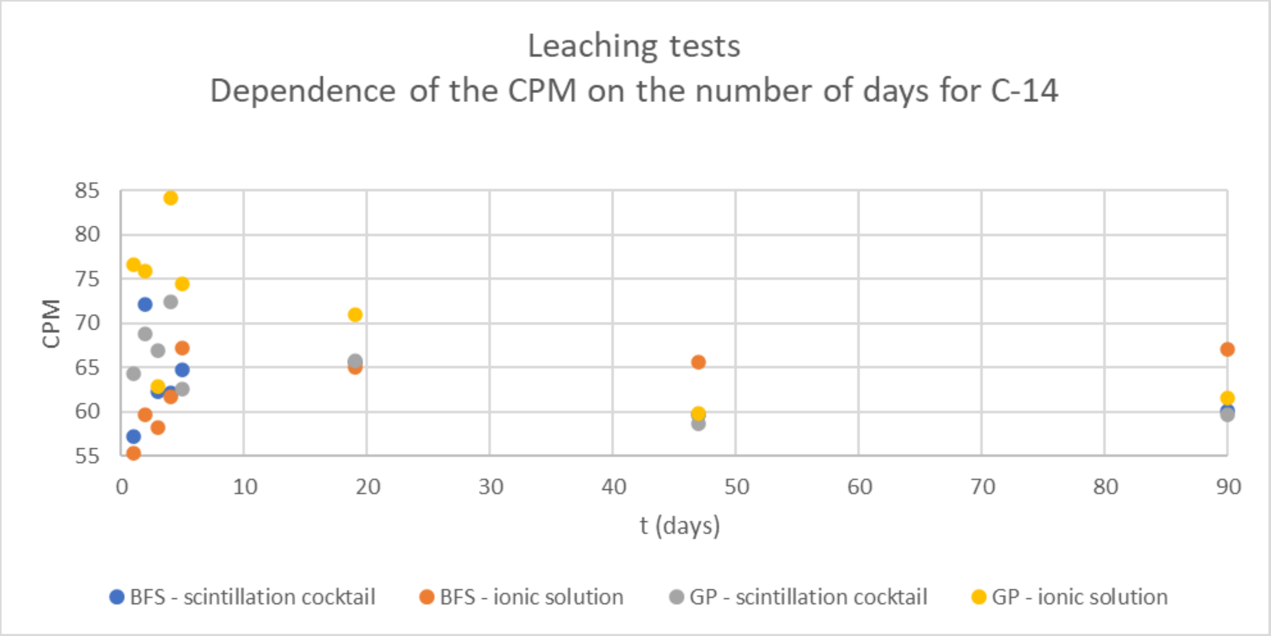


Figure 139 *Leaching tests – Dependence of the CPM on the time for* ^{14}*C*

The Leachability index „Li“ was calculated according to the ANSI method. The Leachability index comprises a dimensionless value that is calculated from the experimentally obtained effective diffusivity value for a given radionuclide. It characterises the leaching properties of a given solidified material.

$$L_i = \frac{1}{10}\sum_{10}^{1}\left[\log(\beta / D_i\right]$$

where

ß = defined constant 1.0 cm^2/s

Di = effective diffusivity for a given radionuclide cm^2/s, $D = \pi\left[\frac{a_n / A_0}{(\Delta t)_n}\right]^2\left[\frac{V}{S}\right]^2 T$

The calculated values (the average values of 3 samples from each matrix) are shown in Table 95 and Table 96 and in graph form in Figure 140 and Figure 141.

Table 95 *Results of the leaching of ^{63}Ni in Li*

^{63}Ni	**Li**			
Days	**BFS - scintillation cocktail**	**BFS - ionic solution**	**GP - scintillation cocktail**	**GP - ionic solution**
1	9.06	9.24	9.09	9.07
2	8.45	8.57	8.42	8.41
3	8.22	8.27	8.17	8.18
4	8.16	8.21	8.05	8.03
5	8.07	8.12	8.03	8.02
19	9.88	9.89	9.55	9.62
47	9.82	9.69	9.64	9.68
90	9.93	10.13	9.9	9.92

Table 96 *Results of the leaching of ^{14}C in Li*

^{14}C	**Li**			
Days	**BFS - scintillation cocktail**	**BFS - ionic solution**	**GP - scintillation cocktail**	**GP - ionic solution**
1	10.29	10.51	10.15	9.98
2	9.33	9.68	9.33	9.23
3	9.22	9.47	9.12	9.16
4	9.07	9.27	8.9	8.76
5	8.93	9.08	8.92	8.75
19	10.82	11.01	10.79	10.71
47	11.04	11.15	11.02	10.99
90	11.08	11.18	11.08	11.01

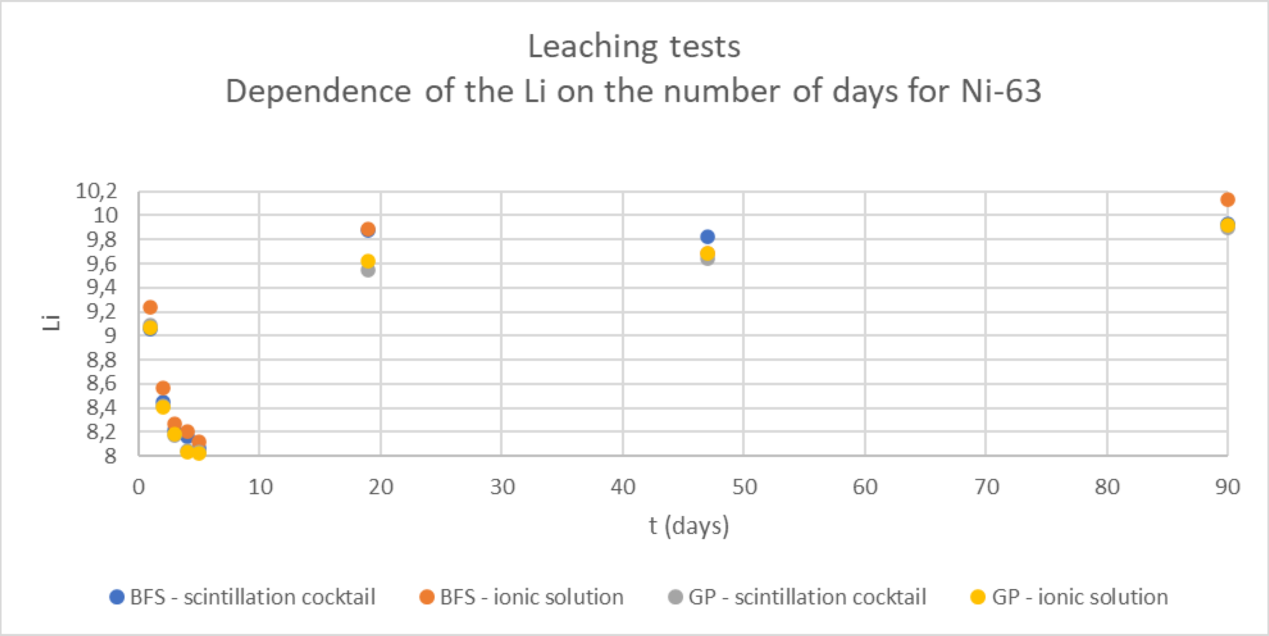


Figure 140 *Leaching tests - Dependence of Li on the time for ^{63}Ni*

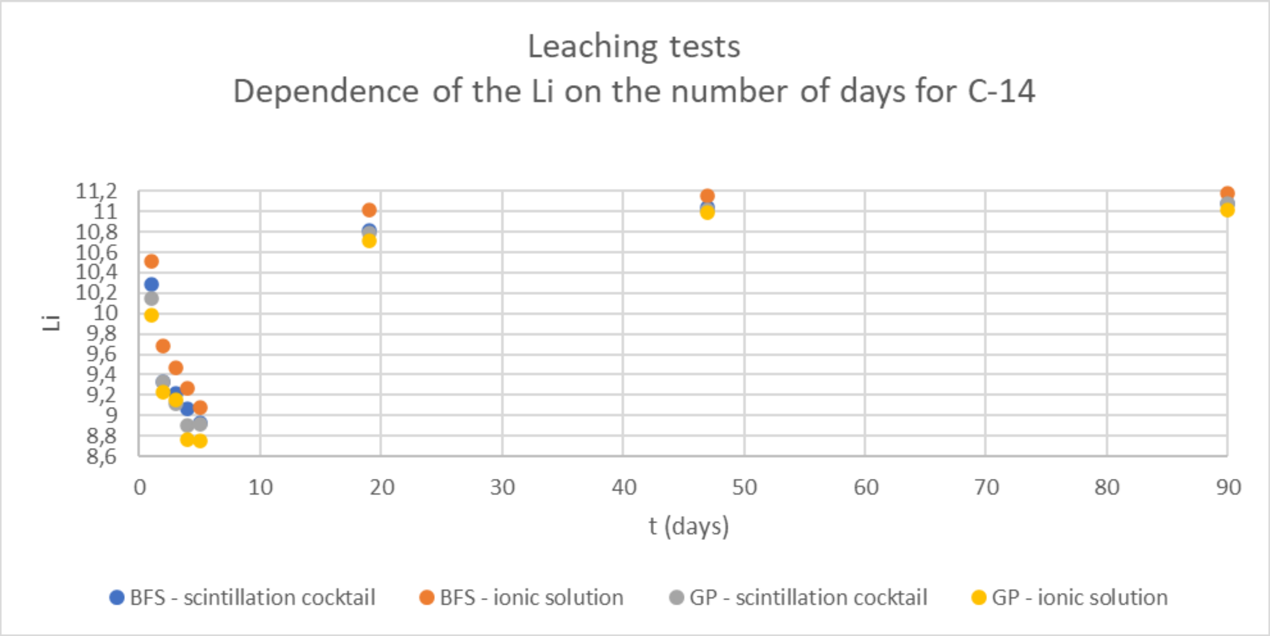


Figure 141 *Leaching tests - Dependence of Li on the time for ^{14}C*

6.1.2.3.1 Results of the leaching tests

The required minimum value of the leachability index „Li“ 8 was attained for all the tested matrices (Table 95 and Table 96).

It is clear from the graphs in Figure 140 and Figure 141 that both of the tested radionuclides ^{63}Ni and ^{14}C evinced decreasing Li values in the first 5 days of leaching both BFS and GP matrices.

The Li values for the leaching intervals 19, 47 and 90 days were in the range 9.55 – 10.13 for ^{63}Ni and 10.71 – 11.18 for ^{14}C.

The BFS matrix exhibited the highest Li (^{63}Ni max. Li = 10.13 on the BFS – ionic solution, ^{14}C max. Li = 11.18 on the BFS – ionic solution).

Acceptable leachability index „Li" values were obtained for both radionuclides, ^{63}Ni and ^{14}C. It can be stated that both the BFS and GP matrices are suitable for the solidification of these radionuclides at a waste loading of approximately 10 wt%.

6.1.3 UJV tests summary and conclusions

All the activities planned at UJV were completed.

The investigation was conducted of reference formulations with real radioactive waste, i.e. a scintillation cocktail and an ionic solution. Compressive strength, sorption and leaching tests were performed for the ^{63}Ni and ^{14}C radionuclides on blast furnace slag and geopolymer matrices.

Compressive strength: The results revealed adequate strengths in the range 13.28 – 25.71 MPa after 28 days of ageing.

Sorption tests: A slightly higher degree of ^{63}Ni sorption efficiency was detected on the geopolymer matrix than on the blast furnace slag matrix. Conversely, the blast furnace slag matrix exhibited a higher ^{14}C sorption efficiency.

With respect to the two different weight loadings (0.5 g and 1 g), samples with lower weights (0.5 g) evinced a higher degree of ^{63}Ni sorption efficiency on the BFS matrix, while the samples with higher weights (1 g) evinced a higher degree of ^{63}Ni sorption efficiency on the GP matrix. A higher ^{14}C sorption efficiency was exhibited by the 1 g samples than the 0.5 g samples with respect to both matrices.

Leaching tests: The results led to the following conclusion: blast furnace slag and geopolymer matrices are suitable for the solidification of the radioactive wastes considered in the study – a scintillation cocktail and an ionic solution, as indicated by the attainment of the required minimum leachability index value of 8 for the monitored radionuclides.

The results of the tests confirmed that blast furnace slag and geopolymer matrices are suitable for the solidification of ^{63}Ni and ^{14}C at a radioactive waste filling of approximately 10 wt%.

6.2 POLIMI – MK matrix

POLIMI considered two real radioactive liquid organic wastes to be directly conditioned in the MK-based matrix:

- Liquid scintillation cocktail (indicated as *LSC* in the following), consisting in a mixture of Ultima Gold LLT (Perkin Elmer) and AquaLight+ (Hidex) cocktails in unspecified proportions, containing ^{63}Ni;
- *TODGA* waste (0.2 mol/L N,N,N,N Tetraoctyl Diglycolamide in kerosene + 5% v. 1-octanol) employed for research activities on spent fuel reprocessing, containing ^{241}Am, ^{244}Cm and ^{152}Eu. This type of waste is similar in physical properties to TBP/dodecane.

Among the three formulations optimized within this task, the MK-based matrix proved to be the best suited for these real wastes. Specimens resulting from the conditioning of the two types of wastes were studied in terms of compression resistance and leaching behavior.

6.2.1 Real waste characterization

The wastes available at POLIMI were characterized in terms of radiological content and relevant physico-chemical properties prior to their conditioning.

LSC waste presents an activity concentration of 19.8 Bq/L of ^{63}Ni, plus a concentration of stable Ni carrier of 94 mg/L. Moreover, the spent cocktail is constituted by 20% v. of 1 mol/L nitric acid. The content of Ni carrier and HNO_3 are a result of the previous use of the cocktail, i.e. radiochemical analyses. Moreover, *LSC* waste was additionally doped with 5 mg/L of stable Cs to investigate the leaching behavior of this element in resulting waste forms as required by the Italian regulator.

TODGA waste presents negligible water content. On the other hand, the spent solvent contains 0.2 mol/L of HNO_3 due to the contact with 3 mol/L HNO_3 feed during the solvent extraction process in which it was originally employed. TODGA elemental composition is reported in Table 97.

Table 97 *Elemental content of TODGA waste from POLIMI.*

Element	Concentration
^{152}Eu	3.8 Bq/g
^{241}Am	2.7 Bq/g
^{244}Cm	3.1 Bq/g
Ce (stable)	1.1 g/L
Nd (stable)	0.8 g/L
Eu (stable)	1.3 g/L

6.2.2 Sample preparation

A MK-based geopolymer was employed by POLIMI for the studies on real waste encapsulation (Metamax®, KOH and Betol K-5020T activators, molar ratios as in *Figure 39*).

LSC waste was conditioned with no added surfactant at 30% v. loading. The water content of the waste was subtracted from the water necessary for the preparation of the matrix, so to achieve the same W/B ratio. The high-shear mixing protocol illustrated in Figure 56 was adopted for this waste.

TODGA waste was conditioned following the mixing protocol illustrated in Figure 66. In particular, the waste was pre-emulsified with the activation solution thanks to Tween-80 surfactant (5% wt. of surfactant with respect to the loaded waste). All samples were cured for 28 days at >90% RH prior to being employed for their intended use.

For both wastes, 2.5 cm diameter x 4 cm height cylinders were manufactured to be employed for leaching tests. Furthermore, 5 cm equilateral cylinders were also prepared to undergo compression resistance testing. For this second waste geometry, a surrogate inactive waste was employed. This replicated in all aspects the physico-chemical composition of the real *LSC* and *TODGA* wastes as described above, minus the radioactivity content. After curing and prior to testing, samples for compressive testing were either stored in a humid environment or immersed for 28 days in osmotic water.

Compression resistance was assessed by NUCLECO in accordance with UNI EN 12390:2021. Leaching tests were performed as specified in ANSI/ANS16.1-2019 protocol. The leachant was ultrapure water and was periodically renewed. The test was conducted at room temperature (20 °C ± 1°C).

In addition, phase composition (XRD) and porosity are going to be assessed to shine a light on possible microstructural changes occurred during water immersion.

6.2.3 Results

Preparation of specimen followed the protocols described previously and presented no added difficulties deriving from the characteristic of real wastes. Specimens appeared uniform, dense, and with no macroscopic porosities nor cracks following the curing period. A slight bleeding was noted for all samples (approximately 1% of the total specimen volume). However, very similar bleeding occurs also for the non-loaded matrix, therefore this behavior could not be attributed to the presence of real waste. The results of compression resistance and leaching behavior are reported in the following.

6.2.3.1 Compressive strength

Compressive strength of conditioned *LSC* and *TODGA* wastes, for both storage conditions of 28 days (humid storage and water immersion) is reported in Table 98. Reference values of compressive strength determined for the non-loaded matrix are also reported for comparison. In all cases, no clear detrimental effect of water immersion was noted as the slight changes are within the experimental uncertainty. Compressive resistance of the matrix is significantly affected by the presence of waste, with a maximum decrease of about 50% regardless of the waste considered.

***Table 98** Compressive strength measured for non-loaded MK matrix ("None") and for conditioned LSC and TODGA wastes. Values were determined after 28 days of either humid storage or static immersion performed after 28 days of curing. Measured values present a 5% relative uncertainty.*

Waste	**Immersed**	**Compressive strength (MPa)**
None	NO	18.6
	YES	16.1
LSC	NO	9.6
	YES	11.1
TODGA	NO	12.1
	YES	9.3

6.2.3.2 Leaching behavior

The pH of the leachates was determined by litmus paper and the values are reported in Figure 142. As could be noted, slightly lower values are obtained for real waste, especially for *LSC* waste. This outcome is coherent with the non-negligible amount of HNO_3 contained in this real waste, as described in paragraph 6.2.1.

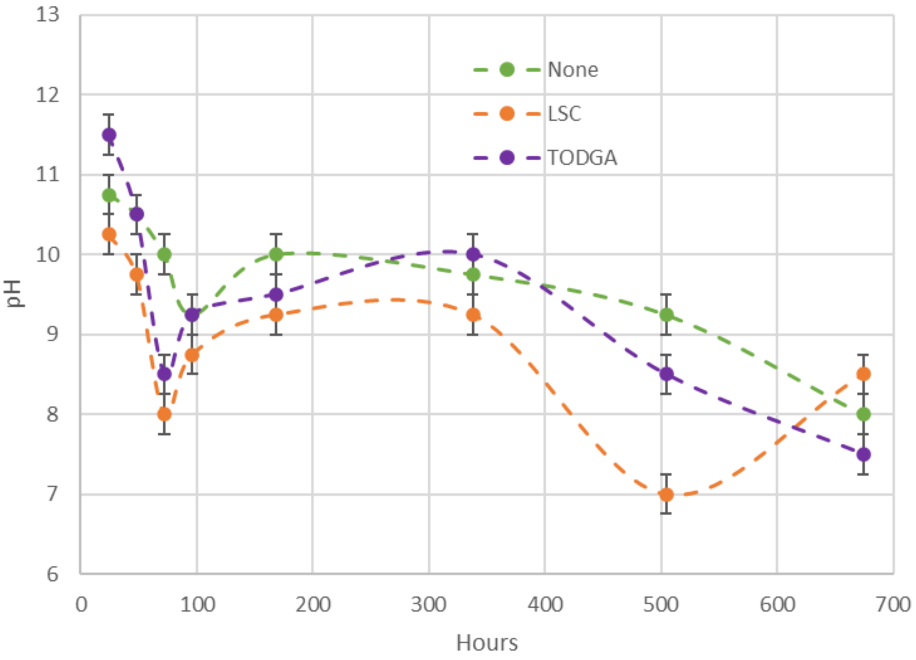


Figure 142 *pH of the leachates for non-loaded MK matrix ("None") and conditioned LSC and TODGA wastes*

Analysis of leachates were attempted via liquid scintillation counting (for ^{63}Ni in *LSC* waste) and gamma+alpha spectrometry (for ^{152}Eu, ^{241}Am and ^{244}Cm in *TODGA* waste). In all cases, leachates presented activity concentrations of the analytes below the detection limits of the adopted radiometric techniques.

It was therefore decided to base the study of leaching behavior on the non-radiometric quantification of suitable surrogate elements naturally present in the wastes which possess the same, or at least very similar, chemical behavior of the radionuclides, namely:

- Ni in place of ^{63}Ni (*LSC* waste)
- Eu in place of ^{152}Eu (*TODGA* waste)
- Ce, Nd, Eu as surrogates of tri- and tetra-valent actinides (*TODGA* waste).

Quantification of these elements (and additionally of Cs for *LSC* waste) via ICP-MS proved successful thanks to a lower detection limit of the technique and higher concentration of the surrogates with respect to their radioactive counterparts. Just in a few exceptions, the concentration of some inactive analytes was found to be below the detection limit. In these cases, the calculations were conservatively performed imposing the concentration equal to the detection limit values.

Leachability indices of the two conditioned wastes are reported in Table 99. No significant differences were noted with respect to the previously determined leaching behavior of the non-loaded matrix, which was assumed as reference. Only in the case of Ni for the conditioned *LSC* waste, a lower immersion stability was noted. The reason for this behavior remains unclear. It may be speculated that the acidity of the *LSC* waste might have played a role in worsening the leaching resistance of the matrix, but this hypothesis will need to be further investigated via microstructural characterizations (XRD and porosity).

Table 99 Leachability indices for non-loaded MK matrix ("None") and conditioned LSC and TODGA wastes.

Waste	**Ni**	**Cs**	**Ce**	**Nd**	**Eu**

None	10.1 ± 0.3	9.5 ± 0.2	11.1 ± 0.2	10.9 ± 0.2	11.2 ± 0.3
LSC	8.2 ± 0.3	9.3 ± 0.2	-	-	-
TODGA	-	-	>11.5*	>11.2*	>12.5*

* lowest estimated value based on limit of detection of the analyte.

Release of the organic component was also evaluated via periodic chemical oxygen demand (COD) measurements on collected leachates. This measure was performed only for the specimens containing *LSC* waste, as in this case the leachates proved to be homogeneous. In the case of *TODGA* waste, the negligible solubility of kerosene in water would hinder obtaining a representative and homogeneous sample for COD determination. Nevertheless, no organic drops were evidenced by visual inspection of the leachants surface. Correlation between measured COD and actual organic waste content in the leachates was determined through calibration with a standard solution prepared *ad hoc*. A cumulative release of 12.5% of the initial organic content was noted after 28 days of immersion, as reported in Figure 143. After such a period, further organic release becomes negligible. By comparison, organic release from an identical sample prepared with fresh cocktail (i.e. containing no water and acid, “Surrogate LSC”, blue curve) is also reported in the graph. A significantly higher – more than double – organic release can be noted in the case of encapsulation of the real LSC waste. Also in this case, as for the leaching behavior of Ni, the acidity of the waste might have influenced the stability of the final waste form. Additional XRD and porosity measurements are going to be carried out to elucidate this point.

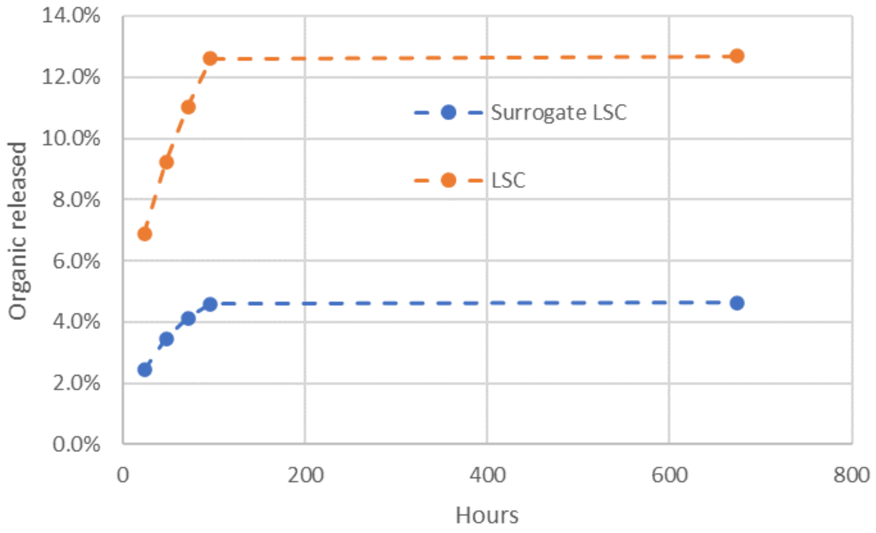


Figure 143 *Cumulative percentage organic release for conditioned LSC real waste (orange) and surrogate waste (blue).*

6.3 NUCLECO

6.3.1 Type of real waste tested

Organic wastes of various kinds from decommissioning activities are stored at the Caorso power plant. Some of these liquids are oily. Only in some of them the presence of radiological activity (mainly Cs-137 and Co-60) was detected.

To limit the use of radioactive substances as much as possible during the activities conducted with the real waste, it was decided to test a waste with very low activity, below the limits of MDC values. The following Table 100 shows the chemical-physical characterization of the waste used.

Table 100 *Chemical-physical characterization of the real waste*

Parameter	Value	Unit of measurament
As	2,06	µg/L
Cd	1669,19	µg/L
Cr	56,88	µg/L
Fe	181,76	µg/L
Hg	3,05	µg/L
Ni	156,59	µg/L
Pb	20,91	µg/L
Zn	2147,54	µg/L
Density	0,89	g/mL
% H_2O	0,87	%
Flash point	> 220	°C
TOC	268103,10	mg/L
COD	814230,70	mg/L
Cationic surfactant (CTAB)	146,10	mg/L
Anionic surfactant (MBAS)	<0,05	mg/L
Non-ionic surfactant (BiAS)	1,72	mg/L
Nitrate (NO_3^-)	1379,80	mg/L
Ammonia (NH_3)	94,27	mg/L
Chloride (Cl^-)	<1,00	mg/L
Sulphate (SO_4^{2-})	74,20	mg/L
pH	7,03	
Hydrocarbon	100	%
Aromatic compounds	0	%

6.3.2 Tested conditioning formulation

In this work 3 formulations have been tested: NNL, metakaolin based, SCK-CEN, slag based and KIPT, mix based. The following Table 101 shows the 3 tested formulations:

***Table 101** Formulations tested with the real waste (formulation ratios are expressed on a weight-to-weight basis)*

Formulation	Raw materials	Activating solution	Formulation parameters
MK based	METAMAX	Betol K 5020T H_2O KOH	Waste/Mixture = 0,19 MK/Mixture = 0,26 Betol/Mixture = 0,33 KOH/Mixture = 0,08 Additional H_2O/Mixture = 0,14
BFS based	BFS from ECOCEM (France) Sand	NaOH 10M Na_2SiO_3 H_2O	Waste/Mixture = 0,11 BFS/Mixture = 0,41 Sand/Mixture = 0,25 Na_2SiO_3/Mixture = 0,013 NaOH 10M/Mixture = 0,06 Additional H_2O/Mixture = 0,16
MIX (BFS/FA/MK) based	BFS from Buzzi (Italy) FA from Italy METAMAX	Betol K 5020T H_2O KOH	Waste/Mixture = 0,15 BFS/Mixture = 0,17 FA/Mixture = 0,28 MK/Mixture = 0,12 Betol/Mixture = 0,13 KOH/Mixture = 0,07 Additional H_2O/Mixture = 0,08

6.3.3 Tests carried out and Results

Two types of tests were conducted:

- Rheological (workability, setting time, presence of bleeding, density);
- Physical-mechanical (compressive strength, thermal cycling, immersion and leaching).

A brief description of the tests performed follows:

Workability

The test is performed by the shake table method. Geopolymeric mortar is poured inside a truncated ring centered on a glass disk. After the ring is removed, the test consists of spreading the mortar following the execution of 15 shakes and measuring the percent change in the diameter of the mix from the initial.

Setting time

The setting time of geopolymer mortar is measured in accordance with UNI EN 196-3:2017 Standard, with an automatic Vicat needle. A needle penetrates the mortar with a pre-set frequency. For each penetration, the depth reached by the needle is measured, up to the point where the needle no longer penetrates due to hardening of the matrix.

Presence of bleeding

After the preparation of a dough, any bleeding of liquid at the time of stopping mixing is recorded qualitatively. The same monitoring is performed on specimens, during the setting phase and in the first few days of curing.

Density

Density is measured on both the fresh dough and hardened specimens by performing the mass/volume ratio.

Compressive strength

The compressive strength test is performed in accordance with UNI EN 12390-3:2019 Standard. The test is performed on cylindrical specimens with a diameter and height of 50 mm. The load gradient is set on the equipment, after which the machine detects the maximum load (breaking load, expressed in kN) and converts it to compressive strength (N/mm^2).

Thermal cycling

The test is performed on cylindrical specimens with a diameter and height of 50 mm. The specimens are placed inside a climatic chamber and subjected to 30 24-hour thermal cycles (total time 30 days). During each cycle the temperature varies from -40°C to +40°C and the relative humidity is maintained at 90 percent (within the climatic range in which this is allowed).At the end of the test, the specimens are inspected to record any lesion formation during the cycles and then these are subjected to compression.

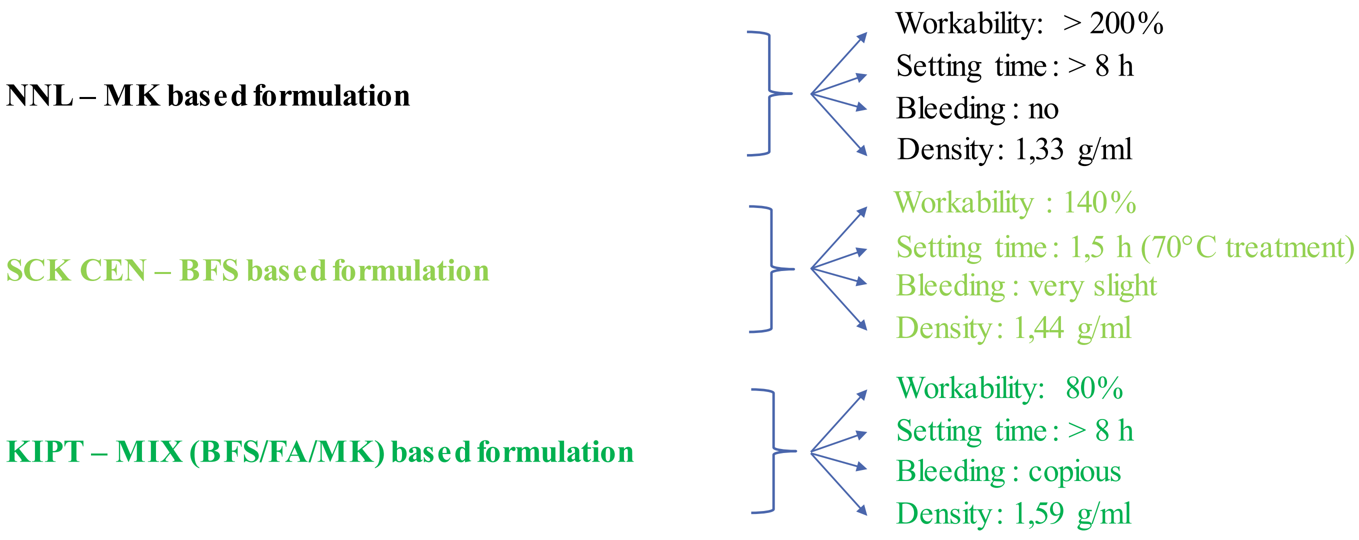
Immersion

The test is performed on cylindrical specimens with a diameter and height of 50 mm. The specimens are subjected to immersion in water for a period of 90 days. At the end of the test, the specimens are inspected to record any lesion formation during immersion, and then these are subjected to compression.

Leaching

The test is performed on cylindrical specimens with a diameter and height of 50 mm, in accordance with ANSI/ANS-2019 Standard. A known amount of gamma source (Cs-137) is added to the waste before conditioning. From the weight of the specimens, it is therefore possible to trace the initial activity of the specimens. During the test, the specimens are subjected to several immersion baths, which are then analysed by gamma spectrometry to determine the activity of the tracer in the leachate. Using the mathematical equations given in the Standard, the matrix leachability index, which is the inverse of the logarithm of diffusivity, is then determined.

The results of the rheological tests are summarized in Figure 144.



NNL – MK based formulation

Workability: > 200%
Setting time: > 8 h
Bleeding: no
Density: 1,33 g/ml

SCK CEN – BFS based formulation

Workability: 140%
Setting time: 1,5 h (70°C treatment)
Bleeding: very slight
Density: 1,44 g/ml

KIPT – MIX (BFS/FA/MK) based formulation

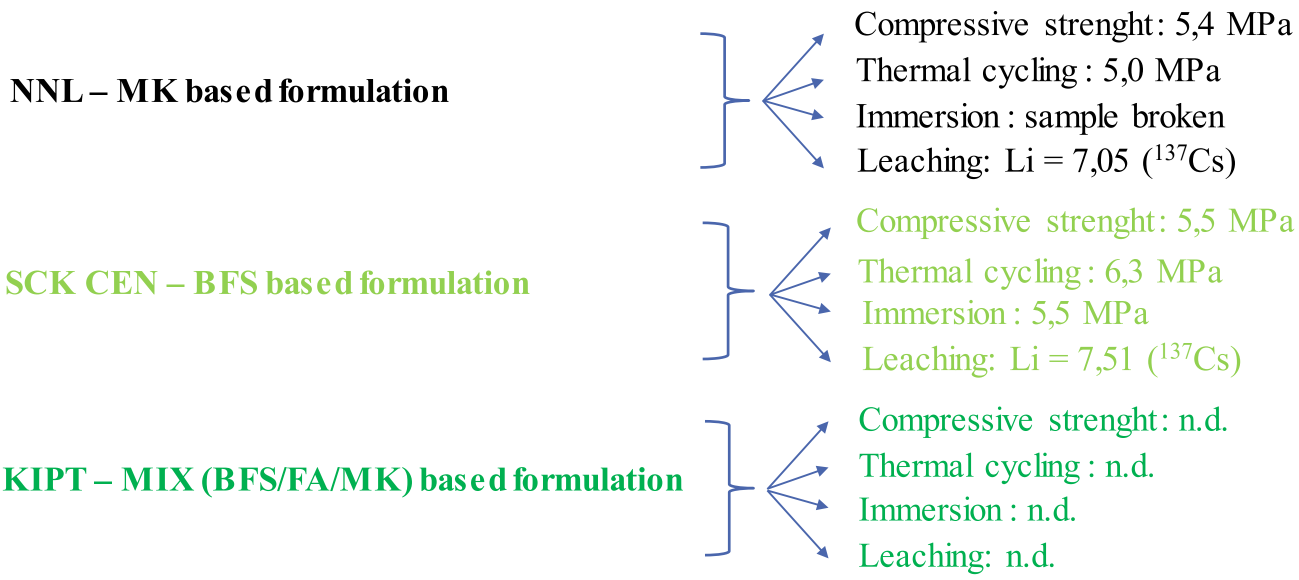
Workability: 80%
Setting time: > 8 h
Bleeding: copious
Density: 1,59 g/ml

Figure 144 *Summary results of rheological tests*

The following considerations can therefore be made:

- The MK-based mixture shows high workability, long setting times, absence of bleeding and a density of 1.3 g/ml;
- The BFS-based mixture shows good workability, fairly short setting times due to the heat treatment at 70°C, very slight bleeding and a density of 1.44 g/ml;
- As regards the MIX(BFS/FA/MK)-based mixture, differently from what was seen in previous tests with Nevastane and Shellspirax oils, the incorporation of real waste is not good. Copious bleeding was found and for this reason it was decided not to carry out mechanical tests on the specimens.

The results of the mechanical tests are summarized in Figure 145.



NNL – MK based formulation

Compressive strenght: 5,4 MPa
Thermal cycling : 5,0 MPa
Immersion : sample broken
Leaching: Li = 7,05 (^{137}Cs)

SCK CEN – BFS based formulation

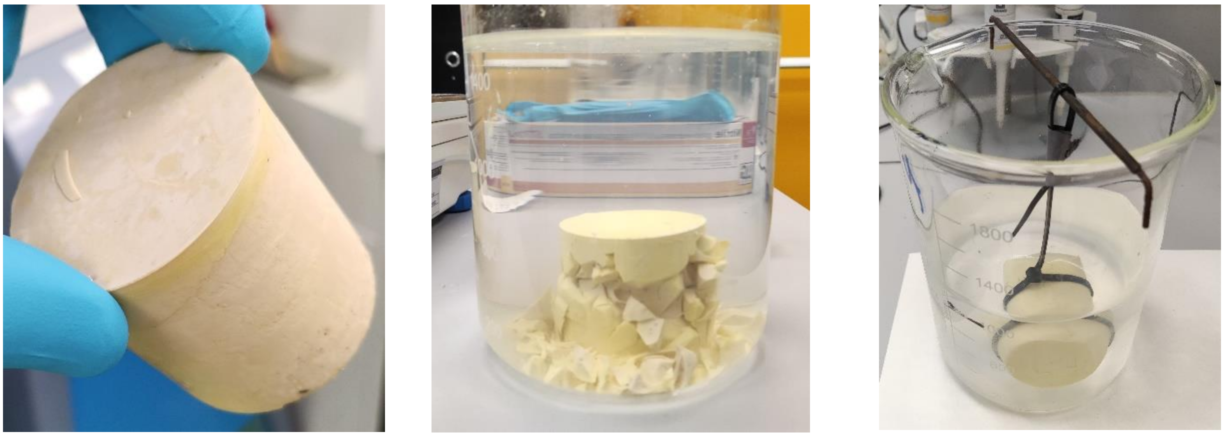
Compressive strenght: 5,5 MPa
Thermal cycling : 6,3 MPa
Immersion : 5,5 MPa
Leaching: Li = 7,51 (^{137}Cs)

KIPT – MIX (BFS/FA/MK) based formulation

Compressive strenght: n.d.
Thermal cycling : n.d.
Immersion : n.d.
Leaching: n.d.

Figure 145 *Summary results of mechanical tests*

Photographic documentation of the specimens and tests performed is reported in Figure 146, Figure 147 and Figure 148.



MK-based specimen

Immersion test

Leaching test

Figure 146 *MK based formulation*

BFS-based specimen Compressive strength test Immersion test

Figure 147 *BFS based formulation*

MIX-based specimens Oil bleeding

Figure 148 *MIX based formulation*

The following considerations can therefore be made:

- The mechanical resistances are rather low;
- The behavior of the MK-based formulation during the immersion test is very particular. The specimen is destroyed after a few seconds;
- Despite the problems encountered during the immersion test, the leaching results on the MK-based specimens are quite good;
- The leaching results are quite good even for the BFS-based formulation.

The conclusions drawn after this test campaign are the following:

- The MK-based and BFS-based formulations incorporate the real waste well and generally show good rheological properties (good workability, long setting times, and no or little bleeding);
- The MIX (BFS/FA/MK)-based formulation doesn't incorporate the real waste as well as it does with Nevastane and Shellspirax oils. Tests on specimens have not been conducted;
- The compressive strength values of the tested formulations are all quite low (between 5 and 6 N/mm^2);

- Specimens made with the MK-based formulation disintegrate after a few seconds when immersed in water. However, this doesn't happen if curing of the specimen is carried out under saturated humidity conditions (the specimen used in the leaching test in fact, matured inside the closed mold and therefore in conditions of humidity saturation, didn't disintegrate);
- Thermal cycling (30 cycles from -40°C to +40°C) doesn't create cracks to tested specimens.

7 Investigation of direct conditioning process scale up

7.1 CV Rez – Research Centre Rez

Within the PREDIS WP5, CV Rez focused on two tasks. In Task T5.3.5, the CV Rez efforts was dedicated to scale-up experiments for the geopolymer formulations selected in Task 5.5.5 with the aim to advance the understanding and application of geopolymers on a larger scale, contributing to developing robust and scalable formulations. Secondly, in Task T5.4, CV Rez work was focused on the durability assessment of the BFS formulation. This involved evaluating the long-term performance and stability of geopolymers, to assess their reliability under various conditions.

7.1.1 Scale-up solidification device

In the scope of Task T5.3.5, CV Rez conducted scale-up experiments involving directly conditioning a liquid organic RW surrogate. For this purpose, CV Rez used a solidification device capable of scale-up operations, the dimensions of which are presented in Figure 149.

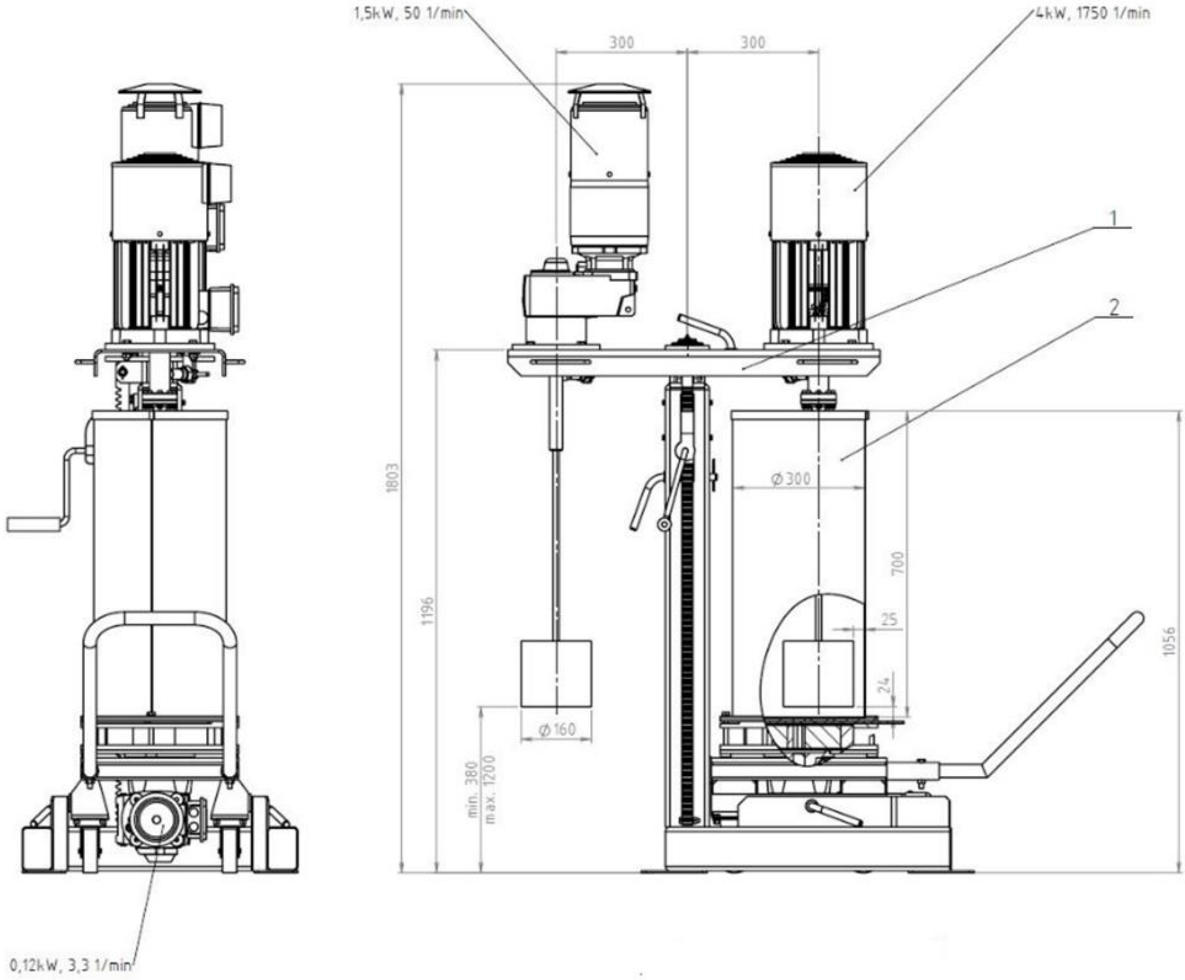


Figure 149 *Solidification device design*

The device is equipped with a top mixer affixed to a movable shoulder which facilitates horizontal and vertical movement within the drum. The mixer offers rotational options in both right and left directions. Complementing this, the device features a drum rotator that rotates independently of the mixer. The solidification device can accommodate drums with either 50 L (Figure 150) or 100 L capacities.

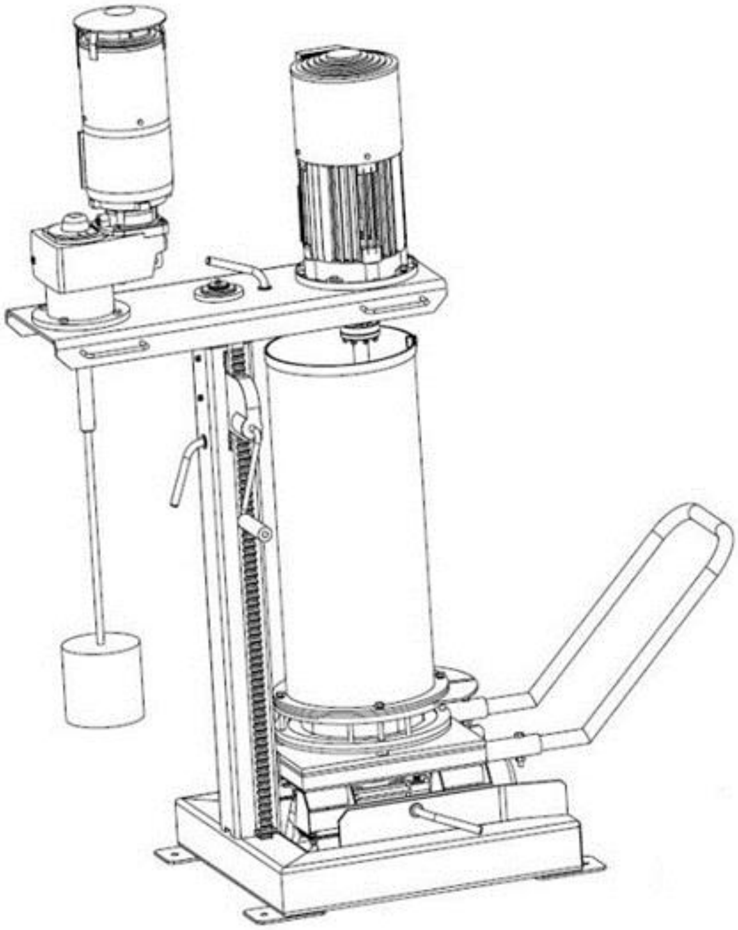


Figure 150 *Solidification device design with a 50 L drum*

7.1.1.1 50 L drum

The 50 L drums are 704 mm high and 303 mm in diameter. These drums are constructed from structural steel S235JRG1. The lid has five holes to insert thermocouples; the layout is shown in Figure 151. Each thermocouple is equipped with a triad of temperature sensors (bottom, middle and top) situated at distances of 230, 290, and 570 mm from the base of the drum post-insertion. Surface thermocouples with one temperature sensor each were affixed to the external surface of the drum, positioned at distances of 100, 200, 300, 400, and 500 mm from the drum base.

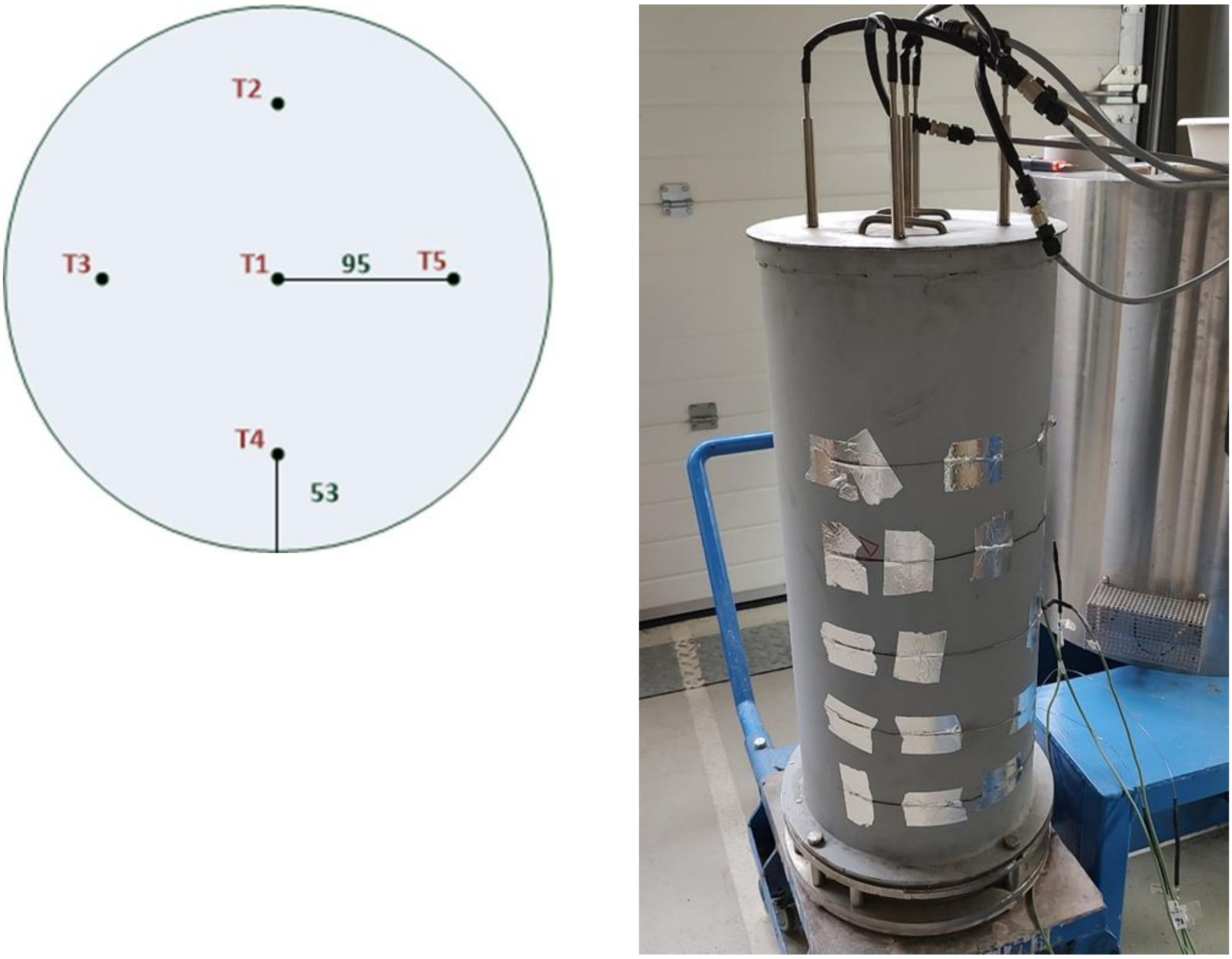


Figure 151 *Thermocouple layout on the lid (left) and on the surface of the 50 L drum (right)*

7.1.1.2 100 L drum

The 100 L drum has a height of 820 mm, a diameter of 482 mm, and a maximum total volume of 120 L. Fabricated from a 0.7 mm thick steel sheet; the drum is sealed with a 4.4 mm thick steel lid. A specially designed lid featuring six entry points for thermocouples is shown in Figure 152. Each thermocouple is equipped with three temperature sensors (bottom, middle and top) situated at distances of 25, 325 and 675 mm from the base of the drum post-insertion. Surface thermocouples with one temperature sensor were positioned at 100, 200, 300, 400, 500 and 600 mm from the drum base. The temperature sensor layout was designed with SCK-CEN to model the overall temperature distribution in the drum.

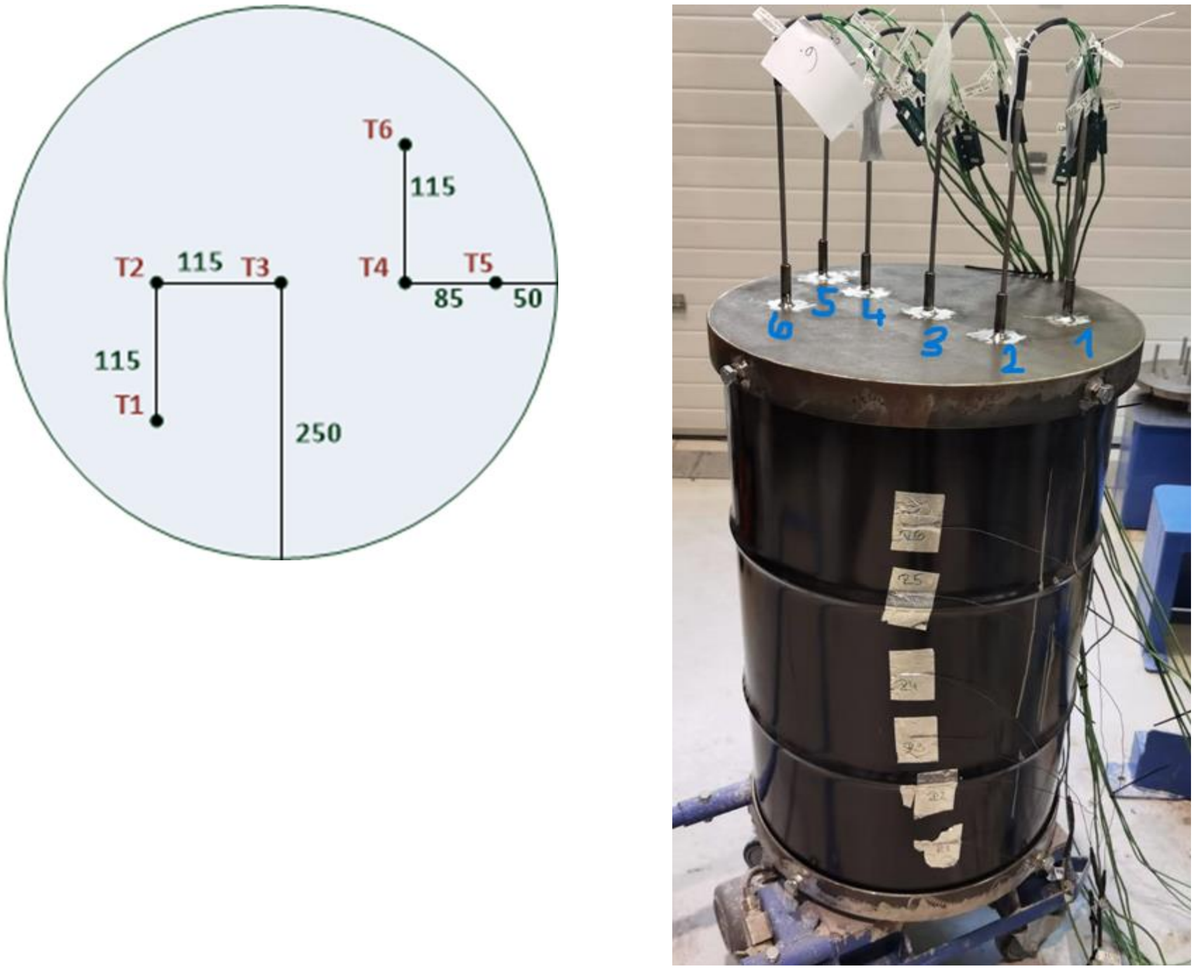


Figure 152 *Thermocouple layout on the lid (left) and on the surface of the 100 L drum (right)*

7.1.2 Scale-up experiments with MK-based geopolymers

CV Rez performed multiple testing experiments before the T5.3.5 evaluating the MK available in the Czech Republic. The geopolymer mixes Baucis LK, Baucis LBNa and Baucis LNa are commercially available from České Lupkové závody a.s. Baucis LK and LNa consist of MK Mefisto L05 and Baucis LBNa of metakaolin Mefisto LB05. A sodium silicate is used as an alkaline activator for both Baucis LBNa and Baucis LNa, and potassium silicate is used for Baucis LK. After initial testing, the MK Mefisto L05 with potassium silicate (35 wt. %) was used as an activator for the scale-up experiments within T5.3.5. The chemical and physical properties of the Mefisto L05 MK declared by the manufacturer are shown in Table 102 *and*

Table **103**.

Table 102 *Composition of the MK used for scale-up experiments*

Mefisto L05		
Oxides	**Typical content (wt. %)**	**Guaranteed content (wt. %)**
Al_2O_3	40.10	min. 38.0
SiO_2	54.10	max. 57.0
K_2O	0.80	max. 0.9
Fe_2O_3	1.10	max. 1.80
TiO_2	1.80	max. 2.00
MgO	0.18	max. 0.4
CaO	0.13	max. 0.2

Table 103 *Physical properties of the MK used for scale-up experiments*

Mefisto L05		
Physical properties	**Typical value**	**Guaranteed value**
Loss during annealing (%)	2.20	0.3 - 0.4
Moisture (%)	0.50	-
K_2O Specific surface (m^2/g)	12.69	-
Pozzolanic activity (°C)	4.30	min. 4.0
Degree of whiteness	60.00	-

7.1.2.1 50 L scale-up

7.1.2.1.1 Test with no added oil

The MK formulation was first tested at the 50 L drum version of the scale-up. The formulation details can be referenced in Table 104.

Table 104 *The formulation used for 50 L scale-up experiment with no added oil*

Formulation	**Weight (kg)**
MK	36
Alkali activator	24
Nevastane	-
Surfactant	-

The MK and alkali activator were mixed in stages. Based on preceding assessments, it was decided that optimal results are achieved by introducing the alkali activator first, followed by adding MK to improve workability and increase homogeneity. The mixing procedure was executed at a speed of 900 rpm, with the entire process lasting 20 minutes. The mixing process is illustrated in Figure 153.

Figure 153 *Mixing process*

Subsequently, the drum was securely sealed with a lid, and thermocouples were inserted into the tubes and affixed to the external surface of the drum. The temperature profiles are shown in Figure 154 *and* Figure 155.

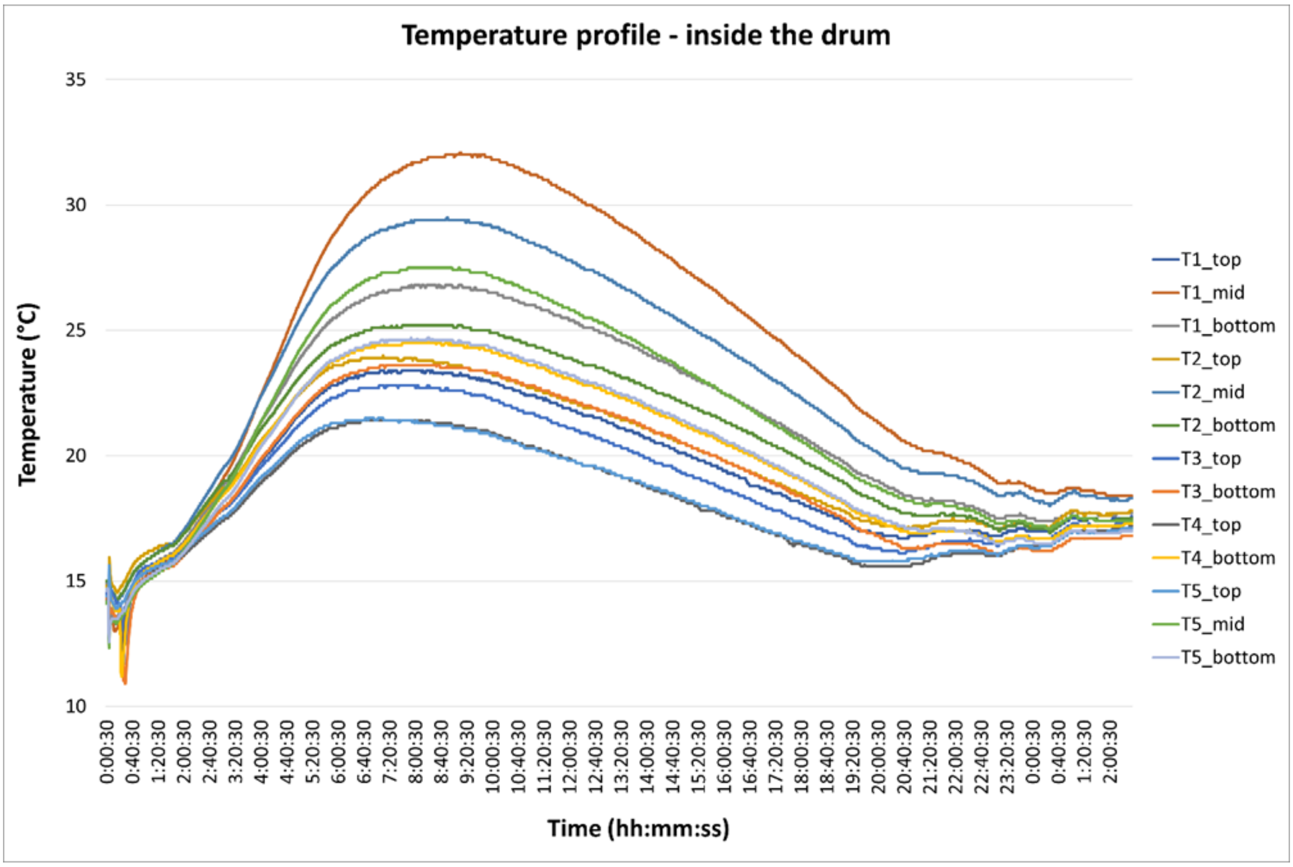


Figure 154 *Temperature profile inside the drum*

The temperature within the drum exhibited a rapid ascent, peaking after 9 hours of mixing. The highest recorded temperature, reaching 32.08 °C, was registered by the middle-temperature sensor of thermocouple T1 (positioned approximately in the middle of the drum), as illustrated in Figure 151. The temperatures decreased gradually, eventually stabilising after one day and three hours.

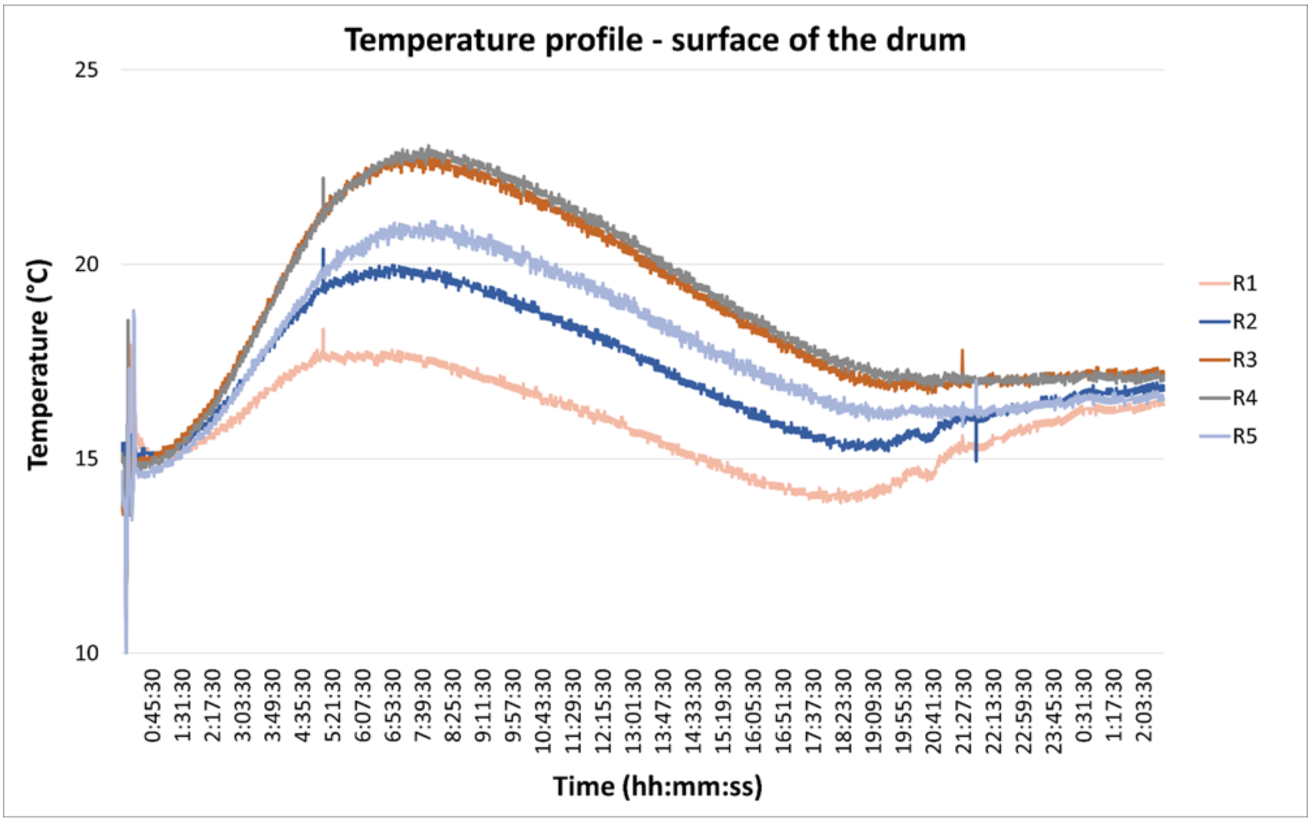


Figure 155 *Temperature profile on the outside surface of the drum*

External drum surface temperature peaked at 23 °C, recorded at location R4. The thermocouples on the drum surface were placed at varying distances from the bottom of the drum: R1 at 50 cm, R2 at 40 cm, R3 at 30 cm, R4 at 20 cm, and R5 at 10 cm.

Post-test completion, an examination was performed involving the dry cutting of the drum base to assess both homogeneity and the overall condition of the cured geopolymer. The findings, as shown in Figure 156, reveal a uniform and crack-free geopolymer composition.

Figure 156 *Geopolymer composition at the bottom of the drum after curing*

7.1.2.1.2 Test with 10 wt. % Nevastane

Following the successful test without added oil, a subsequent experiment was conducted incorporating 10 wt. % of Nevastane, the formulation details are outlined in Table 105.

Table 105 *The formulation used for 50 L scale-up experiment with added oil*

Formulation	Weight (kg)
MK	36
Alkali activator	24
Nevastane	6
Surfactant	-

Adhering to the same experimental protocol, the MK and alkali activator were initially combined until homogenous, followed by adding Nevastane and mixing for an additional 10 mins. The total mixing time was 30 minutes. The progress of the mixing and the solidified geopolymer is depicted in Figure 157. After curing, the drum was cut at the base, revealing a homogenous geopolymer structure with no visible cracks.

Figure 157 *Geopolymer composition during mixing (left), after curing (middle) and cut bottom of the drum after curing (right)*

The inside drum temperature data are shown in Figure 158.

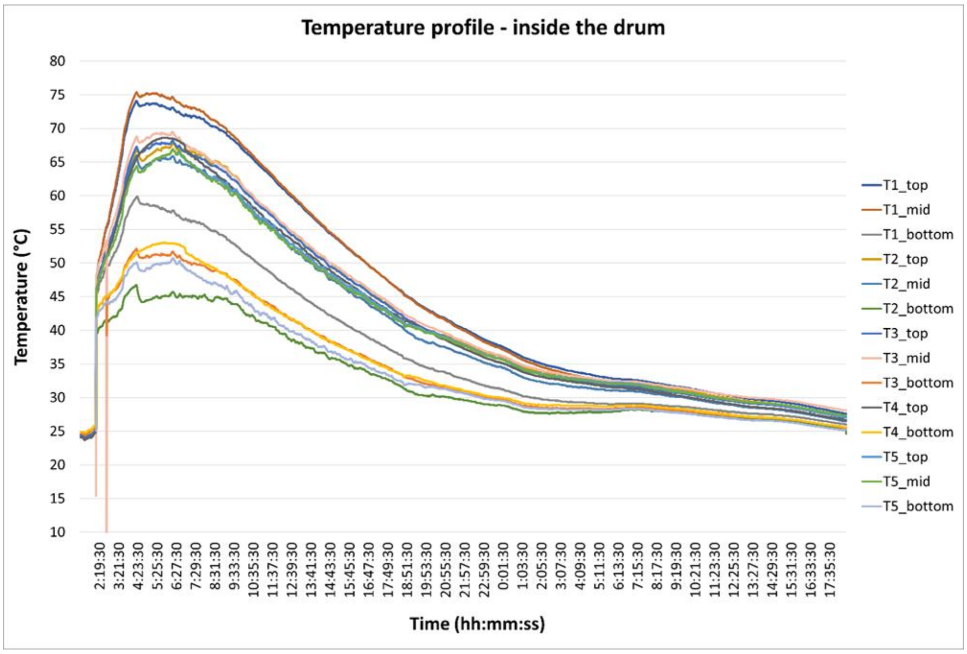


Figure 158 *Temperature profile inside the drum*

The temperature within the drum increased rapidly and peaked after 4 hours of mixing. The highest temperature of 75.40 °C was registered by the middle-temperature sensor of thermocouple T1. The temperatures then gradually decreased and eventually stabilised at ambient temperature around 25 °C.

7.1.2.2 100 L scale-up

7.1.2.2.1 Test with 10 wt. % Nevastane

After the successful 50 L drum test, a test with 10 wt. % of Nevastane in 100 L drum was performed. The formulation is shown on Table 106.

Table 106 *The formulation used for 100 L scale-up experiment with added oil*

Formulation	**Weight (kg)**
MK	109
Alkali activator	73
Nevastane	18
Surfactant	-

The experimental methodology mirrored that of the 50 L drum, where the MK and alkali activator were gradually dosed in three stages and mixed until homogenous. Subsequently, Nevastane was gradually added. The total mixing duration was 45 minutes, with the mixer operating at a speed of 1000 rpm. A visual representation of the mixing process is depicted in Figure 159.

Figure 159 *Geopolymer mixing*

Following this, the drum was sealed with a lid, and thermocouples were inserted into the tubes in the lid (arrangement shown in Figure 151) and affixed to the external surface of the drum. Temperature profiles are shown in Figure 160 *and* Figure 161.

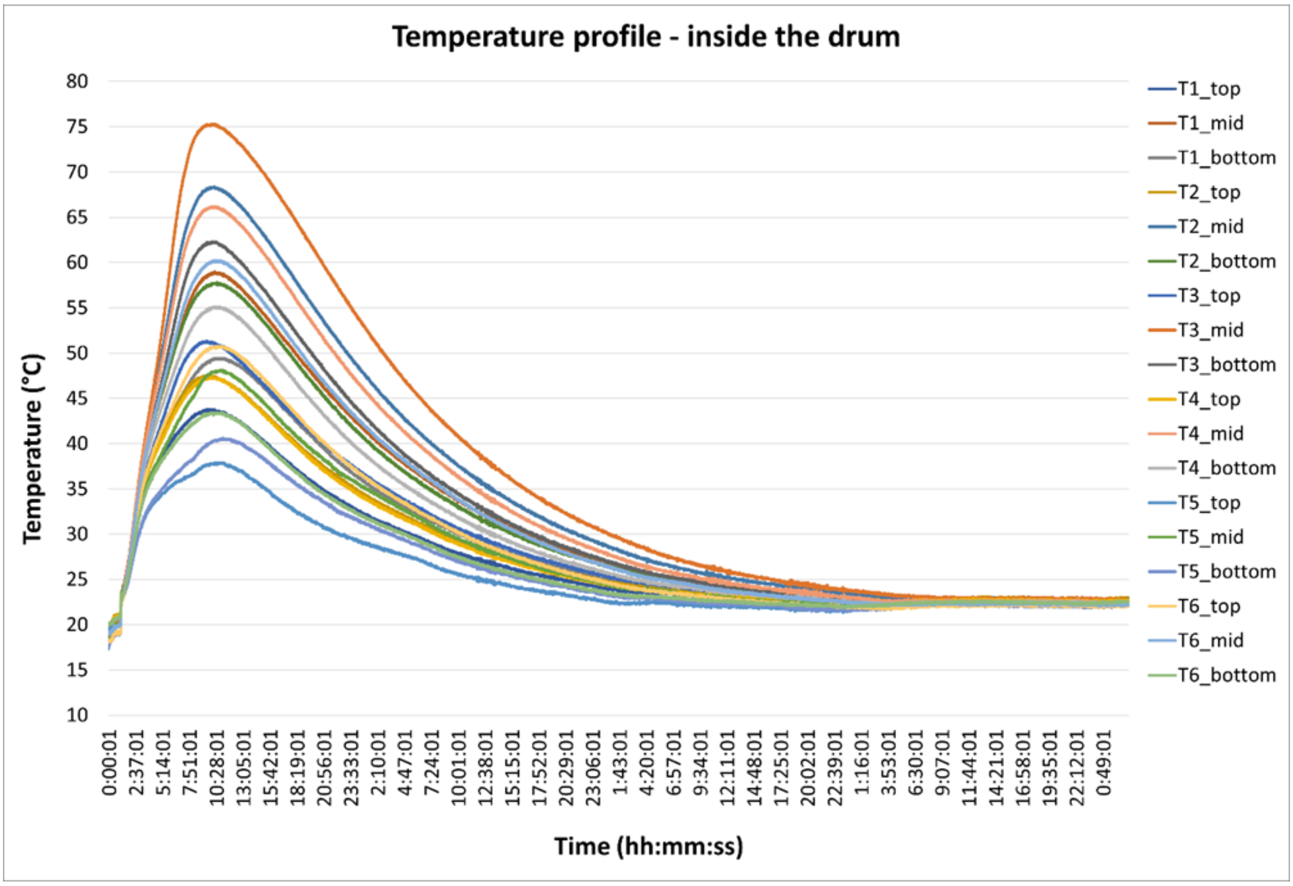


Figure 160 *Temperature profile inside the drum*

Temperature profiles revealed a substantial increase in the temperature within the drum, peaking after 9 hours of mixing. The highest temperature, measured by the middle-temperature sensor of thermocouple T3, reached 75.23 °C. Subsequently, a gradual decrease in internal drum temperature was observed over the course of three full days.

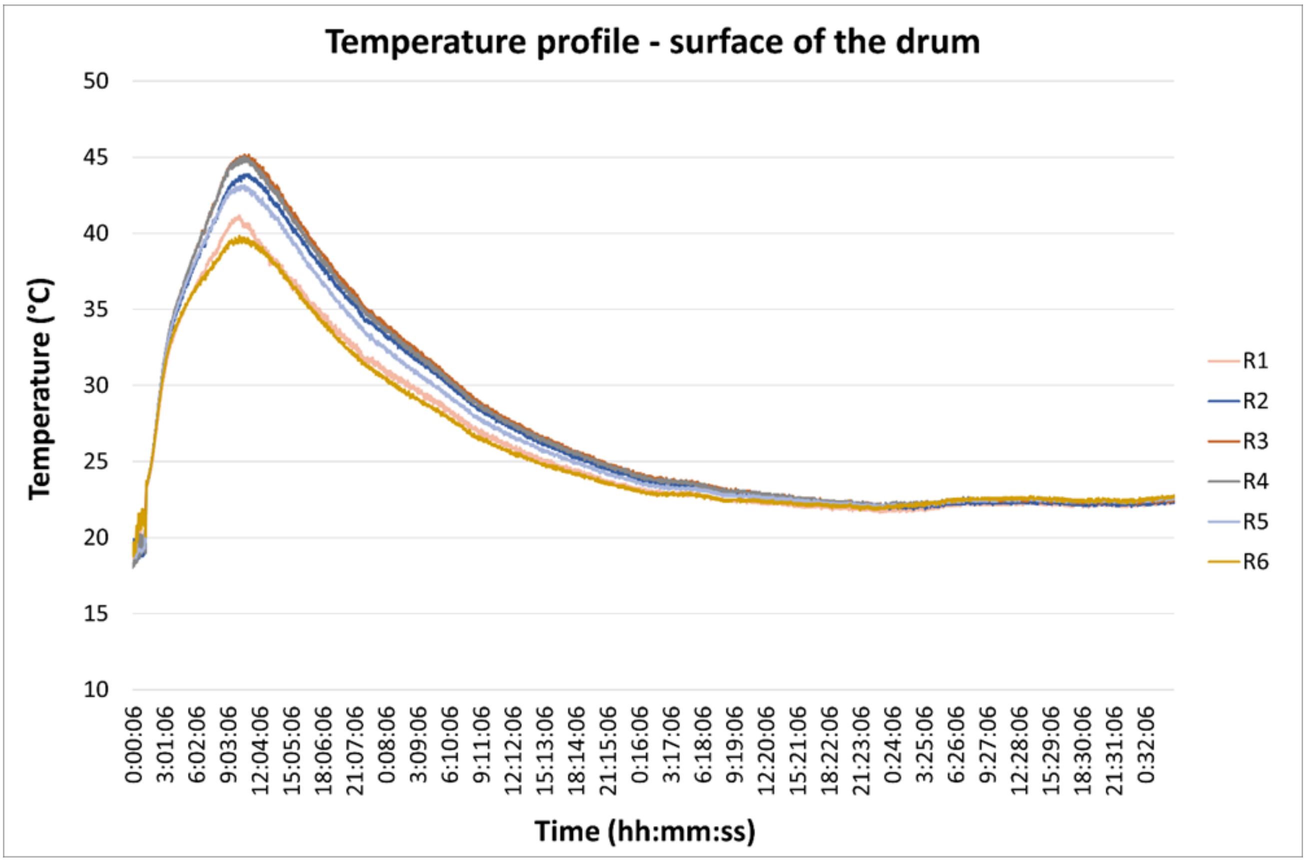


Figure 161 *Temperature profile on the outside surface of the drum*

The external temperatures peaked at 45.17 °C on thermocouple R3. The positioning of surface thermocouples on the drum labelled as R1 through R6 were at distances of 15 cm, 25 cm, 35 cm, 45 cm, 56 cm, and 65 cm from the drum's base, respectively.

Wet coring was conducted after a curing period of 20 days with the HILTI DD 350-CA diamond drilling system. Three cylindrical samples, each with a 100 mm diameter, were extracted from locations shown in Figure 162.

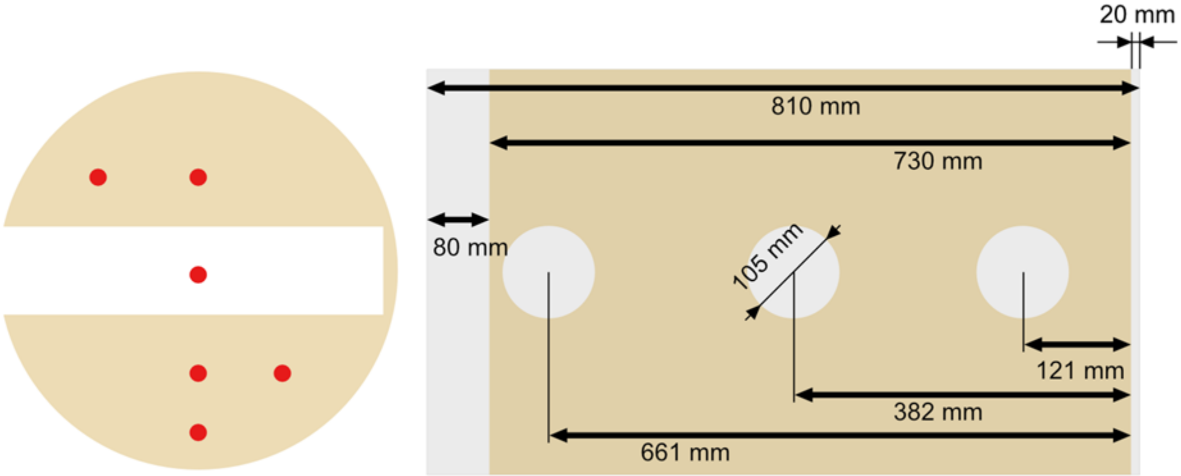


Figure 162 *Positions of the coring samples*

It is noteworthy that visible cracking observed in the samples was primarily attributed to manipulations during the coring process and the presence of steel tubes accommodating thermocouples. The samples from coring are shown in Figure 163.

Figure 163 *Samples extracted from the bottom, centre and top of the drum (left) and a close-up photo of the drilled hole in the drum (right)*

The compressive strength analysis of the samples was performed using MTS 300 Exceed® device according to the Czech National Standard CSN EN 12390-3 Testing hardened concrete - Part 3: Compressive strength of test specimens. The determined compressive strength was 21 MPa. The samples were then also measured for porosity using mercury porosimeter AutoPore IV 9500. The pores measuring 0.01 µm in size were predominant within the sample matrix and the outcomes of porosity analysis are shown in Figure 164.

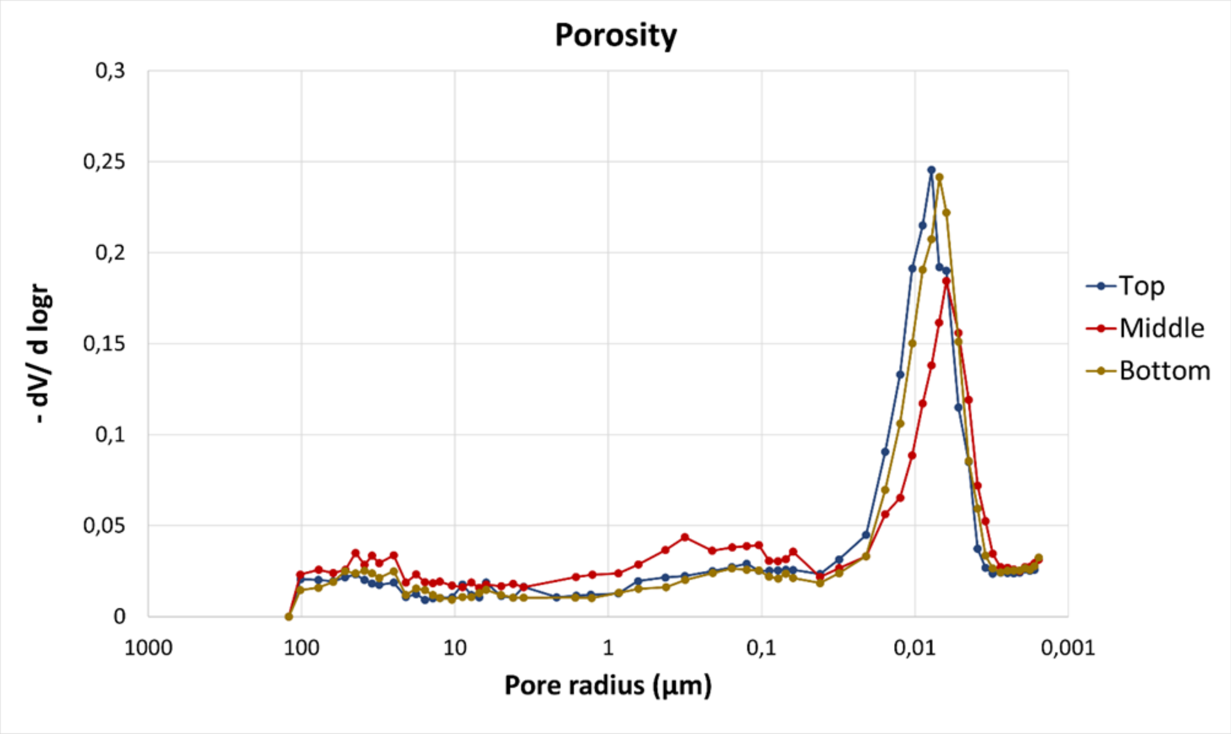


Figure 164 *The porosity of samples from coring*

Each sample was also analysed for the specific surface area using the 3Flex Adsorption Analyser, Micromeritics. The corresponding results are shown in Table 107.

Table 107 *Results of the surface area and pore volume analysis*

Coring sample	**BET surface area (m^2/g)**	**D-H Desorption cumulative surface area of pores between 1.7 - 300 nm diameter (m^2/g)**	**D-H Desorption cumulative volume of pores between 1.7 - 300 nm diameter (cm^3/g)**	**D-H Desorption average pore diameter (nm)**
Top	7.68	11.50	0.04	13.62
Middle	6.88	10.14	0.03	11.96
Bottom	6.74	9.43	0.03	14.30

The pore structures in the coring samples (Figure 165*)* were also examined using a stereoscopic microscope SMZ 171 T-LED from Motic equipped with a MOTICAM S12 camera.

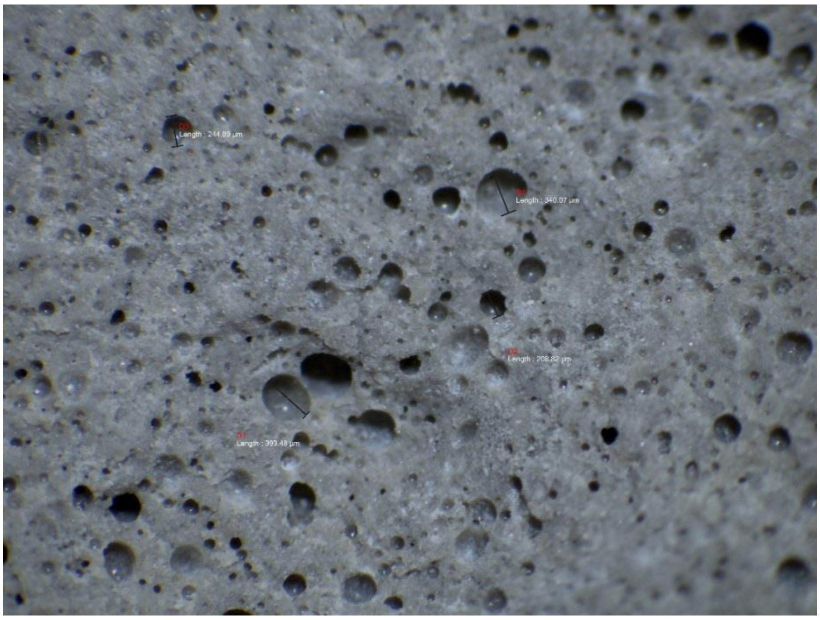


Figure 165 *Stereoscopic microscope images of the coring sample*

7.1.2.2.2 Test with 20 wt. % Nevastane

After the successful integration of 10 wt. % Nevastane, a subsequent experiment involving the addition of 20 wt. % Nevastane was conducted, with the formulation details outlined in Table 108.

Table 108 *Formulation used for 100 L scale-up experiment with 20 wt.% added oil*

Formulation	**Weight (kg)**
MK	102
Alkali activator	68
Nevastane	34
Surfactant	-

Following the same experimental protocol, the MK and alkali activator were added in three doses. Afterwards, Nevastane was added, and the matrix was thoroughly mixed until homogenous. The mixing process was performed at a speed of 1000 rpm and lasted 45 minutes (Figure 166).

Figure 166 *Mixing process*

The drum was sealed with a lid, and thermocouples were inserted into the drum and attached to the drum surface. Temperature profiles are shown in Figure 167 *and* Figure 168.

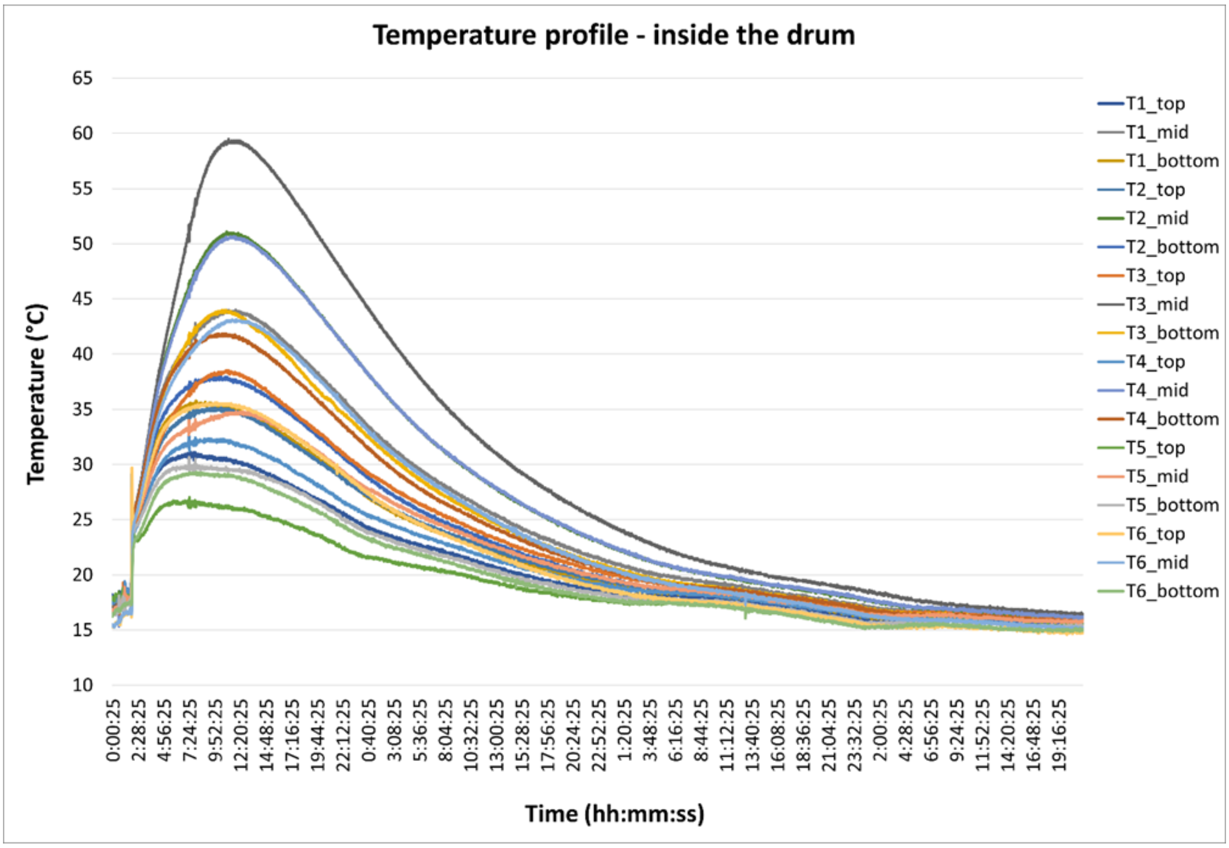


Figure 167 *Temperature profile inside the drum*

The temperature profile within the drum was similar to the previous experiments, reaching the highest value after 11 hours. The highest recorded temperature measured by the middle-temperature sensor of thermocouple T3 was 59.47 °C. Compared to the experiment with 10 wt. % Nevastane it was over 15 °C lower. Subsequently, temperatures gradually decreased, stabilising after three full days around 15 °C.

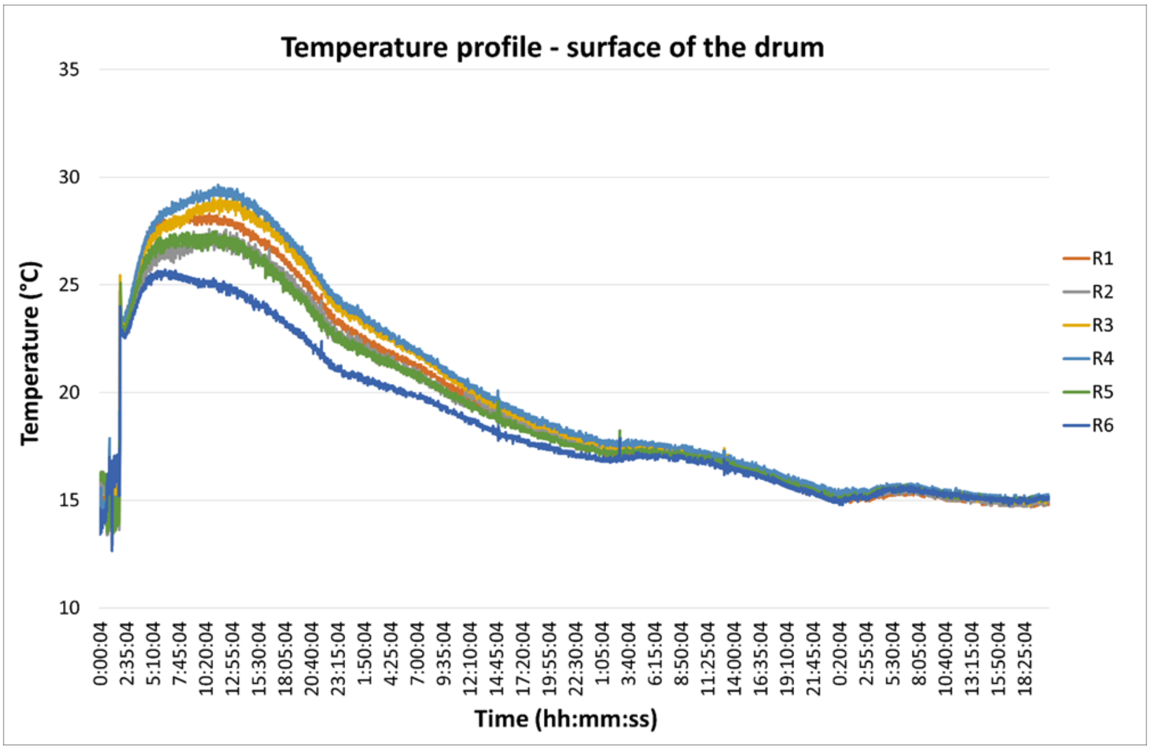


Figure 168 *Temperature profile surface of the drum*

The external temperature on the surface of the drum reached a maximum of 29.64 °C on R4. Surface thermocouples were labelled from R1 to R6 and positioned at distances at distances of 15 cm, 25 cm, 35 cm, 45 cm, 56 cm, and 65 cm from the bottom of the drum, respectively.

The curing period preceding the coring was six days. Wet coring was performed using a drilling system identical to the one used in the 100 L drum experiment with 10 wt. % Nevastane. To prevent the breaking of the samples and for easier manipulation, a smaller drilling head was selected to obtain samples with an 80 mm diameter. The coring locations are shown in Figure 169.

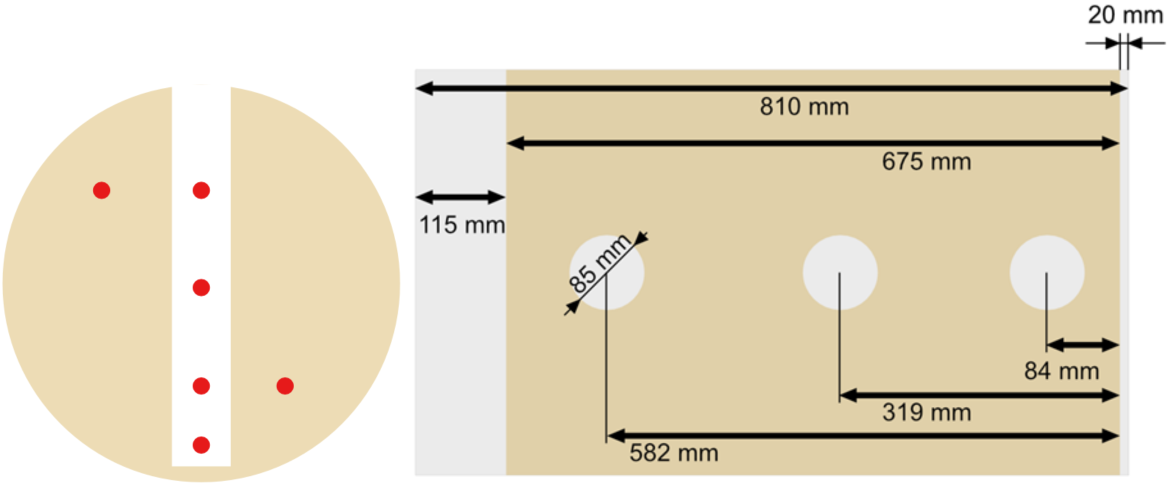


Figure 169 *Positions of the coring samples*

In contrast to the prior 100 L experiment, no visible cracks were observed, and all three samples were successfully extracted without damage (Figure 170). The geopolymer matrix exhibited homogeneity, with minor visible pore patches primarily concentrated at the top sample.

Figure 170 *Samples extracted from the top, centre and bottom of the drum (left) and a close-up photo of the pores in the top sample (right)*

During the coring of the drum, sufficient sample material was obtained for the further division of each sample into three equal segments. These segments were then analysed for compressive strength using the same protocol employed in the previous tests. The average resulting compressive strength values are presented in Table 109. Lower compressive strength compared to previous 100 L drum samples was probably due to shorter curing time.

Table 109 *Compressive strength analysis of the cored samples*

Sample	**Compressive Strength (MPa)**
Top	15.6
Middle	12.3
Bottom	15.6

A porous structure was observed on this sample using the stereoscopic microscope (Figure 171*)*. A contrast in colour was evident between the surface and near-surface with the inner part of the sample, likely due to the influence of air.

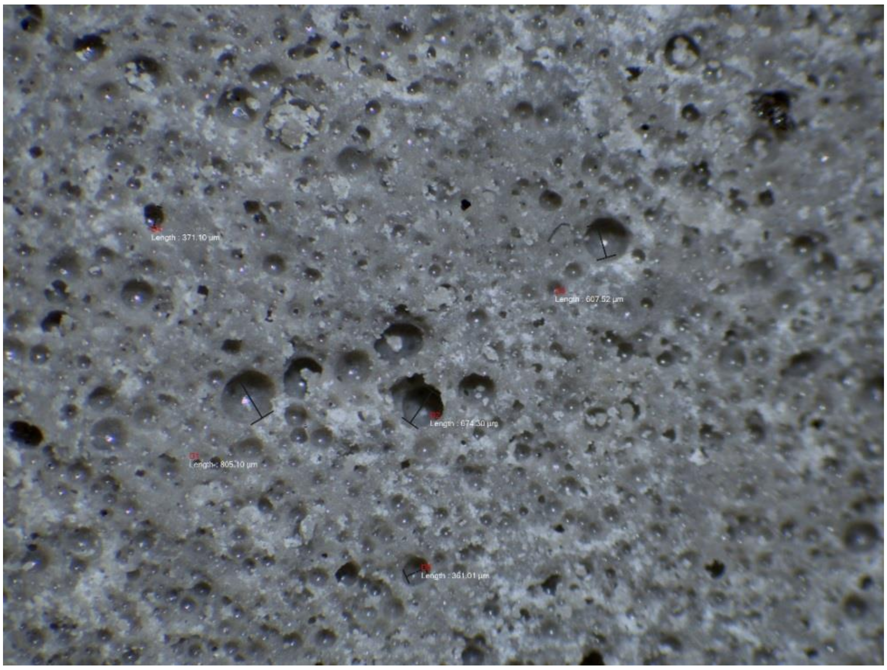


Figure 171 *Stereoscopic microscope images of the coring sample*

7.1.3 Scale-up experiments with BFS-based geopolymers

A supplementary scale-up evaluation involving the BFS formulation was performed, following the SCK-CEN formulation preparation protocol. The preparation procedure remained consistent, with only a marginal extension of time attributable to the increased volume of the mixture. Finely ground granulated BFS sourced from Trinec Iron and Steel Works was used, along with locally obtained quartz sand as the added component. The XRD analysis of the BFS is shown in Figure 172.

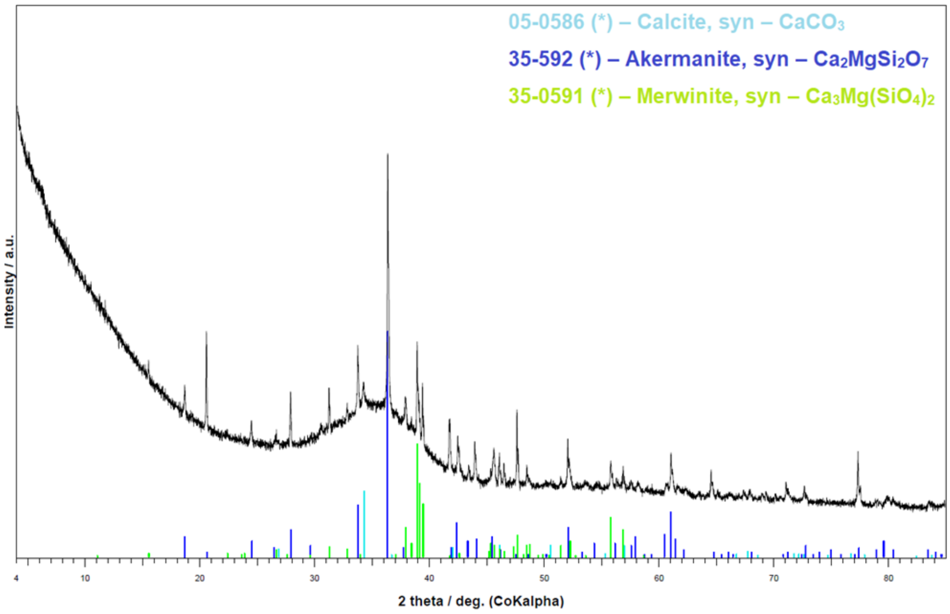


Figure 172 *XRD analysis of used BFS*

The geopolymer preparation protocol was the same as for the laboratory scale. The alkali activator was prepared by combining Sodium silicate (Sigma-Aldrich) and Sodium hydroxide (Penta), while

Tween® 80 (Sigma-Aldrich) was used as a surfactant. The activating solution which had to be divided into three equal parts due to the volume consideration was prepared 24 hours in advance of the scale-up mixing. Preceding the sample preparation, the total amount of Nevastane and Tween® 80 were divided into three equal parts due to volume and mixed for 10 minutes. Subsequently, the granulated BFS and activating solution were combined until homogenous, following which the oil-surfactant emulsion was introduced, succeeded by the addition of sand to the mixture. The detailed formulation is presented in Table 110, and the associated temperature profiles are graphically illustrated in Figure 173 *and* Figure 174.

Table 110 *Formulation used for BFS 50 L scale-up experiment with 10 wt.% added oil*

Formulation	**Weight (kg)**
BFS	23.27
Sodium silicate	0.76
Sodium solution	3.12
Additional water	8.86
Quartz sand	14.00
Nevastane	5.00
Surfactant	0.75

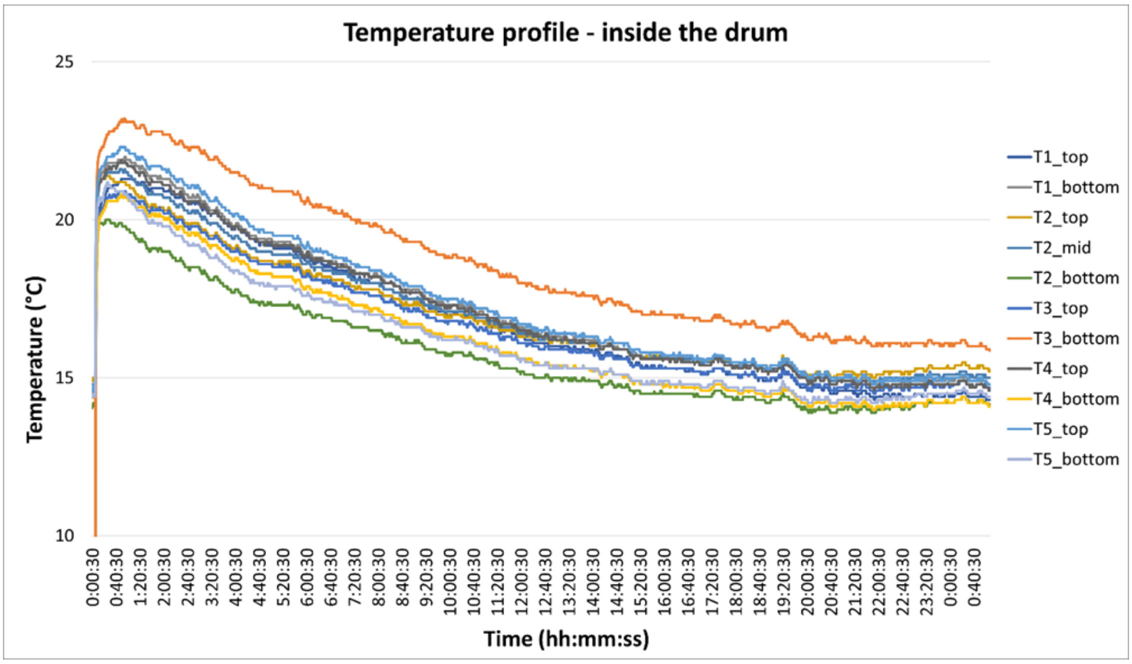


Figure 173 *Temperature profile inside the drum*

The internal drum temperature reached the highest temperature of 23.20 °C registered by the bottom sensor of the thermocouple T3 after 23 minutes of mixing. Subsequent temperature trends within the drum decreased, levelling off after 25 hours at around 15 °C.

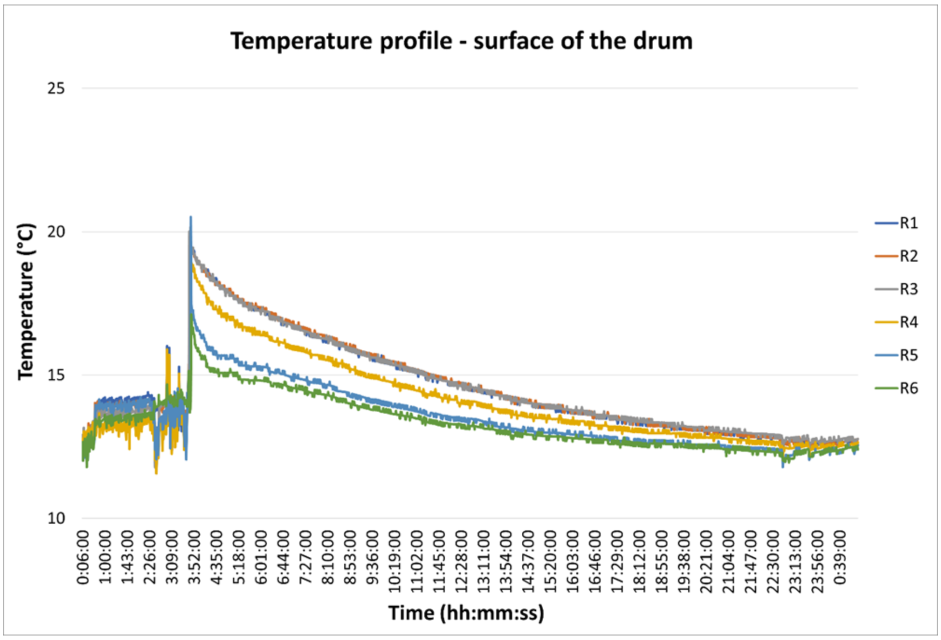


Figure 174 *Temperature profile surface of the drum*

On the surface of the drum, the temperature peaked at 20.52 °C on R1. Surface thermocouples labelled as R1, R2, R3, R4, R5 and R6 were placed at 10, 20, 30, 40, 50 and 60 cm respectively from the drum base.

The after-curing analysis of the solidified sample (Figure 175) revealed suboptimal texture; the sample exhibited softness, preventing the extraction of a suitable sample for compressive strength testing. Additionally, visual observations indicated the likelihood of separated yet solidified phases, particularly at the upper section of the drum.

Figure 175 *Solidified sample of the BFS 50 L scale-up experiment*

Overall, the scale-up experiments provided valuable insights into the behaviour of geopolymers in larger scale drums. While further optimisation of the BFS-based geopolymer preparation protocol is needed the MK-based scale-up experiments demonstrated the feasibility for direct solidification of liquid organic waste.

8 Conclusions

The experimental activities conducted for the investigation, development, and assessment of innovative direct conditioning solutions for Radioactive Liquid Organic Waste, showed that specific formulations based on metakaolin, blast furnace slags and innovative mixes of raw materials have very promising results in terms of improving waste loadings and waste form properties compared to traditional cementitious waste forms.

Metakaolin-based formulation:

Encapsulation of up to 50 vol% of simple high viscosity oil (Nevastane EP100) can be achieved for mid-point formulations based on Metakaolin ($SiO_2/K_2O = 1.2$, $H_2O/K_2O = 13$, $K/Al = 1.2$). Experimental tests demonstrated the possibility to incorporate up to 30 vol.% of TBP-dodecane and scintillation cocktails. The addition of specific surfactant is needed only for TBP-dodecane mixture.

With high RLOW loadings the mixing methodology may become important in incorporating oil in the GP formulation (effect of shear). RLOW loading affects GP viscosity/fluidity: by increasing oil loading, an increase of viscosity / decrease of fluidity is observed. The compressive strengths develop rapidly by 7d and are reduced by increasing RLOW loading.

Mid-point formulations are characterised by high heats of dissolution of the MK powder, with lower heat of dissolution for Argicem® GP system compared to the Metamax® GP system.

No oil leaching was observed, but in the case of specimens containing scintillation cocktail cracks were observed and positive TOC values were obtained in the leaching tests.

Longer term monitoring of formulations is required to prove the long term RLOW retention and product stability.

Blast Furnace Slag-based formulation:

Encapsulation of up to 30 vol% of simple high viscosity oil (Nevastane EP100) and complex low viscosity (Shellspirax) oil can be achieved in BFS-based geopolymer. It was not possible to achieve comparative waste loading (up to 30 vol%) with TBP-Dodecane and scintillation cocktail.

Concentration of alkaline activating solution and type of oil affect the setting time, while waste loading does not seem to have any significant effect on setting. The presence of immobilised oil in samples delayed the geopolymerization up to 7 days after which it did not have any additional recorded effect. Higher NaOH accelerates geopolymerization while high Sodium Silicate content seems to delay the process. The total alkaline content (both NaOH and Sodium Silicates) additionally controls the geopolymerization (heat release) after 7 days. The strength of the samples is strongly affected by the w/b ratio and waste loading.

The effect of the variability in raw materials has been studied and it was noted that the oil incorporation and mechanical strengths are affected by BFS composition and fineness.

Mix-based formulation:

Encapsulation of up to 30 vol% of simple high viscosity oil (Nevastane EP100) and complex low viscosity (Shellspirax) oil can be achieved without any surfactant. On the basis of rheology measurement of selected geopolymeric pastes it has been shown that the composites behave as a yield stress fluid with a dependence of the viscosity with the shear rate. As the oils content increases the viscosity of paste and corresponding shear stress increases.

A collaborative work was performed to study the influence of raw materials variability on the optimised reference formulation. It was highlighted that changing in raw materials (mainly different BFS), mixing protocols and curing conditions have a great impact on the oil incorporation and on the mechanical properties of the final waste form. The storage conditions and especially the relative humidity plays a crucial role on the hardened properties of the alkali activated materials/OL composites.

Robustness study conducted by varying in content of six different formulation parametres showed a compressive strength of 5 MPa and higher and a range of flowability between 75%-90%. Some bleeding has been observed in some samples, mainly with Nevastane oil.

Surfactants are needed to correctly emulsify the TBP-dodecane. Using Glucopon as surfactant, it was possible to incorporate TBP-dodecane at a rate of 30 vol% and the resulted specimens had a compressive strength higher than 15 MPa.

Tests with Real RLOW and process scale-up

The results of the tests on incorporation of real RLOW in the optimised reference formulations confirmed that blast furnace slag-based geopolymer matrices are suitable for the incorporation of real scintillation cocktail and an ionic solution containing 63Ni and 14C with a waste loading of about 20 vol%.

For the real scintillation cocktail and solvent waste incorporation in Metakaolin-based geopolymer it was observed that compressive strength is significantly affected by the presence of real waste, with a maximum decrease of about 50% regardless of the waste considered. Regarding the leaching behaviour no significant differences were observed between the matrix without ROLW (assumed as reference) and the ones with real waste.

For the real oil waste, a good incorporation rate was obtained for the MK-based and BFS-based formulations while the Mix-based one didn’t incorporate the real oil waste and it was not possible to prepare mortar specimens for testing. The real oil affected the compressive strength of the matrices and for the MK-based formulation it was highlighted that the curing conditions affect the stability of the samples if immersed in water.

Process scale-up tests were conducted with both MK-based and BFS- based formulations and Nevastane oil. The experiments provided valuable insights into the behaviour of geopolymers in larger scale drums. While further optimisation of the BFS-based geopolymer preparation protocol is needed, the MK-based scale-up experiments demonstrated the feasibility for direct solidification of liquid organic waste.

The work performed within Task 5.3 of the PREDIS project lasts for more than 3 years and involved the participation of different Partners coming from different European countries, with different background and experience in the field of RLOW conditioning. A continuous collaboration and exchange of information and data between the Partners allowed the project to reach its goal.

The results of the project can be used by Waste Management Organisations and Waste Owners who deal with RLOW that, due to their radiological and physicochemical characteristics, don’t meet the acceptance specifications for industrial treatment plants and constitute radioactive waste without management route.

9 References

[1]. A.J. Fuller (2021) “Input Data Synthesis Report”, Deliverable D5.1 of the H2020-PREDIS Project

[2]. IAEA Technical Reports Series No. 427. “Predisposal Management of Organic Radioactive Waste” International Atomic Energy Agency Vienna, 2004

[3]. IAEA Technical Reports Series No 421. “Management of Waste Containing Tritium and Carbon-14” International Atomic Energy Agency Vienna,2004

[4]. S. Wickham (2020) “Selection of candidate wastes”, Milestone 30 of the H2020-PREDIS Project

[5]. M. Fournier and D. Lambertin (2020) “Identification of exploratory conditioning options”, Milestone 31 of the H2020-PREDIS Project

[6]. Yury Pokhitonov, Vasiliy Babain, Vladislav Kamachev, Dennis Kelley. Waste Management, Decommissioning and Environmental Restoration for Canada’s Nuclear Activities, September 11-14, 2011 “Russia: results and prospects of liquid solidification experiments at Rosatom sites”

[7]. “Choice of 3 reference formulations to be further studied”, Milestone 32 of the H2020-PREDIS Project

[8]. M. Guerra, R. Sciacqua (2021) “Screening study results & Selection of reference formulations”, Milestone 33 of the H2020-PREDIS Project

[9]. F. Pancotti, C. Bucur (202) “Optimised formulations for reference formulations”, Milestone 34 of the H2020-PREDIS Project

[10]. E. Mossini et al. “Pre-impregnation approach to encapsulate radioactive liquid organic waste in geopolymer”, J. of Nucl. Mater., V. 585 (2023), 154608

[11]. B. Liguori, I. Capasso, M. De Pertis, C. Ferone, R. Cioffi, Geopolymerization Ability of Natural and Secondary Raw Materials by Solubility Test in Alkaline Media. Environments, Vol. 4, p. 56-68, 2017

[12]. B. Uzal, L. Turanli, H. Yücel, M.C. Göncüoğlu, A. Çulfaz, Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan. Cement and Concrete Research, Vol. 40, p. 398-404, 2010

[13]. J. Davidovits, Geopolymers. Journal of Thermal Analysis, Vol. 37, p. 1633-1656, 1991

[14]. A. Galkin, et al., Dual solidification process of BN-350 liquid radioactive waste using high technology polymers and newly designed encapsulation techniques. INIS-US-19-WM-15198, 2015

[15]. Z.Xu, L.Cai, X.Liang, and S.Lyu, “Insight into trichloroethene removal in alkaline condition with the presence of surfactant based on persulfate system,” *J. Environ. Chem. Eng.*, vol.10, no.5, p.108492, 2022.

[16]. C.Reeb, C.A.Davy, C.Pierlot, M. Bertin, V.Cantarel, and D.Lambertin, “Emulsification of low viscosity oil in alkali-activated materials,” *Cem. Concr. Res.*, vol.162, p.106963, 2022.