DIRECT CONDITIONING OF LIQUID ORGANIC RADIOACTIVE WASTE INTO A GEOPOLYMER MATRIX

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ABSTRACT

The management and disposal of liquid organic radioactive waste pose significant challenges due to their hazardous nature and long-term environmental impacts. Conventional methods, such as incineration and solvent extraction, often result in secondary waste streams or generate harmful emissions. To address these issues, we investigate a novel approach for directly conditioning the liquid organic radioactive waste into a geopolymer matrix. A series of experimental tests were conducted to evaluate the feasibility and effectiveness of the direct conditioning method. Engine oil was used as a simulated organic radioactive waste and mixed with blast-furnace slag, alkali activators, and other additives to form a homogeneous geopolymer mixture. The mixture was then cured under controlled conditions, allowing the formation of a hardened geopolymer matrix incorporating the liquid organic radioactive waste. Various techniques, including UV/Vis spectroscopy, X-Ray Diffraction (XRD), microscopy and compressive strength tests, were employed to characterise the physical, chemical, and mechanical properties of the resulting geopolymer waste forms. Compressive strength tests demonstrated that the geopolymer waste forms exhibited satisfactory mechanical performance, suggesting their potential suitability for long-term storage and disposal of liquid organic radioactive waste. Furthermore, leaching experiments were conducted to assess the leachability of oil and selected elements from the conditioned waste form. The results revealed very low oil leaching, indicating high immobilisation efficiency. Overall, this study demonstrates the successful direct conditioning of liquid organic radioactive waste into a geopolymer matrix using blast furnace slag alkali-activated binder. The results highlight the potential of this approach as a sustainable and effective solution for the immobilisation and safe disposal of liquid organic radioactive waste streams. Further research and optimisation are necessary to expand the application of this technique to other liquid organic waste types and evaluate its long-term performance under various environmental conditions.

1 INTRODUCTION

Managing liquid organic radioactive waste (LORW) poses a significant challenge in nuclear industries due to its hazardous nature and long-term environmental impact [1]. Conventional treatment methods, such as incineration or absorption into porous material before solidification, have limitations and may not always provide a sustainable and environmentally friendly solution [2]. In recent years, alternative approaches utilising geopolymer matrices have emerged as promising options for the direct conditioning of LORW.

Geopolymers are inorganic, amorphous aluminosilicate materials synthesised through the alkaline activation of either metakaolins or industrial by-products, such as blast furnace slag (BFS) and fly ash [3][4][5][6]. In addition to being cured under normal temperature and pressure conditions, geopolymers offer numerous advantages, including but not limited to excellent resistance to acids and heat, increased resistance to leaching, robust structural integrity, and mechanical stability [7]. Unlike cement, the setting mechanism of geopolymers relies on rapid polymerisation rather than hydration, resulting in a significantly shorter curing time [8]. They are also often considered environmentally friendly due to their lower greenhouse gas emissions than cement [9][10]. These characteristics suggest that geopolymers hold the potential for long-term stability, making them a promising material candidate for solidifying radioactive waste.

This paper presents an experimental study on the direct route of conditioning organic waste into the geopolymer matrix. That involves directly incorporating the organic liquid, motor oil in our case, into a geopolymer mortar . The geopolymer paste slurry is created by mixing BFS as a solid precursor with an alkaline solution as an activator [11]. The investigation will involve a range of parameters, including varying surfactant type and concentration, curing conditions, and evaluation of the resulting geopolymer structural, mechanical, and leaching properties to assess waste immobilisation efficiency. Overall, this research seeks to advance the understanding of the direct conditioning process of LORW in geopolymer matrices and contribute to developing innovative strategies for the safe and efficient immobilisation of liquid organic radioactive waste. Successful direct conditioning of liquid organic radioactive waste into geopolymer matrices could offer a sustainable solution for managing this challenging waste stream, reducing potential environmental hazards, and minimising the risk of contaminant release.

2 METHODOLOGY

2.1 Materials and sample preparation

In all experiments, finely ground granulated BFS (Ecocem Benelux) provided by SCK-CEN was used, along with locally sourced quartz sand as the added component. The alkali binder combined Sodium silicate (Sigma-Aldrich) and Sodium hydroxide (Penta). The waste oil used in the experiments was Mogul TB 32. The study evaluated the performance of three distinct surfactants: Tween® 80, Sodium Dodecyl Sulfate (SDS), and Glucopone 600 CS UP solution (all Sigma-Aldrich).

The sample preparation protocol was conducted at the laboratory scale. The activating solution was prepared 24 hours before the actual sample preparation. This involved dissolving Sodium silicate in a solution of 10M Sodium hydroxide and demineralised water. Before the main sample preparation, a mixture of motor oil Mogul and a surfactant was mixed for 10 minutes. Following this, the BFS and activating solution were blended for 3 minutes, after which the oil-surfactant emulsion was incorporated, and the mixture was further mixed for 10 minutes. Subsequently, the sand was added to the mixture and mixed for 3 minutes.

A thoroughly mixed geopolymer paste was cast into cubic molds, each with dimensions of 50×50×50 mm. After casting, the samples were left to harden. Following this, the samples were demolded, weighted and subjected to a controlled curing process for 28 days. The controlled conditions were: one in a dry environment and the other in a humid environment, both maintained at laboratory temperature. The humid condition was established by placing the samples in a sealed container positioned above the demineralised water's surface, ensuring the sample remained untouched by the water.

2.2 Sample analysis

The key objectives of this research were to assess the feasibility of incorporating motor oil-based liquid organic waste into an alkali-activated BFS, to evaluate the mechanical and chemical stability of the resulting geopolymer composite, investigate the leaching behaviour and the immobilisation efficiency of the liquid organic waste within the geopolymer matrix and to analyse the microstructural properties and phase composition of the geopolymer composite through advanced characterisation techniques.

The cured samples were tested for compressive strength using an MTS 300 Exceed® device in accordance with Czech National Standard CSN EN 12390-3 Testing hardened concrete - Part 3: Compressive strength of test specimens.

Samples, containing the surfactants Tween® 80 and SDS at concentrations of 0.45 wt% and 0.75 wt%, and cured in dry and humid curing conditions, were subsequently subjected to a 91-day leaching test in demineralised water. At specific intervals (2, 7, 14, 28, 56, and 91 days), the demineralised water was replaced and analysed for the presence and concentration of the oil and leached elements. The leachate's pH and conductivity were measured using a WTW pH/Cond 3320 Multi-Parameter Portable Meter (Xylem Analytics). Calcium values were determined through titration, while silicon and iron concentrations were determined using a UV/Vis Spectrophotometer Jenway 6850 (Cole-Parmer Instrument Company).

Diffraction patterns were collected with a Malvern PANalytical Empyrean, series 3 diffractometer equipped with a conventional X-ray tube (Co K_α radiation, 40 kV, 30 mA, line focus), multicore optics and a linear position sensitive detector PIXCel3D detector. In this case, we used conventional Bragg Brentano geometry with the iCore optical module set with a 0.03 rad Soller slit, a 0.25° divergence slit and a 14 mm mask in the incident beam. The dCore optical module set with a 0.25°anti scatter slit and 0.04 rad Soller slit was used in the diffracted beam. X-ray patterns were collected in the range of 5 to 85 deg. 2theta with the step of 0.013 deg and 600 sec/step producing a scan of about 4 hours 11 minutes. Samples were adjusted for analysis in the standard sample holder with “backloading”. XRD patterns were not pre-treated before interpretation as no background correction was needed. Qualitative analysis was performed with the HighScorePlus software package (Malvern PANalytical, The Netherlands, version 5.2.0) [12] and PDF-4+ database [13].

3 RESULTS AND DISCUSSION

3.1 Surfactant addition

In our initial experimentation phase, we utilised a waste load of 5 wt% while investigating the performance of three different surfactants — SDS, Glucopone, and Tween® 80 — at varying concentrations of 0.15, 0.3, 0.45 and 0.75 wt%. The initial trials using 0.15 and 0.3 wt% of these surfactants produced unsatisfactory outcomes. Although the samples demonstrated sufficient hardening, a significant oil release was noticeable. In response to this issue, we raised the surfactant levels to 0.45 and 0.75 wt%, resulting in enhanced homogeneity and decreased oil release from the sample during the hardening period. During these experiments, challenges arose regarding the surfactant Glucopone. As we increased the surfactant quantity, we encountered difficulties effectively mixing the oil and Glucopone. Furthermore, an additional complication arose as the Glucopone within its original container solidified over time, thus requiring heating to restore it to its liquid state.

The analysis of the compressive strength results (Fig. 1) showed that the introduction of waste oil with surfactant has resulted in a reduction in compressive strength compared to the standard sample (the BFS formulation without added oil and surfactant), which exhibited a compressive strength of 48.25 MPa. The compressive strength values varied from 17 to 26.4 MPa depending on the surfactant type and concentration. Across all surfactants, there was a notable trend where the compressive strength tended to decrease as the surfactant concentration increased. This suggests that higher surfactant concentrations might lead to weaker overall strength in the samples. There is no consistent pattern across all surfactants and concentrations when comparing dry to humid curing conditions, indicating a complex relationship between surfactants and the curing environment. Glucopone's inconsistent performance, including mixing challenges and solidification suggests that it might not be a favourable choice for this application. Therefore, we conducted subsequent experiments only with the other two remaining surfactants.

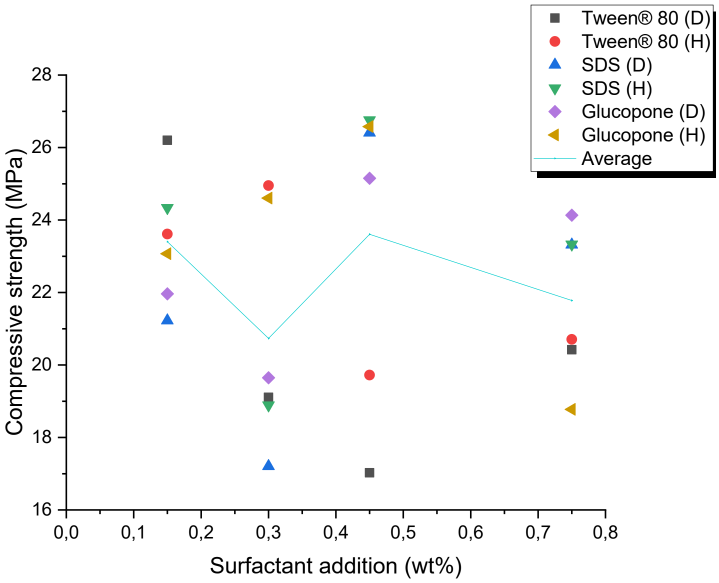

Fig. 1 Compressive strength variation with different surfactant, surfactant concentration and curing conditions (D - dry, H – humid).

3.2 Leaching experiments

The analysis of leachate and subsequent sample characterisation post-leaching experiments provided valuable insights into the behaviour of the samples across varied curing conditions and surfactant concentrations. These insights highlighted clear patterns in waste oil behaviour, demonstrating an initial release phase followed by limited or negligible oil release as time progressed as shown in Fig. 2.

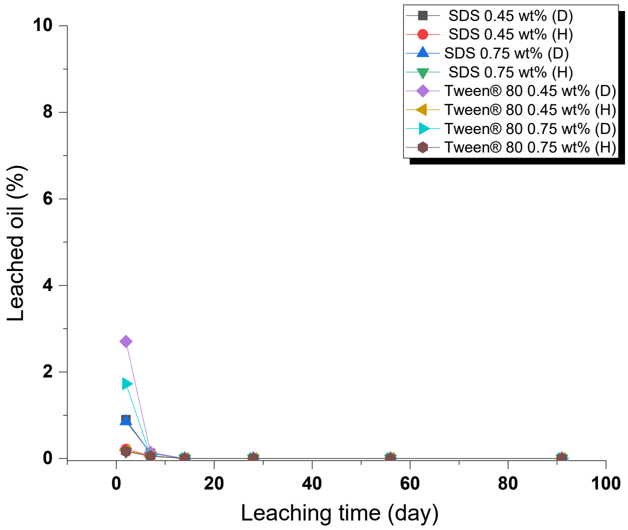

Fig. 2 Oil release from geopolymer samples in demineralised water

The amount of leached oil in the initial phase was lower in samples that were cured in humid conditions, indicating the role of humidity in speeding up leaching mitigation. In the case of samples with SDS at 0.45 wt%, it is evident that there is an initial leaching observed at day 2, followed by a rapid reduction in subsequent days, eventually reaching zero from day 14 to 91. Similarly, for the sample with SDS at 0.75 wt%, both dry and humid conditions exhibit a similar pattern. In contrast, samples with Tween® 80 at 0.45 wt% show higher initial leaching levels, particularly in dry conditions, which decrease from day 14 to a negligible level. Comparable behaviour is observed for samples with Tween® 80 at 0.75 wt%, suggesting that despite initial releases, both surfactants tend to stabilise over time.

Following the analysis of oil leaching, our assessment extended to the calcium, silica (Fig. 3) and iron leaching as these elements are fundamental parts of the geopolymer structure, and tracking their leaching provides insights into potential impacts on structural integrity and mechanical properties over time. The results then help to evaluate the material's long-term durability and stability under real-world conditions. Throughout the experiment, calcium leaching had a consistent upward trend across all samples. The initial values, ranging from 5.2 to 9.6 mg/l on day 2, increased to a range of 28.5 to 31.3 mg/l by day 91. The impact of SDS surfactant concentration on calcium leaching was only minor, whereas higher levels correlated to a slight increased leaching. Similar tendencies were observed with Tween® 80. Additionally, when comparing leaching between dry and humid-cured samples, there was evidence of data variability, which could potentially be attributed to experimental factors or interactions among parameters.

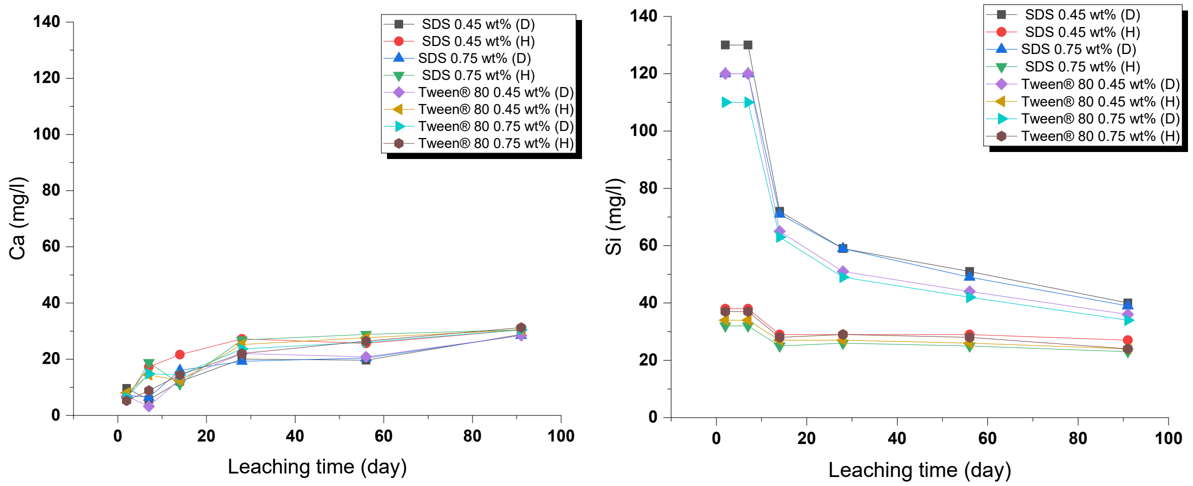

Fig. 3 Leaching of calcium and silica from geopolymer samples in demineralised water.

Leached silica concentrations were consistently higher in the dry-cured samples, regardless of surfactant types and concentrations, with initial values ranging from 110 to 130 mg/l on day 2. Following the initial steep decrease in leached amounts (ranging from 63 to 72 mg/l) between days 7 and 14, the decline slowed, stabilising at 34 to 40 mg/l by day 91. The humid-cured samples began with initial values ranging from 32 to 38 mg/l on day 2. Similar to the dry-cured samples, the humid-cured samples displayed an evident reduction in leached silica between days 7 and 14, although the decrease was comparatively less pronounced. Following this initial decrease, the humid-cured samples maintained a relatively consistent range of leached silica values, with only minor fluctuations occurring between 24 and 29 mg/l over the duration of the leaching experiment. Although the leached iron concentrations were significantly lower in comparison to those of silica and calcium, they displayed a similar pattern, with the highest concentrations on days 2 and 7, ranging from 0.05 mg/l to 0.14 mg/l, followed by a decrease to the values below the detection limit later in the leaching experiment. This pattern remained consistent regardless of curing conditions or added surfactants.

As mentioned previously, the leachate was subjected to pH and conductivity analysis, the outcomes of which are shown in Fig. 4. The conductivity values mirrored those observed in silica leaching. However, there was a greater degree of variability among samples that utilised different surfactant types and concentrations. The conductivity values were consistently higher within the dry-cured samples, from 194 to 224 µS/cm on day 2. Following a sharp decrease between days 7 and 14 to approximately half of the initial value, the values stabilised. The humid-cured samples displayed initial conductivity values from 141 to 164 µS/cm. There was an initial decline similar to the dry-cured samples, yet less steep followed by a slight increase. The values reached a stable range of 83 to 87 µS/cm by day 91. The differences in conductivity values among samples that utilised different surfactant types and concentrations were less pronounced than with the dry-cured samples.

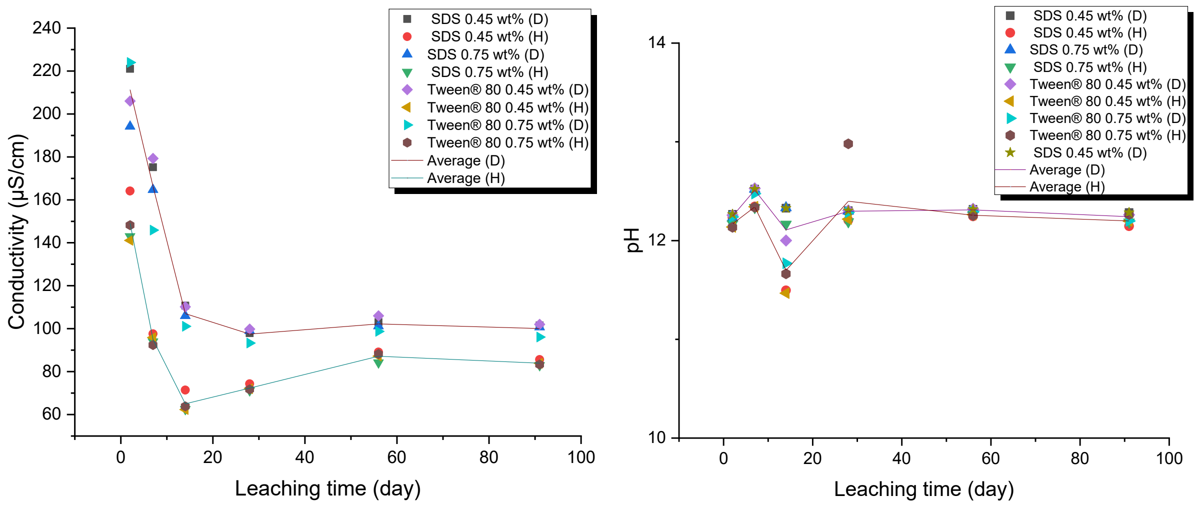

Fig. 4 Electric conductivity (left) and pH (right) values during leaching.

After completing the leaching experiments on day 91, the samples were shortly dried at laboratory temperature and analysed for compressive strength. The outcomes of this analysis have been documented in Tab. 1. The observed increased compressive strength after leaching could be attributed to several factors. The leaching out of soluble components might have helped reduce potential weakening effects arising from the concentration of alkali-rich regions during the initial curing stages. Leaching may have resulted in a denser and more compact microstructure within the geopolymer samples, characterised by enhanced inter-particle bonding and reduced porosity. Despite the variation in compressive strength values observed between the samples before and after leaching, it remains noteworthy that all samples continue to meet the Waste Acceptance Criteria (WAC) for the disposal of radioactive waste in terms of compressive strength characteristics.

Tab. 1 Compressive strength evaluation before and after exposure to leaching.

Surfactant addition (wt%)		Compressive strength before leaching (MPa)	Compressive strength after leaching (MPa)
Tween® 80 (D)	0.45	17.03	31.37
	0.75	20.42	29.75
Tween® 80 (H)	0.45	19.72	28.59
	0.75	20.71	24.96
SDS (D)	0.45	26.41	34.55
	0.75	23.32	29.37
SDS (H)	0.45	29.73	29.97
	0.75	22.30	27.56

3.3 XRD analysis

XRD analysis was conducted on various samples. The initial analysis focused on the used BFS raw material (Fig. 5), primarily containing amorphous SiO_2 with traces of $CaCO_3$. The second analysis involved the standard sample, prepared without any added oil or surfactant (Fig. 6), while the third analysis examined the sample where waste oil and a 0.75 wt% concentration of Tween® 80 were added (Fig. 7).

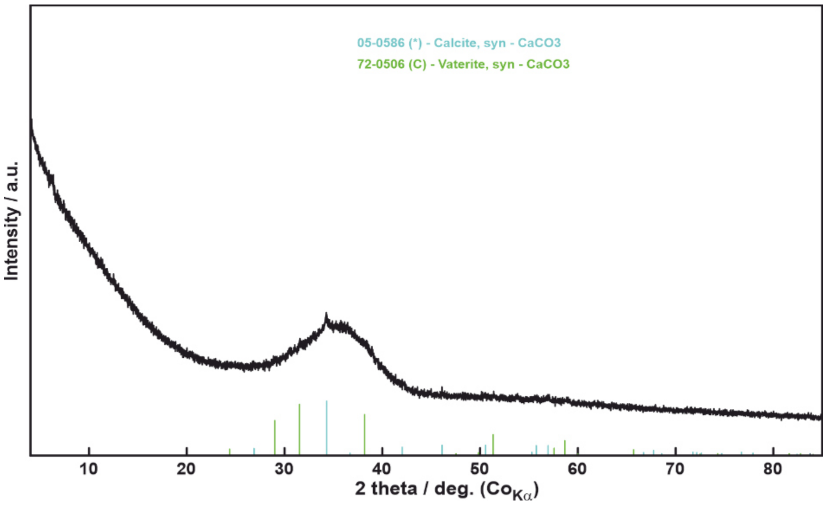

Fig. 5 XRD analysis of BFS raw material

The observed differences in mineral composition between the geopolymer samples can be attributed to the complex interplay of chemical reactions and interactions that occur during the geopolymerisation process, as well as the influence of the added oil and subsequent leaching process. In the geopolymer samples, minerals like quartz, feldspar and mica can be associated with incorporated sand. Additionally, tobermorite and hydrotalcite are commonly associated with the reaction products of the geopolymerisation process forming due to the alkali activation of the BFS. The presence of these minerals signifies the formation of a stable geopolymer matrix. Identifying wollastonite in the sample suggests a specific reaction during synthesis and curing. However, it's noteworthy that wollastonite typically forms at elevated temperatures, which are not typically achieved during the geopolymerisation process.

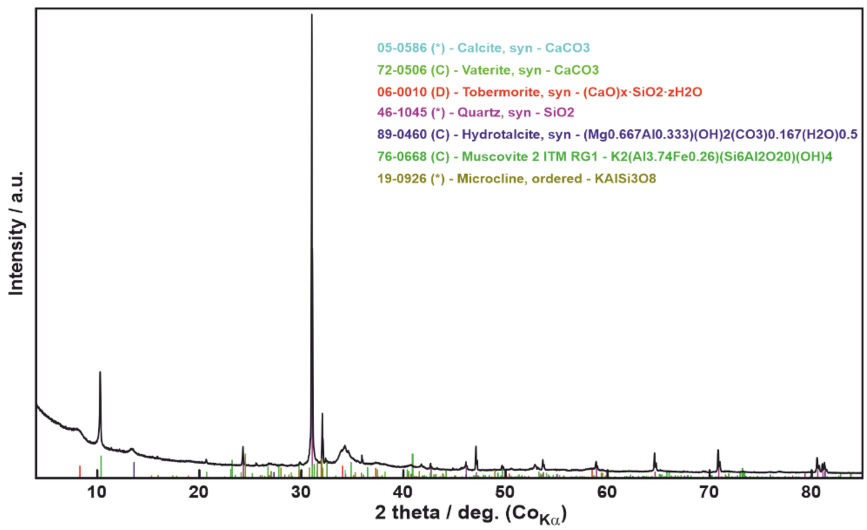

Fig. 6 XRD analysis of a standard sample prepared without oil and surfactant addition.

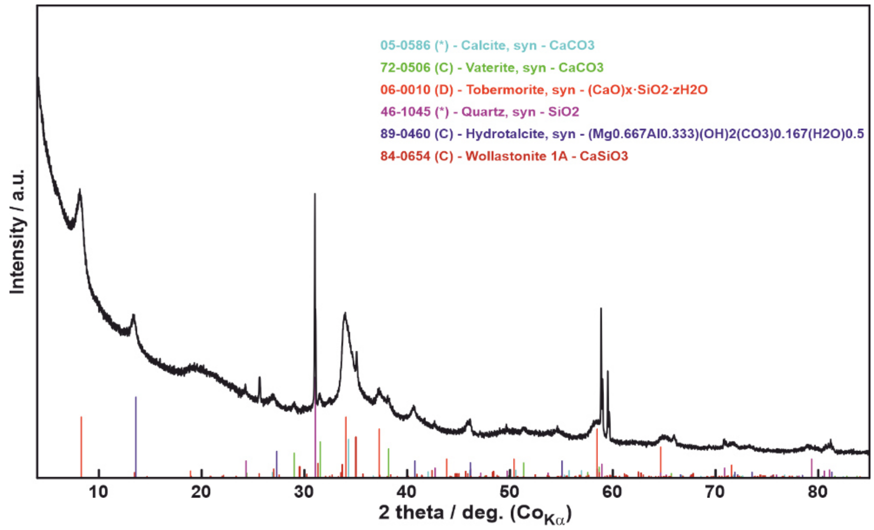

Fig. 7 XRD analysis of sample with 5 wt% waste oil and 0.75 wt% Tween® 80.

3.4 Microscope

In our analysis, we used a stereoscopic microscope, specifically the SMZ 171 T-LED model from Motic, equipped with a MOTICAM S12 camera to examine the samples (Fig. 8). Within our observations, the left image portrays the standard sample, without any oil addition, while the right image shows the sample with added waste oil. In both images a magnified view of the grains of quartz sand incorporated into the samples was visible. We detected the presence of fractures within the samples, particularly concentrated towards their edges. These fractures are visible indicators of the stress and deformation experienced by the samples. A contrast in colour is evident between the surface and near-surface regions of the samples, likely due to the influence of factors such as water and air during curing, leaching, and drying. The pore structures in the samples were also examined. The standard sample displayed significantly smaller and less frequent pores than those with added waste oil. The sample with added waste oil exhibited larger and more pronounced pores, signifying a clear impact on its porosity and permeability. These findings underscore the role of added oil in modifying the material's microstructure, influencing its physical properties and behaviour.

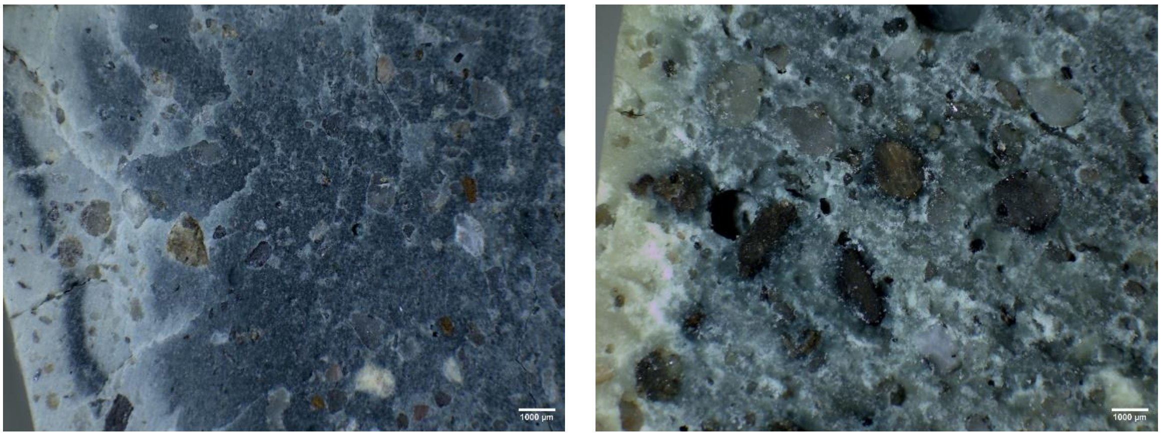

Fig. 8 The stereoscopic microscope images of the sample without added waste oil (left) and with waste oil and surfactant mixture (right).

4 CONCLUSION

This study explores an innovative approach for addressing the management and disposal challenges associated with liquid organic radioactive waste (LORW), known for its hazardous nature and long-term environmental impact. Conventional disposal methods often generate secondary waste streams and emissions, highlighting the need for sustainable alternatives. In this context, we investigated the direct conditioning of LORW into a geopolymer matrix, which offers promising prospects. Using engine oil as a surrogate for LORW, we combined BFS, alkali activators, and surfactants to create homogeneous geopolymer mixtures, which were cured under controlled conditions to form hardened geopolymer matrices incorporating the liquid organic waste. We employed multiple characterisation techniques, to assess the physical, chemical, and mechanical properties of the geopolymer waste forms. The results of this study provide several key insights. First, compressive strength tests indicated that the geopolymer waste forms exhibited satisfactory mechanical performance, suggesting their potential suitability for the long-term storage and disposal of LORW. However, adding waste oil with surfactants resulted in a reduction in compressive strength compared to the standard geopolymer samples, with a notable trend of decreasing strength as surfactant concentration increased. The choice of surfactant and curing conditions also played a significant role in shaping the compressive strength outcomes, indicating a complex relationship between surfactants and the curing environment. Leaching experiments revealed promising results, with very low oil leaching observed, indicating high immobilisation efficiency. Additionally, leaching studies on calcium, silica, and iron indicated their initial release, followed by stabilisation. The conductivity values mirrored trends in silica leaching, with variations among surfactant types and concentrations. XRD analysis demonstrated variations in mineral composition between geopolymer samples, suggesting complex chemical reactions during geopolymerisation and the influence of oil and leaching on mineral phases. Microscopic examination of the samples revealed fractures, colour variations, and distinct pore structures, further highlighting the impact of added oil on the material's microstructure. In conclusion, this research demonstrated the direct conditioning of liquid organic waste into geopolymer matrices using BFS alkali-activated binders. The findings highlight the potential of this approach as a potential solution for the immobilisation and safe disposal of liquid organic radioactive waste streams. However, further research and optimisation are necessary to expand its applicability to other types of liquid organic waste and evaluate long-term performance under diverse environmental conditions.

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REFERENCES

[1] Technical Reports Series No.427: Predisposal Management of Organic Radioactive Waste, IAEA 2004, Vienna

[2] TECDOC-656 Treatment and conditioning of radioactive organic liquids, IAEA 1992, Vienna

[3] R. S. Krishna, J. Mishra, M. Zribi, F. Adeniyi, S. Saha, S. Baklouti, F. U. A. Shaikh, H.S. Gökçe, "A review on developments of environmentally friendly geopolymer technology", Materialia, Volume 20, 2021.

[4] T. Hertel, Y. Pontikes, "Geopolymers, inorganic polymers, alkali-activated materials and hybrid binders from bauxite residue (red mud) – Putting things in perspective", Journal of Cleaner Production, Volume 258, 2020, https://doi.org/10.1016/j.jclepro.2020.120610.

[5] S. S. Mohapatra, J. Mishra, B. Nanda, S. K. Patro, "A review on waste-derived alkali activators for preparation of geopolymer composite", Materials Today: Proceedings, Volume, 2022, pp. 440–446.

[6] P. Duxson, A. Fernández-Jiménez, J. L. Provis, G. C. Lukey, G C, A. Palomo, J. S. J. van Deventer, "Geopolymer technology: the current state of the art", Journal of Materials Science, Volume 42, Issue 9, 2007, DOI:10.1007/s10853-006-0637-z

[7] N.B. Singh, B. Middendorf, "Geopolymers as an alternative to Portland cement: An overview", Construction and Building Materials, Volume, 2020, https://doi.org/10.1016/j.conbuildmat.2019.117455.

[8] N. A. Girke, H.-J. Steinmetz, A. Bukaemsky, D. Bosbach, E. Hermann, I. Griebel, "Cementation of Nuclear Graphite Using Geopolymers", IAEA-TECDOC-1790, IAEA 2016.

[9] E. R. Vance, D. S. Perera, "Geopolymers for nuclear waste immobilisation", Geopolymers: Structures, Processing, Properties and Industrial Applications, 2009, pp. 401–420.

[10] R. Firdous, D. Stephan, J. N. Yankwa Djobo, "Natural pozzolan based geopolymers: A review on mechanical, microstructural and durability characteristics", Construction and Building Materials, Volume 190, 2018, https://doi.org/10.1016/j.conbuildmat.2018.09.191.

[11] Ch. Reeb, Ch. Pierlot, C. Davy, D. Lambertin, "Incorporation of organic liquids into geopolymer materials - A review of processing, properties and applications", Ceramics International, Volume 47, Issue 6, 2021, https://doi.org/10.1016/j.ceramint.2020.11.239.

[12] T. Degen, M. Sadki, E. U. König, G. Nénert, "The HighScore suite", Journal of Powder Diffraction, Volume 29, 2014, Suppl. S2, S13 - S18, http://doi.org/10.1017/S0885715614000840.

[13] PDF-4+ database, International Centre for Diffraction Data, Newtown Square, PA, U.S.A. release 2023.