Direct Conditioning Of Molten Salt Arising From The Thermal Treatment Of Solid Organic Waste

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ABSTRACT

Organic radioactive waste is generated during the operation and decommissioning of nuclear facilities. This includes both solid (spent ion-exchange resins) and liquid (scintillation cocktails, oils, organic solvents) wastes. Therefore, it is essential to focus on the possibilities for processing, reduction, and disposal, not just due to its radioactivity content but also due to its chemical composition. It is expected that not all organic radioactive wastes will be suitable for direct conditioning due to their high volume and instability in the expected conditions in the final repositories. Thermal treatment offers a potential route to process this type of waste and Molten Salt Oxidation (MSO) was identified as one of the possible pathways for radioactive organic waste treatment. In the MSO process, the organic waste is dosed, together with oxidising medium, under the surface of the molten salt, where flameless oxidation occurs. The non-combustible inorganic substances, such as heavy metals or radionuclides, are trapped in the molten salt, which can be further processed. The study aimed to determine the possibility of direct conditioning of resulting molten salt, which arises as the secondary waste after the combustion of spent ion exchange resins in the geopolymer matrix. After initial tests, a geopolymer of the commercial name LK was chosen as the most suitable choice. The series of experiments were then performed with 5, 10, 15, 20, 25, 30, 35 and 40 wt.% of spent MSO salt added to the matrix. Adding more than 40 wt.% alkali salt into the matrix wasn't possible as the mixture could no longer be thoroughly stirred. The samples were cured in different conditions, such as in mold, air dry, and in the dryer for 24 hours at 65 °C. Mechanical strength and XRD composition analysis were performed on the prepared samples. The results showed increased mechanical strength after adding 20 wt.% or more alkali salt.

1 INTRODUCTION

Radioactive waste generated during the operation and decommissioning of nuclear facilities can include both organic and inorganic solid and liquid waste. Some organic wastes proved to be a challenge to process by existing methods and therefore, alternative approaches were studied. Molten Salt Oxidation (MSO) is a promising thermal treatment process identified as one of the potential routes to process and reduce the volume of organic radioactive waste

such as oils and ion exchange resins and other hazardous wastes, including herbicides, pesticides, dioxins, PCBs, halogenated plastics, or chemical warfare agents. It is suitable for many wastes, including solid, liquid, and mixed wastes [1]. The processed waste is fed through the dosing system and oxidising medium into the reactor vessel. The reactor vessel contains molten salt, typically an individual alkali carbonate such as sodium, potassium and lithium carbonate or their eutectic mixture. Waste is fed underneath the surface of the molten salt, which has a temperature range of 400 – 950 °C and where flameless oxidation occurs. The organic components undergo oxidation at these temperatures and are converted mainly into CO_2 and water vapour. Carbon monoxide and some hydrocarbons could be produced due to incomplete oxidation in the reactor vessel therefore, a two-reactor system is convenient for the complete oxidation of complex organic wastes. The acid gases containing halogens, sulphur, and phosphorus, formed during the oxidation of some wastes, are neutralised in the salt melt, forming corresponding stable salts. The non-combustible substances such as heavy metals and radionuclides are trapped in the molten salt [2][3]. 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. The spent salt can either be recycled to minimise the amount of secondary waste and reduce the consumption of fresh salt or it can be disposed of as solid waste.

In drum cementation, using Portland-based types of cement is a common solidification process. Cement, however, is subject to chemical degradation, due to water or acidic condition, which can cause calcium from the solid matrix to leach out. This phenomenon challenges waste storage safety and sustainability [4]. This leads to a focus on the possibilities of improving the solidification method using cement as well as finding an alternative solidification method. One of the potential routes is using geopolymers instead of cement. Geopolymers are inorganic polymers which are considered class green due to producing less greenhouse gas than cement [5]. Geopolymers are prepared by the polycondensation reaction of an aluminosilicate precursor with an alkali activator solution at normal temperature and pressure. A wide variety of aluminosilicate precursors are available for geopolymer manufacturing, such as metakaolin, blast furnace slag, fly ash, etc. [6][7]. Besides curing at the normal temperature, the geopolymers have other advantages such as but not limited to high acid and heat resistance, higher leaching resistance, high structural integrity, and mechanical stability. The setting mechanism of geopolymer is based on rapid polymerization rather than hydration as with cement and is, therefore, much faster [8]. These characterisations suggest that geopolymers could be long-term stable and, therefore, potentially usable material for radioactive waste solidification.

2 EXPERIMENTAL PART

2.1 Materials

A spent sodium carbonate salt from the thermal treatment of the ion exchange resin (Purolite C100 H) in the MSO process was used.

The geopolymers Baucis LK, Baucis LBNa and Baucis LNa used for experiments are commercially available from České Lupkové závody a.s. Baucis LK and LNa consist of metakaolin 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. The chemical composition of the Mefisto metakaolins declared by the manufacturer is shown in Table 1.

Table 1: The chemical composition of metakaolin Mefisto L05 and LB05

	Mefisto L05	Mefisto LB05
	Mass, wt.%	
Al_2O_3	40.10	37.50
SiO_2	54.10	54.40
K_2O	0.80	1.10
Fe_2O_3	1.10	3.50
TiO_2	1.80	1.30
MgO	0.18	0.25
CaO	0.13	0.28

2.2 Sample preparation and analysis

The sample preparation procedure was performed according to the recipe of the geopolymer manufacturer. For experiments with sodium carbonate from the MSO process, the alkali salt was ground into a fine powder and dried. The specified quantity of salt was then dried and mixed with the metakaolin into a homogeneous mixture before the alkali activator was added. The mixing time of the metakaolin or metakaolin and salt mixture with the alkali activator was 15 minutes. After this time, a well-stirred geopolymer paste was cast into cubic molds with dimensions 50×50×50 mm and vibrated for air bubble elimination. The samples were wrapped in aluminium foil and placed in a plastic bag and left to cure for seven days. After this designated time, the samples were demolded and the compressive strength analysis 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 MTS 300 Exceed® device according to the Czech National Standard CSN EN 12390-3 Testing hardened concrete - Part 3: Compressive strength of test specimens.

X-ray diffraction patterns (XRD) were collected using PANalytical X´Pert PRO diffractometer equipped with a solid-state X-ray tube (Co-Kα radiation, 40 kV, 30 mA), detector PIXcel 3D-Medipix3 (1D mode), and iCore and dCore optics in the primary and diffracted beam respectively.

3 RESULTS AND DISCUSSION

3.1 Geopolymer selection

Different sets of experiments were performed. The first experiment consisted of preparing samples of all three geopolymer recipes and adding a specific amount of metakaolin to determine which geopolymer has the best compressive strength properties. In these samples, an addition of 5, 10, 15 and 20 wt.% more relevant metakaolin was added into the mixture as a binder for better performance. This modification resulted from previous experiments and consultations.

The best performance in the compressive strength test with adding extra metakaolin had Baucis LK with its compressive strength between values 50 to 80 MPa depending on the extra amount of added metakaolin and was therefore determined as the most suitable for the subsequent experiments. Baucis LNa sample with 10 wt.% addition of metakaolin saw a drop in its compressive strength compared to 5 wt.% addition, but samples with higher metakaolin addition had an increasing trend of compressive strength. Compressive strength values of Baucis LBNa samples decreased from 56 to 36 MPa with extra added metakaolin. The comparison of Baucis LK, LBNa and LNa is shown in Figure 1. The reason for the different compressive strength values between tested geopolymer mixtures is mainly due to their chemical composition.
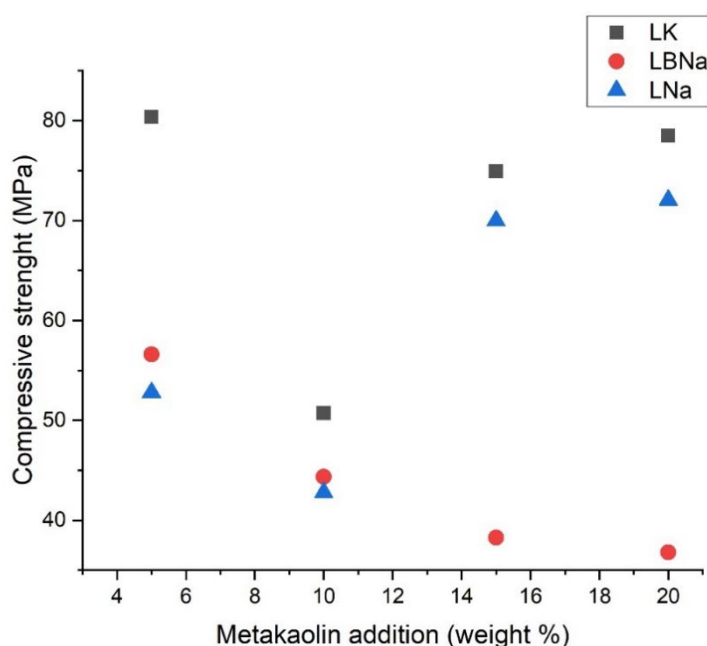

Figure 1: Comparison of the different geopolymers

3.2 The effect of curing time

In order to investigate the effect of curing time on the compressive strength, three sets of Baucis LK samples with the addition of 5, 10 and 15 wt.% of metakaolin were prepared (LK5, LK 10 and LK15) and cured for the different time periods. The curing times were set at 7, 14 and 21 days. As can be seen in Figure 2, the curing time positively influenced the compressive strength values at all three geopolymer mixtures, which is due to the continuous polymerisation process. Longer curing time resulted in higher compressive strength, similar to what was reported in other studies [9][10]. The LK5 mixture showed smaller compressive strength compared to LK10 and LK15. The highest compressive strength values were measured for LK15 and were 60, 72 and 82 MPa after 7, 14 and 21-day curing, respectively. It can be observed that the addition of the metakaolin on the top of the recipe increased the compressive strength values; however, more added metakaolin content also increases the mixture viscosity. Adding more than 15 wt. % of the metakaolin made mixing very difficult and increased the porosity of the samples, which then had a negative effect on the resulting geopolymer properties.
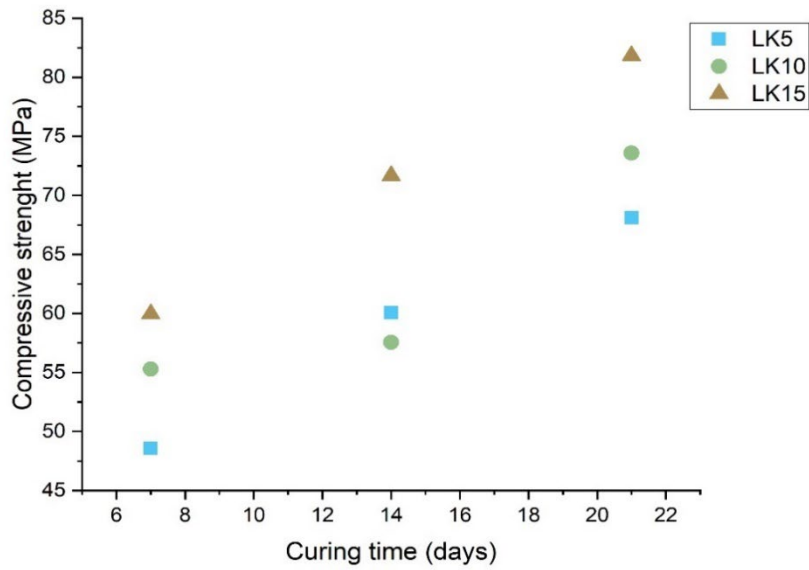
Figure 2: The effect of curing length of compressive strength

3.3 The effect of salt addition

As the LK10 and LK15 mixtures showed higher values of compressive strength in previous tests they were then used for the experiments where a set amount of an MSO spent salt was added to the mixture instead of metakaolin. The resulting samples after curing are shown in and the results of compressive strength analysis are shown in Figure 3.
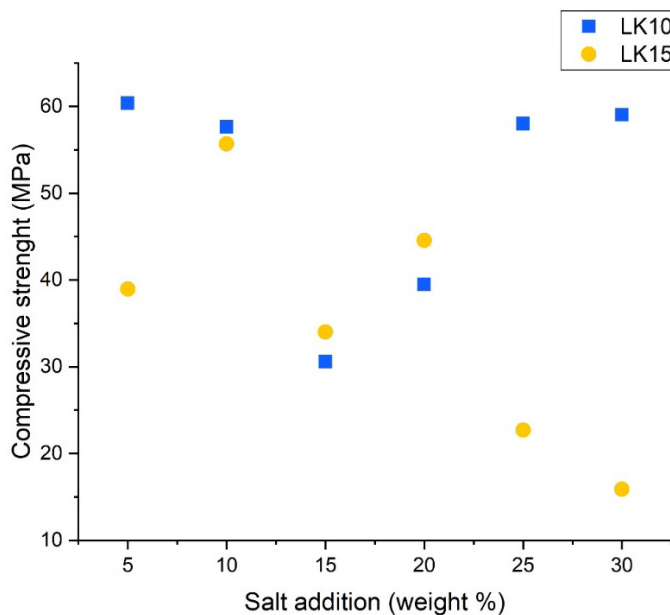

Figure 3: The effect of salt addition on compressive strength

Both geopolymer mixtures had a similar compressive strength value at 10, 15 and 20 wt.% load of salt. Significantly higher compressive strength of 58 and 59 MPa was observed at samples LK10 with 25 and 30 wt.% salt additions, respectively, compared to the LK15 samples with the same amount of salt addition where the values were 23 and 16 MPa. It can be stated that adding more metakaolin together with higher loads of salt leads to higher viscosity and difficult mixability, which then negatively affects the strength properties. The unsatisfactory results of the LK15 mixture meant that further increase of metakaolin addition together with the addition of salt as a waste load was unsuitable. Because overall better results have been seen with LK10 it was then determined to use it for the temperature experiment.

Metakaolin samples and cured geopolymer samples with salt addition were analysed on an XRD diffractometer to compare the composition of metakaolin and the resulting geopolymer with MSO salt. The XRD spectrum of Baucis LK metakaolin can be seen in Figure 4 and the XRD spectrum of the resulting geopolymer is shown in Figure 5.
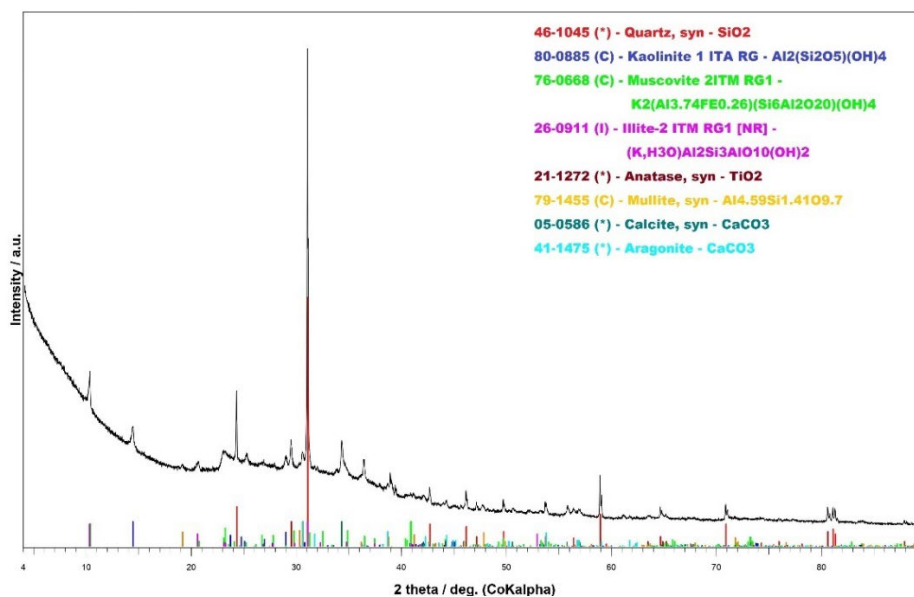

Figure 4: XRD analysis of Baucis LK metakaolin

The analysis has shown the presence of gaylussite and thermonatrite in the resulting geopolymer. Thermonatrite is an evaporite consisting of sodium carbonate and gaylussite is a hydrated form of the sodium-calcium carbonate, which is usually unstable and formed at an early stage in the activated geopolymer paste. It then slowly decomposes in H_2O, leaving $CaCO_3$ as stable calcite or aragonite. These two minerals are usually present in geopolymers where an alkalic activator which contains sodium is presented; however, geopolymer mix Baucis LK uses potassium silicate as an activator. The most probable reason for their formation is the presence of sodium in the MSO salt, which reacts with the geopolymer mix during the process.
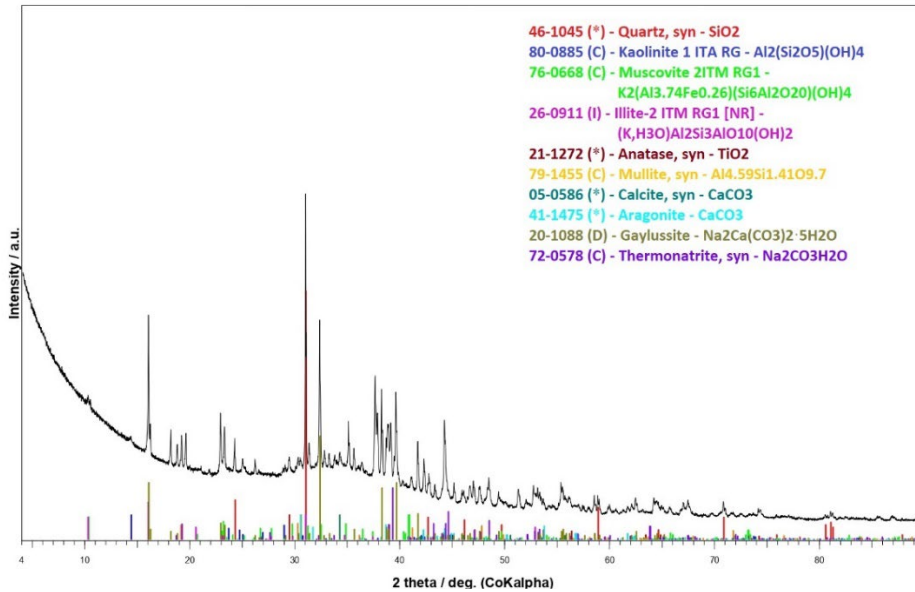
Figure 5: XRD analysis of Baucis LK geopolymer mixture with MSO salt

3.4   The effect of temperature

In the next experiment, the influence of curing temperature on compressive strength was studied using the geopolymer mixture LK10. One set of samples with 5, 10, 15, 20, 25 and 30 wt.% spent MSO salt addition was cured as the samples in the previous experiments. The other samples were removed from the mold after 24 hours and placed into the laboratory drier for 24 hours at 65 °C. The results presented in Figure 6 have shown that the standardly cured samples had overall higher compressive strength than the samples cured at a higher temperature.
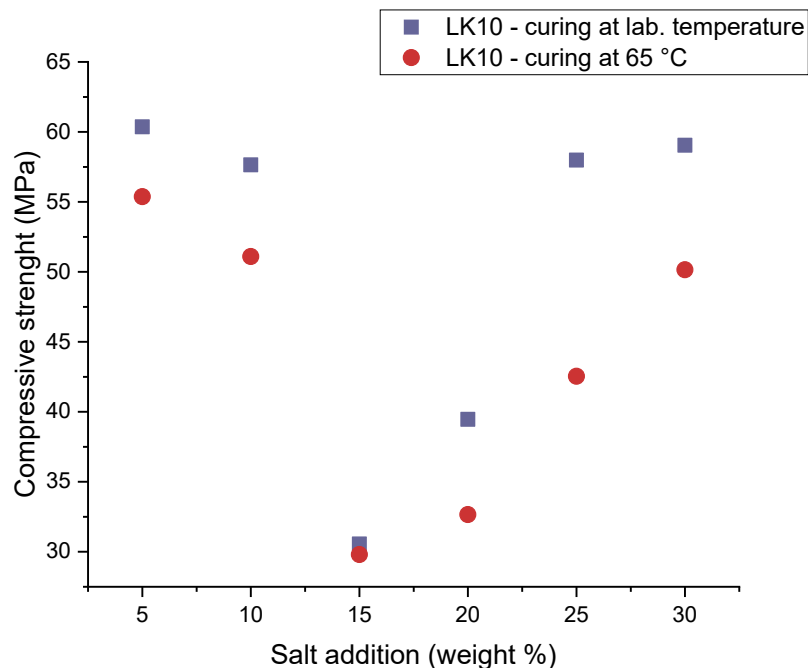

Figure 6: The effect of curing temperature on compressive strength

Overall lower compressive strength values were seen in the samples which were cured at the higher temperature, which was in contrast to the results seen in another study [11]. It is possible that a sudden change in temperature influenced the microstructure of the samples, as some small cracks were observed on the surface. A gradual rise in temperature would therefore be more beneficial.

The unexpected drop in the compressive strength values at samples with 15 and 20 wt. % salt addition was most likely caused by inhomogeneous moisture content in MSO salt. Sodium carbonate is very hygroscopic and even though the salt was homogenised, it is possible that the moisture content varied slightly in each batch used for sample casting. This variation in moisture content then affects the W/S ratio in the mixture and, subsequently, the reaction in the polymerization process.

4   CONCLUSION

In this study, several experiments were performed to determine the suitability of using commercially available geopolymers Baucis for direct conditioning of spent salt from the MSO process. After initial testing of three different geopolymers Baucis LK, LNa and LBNa, a Baucis LN was selected based on the highest compressive strength values of 50 to 80 MPa depending on the mixture ratio compared to the other two. These values suggest that the resulting product would be durable in case of an unexpected event. The effect of curing time was determined by letting the samples of LK geopolymer cure for a different time. The compressive strength increased with the length of curing. In this experiment samples, LK10 and LK15 showed a higher compressive strength of values 55, 58 and 74 MPa (LK10) and 60, 72, and 82 MPa (LK15) compared to LK5 with values of 49, 60 and 68 MPa after 7, 14 and 21-day curing, respectively. The LK10 and LK15 mixtures were therefore used for direct conditioning of spent salt.
In the direct conditioning experiments, metakaolin was replaced with 5, 10, 15, 20, 25 and 30 wt% of spent salt from the MSO process. In the case of 5, 25, and 30 wt% of salt additions, the LK10 samples were significantly more durable with values of 60, 58, and 59 MPa than LK15 with values of 39, 23 and 16 MPa, respectively. In the case of 10, 15 and 20 wt%, the compressive strength values of LK10 and LK15 samples were similar. The performed XRD analyses confirmed the presence of gaylussite after 7 days of curing, which would indicate a positive effect on the stability of the geopolymer, however, it is necessary to further test its presence in samples with a longer curing period. For the final experiment on the influence of the curing temperature, geopolymer LK10 samples were prepared and cured at laboratory temperature and a temperature of 65 °C. Samples that were cured at a higher temperature had overall lower compressive strength. The above results indicate the possibility of using Baucis LK geopolymer to stabilize salt directly after the thermal degradation of ionex using the MSO process. However, more experiments need to be performed together with additional analysis of the cured samples, such as leaching experiments and radiation stability tests.

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