

Sustainable tuff-based geopolymers for encapsulation of radioactive solid organic waste

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Abstract

The broad range of nuclear applications makes the generated radioactive waste very different in terms of physical and chemical forms, activity concentrations, and types of contamination. Such a variety results in an equally wide spectrum of waste management strategies, which must be carefully addressed in virtue of waste-inherent hazards. Among all, radioactive solid organic waste is particularly challenging to manage because of its nature, which typically exhibits flammability, dispersivity, and swelling. Such features are incompatible with common encapsulation matrices. In the recent years, geopolymers, mainly based on metakaolin, emerged as a promising class of materials. In this work, alkaline geopolymerization of highly zeolitized volcanic tuff and some industrial by-products has been investigated at laboratory scale as an economically and environmentally sustainable process for the conditioning of radioactive solid organic waste.

Introduction

The problem of radioactive waste disposal is known since the first use of radioactivity. Nowadays, radiations are employed in research, medical, and industrial applications [1]. Consequently, the produced waste takes different physical and chemical forms, having various activity concentrations and types of contamination. This results in an equally wide variety of options for the management of the waste, which must be carefully performed in virtue of its inherent radiological, biological, chemical, and physical hazards [2]. Some radioactive waste, for reasons related to its origin and specific characteristics, does not allow management through traditional operations, like direct cementation and bituminization, and, therefore, is in continuous accumulation while waiting for an appropriate disposal protocol to be developed [3]. Such a waste is referred to as “challenging”, and radioactive solid organic waste (RSOW) belongs to this class. Examples of RSOW are the spent ion-exchange resins used for the decontamination of radioactive liquid wastes and in nuclear power plants for the control of the chemical quality of the water, and protective equipment, such as plastic gloves and other consumables [4]. Management problems for RSOW, when directly encapsulated, arise from the presence of the organic component, which easily stores water, causing swelling of the matrix [5]. In addition, flammability and other chemical instabilities need pre-treatment processes to transform the waste into more stable products, possibly suitable for long-term disposal. In recent years, the innovative class of geopolymeric materials has proved to be a valid alternative to Portland cement for the encapsulation of RSOW because of their better affinity with the waste, excellent mechanical and physical properties, lower cost, and minor environmental footprint, characteristics which place them in a category of new environmentally sustainable materials [6, 7].

Geopolymers, introduced by Joseph Davidovits in the late '70s, are a class of inorganic, polymeric, amorphous aluminosilicate materials, generally synthesized at room or slightly higher temperature by reaction of an aluminosilicate powder with a concentrated alkali metal silicate and hydroxide solution [8, 9]. Aluminosilicates are the most abundant minerals in the Earth's crust, and many of them resulted to be suitable precursors for the synthesis of geopolymers due to their high contents of reactive aluminium

and silicon [10]. In particular, the interest has been focused on pozzolanic materials, as they are naturally occurring or they can be obtained as industrial by-products, and chemically react in presence of alkaline solutions at room temperature and ambient pressure to produce compounds with binding properties [11]. In this work, geopolymerization has been achieved with the use of an Italian tuff of volcanic origin with a predominant zeolitic mineralogical composition, and a series of industrial by-products, such as ground-granulated blast-furnace slag (GGBFS) and fly ash (FA). The presence of zeolites, hydrated aluminosilicate minerals characterized by highly regular nanocavities, is expected to enhance ion-exchange processes between the matrix and the encapsulated waste, thus resulting in stronger interactions and leaching resistance compatible with long-term storage [12]. Moreover, the exclusive use of natural and recycled materials, with activation provided by cheap reactants, makes the process sustainable from an economic and environmental point of view.

Materials and Methods

Geopolymerization has been carried out using a Zeolite Fertenia volcanic tuff (VT), and FA and GGBFS, the latter kindly provided by the Kharkiv Institute of Physics and Technology, without further processing. Alumina (purchased from MERCK) was added to the grouts for Si/Al balance, while sodium hydroxide (purchased from MERCK) and osmotic water were used for activation of the pastes. The inorganic ashes encapsulated as surrogate waste come from the IRIS plant managed by the French Alternative Energies and Atomic Energy Commission. Such residues were preliminary blended with a grinder. The VT is rich in both silica and alumina ($\text{SiO}_2 + \text{Al}_2\text{O}_3 > 65\%$ wt.), while the amount of these compounds in the other materials is lower: $> 60\%$ wt. for FA, $> 45\%$ wt. for GGBFS, and $> 55\%$ wt. for the surrogate waste. Calcium content is particularly high for GGBFS (CaO around 45% wt.), while iron is present in the FA ($\text{Fe}_2\text{O}_3 > 20\%$ wt.).

Precursors and additives for geopolymerization were weighed, and mixed for about 10 minutes at 40 rpm speed. Once mixed, the geopolymeric paste was poured into equilateral cylindrical moulds with dimensions of 5 cm, and vibrated for few minutes to eliminate air inclusions and flatten the upper surface. The amounts of each reagent used in formulations A, B, C, C-10, C-20, and D vary: GGBFS and FA are increased from A to D in the range 14–33% wt., while the VT is decreased from 34% wt. to 0% wt. In particular, formulation D is prepared without VT, while formulation C was loaded with 10% wt. and 20% wt. of surrogate RSOW in samples C-10 and C-20 respectively. Oxide ratios, expressed in mol/mol, are kept around 4.3 for $\text{SiO}_2/\text{Al}_2\text{O}_3$, 1.1 for $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, and 12.5 for $\text{H}_2\text{O}/\text{Na}_2\text{O}$. Four distinct curing environments have been tested: in-mould, open beaker, sealed beaker, and water-saturated sealed beaker.

X-ray powder diffraction (XRD) on hardened grouts was carried out using a Bragg-Brentano diffractometer with a copper K_α source. Thermogravimetric analyses were performed using a Mettler Toledo TGA1 XP1 thermogravimetric analyser, heating the geopolymerized samples from 25 to 800 °C with a rate of 10 °C/min, under air atmosphere (mass flow: 100 ml/min). Fourier transform infrared (FTIR) spectroscopy was carried out on hardened grouts powders using a Thermo Nicolet 6700 spectrometer coupled to a FTIR Thermo Nicolet Continuum microscope with MCT detector providing 128 acquisitions, with spectral windows between 650 and 4000 cm^{-1} , and a resolution of 4 cm^{-1} . Analyses have been performed via μ -FTIR spectroscopy in attenuated total reflectance mode with a silicon crystal and an incidence angle of 53°. Resulting spectra were extracted using Omnic 7.1. Mass spectrometry was performed with a PerkinElmer NexION 2000 inductively coupled plasma mass spectrometer, with calibration curves obtained with Inorganic Ventures CMS-x standards. The samples were prepared by diluting the aqueous samples with a 0.14 M ultrapure nitric acid solution. Ultrapure water in sample dilutions for inductively coupled plasma-mass spectrometry (ICP-MS) is Milli-Q gradient from MilliporeSigma. Compression tests were carried out according to the UNI EN 12390-3:2019 standard. Specimens have been compressed by a gradually increasing load applied by the platens of a compression-testing machine. The maximum compressive strength is derived by dividing the maximum load by the upper surface area of the specimen.

The ANSI/ANS-16.1-2003 protocol was followed to derive the leachability indices of the matrix constituents, i.e., silicon, aluminium, sodium, and calcium. A set of capped jars was suitably conditioned and filled with ultrapure water, and the cylindrical geopolymeric samples were immersed the solution. In order to monitor the species release, the leachant was periodically renewed after 2, 5, 24, 48, 96, and 168 hours, for a total period of two weeks. Leachates were diluted with 0.14 M ultrapure nitric acid and analysed via ICP-MS, while geopolymeric specimens underwent post-mortem compression testing.

Results and Discussion

The above-described formulations, prepared with 10-days in-mould curing, exceed the minimum requirement of 5 MPa imposed by the waste acceptance criteria (WAC), indicating a promising synergy between the zeolitized VT and the recycled FA and GGBFS. The development of mechanical strength increases in time in a non-linear way, doubling after 28 days of curing the compressive strength value at 10 days. Longer curing times, up to 6 weeks, were investigated only for formulations B, C, and C-10, which far exceeded 10 MPa. By visual inspection, the specimens exhibit air inclusions and cavities originating from the unsuitable casting of the grouts, which certainly worsens the mechanical properties. The influence of the curing environment is relevant and involves significant changes in the sample both from the aesthetic point of view, as shown in Figure 1, and from the point of view of mechanical strength. The optimal curing condition is the water-saturated sealed beaker, which, with the moisture saturation of the environment, prevents the rapid drying of the specimens, responsible for shrinkage and the formation of cracks. Geopolymers exposed to air during curing became superficially covered with a white phase, identified via XRD as sodium carbonate, caused by carbonation of the alkaline activator. Samples with curing in a water-saturated environment do not develop surface carbonation, even when re-exposed to air. Mechanical properties of geopolymers undergoing in-mould or sealed curing have behaviour somewhat in between the matrices exposed to air and those cured in water-saturated sealed beakers.

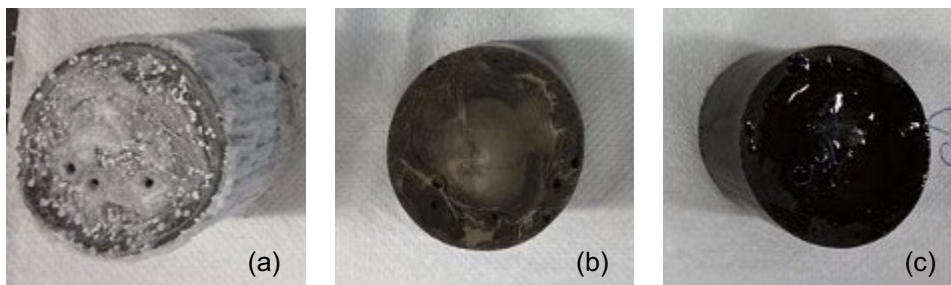


Figure 1: Specimens having undergone three different curing conditions: (a) in-air; (b) sealed beaker; (c) water-saturated sealed beaker.

The properties of the geopolymer formulations were investigated by TGA, FT-IR, and XRD on hardened paste powders. The former confirmed good stability at elevated temperatures, with low mass losses exclusively attributable to evaporation of the structurally-incorporated H_2O of the geopolymer. Phase analyses of the matrices, on the other hand, showed a consistent amorphous content, with the presence of crystalline peaks already present in the solid precursors, mainly in VT. In particular, the peaks of the zeolite are well identifiable, suggesting the preservation of its well-known ion-exchange capability.

Leaching resistance was investigated via ICP-MS by means of water immersion tests for formulations B, C, and C-10. The cumulative release curves of the main constituents of the geopolymer matrices, i.e., sodium, silicon, aluminium, and calcium, are drawn and the leachability indices (LIs) calculated. Overall, the three formulations have very similar behaviours, and the fractions released after two weeks of immersion are promisingly low, highlighting the stability of the matrix. The LIs were found to be well above 7, the minimum limit imposed by WAC for low and intermediate level waste. Furthermore, compression tests performed on the immersed and reference specimens showed that the mechanical strength was not affected by immersion, as the compressive strength values differed of an amount within the uncertainty of the measurements.

Conclusions

This preliminary experimental work successfully managed to obtain and characterize geopolymeric matrices suitable for the encapsulation of RSOW exclusively employing natural materials and recycled industrial by-products precursors for the synthesis, with the use of inexpensive activators and additives. Such geopolymers resulted chemically and thermally stable, and compliant with waste acceptance cri-

teria in both mechanical and leach resistance. Optimal curing conditions have been investigated to increase performance of the matrices without compromising the loading factor. Obtaining geopolymers with good properties has successfully allowed the recycling of industrial by-products from non-nuclear industries as conditioning materials for radioactive waste, making the tuff-based geopolymer more environmentally sustainable than ordinary Portland cement and metakaolin-based geopolymers.

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