

Solidification/Stabilization of Liquid Oil Waste in Metakaolin-based Geopolymer – 17209

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ABSTRACT

Cement-base solidification/stabilization (S/S) is a widely applied technique for the immobilization of inorganic hazardous constituents. However, S/S is considered less compatible with organic liquid wastes (OLW) because organic compounds may inhibit binder hydration. Geopolymers (alumino-silicate materials) are a worthwhile material for applications in which cements are inappropriate. In this study, we propose a direct immobilization process of organic liquid waste in a geopolymer matrix based on the emulsification of OLW in an activating solution, followed by the addition of alumino-silicate source (metakaolin).

At first, the harmlessness of the chemicals contained in the OLW on the geopolymerization was examined through a screening, revealing that only acidic oils should be pre-treated before a direct immobilization. Waste form characterizations with a simulated OLW were measured, showing interesting mechanical and confinement properties. Waste forms containing 20% Vol. of OLW show a mechanical strength higher than 30 MPa in compression and less than 1 % of waste leached over a month in pure water.

INTRODUCTION

Cement-base solidification/stabilization (S/S) is a widely applied technique for the immobilization of inorganic hazardous constituents [1]. S/S is considered less compatible with organic wastes because organic compounds may inhibit binder hydration [2] and are generally not chemically bonded to the binder hydration products, so their retention strongly depends on their physical entrapment. Many studies reported the effect of organic compounds such as 3-chlorophenol, methanol

and 2-chloroaniline, trichlorobenzene on cement binder [3, 4] and clearly demonstrated that even at low concentrations, organic materials can produce significant micro and macro structural changes to the properties of hydrated cement. Organic liquid waste is an important type of radioactive waste in the nuclear industry.

Cementation has been widely used in US facilities to solidify contaminated oil from turbines or pumps [5]. The process was based on the stabilization of an oil in water (O/W) emulsion using emulsifiers and then by addition of Portland cement powder and a setting accelerator to ensure the uniform dispersion of oil in the resulting solid material. With this method, the obtained compressive strength was less than 0.5 MPa with oil incorporation up to 40 wt. % Nevertheless, the material microstructure can be significantly affected by minor waste components. Another approach based on absorption and cementation has been studied by using Nochar polymers for nuclear oil wastes [6].

In the present work, a new technique based on direct solidification/stabilization of oil waste into a geopolymer material [7] has been studied, hereafter referred to as "Geoil composite". The process is based on the emulsification of the oil in an alkali silicate solution, followed by the addition of an alumino-silicate source (metakaolin) to engage the setting of a geopolymer block with an oil emulsion trapped into the solid material.

The aim of this work is to study the effect of the chemicals contained in organic liquid wastes (OLW) on the geopolymerization. Wasteforms with simulated OLW (hexadecane) were characterized using mechanical strength techniques and leaching method in pure water.

MATERIALS AND METHODS

Geoil Composite Preparation

In this work, the alumino-silicate source is activated by oil in a water-glass emulsion instead of a simple water-glass solution. Oil in water-glass emulsion (o/w) was obtained by mixing oil liquid waste in a water-glass solution (molar composition of 1.2 SiO₂:1 Na₂O:12 H₂O) prepared by dissolving sodium hydroxide pellets (VWR, >99%) in a mixture of sodium silicate solution (Betol 52T; Woellner) and osmotically purified water. The emulsion stirring was realized with a high-speed overhead stirrer for 2 h. Metakaolin was purchased under the brand name of Pieri Premix MK from Grace Construction Products. Oil in water-glass emulsions and then the mixing with metakaolin powder were realized with a high-speed overhead stirrer for 5 min. The

geopolymer composition 1 Al₂O₃ : 3.6 SiO₂ : 1 Na₂O : 12 H₂O is similar to another formulation already used for other nuclear applications [8]. The fresh grouts were either directly used for characterizations or cured under air, bag or water before characterizations.

Characterizations

Compressive strengths were performed on 40x40x160 mm prismatic samples (Standard EN196-1). The samples were obtained by pouring fresh pastes into PTFE moulds, vibrated for a few seconds and cured for 4 days at 20°C under 100% relative humidity at atmospheric pressure before extraction from the molds and storage. Scanning Electron Microscopy (SEM) experiments were performed on a FEI Inspect S50 device (acceleration voltage = 15 kV, tungsten filament current = 50 A).

For leaching experiments, Geoil composite with 20% volume fraction of hexadecane with L35 or CTAB surfactants, were immersed in demineralised water. The immersed samples were 40x40x160 mm prismatic samples. The volume of the leachate was 1500 mL. The water solution was renewed at each samples analysis. The sampled leachates were stored at +5 °C before characterizations. No solid precipitation and no organic phase were observed in the leachates. The sampled leachates were then analyzed by Total Organic Carbon.

RESULTS AND DISCUSSIONS

Influence of Chemical Contained in Organic Liquid Waste During Geopolymerization

Incorporation tests were carried out on pure organic liquids selected to represent different chemical functions present in organic liquid waste streams (aliphatic, aromatic, ketone, alcohol, phosphate ...) from nuclear fuel cycle industry. The direct immobilization process is based on the emulsification of the oil in an activating solution. Selected pure organic liquids are shown in Table 1.

Pure organic liquid (20 mL) was emulsified in 50 mL of activating solution with or without surfactant by mechanical agitation during 30 minutes. Results are similar, with a very fast creaming and a total phase segregation in less than 15 minutes, even in the case of DEHP. The density of the activating solution (1.45 kg/L) is much higher than that of all organic liquids. Rapid creaming observed may be related to this very important density difference. These emulsions have been made in an activation







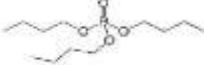



solution, therefore, metakaolin was then added in order to react with the activation solution and obtain a geopolymer composite. Before the addition, the emulsions were stirred during 15 minutes.

With metakaolin addition and without surfactant, results showed oil segregation, several mL of oil was visible above the geopolymer paste. Thus, it is not possible to immobilize oil without surfactant addition. However, with surfactant addition, all the emulsions resulted in a macroscopically homogeneous paste.

After the metakaolin addition, all composites with surfactant hardened to a solid form except the composite containing octanoic acid which remained pasty without any mechanical resistance but without bleeding. This result can be explained because the geopolymerization reaction requires a high pH, confirming the impossibility of direct immobilization of an acid oil.

Solid samples were fractured and calcined at 350 °C for 5 hours in order to observe, by Scanning Electronic Microscopy, the relic footprints of droplets left in the geopolymer by calcined oil. The resulting photographs are shown in Figure 1. All samples exhibit similar morphologies, oil footprints indicating that organic liquids were present in the geopolymer matrix as droplets with a radius of between 5 and 50 μm .

Table 1. Organic liquid selected for screening tests.

OLW	Structure	Function
Octane		Aliphatic
Dodecane		Aliphatic
Hexadecane		Aliphatic
Octanoic Acid		Acid
4-methylpentanone		Ketone
Decanol		Alcohol
TBP		Phosphate
t-butyl benzene		Aromatic
Toluene		Aromatic
DEHP		Aromatic ester

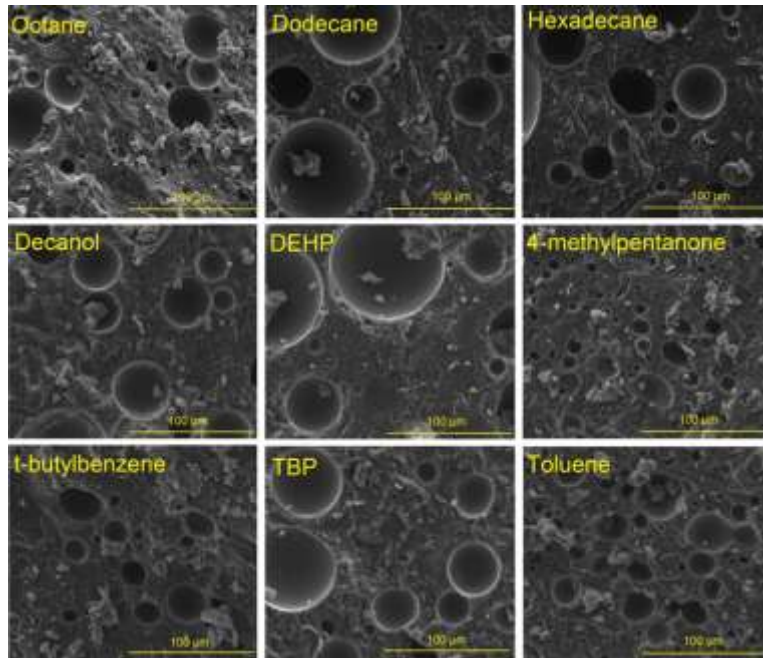


Fig. 1. SEM secondary electron micrograph of Geoil composite containing 20 vol.% of various organic liquid wastes.

Mechanical and Leaching Performance of Geoil Composites

Technical tests related to mechanical properties and leaching were carried out to establish disposal facility waste acceptance criteria at ANDRA (French National Radioactive Waste Management Agency) center for this new waste form. The studies were carried out with a model organic liquid (hexadecane at 20 % vol.)

The compression strengths of geopolymer with or without surfactant and those of composites were measured on samples after 28 days stored under air, water and closed bag (Figure 2). These values are important in the context of using geopolymer matrix as a conditioning binder for nuclear waste. Indeed, a minimum of strength is required for the primary package to be accepted by ANDRA and in order to ensure the integrity of the final package. The minimum compressive strength imposed by ANDRA for a storage acceptance is 8 MPa for homogeneous wastes. We can see in Figure 2 that for pure geopolymers, compressive strengths are between 40 and 50 MPa at 28 days for all conditions (in air, water or bag). This result is consistent with most of the values found in the literature for metakaolin based geopolymer [9].

When the geopolymer contains CTAB surfactant, a significant loss of mechanical properties ($\approx 30\%$) is observed. Under the same conditions with the L35 surfactant, mechanical strengths are comparable to pure geopolymer. We have attributed these

results to the presence of air bubbles in the geopolymer with CTAB surfactant. For hexadecane / geopolymer composites, the presence of the oil droplets leads to mechanical strengths about 20% lower than the paste of pure geopolymer, regardless of the surfactant used. We know that the composite with CTAB incorporates more air, but in the case of the composite, air does not appear to induce an additional loss. We can conclude that with a volumetric rate of incorporation of 20% by hexadecane, the composites have satisfactory mechanical strength in regard to the immobilization matrix of nuclear waste.

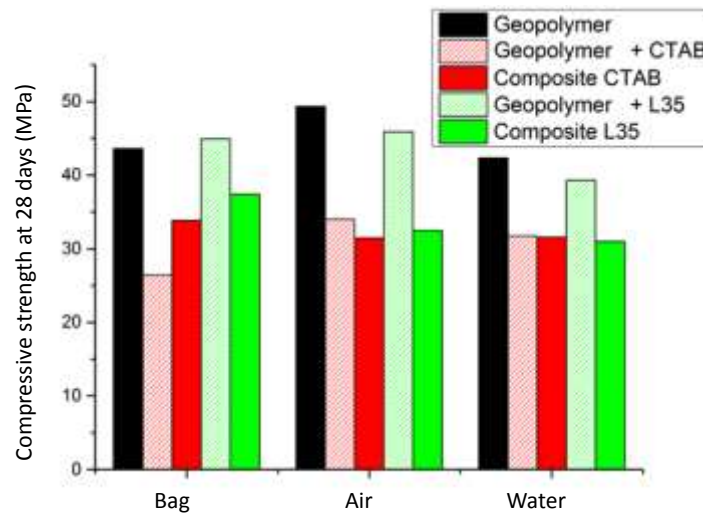





Fig. 2. Compressive strength of geopolymer, geopolymer and surfactants (L35 and CTAB) and Geoil composite (with 20 vol.% of hexadecane) with surfactants at 28 days.

In order to evaluate the leaching performance of Geoil composite with 20 % (Vol.) of hexadecane with CTAB and L35 surfactants in water under static conditions during 30 days, a glass container has been developed with a burette centered on the verticale of the sample (Figure 3). Total organic contents were measured with time (Figure 3). The leaching tests were performed on 4x4x16 prismatic samples. During leaching experiments, organic liquid was never observed in the burette. The cumulative quantity of organic carbon released in the leachate increased linearly as a function of the square root of time. Organic liquid is not dispersible and leaching is very low. The values of total organic content for Geoil composite with 20 % (Vol.) of hexadecane with CTAB and L35 surfactants under leaching are respectively 0.1 % at 40 days and 0.65 % at 36 days.

To study the composite Geoil behavior with 20 % vol. of hexadecane with L35 or CTAB surfactants, we conducted a work on mechanical properties of sample during 21 months under various cured conditions (water, bag and air). The results are reported on Table 2. We can see that samples did not present any efflorescence or macro-cracks. By comparing a geopolymer and a Geoil composite with hexadecane (20 vol.%) aged of 21 months, we found that the compressive strength for Geoil with L35 and CTAB surfactants stored under water decrease about 25% compared to pure aged geopolymer. This result is in agreement with those obtained at 28 days and demonstrated that these Geoil composites retain their mechanical properties for at least 21 months.

Table 2. Compressive strength of Geoil composite with hexadecane (20 vol.%) and geopolymer at 21 months stored under water, bag and air.

	Water storage		Bag storage		Air storage
	L35	CTAB	L35	CTAB	L35
Geoil composite with 20%vol. of hexadecane					
	24.6	22.6	33.1	34	25
Geopolymer	31.7		not tested		not tested

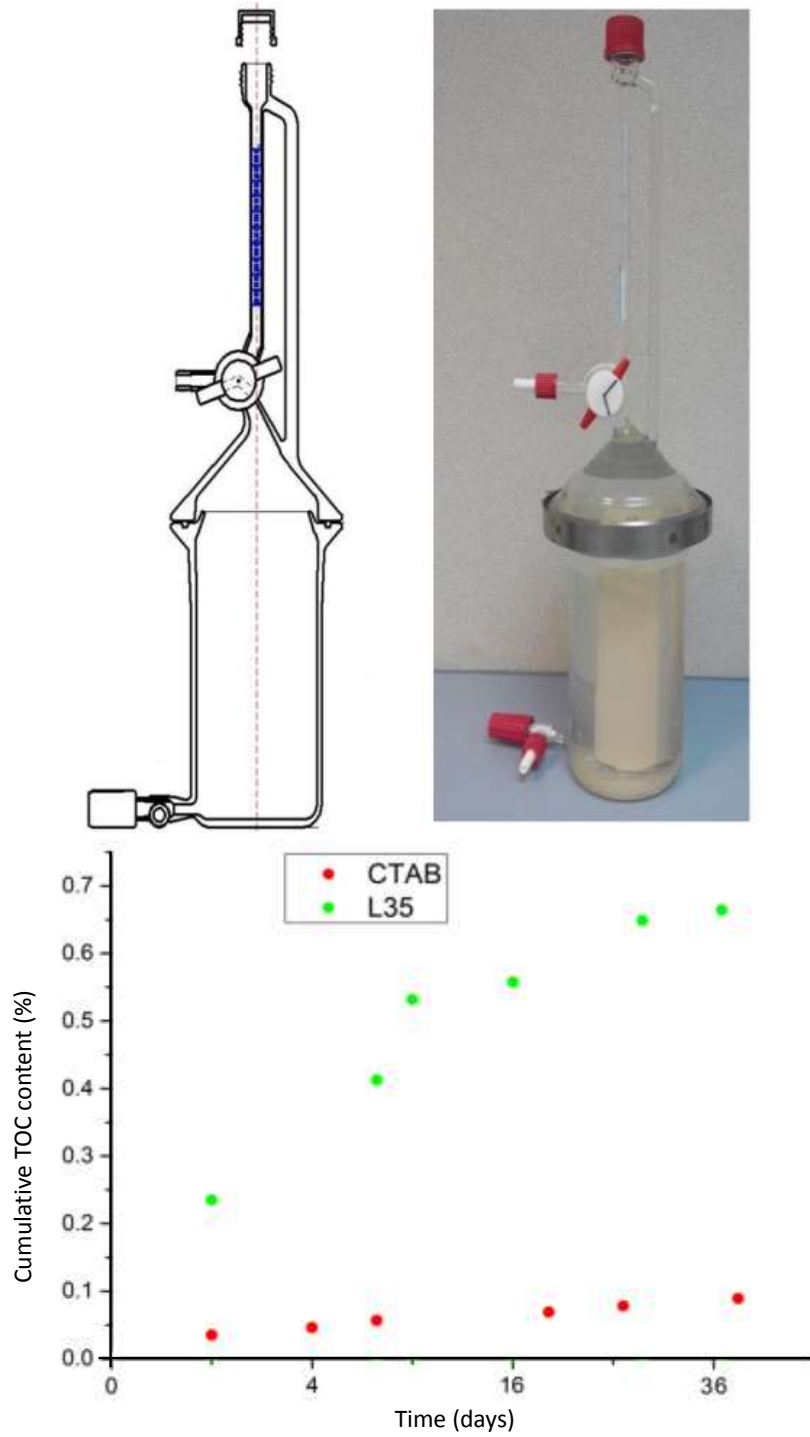


Fig. 3. Leaching cell (left) and cumulative leached TOC versus time for Geoil composite with hexadecane (20 vol.%) with L35 or CTAB.

CONCLUSIONS

The effects of the chemicals contained in selected organic liquid wastes on the geopolymerization were evaluated in a screening study. We demonstrate that only acidic oils required pre-treatment before a direct immobilization. Waste form characterizations with simulated organic liquid waste (hexadecane) were measured, and showed interesting mechanical and confinement properties. Waste forms containing 20% Vol. of OLW have mechanical strengths of more than 30 MPa in compression. In addition less than 1% of organic liquid waste leached over a month in pure water. Long-term tests indicate that Geoil composites retain their mechanical properties and have long term durability.

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