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Improved Geopolymers for Encapsulation of Molten Salts from Thermal Treatment Processes

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ABSTRACT

Organic waste is commonly generated during the operation of nuclear facilities and decommissioning. High prices for repositories force radioactive waste producers to lower the volume of organic radioactive waste. Thermal treatment is one of the key routes for volume reduction, and Molten Salt Oxidation (MSO) is one of the potential processes. In the technology, the organic waste is dosed, together with an oxidising medium, under the surface of the molten salt, where flameless oxidation takes place, and non-combustible materials are trapped in the molten salts. For this study, the process for encapsulation of molten salt waste into an improved geopolymer matrix was conducted. The commercial geopolymer LK was encapsulated with 10 wt.% of volcanic tuff as a filler. The volcanic tuff was chosen for its zeolite richness for radionuclide trapping, good availability, and cost. The experiments were conducted by encapsulating 5, 10, and 15 wt.% of waste salts into the matrix. The mixture was cured under controlled conditions, and its physical and mechanical properties were tested by compressive strength and XRD analysis. Secondly, the molten salts were chemically enhanced for possible encapsulation. The molten salt waste mainly comprises Na_2CO_3 hydrates, which can cause sample instability and cracking. The chemical reaction with calcium hydroxide was conducted to form a more stable $CaCO_3$. The resulting decantate had an average elemental composition of Na:Ca = 52.6:47.4. The resulting salt was encapsulated in a geopolymer with controlled conditions, and its physical and mechanical properties were tested for compressive strength and XRD analysis. The experiments were conducted with 5, 10, and 15 wt.% of enhanced waste added into the matrix. Compressive strength tests demonstrated satisfactory mechanical performance for future use, but more research is needed for possible waste load increase and sample stability.

1 INTRODUCTION

Radioactive waste is generated during the nuclear power plants and facilities. Nuclear power plants and research reactors contribute mostly to these sources [1]. The waste can be divided into several groups based on its radioactivity level: low-level, medium-level, and high-level radioactive waste.[2] The assessment of the reactor pool water confirms the presence of ^{134}Cs and ^{137}Cs as fission products. These elements have special attention due to their long-term radiation risk, high solubility, and environmental mobility. Overall, radioactive waste should be managed to ensure environmental protection. Several approaches are suited for radioactive waste treatment, such as coagulation, membrane filtration and ion exchange. [1-4]

Ion exchange resins (IER) are organic granules utilised for water purification processes and used in the nuclear industry [5]. These resins remove unwanted impurities, ions and other contaminants, e.g., Cs^+, Sr^{2+}, and Co^{2+} ions. Over time, the IER must be regenerated or replaced; when this happens, it must be appropriately disposed of. The direct conditioning of IER waste was studied many times, and few methods for direct immobilisation were developed [6-8]. Yet several problems arise when direct immobilisation occurs, as specific high volume of the IER and high-water absorption causing swelling may damage the immobilisation matrix; the total decomposition of IER into ashes and their volume reduction open new possibilities for immobilisation processes.

One of the suited technologies for IER decomposition is the Molten Salt Oxidation (MSO). This process is based on the flameless decomposition of organic wastes in molten salts. The oxidation is performed by dosage of oxidising medium with the waste below the molten salt's surface [9]. Other non-combustible inorganic substances, i.e., heavy metals or radionuclides, are trapped in the molten salt and can be easily separated. [9-11] All organic carbon-containing wastes, together with excess combustion air, are conducted in the reaction vessel below the level of the salt melt, which has a temperature of 800-950 °C.

The MSO process has several advantages over combustion. The operating temperature depends on the used alkali salts, but it is generally lower than in direct combustion. Alkaline carbonates and their mixtures have melting temperatures from 400 °C to 850 °C. The alkaline molten salt also acts as a scrubber for other acidic substances such as SO_3, SO_4, and NO_x, eliminating the need for a sophisticated flue gas cleaning system. The molten salt has the function of a stable heat transfer medium, which resists thermal shocks. After the decomposition of the organic waste, the molten salt is saturated with heavy metals, products of acid neutralisation and ash. The concentration of inorganic components accumulated in the molten salt increases with the amount of treated waste. Therefore, periodic removal of spent salt is required before a new batch is added. The removed salt is discharged into the water tank, where the salt is partially dissolved. The undissolved part must be taken out and appropriately disposed of. Solidification is one of the convenient methods to dispose of the spent salt.

Cementation is widely used for solidification; however, the cement forms a porous structure prone to structural degradation under acidic conditions or high temperatures [12]. On the other hand, geopolymers are more suited for the alkaline nature of the MSO waste. Geopolymers are inorganic polymers prepared by polycondensation reaction of an aluminosilicate precursor with an alkaline activator at room temperature. Various precursors could be used for the geopolymerisation effect, such as metakaolin, fly ash, blast furnace slag, volcanic tuff, etc. The geopolymers offer higher structural integrity, mechanical stability and high leaching resistance and are suitable for long-term radioactive waste storage. [13]

As our previous work [14] was to study different commercial geopolymers for MSO waste immobilisation and its effects on mechanical strength, curing time and curing temperature, we decided to improve the used recipe. The volcanic tuff was one candidate, as colleagues [15] used it as part of their geopolymer for MSO waste immobilisation. For the series of LK10 geopolymer, the 10 stands for 10 wt.% of metakaolin added as filler, which improved the physical properties of the samples. We used 10 wt.% of volcanic tuff added instead of our commercial metakaolin for the first experiments with volcanic tuff.

The second series of experiments focused on chemically improving the MSO waste salt into a more suitable form for immobilisation. The reaction between the dissolved MSO salt waste and lime was developed (1).

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + NaOH \tag{1}$$

The product improves the mechanical properties of the final sample, reduces blooming and increases the stability against water immersion.

2 EXPERIMENTAL PART

2.1 Materials

An MSO waste salt was used from thermal treatment of the ion exchange resin (Purolite C100 H) in the MSO process. Table 1 shows the average composition of used spent salt.

Table 1: The phase composition generated from XRD analysis of each sample.

Phase (wt. %)		**R430**	**R431**	**R432**	**R433**	**R434**
Natrite	Na_2CO_3	96.41	96.52	95.07	94.12	96.25
Essenite	$CaFeAlSiO_6$	3.38	3.48	3.32	3.14	3.71
Thermonatrite	$Na_2CO_3 \cdot H_2O$	0.21	-	0.79	1.79	0.04
Trona	$Na_3H(CO_3)_2 \cdot 2H_2O$	-	-	0.81	0.95	-

The geopolymer Baucis LK was used for the experiments, and it is commercially available from the company České Lupkové závody a.s. Baucis LK consists of metakaolin Mefisto L05; its chemical composition is shown in Table 2. An activator solution also commercially available from the same company is a solution of K_2SiO_3. The volcanic tuff was provided for the experiments Politecnico di Milano, and its chemical composition is shown in Table 2.

Table 2: The chemical composition of metakaolin Mefisto L05 and Volcanic tuff. [15,16]

	Mefisto L05	Volcanic tuff
	Mass, wt.%	
Al_2O_3	40.10	17.13
SiO_2	54.10	52.09
K_2O	0.80	6.08
Fe_2O_3	1.10	3.69
TiO_2	1.80	0.52
MgO	0.18	1.94
CaO	0.13	5.77
NaO	-	0.51
H_2O	-	7.98

The enhanced salt prepared by the chemical reaction was prepared by dissolving a quantity of the MSO salt waste in the demineralised water. A stoichiometric amount of $Ca(OH)_2$ was weighted and mixed into a solution to be pipetted. Both solutions were continuously mixed, and the 10 ml of $Ca(OH)_2$ solution was added every 5 minutes until both solutions were completely mixed together. The final sediment was filtered, dried and ground to fine particles, and XRD analyses were conducted. The phase composition of enhanced salt is shown in Table 3.

Table 3: The chemical composition of enhanced salt.

Enhanced salt		Phase composition (wt.%)
Gaylussite	$Na_2Ca(CO_3)_2.5H_2O$	55.9
Calcite	$CaCO_3$	44.1

2.2 Sample preparations

The sample preparation procedure was performed according to the recipe of the geopolymer manufacturer. For experiments with waste salt from the MSO process, the alkali salt was ground into a fine powder and dried. The specified quantity of volcanic tuff and dried salt was mixed with the metakaolin into a homogeneous mixture before adding the alkali activator. The mixing time of the metakaolin and salt mixture with the alkali activator was 15 minutes. After this time, a well-stirred geopolymer paste was cast into cubic moulds with dimensions 50×50×50 mm and vibrated for air bubble elimination. After this designated time, the samples were demolded and cured in three different environments:

- Dry-cured in laboratory conditions
- In a sealable vessel filled with water to study high-level moisture
- Water immersion

After curing, the compressive strength test was carried out. Multiple sample measurements (at least two) were performed for each analysis, and the standard deviation values were less than 10 %.

To determine the weight of the mixture compounds, we used RADWAG WLC 6/A2 scales. The accuracy of the scales is +-1.0 g. The expected uncertainty assigned corresponds to a coverage probability of 95% and the coverage factor k = 2. The compressive strength analysis of the samples was performed using the MTS 300 Exceed® device according to the Czech National Standard CSN EN 12390-3 Testing hardened concrete - Part 3: Compressive strength of test specimens. 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 "back loading".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) [17] and PDF-4+ database [18].

3 RESULTS AND DISCUSSION

3.1 Volcanic tuff addition

The influence of volcanic tuff addition in the commercial geopolymer matrix was studied during this experiment. Based on the improved recipe [14], the tuff added was determined to be 10 wt.% into the matrix. With the waste salt addition, the final geopolymer samples were studied with compressive strength and XRD analysis. The samples with 5, 10 and 15 wt.% waste salt were prepared. Figure 1 shows the compressive strength of LK geopolymer with 10 wt.% of volcanic tuff added. The LK + volcanic tuff with 5 wt.% had the best performance with a dry-cured sample of 79 MPa, but mechanical strength decreased with a high moisture environment and water immersion. The 10 wt.% shows similar mechanical strength in all three environments, but the 15 wt.% samples were cracked and only dry cured was ready for analysis. The samples were not fully solid after 30 days of curing, which led to low mechanical strength.

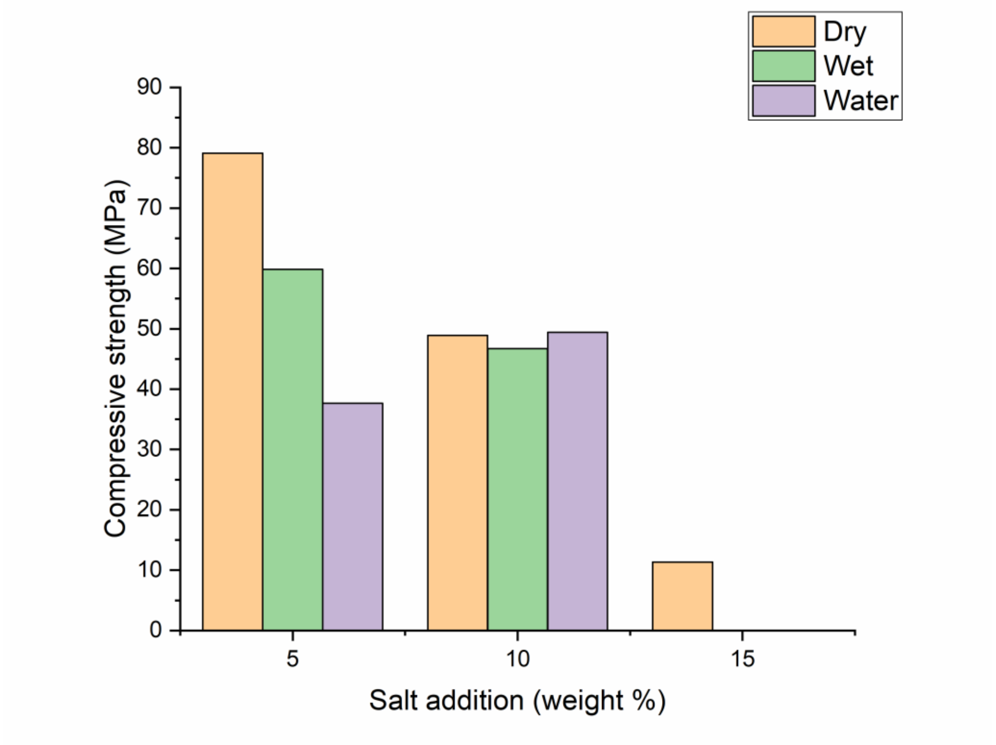

Figure 1: Compressive strength of LK geopolymer with 10 wt.% of volcanic tuff and with salt addition.

The XRD analysis of the sample with 5 wt.% waste salt is shown in Figure 2. The analysis showed the presence of typical compounds of geopolymers with pirssonite and calcite. Pirssonite could form with the sodium-activated geopolymers, but LK uses a potassium activator. This suggests the pirssonite formed by reaction with MSO salt waste from thermonatrite or trona by hydrate decomposition and water loss. The pirssonite is a stable component, which suggests the high compressive strength of the sample.

Figure 3 shows the results of the XRD analysis of the sample with volcanic tuff and 10 wt.% of waste salt added. The XRD shows the presence of trona and gaylussite, which are unstable sodium-calcium carbonates formed during the geopolymer paste's early stages. Gaylussite slowly decomposes in H_2O and forms a more stable form as $CaCO_3$. The presence of sodium-calcium carbonates corresponds with a higher waste load and lower compressive strength. Similar results were obtained during our previous work [14].

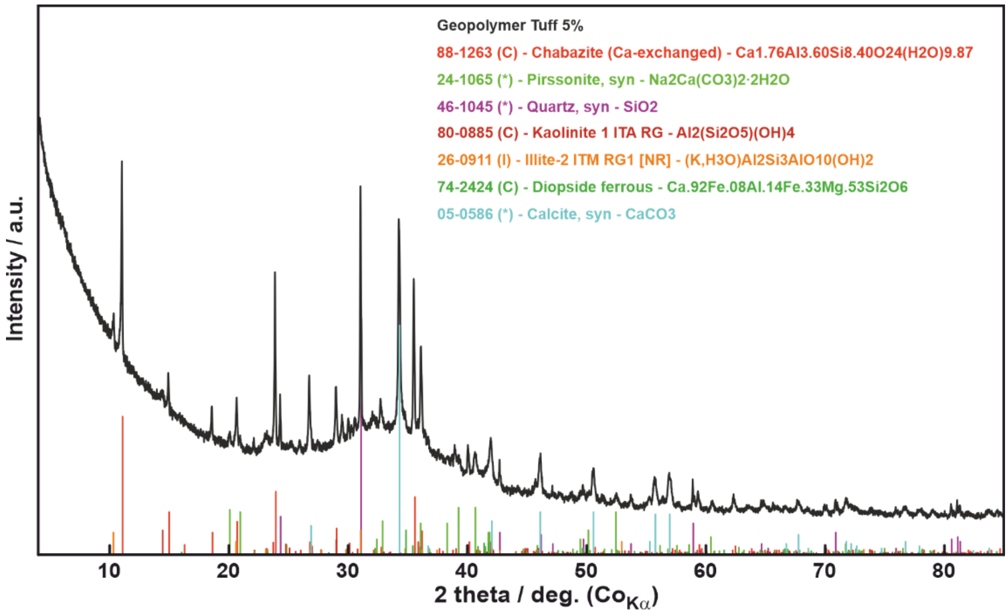

Figure 2: The XRD analysis of LK geopolymer with 10 wt.% of volcanic tuff and 5 w.t% salt addition.

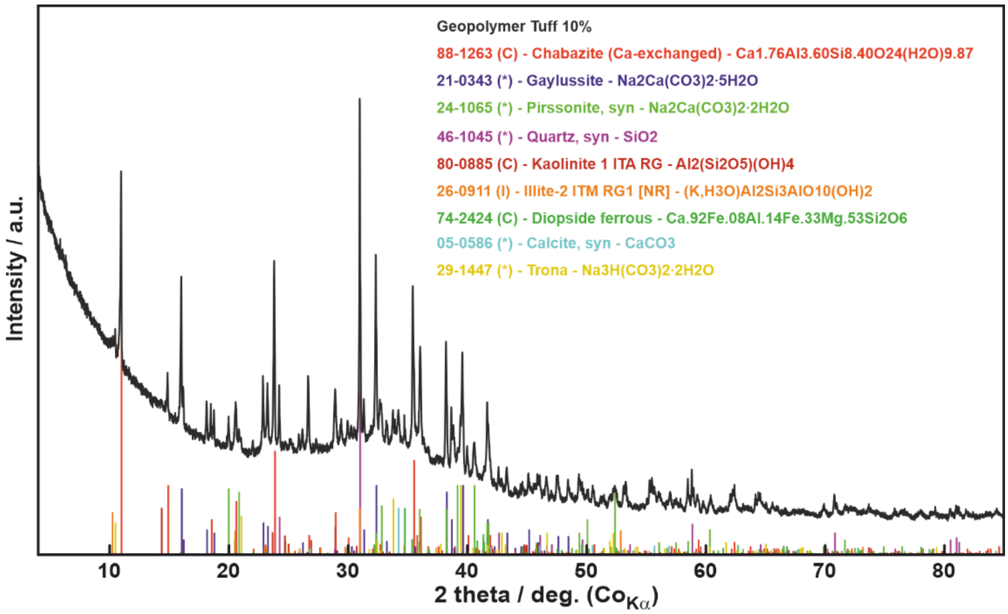

Figure 3: The XRD analysis of LK geopolymer with 10 wt.% of volcanic tuff and 10 wt.% salt addition.

3.2 Enhanced salt

The results showed that MSO waste is difficult to immobilise with no cracking, leaching or long-term stability of the samples. Therefore, improvements were made to change the MSO waste, mainly from $Na_2CO_3.XH_2O$ chemically into a $CaCO_3$-rich salt would have better properties for leaching and mechanical and long-term stability performance. Figure 4 shows the results of the compressive strength analysis of the cured samples. The samples had high mechanical strength in all three conditions, as even water-immersed samples did not crack. The LK10 with 15 wt.% of waste dry cured show lower mechanical strength, only 32 MPa. On the other hand, the wet sample had very high mechanical strength. This could be explained by the slower polymerisation effect in humid conditions, which helped stabilise the sample with less cracking and a more flexible final product. On the other hand, water immersion helped the Na_2CO_3 inside the sample to gain H_2O to form hydrates, which leads to swelling, increasing the inner tension, which helps the cracking of the sample. The XRD analysis of the samples is in progress, and the results will be the subject of our subsequent work.

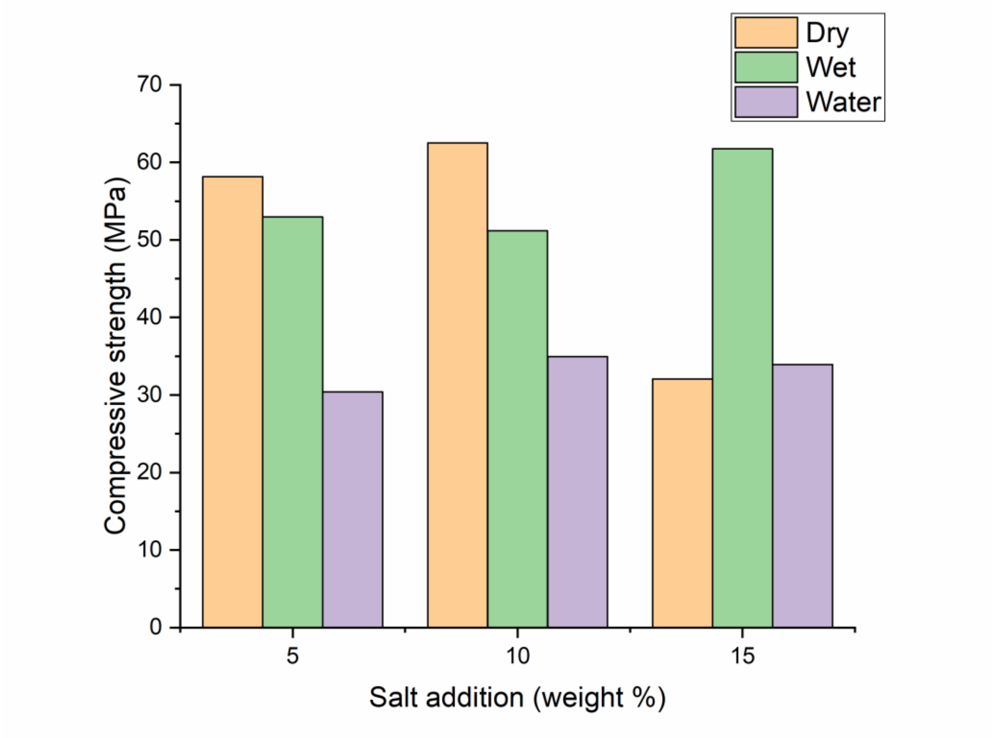

Figure 4: Compressive strength of LK10 geopolymer with enhanced salt addition.

4 CONCLUSIONS

This work aimed to study the potential positive influence of volcanic tuff on the LK geopolymer and to improve MSO salt waste into a suitable form for immobilisation. The samples were cured for 4 weeks in three different conditions. After the curing time, they were subjected to compressive strength and XRD analysis. The best performance had the samples with 5 wt.% of waste loading. The dry-cured sample had 79 MPa compressive strength, and the compressive strength decreased with high moisture content. The samples with 10 wt.% waste load showed similar results in compressive strength, around 50 MPa. The samples with 15 wt.% were not completely cured, and the compressive strength could be conducted only on dry-cured samples with a compressive strength of only 11 MPa. The XRD analysis shows the presence of pirssonite in 5 w.% waste load samples and gaylussite with trona in 10 wt.% waste load samples.

The next series of experiments aimed to improve the MSO salt waste into a suitable form for immobilisation. The high Na_2CO_3 content in the waste had a negative effect on leaching and sample stability. The waste was chemically changed into a mixture with high calcite content. This waste was then immobilised in the LK geopolymer using the LK10 recipe. The results showed very good compressive strength, even for water-immersed samples. Overall compressive strength decreased slowly with higher waste content. This improvement in the MSO salt waste can be the possible route to be immobilised with no negative effects. The XRD analysis and further improvements of the enhanced waste will be the subject of our future work.

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