Incorporation of organic liquid waste in alkali activated mixed fly ash/blast furnace slag/metakaolin-based geopolymers

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ARTICLE INFO

ABSTRACT

The solidification of liquid oils (Shell Spirax and Nevastane EP 100) used as simulants of radioactive liquid organic waste (RLOW) in a specifically developed mix fly ash, blast furnace slag and metakaolin based geopolymer was studied in the present work. The process consists of obtaining the geopolymer paste slurry, produced by dispersing the solid precursors in the aqueous alkaline solution, and then adding RLOW via direct incorporation into the slurry under mixing to create an emulsion, before the geopolymer hardens. Geopolymer/oil composites have been prepared with various oil content (10, 20, 30 and 40 %v.), and subsequently characterized to verify their compliance with basic waste acceptance criteria. The positive role of the addition of a superplasticizer, to improve the fluidity of the paste, the density, and the homogeneity of the structure of geopolymer hardened materials was also demonstrated. The mechanical and engineering properties of the pastes and of solidified materials have been verified via rheological measurements and compressive strength tests. The optimized reference formulation loaded with 30 %v. oil waste has been tested in terms of raw materials variability and mixing proportion as part of a robustness study. Finally, the possibility to incorporate in the developed formulation other surrogated RLOW (tributyl phosphate/dodecane (30/70) and Liquid Scintillation Cocktail) has been studied with promising results.

1. Introduction

Radioactive liquid organic waste (RLOW) resulting from industrial nuclear activities, nuclear research centers and medical applications, shows a great variability.

Typical examples of such waste include oils, scintillation liquids employed for radiochemical analysis, extraction solvents and other miscellaneous solvents arising from various operations.

The volume of these wastes is small by comparison with other classes of radioactive waste such as radioactive aqueous effluents. However, by contrast, RLOW require management steps that not only take into account their radioactivity but also their chemical characteristics. This is because both the radioactivity and the organic chemical nature can affect the radiological safety and have detrimental effects on human health and environment.

As any other type of radioactive waste, also RLOWs should be treated and conditioned to produce a stable waste form to meet disposability requirements – so-called waste acceptance criteria (WAC) – of common radioactive waste repositories.

Several technologies exist for RLOW treatment (e.g. incineration, digestion, etc.). Industrial incineration plants are operated in various European countries and can process a part of RLOW produced. However, these industrial treatment units have limited acceptance specifications from radiological and physico-chemical points of view. Since many RLOW do not encounter the acceptance specifications, they effectively lack a well-defined management route.

Currently, incorporation of industrial wastes (liquid and solid) into cementitious materials is a well-known and established practice (Paria

and Yuet, 2011). Also in the radioactive waste management context cementation with Ordinary Portland Cement (OPC) is often used to solidify RLOW (IAEA, 1992). However, the stabilization of RLOW in OPC strongly retards and interferes with cement setting, and organic liquids usually do not form strong chemical bonds within the cement as some inorganic compounds do (Nestle et al., 2001; Pollard et al., 1991). Thus, the use of cement for solidification of radioactive liquid organic waste is affected by a very low achievable waste loading. Due to these issues, geopolymers have been proposed instead of OPC for the conditioning of RLOW; the influence of RLOW on geopolymer properties has in fact been observed as less important (Cantarel et al., 2018; Shi and Fernández-Jiménez, 2006).

Nowadays, geopolymers are one of the most promising materials to replace Portland cement, because of their favorable engineering characteristics including good mechanical properties, low permeability to liquids, resistance to high temperatures and chemical attack, etc. (Duxson et al., 2007). There have been a series of reviews related to geopolymers in the past few years testifying of the increasing interest for these materials (Bai and Colombo, 2018; Liew et al., 2016; Provis and Bernal, 2014; Singh et al., 2015). Geopolymers belong to the family of alkali-activated materials (AAM). Unlike OPC, AAM (and geopolymers) require a strong alkaline (e.g., NaOH, KOH) source to accelerate the dissolution of various inorganic precursors (Cantarel et al., 2018; Provis and van Deventer, 2009). Theoretically, any material composed of reactive silicates and aluminates can be alkali-activated. Usually, geopolymers can be fabricated from natural aluminosilicate raw materials such as metakaolin (MK), alumina and silica or industrial aluminosilicate wastes such fly ash (FA) and blast furnace slag (BFS) mixed with activator solutions containing reactive ingredients (potassium/sodium hydroxide, phosphoric acid, potassium/sodium silicates, etc.).

Three methods are currently being considered for incorporating organic liquids into binders and, more specifically, into geopolymers and AAM: (i) direct conditioning process, (ii) pre-emulsification by means of surfactants before adding the solid precursor, and (iii) pre-impregnation on solid absorbers before adding to the reaction mixture (Cantarel et al., 2015; Reeb et al., 2021). Of course, direct conditioning can be considered as the easiest and cheapest implementation. Nevertheless, some RLOW may require the abovementioned pre-treatment steps to ensure satisfactory incorporation in the inorganic matrix and avoid their coalescence (Mossini et al., 2023).

In the present work, a new technique based on direct incorporation of organic liquids into a mix FA-BFS-MK based geopolymer matrix has been studied. Among the different RLOW types, liquid organic oils (lubricating oils, hydraulic fluids, vacuum pump oils, cutting oils, thermal oils) resulting from nuclear industry activities were considered.

The work has been developed in the framework of the Horizon-2020 PRE-DISposal management of radioactive waste (PREDIS) project which targets the development and implementation of activities for pre-disposal treatment of radioactive waste streams other than nuclear fuel and high-level radioactive waste.

A collaborative work has been conducted to investigate, develop, and assess RLOW direct conditioning solutions based on geopolymers and alkali-activated materials as conditioning matrices.

The first part of the research work has been performed by the Kharkov Institute of Physics and Technology (KIPT) and was focused on the development of a geopolymer formulation targeting a waste loading capacity of 30–40 %v. In this preliminary phase, two types of industrial lubricating oils were considered. Following an initial screening phase, a reference "Mix" geopolymer formulation (FA-BFS-MK based) has been identified by using Ukrainian raw materials. The Mix-formulation has been tested and optimized in terms of choice and quantity of aluminosilicate precursors, alkaline activators, possible blended binder systems and additives facilitating the organic oil waste incorporation, to achieve waste forms with good rheological and mechanical properties.

The second part of the research work has been conducted by Nucleco, Commissariat à l'énergie atomique et aux énergies alternatives (CEA)

and Politecnico di Milano (Polimi) to study the effect of the variability of raw materials on the properties of the specimen. In particular, the possibility of replacing the Ukrainian raw materials with similar ones, more worldwide available, for reproducing the optimal Mix-formulation was investigated. Hence, the robustness and performance of the Mix-formulation were investigated with regard to the immobilization of different kinds of oils.

Subsequently, some preliminary tests have been performed to study the applicability of the reference Mix-formulation to other types of RLOW, namely liquid scintillation cocktail and TBP/dodecane solutions.

2. Materials and methods

2.1. Ukrainian raw materials

2.1.1. Dry precursors
The chemical composition of Ukrainian raw materials employed in the first part of the research is shown in Table 1. All materials presented a granulometry < 200 μm. Metakaolin was obtained by calcination at 800 °C of kaolin from the Zaporozhye region and was pulverized using an aluminum oxide pestle and mortar. FA (class F), granulated BFS and quartz sand were supplied by thermal power plant Burshtyn (Ivano Frankivsk region), CEMBUDSERVICE Co (Kam'yanske, Dnipro region) and JSC "Novoselivskyi GZK" (Kharkiv region), respectively.

2.1.2. Activating solution
Preparation of activating solution was performed by dissolution of KOH/NaOH in distilled water in a stainless steel (SS) container with the use of a planetary mill. Potassium/sodium liquid glass were then added to the alkaline solution under stirring to obtain a homogeneous solution. Specifically, the following reagents were used: potassium/sodium hydroxide (Novohim, Kharkiv region), potassium liquid glass – UKRSIL 32 (UKRSILICATE LLc, Zaporozhye region) with SiO_2/K_2O molar ratio 3.1–3.3 and sodium liquid glass (Zaporizhskloflus, Zaporozhye region) with SiO_2/Na_2O molar ratio 3.0–3.3.

2.1.3. Additive
Castament FW-10 additive (BASF) was employed in the formulation developed by KIPT. It is a free-flowing powder based on polyethylene glycol which acts both as a plasticizer and as a surfactant. Its use was investigated for high waste loading factors to increase the flowability of the mortar.

2.2. Alternative raw materials

2.2.1. Dry precursors
Different natural alumino-silicate raw materials than the Ukrainian ones have been used by CEA, Nucleco and Polimi to test their influence on the specimen properties: BFS (ECOTRADE, FR), FA (IT), MetaMax MK (BASF, UK).

Their chemical composition in reported in Table 2, as determined by energy-dispersive XRF analysis (Shimadzu EDX-8100).

2.2.2. Activating solution
Betol K 5020 T (Wöllner) and potassium hydroxide (KOH) in solid form have been used in order to replace Ukrainian waterglass UKRSIL 32. Betol K 5020 T is a potassium silicate solution with SiO_2/K_2O mass ratio equal to 1.6 and density of 1.5 g/cm³.

2.2.3. Additives
As alternatives to Castament FW-10, other surfactants were tested in order to facilitate the incorporation of oils and other organic liquids, namely sodium lauryl sulphate (SLS), sodium dodecyl sulfate (SDS), C8-C10-alkyl polyglucoside (Glucopon 225DK) and polyoxyethylene(10) oleyl ether (Brij O10).

Table 1

Chemical composition (%wt.) of Ukrainian dry precursors determined from energy dispersive X-ray fluorescence (XRF) spectrometry.

Material	SiO_2	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Fe_2O_3
Kaolin (Ukr)	51.0	35.5	0.25	0.16	–	0.15	0.27	0.78	–	–	1.05
BFS (Ukr)	40.6	6.02	45.1	3.61	1.74	0.42	0.40	0.30	0.01	0.17	0.62
FA (Ukr)	46.1	18.0	4.10	1.46	0.21	2.10		1.78	–	0.14	22.1
Quartz sand	98.50	0.50	0.10	0.02	–	0.05	0.05	0.08	–	–	0.05

Table 2

Chemical composition (%wt.) of alternative dry precursors employed by CEA, Nucleco and Polimi determined from XRF spectrometry.

Material	SiO_2	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Fe_2O_3
MK (UK)	54.1	42.5	0.1	<0.1	0.2	0.1	0.2	2	0.1	<0.1	0.5
BFS (ECOTRADE)	31.2	8.3	52.9	3.6	1.4	< 0.1	0.4	1	0.3	0.2	0.5
BFS (ECOCEM)	33.6	8.7	49.0	5.1	1.5		0.4	0.8		0.3	0.4
FA (IT)	54.5	20.2	6.4	1.1	1.3	0.5	3.7	1.5	0.7	0.1	9.3

2.3. Surrogate waste

Four types of surrogate RLOW were considered in the present work:

- Nevastane EP 100 (TotalEnergies Lubricants) lubricating oil. Density 0.871 g/cm^3, kinematic viscosity 100 mm^2/s @ 40 °C.
- Shell Spirax (Shell plc) lubricating oil. Density 0.882 g/cm^3, kinematic viscosity 60 mm^2/s @ 40 °C.
- Tributyl phosphate (TBP)/dodecane (30/70 vol ratio) solvent. Density 0.85 g/cm^3, kinematic viscosity 1.50 mm^2/s @ 40 °C.
- Ultima Gold LLT (PerkinElmer) liquid scintillation cocktail (LSC), density 0.96 g/cm^3.

These were selected as representatives of typical organic liquids produced during operation and dismantling of nuclear facilities, spent fuel reprocessing and radiometric analyses.

2.4. Geopolymer preparation

For the initial part of the work dedicated to formulation development performed at KIPT, geopolymers were synthesized with a varying Si/Al ratio. As Al-Si raw materials, MK, FA, BFS and quartz sand from Ukraine were used (Table 1). Mixing of dry components was carried out in a planetary mill with SS ball with rotation speed 200 rpm over 30 min. The final step of the geopolymer paste preparation is to include the Al-Si dry precursors to the alkaline solution. After mixing for 15–20 min in the planetary mill, 30 and 40 mm cubic samples were cast into plastic moulds lubricated with Vaseline. Then, the samples were demolded and stored in open plastic box under indoor ambient conditions (t = 20–25 ^{0}C, relative humidity (RH) = 50–60 %) until testing (7, 14 and 28 days of curing).

Concerning the incorporation of waste, at KIPT geopolymer/oil composites have been made with various oil content (10, 20, 30 and 40 %v.).

To synthetize geopolymers with addition of oils, appropriate amounts of Shell Spirax or Nevastane EP 100 were added to freshly prepared geopolymer pastes and mixed in a planetary mill for 30 min to obtain a homogeneous slurry which was then cast into plastic molds. Then the samples were demolded and stored under indoor ambient conditions with t = 20–25 ^{0}C, RH=50–60 %.

The same two oils were also used during the study of reproducibility of encapsulation performance obtained with different raw materials than the Ukrainian ones, and to perform a formulation robustness study.

In Nucleco, the formulation components were mixed in a planetary mixer in the following order of addition: firstly, water, surfactant and Betol K 5020 T were added, one by one, and mixed at 100 rpm to promote the formation of a higher viscosity solution; then KOH (solid form) was added and mixed with the other components until its complete

dissolution. At this point the dry precursors were added and mixed for 5 min and finally the organic liquid was added and mixed for another 5 min at 100 rpm.

The specimens were removed from the molds after 2–3 days and cured at room temperature, without humidity saturation.

At CEA and Polimi, the preparation of the geopolymer emulsions was performed by firstly mixing the aluminosilicate powder and the alkaline solution for 2 min at 600 rpm then 2 min at 2000 rpm; then gradually adding the organic liquid to the geopolymer paste and mixing for 5 min at 2000 rpm.

To perform compressive strength measurements, samples of cubic geometry (40 x 40 x 40 mm^3) were used. 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 and 95 % RH for 28 days before testing.

To study the applicability of the reference formulation to other types of waste, TBP/dodecane (30/70) and LSC Ultima Gold LLT have been used as RLOW surrogates by CEA and Polimi. These wastes were conditioned with the same protocol adopted for oils.

2.5. Test protocols

Geopolymer pastes were characterized via several techniques at the various stages of the present study, both during formulation development and in the evaluation of robustness.

2.5.1. Rheology

Rheology measurements were performed by KIPT by using a rotational viscometer (Brookfield LVDV-II+Pro). Rheological behavior of geopolymeric pastes 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 rates in the range 0.1 to 22 s^{-1}.

2.5.2. Flowability, bleeding and setting time

The flowability tests have been performed by Nucleco by means of a shake table. A special truncated cone ring is positioned in the center of a circular glass top, with which the table is equipped, and filled with fresh mortar. After lifting the ring, the mortar is subjected to 15 shocks, for a total time of 15 s, following which the spreading of the mortar on two orthogonal diameters is measured. Flowability (or consistency), expressed as a percentage, is given by the following equation (UNI, 1972) (1):

$$Flowability(\%) = \frac{(d_m - d)}{d} \times 100 \qquad (1)$$

where:

- d_m is the average of the two diameters measured after spreading;
- d is the internal diameter of the truncated cone ring (100 mm).

The bleeding was assessed by Nucleco, by visual analysis of the specimens, during and after casting, until setting was complete.

The setting time values of the prepared fresh geopolymer pastes were determined by a Vicat apparatus (UNI EN, 2017). A special cylindrical ring is positioned in the center of a circular plastic plate and filled with the mortar to be examined, immediately after the end of the mixing of the components (time zero). The surface of the mortar is leveled with a spatula and the sample is placed on a Vicat Needle device, in the dedicated area. The frequency of penetration of the needle into the mortar is set before starting the test. The time elapsed between the instant zero and that in which the distance between the needle and the bottom plate is 4 ± 1 mm is considered as the initial setting time of the mortar. The time elapsed between the instant zero and that in which the needle, for the first time, does not penetrate more than 0.5 mm into the specimen is considered as the final setting time of the mortar. To determine the measurement uncertainty, the setting time test for every mixing proportion was conducted twice.

2.5.3. Heat flow

The reactivity of both geopolymer pastes, with and without surfactant, was assessed in their freshly prepared state using isothermal microcalorimetry. The measurements were conducted using a TAM-air microcalorimeter (TA Instrument). Immediately after mixing, approximately 2 g of geopolymer paste was placed into sealed glass containers, which were subsequently loaded into the calorimeter. The heat flow was monitored over time at a constant temperature of 25 °C and cumulative heat is then calculated.

2.5.4. Compressive strength

Both cubes (40 x 40 x 40 mm^3) and cylinders (Ø20 mm, H 30 mm and Ø50 mm, H 50 mm) were employed for compressive strength testing. Geopolymer samples have been characterized after 7, 14 and 28 days of curing time. Despite the use of samples with non-standard nominal sizes, a test procedure equivalent to national standards (EN, 2016; UNI EN, 2019) was followed.

2.6. Waste acceptance criteria

For the scope of this work a preliminary set of WAC based on the ones enforced in Ukraine, Italy and France was defined for the optimization of geopolymer production parameters: setting time $\leq$ 48 h, absence of significant defects, e.g. cracks or deformations, and homogeneous structure with absence of voids. Concerning minimum compressive strength, different WAC are available: 5 MPa in Ukraine, 8 MPa in France and 10 MPa in Italy. Hence, a minimum compressive resistance of 5 MPa was identified, with a value > 10 MPa considered as ideal.

3. Results and discussion

3.1. Selection of the optimal formulation

Several experiments were performed by KIPT without RLOW to identify an optimal geopolymer formulation with Si/Al ratio of 2, which is considered an ideal target to achieve good compressive strength and chemical stability (Castillo et al., 2021; He et al., 2016). Selected compositions of geopolymer are presented in Table 3. Variable proportions of raw materials were considered, as they can affect the behavior of the geopolymer paste during curing, and compressive resistance of resulting specimen. In particular, it is known that any excess of alkaline solution is more likely to induce crystallization on the surface in the form of white salt deposits (efflorescence) (Mierzwiński et al., 2018; Simão et al., 2021). In this initial stage, visual inspection has been the preliminary selection criterion to identify the most promising formulations.

Table 3
Composition of investigated formulations.

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$_2$SiO$_3$	46			11	
K$_2$SiO$_3$		46	33		11
NaOH	6			9	
KOH		6	6		9
H$_2$O	12	12	8	12	12

After 28 days of curing, samples of compositions No. 1 and 2 presented cracks and deformations, as illustrated in Fig. 1. The presence of cracks in the samples can probably be explained by irregular drying and shrinkage, evaluated at approximately ~2% of nominal sample size. This fact can be likely attributed to the evaporation of free water (Kuenzel et al., 2012). The specimens of compositions No. 3, 4 and 5 did not show visually significant defects, and appeared dense and homogeneous. This improved geometrical stability is likely due to the presence of additional formulation constituents such as sand, FA and BFS (Kuenzel et al., 2014; Yang et al., 2017).

Additional quantitative properties have been considered for the choice of the optimal formulation, namely density, setting times, and compressive strength. These characteristics of geopolymer compositions No. 3–5 are presented in Table 4.

Formulation No. 3 presented the lowest mechanical strength. For compositions No. 4 and 5 a denser structure and a slightly higher compressive strength were noted. This is coherent with the fact that FA and BFS are known to participate in the geopolymerization reaction and a higher content of CaO in the FA and BFS (compositions No. 4 and No. 5) results in improved compressive strength of geopolymer due to the formation of hydrated products, such as calcium silicate hydrate (Diaz et al., 2010; Pilehvar et al., 2018).

It should be noted that the use of KOH in the activating solution leads to an increase in compressive strength compared to NaOH: 32 MPa (28 d, No. 5) as opposed to 25 MPa (28 d, No. 4) (García-Mejía and de Lourdes Chávez-García, 2016; Lizcano et al., 2012). This is also coherent with the fact that formulation No. 3 has a compressive strength close to that of formulation No. 4, despite not containing FA and BFS.

Considering that composition No. 5 is characterized with best properties, that formulation (referred to in the following as "optimized formulation") was the selected geopolymeric matrix employed for further studies with the RLOW simulant.

The incorporation of increasing amounts (10, 20, 30 and 40 %v.) of RLOW surrogate (Shell Spirax and Nevastane EP 100 oils) in the optimized formulation was then tested. The fresh paste and the solidified samples have been characterized and the results are shown in Table 5.

For content of oils ranging between 10 and 30 %v., all samples have similar setting time, compatible to the selected WAC, acceptable density and do not present visible defects. Although the compressive strength decreases at increasing oil loading factor, the minimum WAC of 5 MPa is satisfied up to 30 %v. loading. In case of 40 %v. oil content, samples loaded with Nevastane EP 100 met the compressive strength WAC. On the contrary, mechanical characteristics of the samples containing 40 %v. Shell Spirax oil worsen and visible cavities (voids) are present. These are due to very high viscosity of the paste, which exceeded the capabilities of the employed instrumentation[1] and also hindered an effective casting. In this latter case, the use of an additive is fundamental to

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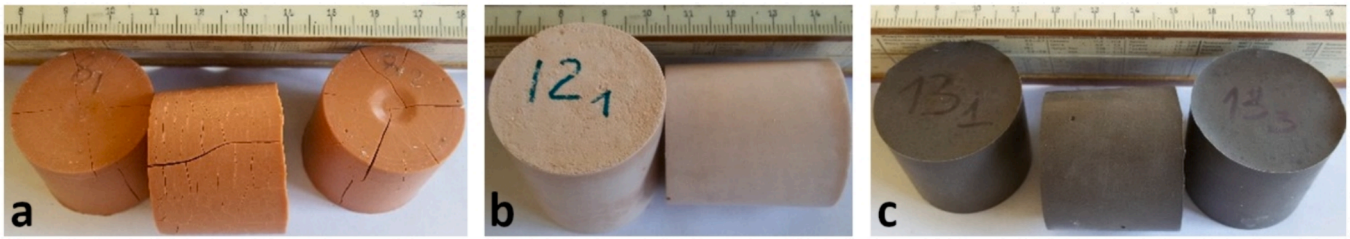[1] The available viscometer (Brookfield LVDV 2 Pro) is intended for low viscosity measurements.

Fig. 1. Geopolymer samples after 28 days of curing: a) MK based (composition No. 1, 2); b) MK-sand based (composition No. 3); c) FA-BFS-MK based (composition No. 4, 5).

Table 4
Physical and mechanical characteristics of geopolymer formulations No. 3–5.

Parameter	Composition No.		
	3	4	5
Vicat Setting time, start/finish (h)	8/48	4/24	4/20
Density (g/cm³)	1.75	1.83	2.15
Compressive strength at 7/14/28 d (MPa)	12/15/22	13/20/25	22/28/32

Table 5
Physical and mechanical characteristics of optimized geopolymer formulations with increasing loading of the two oil waste simulants.

Parameter	Optimized geopolymer with Shell Spirax/Nevastane EP 100 oils content (%v.)					
	0	10	20	30	40	40 + 0.5 %wt. Castament FW-10
Setting time, start (h)	4	3/3	4/3	4/4	5/4	4/-
Setting time, finish (h)	20	22/20	22/20	24/24	36/24	24/-
Density (g/cm³)	2.15	2.10/2.12	1.96/1.98	1.88/1.90	1.65/1.80	1.82/-
Compres. Strength, 7 d (MPa)	22	12/12	10/10	8/8	5/7	7/-
Compres. Strength, 14 d (MPa)	28	15/15	12/13	10/10	6/9	9/-
Compres. Strength, 28 d (MPa)	32	22/24	15/16	12/13	7/11	11/-

improve the fluidity of the loaded geopolymer. To quantify the effect of Castament FW-10 additive on the behavior of the geopolymeric pastes, rheology measurements were performed. Rheograms of the optimal geopolymeric formulation and the paste with different content of oil Shell Spirax are presented in Fig. 2.

It is worth noting that the rheograms of the paste with different content of Shell Spirax are analogous to rheograms of the paste with corresponding content of Nevastane EP 100. Therefore, Fig. 2. only reports the rheograms of the paste with different content of Shell Spirax oil.

It was determined that pastes of all compositions show decreasing viscosity at increasing shear rate, which indicates the pseudoplastic behavior of the tested materials. As the oils content increases from 10 up to 40 %v., the viscosity of the paste and the related shear stress increase at all researched shear rates. Accordingly, geopolymeric paste with 40 % v. oil content is characterized by the greatest tendency to the structuration (highest value of shear stress – see Fig. 2 (b)).

The addition of the surfactant Castament FW-10 (0.5 %wt.) into the paste results in a significant decrease of viscosity and allows to obtain higher quality samples presenting a dense and homogeneous structure and compliant with WAC, even for the highest waste loading tested (Fig. 3). The positive influence of Castament FW-10 addition on structure improvement of the geopolymer is related with the typical effect of surfactants that causes a decrease in surface or interfacial tensions. Thus, the increased fluidity of the paste allows to obtain a denser and more uniform specimen during casting. In addition, Castament FW-10 also contains lithium and calcium which accelerate the setting time of the geopolymeric paste containing 40 %v. of Shell Spirax (Table 5), further improving compliance with WAC.

3.2. Variability of raw materials

In order to reproduce the KIPT formulation by replacing UKRSILL waterglass with Betol K 5020 T, some adjustment in the proportions of silicate solution, KOH and H_2O were made in order to keep the same SiO_2/K_2O molar ratio and total water content in the activating solution (see Table 6). Different raw materials were tested by Nucleco and CEA to reproduce the optimized formulation identified by KIPT. Polimi performed additional tests using the same materials as CEA.

Namely, Nucleco and CEA employed different BFS as reported in Table 6. The chemical composition of the alternative dry precursors
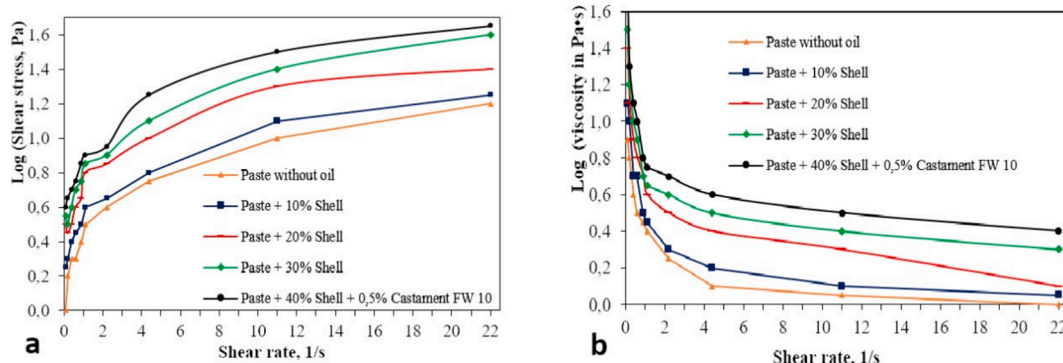

Fig. 2. Rheograms of optimal geopolymeric formulation with different content of Shell Spirax oil.
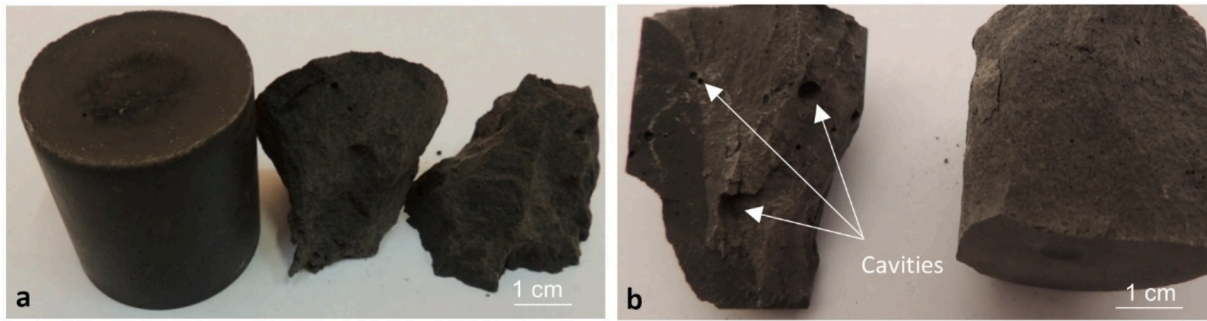
Fig. 3. Geopolymer samples with 40 %v. waste loading after 7 days of curing: a) with Nevastane EP 100; b) with Shell Spirax (left – without Castament FW-10, right – with 0.5 %wt. of Castament FW-10). Cavities are visible in presence of Shell Spirax with no surfactant.

Table 6
Raw materials and quantities employed by Nucleo and CEA to replicate the optimized formulation developed by KIPT.

KIPT optimized Formulation		Nucleco materials		CEA materials	
Component	% wt.	Component	% wt.	Component	% wt.
Fly Ash (Ukr)	34	Fly Ash (Italy)	34	Fly Ash (Italy)	34
BFS (Ukr)	20	BFS (ECOTRADE)	20	BFS (ECOCEM)	20
Metakaolin (Ukr)	14	MK (UK)	14	MK (UK)	14
UKRSILL 32	11	Betol K 5020 T	15.4	Betol K 5020 T	15.4
KOH	9	KOH	8.4	KOH	8.4
H_2O	12	H_2O	10	H_2O	10

employed by CEA, Nucleo and Polimi is reported in Table 2.

Some preliminary tests have been performed by Nucleo and CEA on the reference formulation with and without oil and different results have been obtained. Indeed, the encapsulation of oil wastes with the two formulations based on alternative materials required slightly different approaches depending on the raw materials employed.

For studies performed by Nucleo, to obtain the emulsion samples with 30 %v. of oil waste a small amount of surfactant (0.5 %wt. sodium lauryl sulphate – SLS) was needed.

Similar tests on oil incorporation have been made by CEA but a different observation was made. In this case the 30 %v. of Nevastane oil could be easily incorporated into samples without any surfactant, suggesting that higher loading factors could be achieved with the employed

formulation. It was decided to test different surfactants (sodium dodecyl sulphate – SDS, Brij O10 and Glucopon) with constant proportion of 0.5 %wt. in the challenging condition of 50 %v. of waste (Nevastane EP 100) loading. As can be seen in Fig. 4 the best emulsification and stability was obtained with the non-ionic Glucopon surfactant. This may be due to the higher solubility of Glucopon, the viscosity of the geopolymer grout and the size of the surfactant molecules playing a crucial role on both the emulsification and stability of the geopolymer emulsion.

The difference in the need to use surfactants to achieve 30 %v. waste loading noted between Nucleo and CEA formulations, and resulting mechanical strengths as reported in Table 7, may be attributed to the different BFSs used by the partners while preparing the samples (ECO-CEM BFS used by CEA, ECOTRADE BFS used by Nucleo).

Moreover, mixing system and curing conditions (temperature & relative humidity) proved to have a crucial role on the emulsification process and in the final mechanical properties of the specimens. At CEA, the samples were demolded 24 h after casting and were cured at 20 °C and with a relative humidity higher than 90 %. The appearance of cracks, due to the evaporation of the free water entailing a drying shrinkage, was observed in case of 50 % relative humidity (Fig. 5).

Heat flow evolution during curing was also assessed by CEA, revealing that incorporation of oil does not affect the geopolymerization of process as reported in Fig. 6. In fact, the two heat flow curves for

Table 7
Compressive strength of Mix-formulations employing different raw materials tested by Nucleo and CEA in absence of waste and with 30 %v. oil loading.

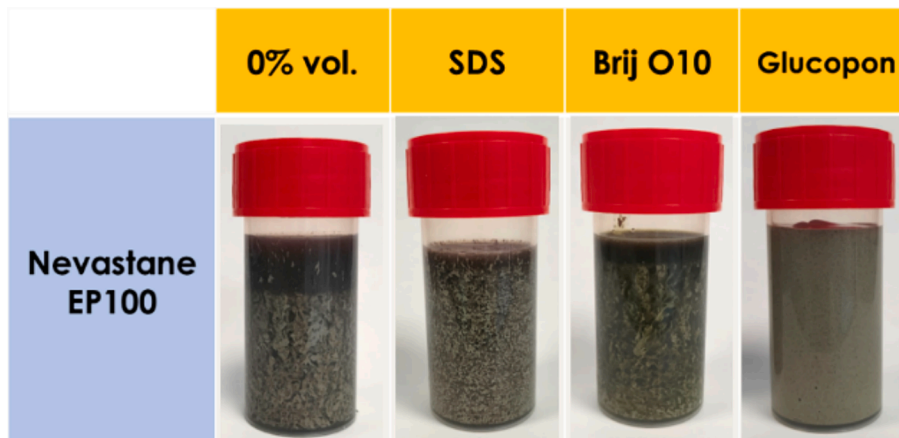| Alternative raw materials	No waste (MPa)	30 %v. Nevastane EP 100 (MPa)
Nucleo	20 ± 2	8 ± 1
CEA	55 ± 3	23 ± 2

Fig. 4. Samples with 50 %v. of Nevastane EP100 oil and different surfactants for the CEA formulation.
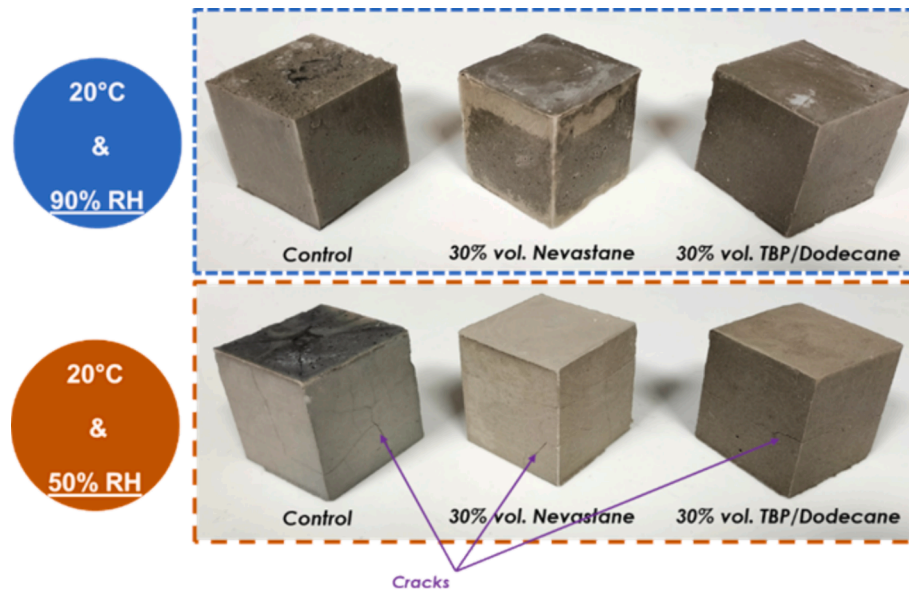
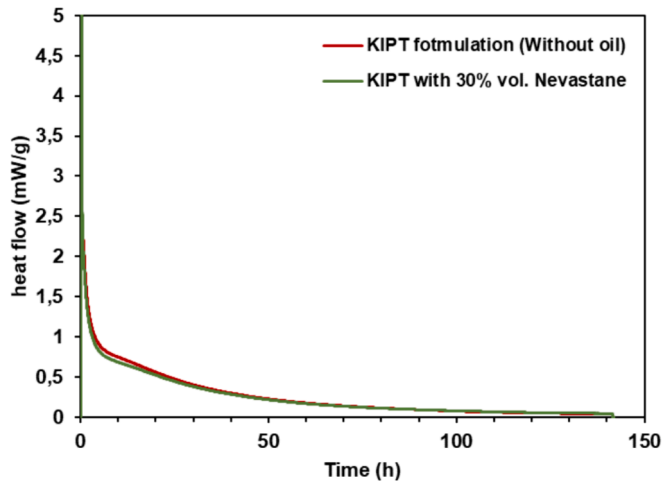**Fig. 5.** Influence of storage conditions on the integrity of the solid samples.

Fig. 6. Heat flow evolution for KIPT formulation reproduced by CEA with and without Nevastane EP 100 oil.

Table 8

Geopolymer formulations considered during robustness study trials in Nucleco with a $\pm$ 2 %wt. variation in materials content.

Formulation ID	FA	BFS	MK	Betol	KOH	H$_2$O
Ref. formulation w/o waste (0)	**28**	**16**	**11**	**13**	**7**	**8**
1	−2	−2	0	−2	2	2
2	2	2	−2	−2	2	0
3	2	−2	−2	2	0	2
4	0	−2	−2	−2	−2	−2
5	0	2	2	2	2	2
6	−2	0	−2	2	2	−2
7	−2	−2	2	2	−2	0
8	2	2	0	2	−2	−2
Ref. formulation w/ waste (9)	**28**	**16**	**11**	**13**	**7**	**8**
10	−2	2	−2	0	−2	2
11	2	−2	2	0	2	−2
12	−2	2	2	−2	0	−2
13	2	0	2	−2	−2	2

sample with and without oil waste are nearly identical, thus confirming the effectiveness of geopolymer binders in encapsulating organic liquids. It is in fact known that, unlike geopolymers, Portland cement experiences retarding effects on hydration in the presence of organic compounds (Nestle et al., 2001; Trussell and Spence, 1994). Even at low concentrations, these compounds induce significant changes in hydrate properties, thereby affecting the microstructural and engineering characteristics of the final composite.

3.3. Robustness study

In total 13 formulations (presented in Table 8) were prepared for each of the two oils (A − Nevastane-based, B − Shellspirax-based) as part of the formulation robustness evaluation. Relative proportions of the six constituents (FA, BFS, MK, Betol, KOH and water) were varied by $\pm$ 2 %wt. in order to assess to which extent a change in the formulation composition could affect the final properties of the samples.

This study aimed at assessing the robustness of the formulation towards a scaleup in large scale facilities, where small deviations from the prescribed composition might occur. In all cases the oil waste loading

(30 %v.) and the proportion of surfactant (0.5 %wt.) were kept constant.

Results on flowability, setting time and compressive strength are presented Fig. 7 and Fig. 8. For comparison, the reference formulation containing no oil waste (indicated as "0″) is also reported in the graphs. In Fig. 7 only data concerning samples prepared with Nevastane EP 100 oil are reported, as corresponding results obtained with Shell Spirax were identical. This finding indicates that flowability and setting time of the formulation are essentially independent on waste type and are only marginally influenced by small variations in materials content.

By comparing the reference formulation with and without added oil (samples 0 and 9-A), it can be seen that initial and final setting times are retarded by approximately 30 − 40 min by the presence of the waste. These values are significantly lower from those obtained employing Ukrainian raw materials (see Table 5), which resulted in much longer setting times, thus indicating that the source of precursors can significantly affect the properties of the paste.

Concerning compressive strength, all samples measured > 5 MPa at 28 days, thus confirming the robustness of the formulation and the acceptability of resulting specimens. However, for samples 1A, 2A and 6A with Nevastane EP 100, as well as sample 1-B with Shell Spirax, bleeding of oil was observed. This fact should be further investigated, as waste bleeding could impair disposability.
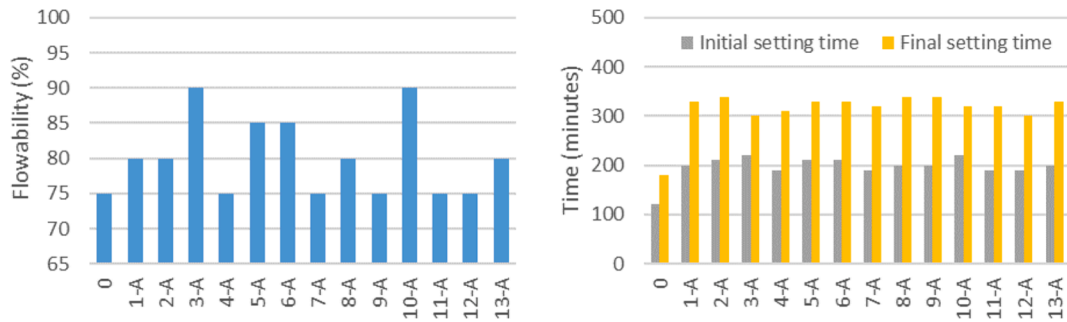
Fig. 7. Robustness study: flowability and initial/final setting times for sample containing Nevastane EP 100. Sample 0 refers to the reference formulation with no waste.
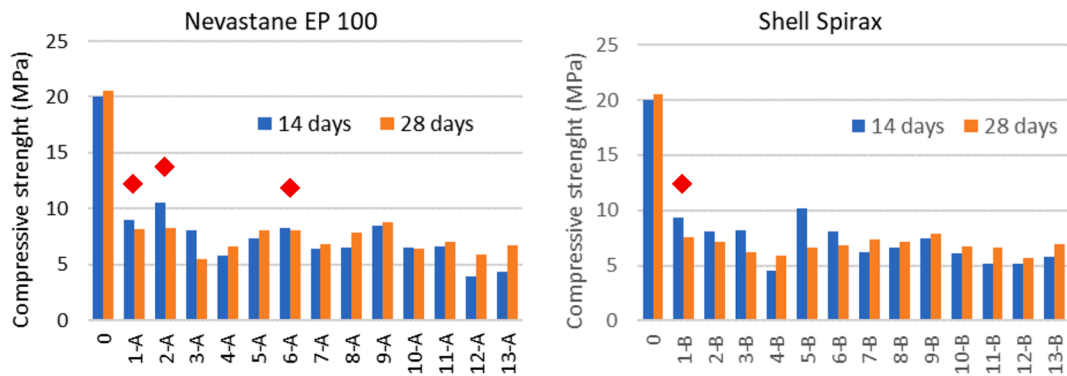

Fig. 8. Robustness study: compressive strength at 14 and 28 days (mean relative uncertainty ± 10 %). Samples where some bleeding was observed are indicated with the red diamonds. Sample 0 refers to the reference formulation with no waste.

3.4. Encapsulation of other surrogate RLOW

Preliminary tests were also conducted to assess the possibility of directly encapsulating 30/70 TBP/dodecane and LSC in the developed formulation. The tests were conducted with the raw materials employed by the CEA as reported in Table 6.

Up to 30 %v. of LSC could be encapsulated by Polimi with no modifications to the mixing protocol. For this type of waste, no surfactant was needed as the scintillation cocktail already contains emulsifiers. Resulting specimen appeared dense, with no superficial defects and no bleeding. Compressive resistance of loaded specimen amounted to 23 ± 1 MPa, to be referenced with 44 ± 2 MPa measured for the non–loaded specimen prepared by Polimi. This latter value is also comparable with the corresponding one obtained by CEA and reported in Table 7.

In case of TBP/dodecane, a 30 %v. loading could be achieved by CEA with the use of 0.5 %wt. Glucopon surfactant, providing a stable emulsion and uniform cured specimen. Resulting compressive strength after 28 days of curing is 18 ± 2 MPa. Similarity of compressive strength of LSC- and TBP/dodecane-loaded specimen with data reported in Table 7 for oil suggests that, when the same raw materials are employed, the main factor affecting compressive strength is the amount of encapsulated waste, and not its nature, if the waste is well incorporated and the emulsion is stable.

SEM observations were also conducted on cured samples, as reported in Fig. 9. The reference formulation with no waste shows few cavities which are due to the entrainment of air during the mixing process. For the two samples with oil and TBP/dodecane, the size of the cavities ranges between 30–150 μm, indicating a good dispersion of the organic liquid.

Finally, as discussed earlier on the benefit of using AAM instead of OPC, also in case of encapsulation of TBP/dodecane heat flow measurements did not show any impact on the geopolymerization reaction
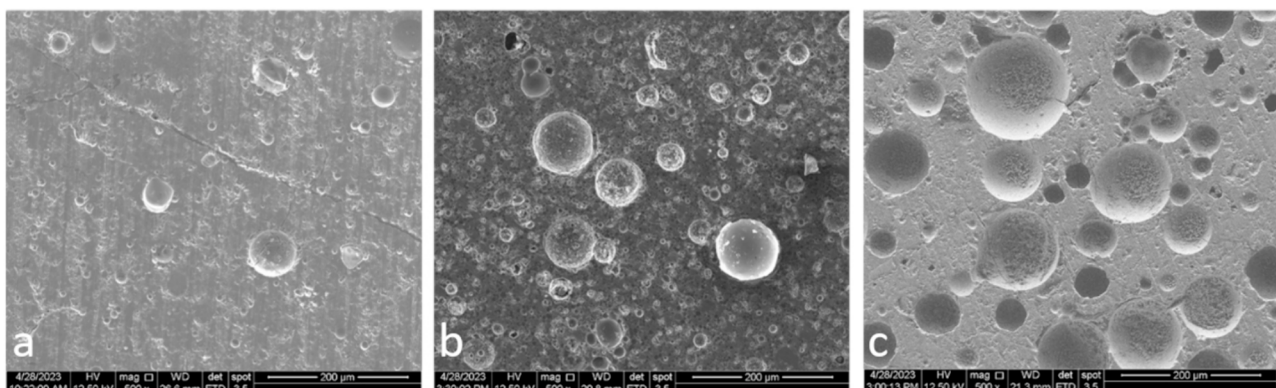

Fig. 9. SEM analysis for the consolidated materials: a) without waste; b) with 30 %v. TBP/dodecane; c) with 30 %v. Nevastane EP 100.

due to the presence of the organic liquid.

4. Conclusions

Geopolymer formulations with various ratios of Al-Si raw materials and different types of alkaline activators were investigated for the incorporation of RLOW, with particular regard to industrial lubricating oils. An optimal composition based on FA, BFS, MK, liquid potassium glass, potassium hydroxide and distilled water was developed. The obtained samples are characterized by a dense, homogeneous structure, with setting time and compressive strength compliant with adopted WAC.

The present study highlighted that a change in raw materials (mainly different BFS), mixing protocols and curing conditions can 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 and integrity on the properties of the hardened specimen.

An incorporation rate of Nevastane and Shellspirax oil up to 30 %v. can be achieved by the developed formulation without a surfactant. Higher waste loading factors could be achieved by using specific additives such as superplasticizer to decease the viscosity and surfactants. Differences in achievable loading of waste, as well as the need to rely on surfactants are likely due the different raw materials employed.

The robustness study confirmed that the developed geopolymer formulation presents a compressive strength of at least 5 MPa when loaded with 30 %v. of oil waste, and a range of flowability between 75 %-90 %, irrespectively of small variations in its composition. Some bleeding has been observed in some samples, mainly with Nevastane oil.

Preliminary data indicate that the developed formulation is also adequate for the immobilization of other RLOW, such as TBP/dodecane mixtures and LSC, with a compressive strength higher than selected WAC at 30 % of volume loading.

Funding sources

CRediT authorship contribution statement

Sergey Sayenko: Writing – original draft, Conceptualization. **Yevhenii Svitlychnyi:** Writing – review & editing, Methodology, Investigation. **Volodymyr Shkuropatenko:** Investigation, Formal analysis. **Federica Pancotti:** Writing – review & editing, Project administration. **Simona Sandalova:** Writing – original draft. **Arnaud Poulesquen:** Writing – review & editing, Supervision. **Isabelle Giboire:** Project administration. **Abdelaziz Hasnaoui:** Validation, Investigation. **Davide Cori:** Writing – review & editing, Investigation. **Gabriele Magugliani:** Writing – review & editing, Investigation. **Eros Mossini:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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