Impregnation of oil on surfactant-clay particles: Solid/liquid interaction in geopolymers

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Introduction

Geopolymers are emerging as innovative materials in the construction industry, formed through the chemical reaction between aluminosilicate components and alkaline activators [1]. In comparison to traditional Portland cements, geopolymers offer a more sustainable production process, as they do not require high-temperature calcination, leading to significantly lower carbon dioxide emissions. Geopolymers also boast superior mechanical properties, such as greater durability and resistance to chemical degradation, which can enhance the longevity of structures. Additionally, they provide better thermal insulation and faster curing times [2]. However, while geopolymers present these compelling benefits, their widespread adoption is hindered by the need for consistent raw material supply, comprehensive understanding of long-term performance, and compliance with existing industry standards and regulations.

Currently, geopolymers have proven their efficacy in building containment structures for nuclear waste, especially for chemically non-reactive organic liquids, like mineral oils [3]. In such applications, it is possible to immobilize up to 20 %v/v of oil within the matrix. Nevertheless, handling chemically reactive organic liquids is more delicate due to their tendency to degrade upon contact with their surroundings [4]. These liquids encompass vegetable oils, cutting fluid bases essential for operations within nuclear power plants, and TriButyl Phosphate (TBP). TBP finds particular significance in the PUREX (Plutonium-Uranium extraction) process, where it serves as solvent for the extraction of plutonium and uranium from irradiated nuclear fuel by forming a complex with these elements during solvent extraction stages.

Solid impregnation, as an intermediary step before immobilization in a cementitious matrix, offer advantages. Its key benefit lies in its non-destructive nature [5], enabling the adsorption of organic liquids onto a solid substrate early on. This adsorbed mixture can then be seamlessly integrated into the cement slurry in a solid form, simplifying the process compared to liquid introduction. When considering impregnation techniques, two primary approaches emerge: one utilizes the precursor materials of the immobilization matrix to trap the organic liquid, while the other employs external filler or charge to adsorb the liquid before immobilization. The choice between these methods depends on various factors, including waste characteristics, chemical properties, and specific disposal or containment requirements.

This study investigates the adsorption of oils from nuclear waste onto particles like metakaolin, diatomaceous earth, and sepiolite. These particles, functionalized with surfactants such as decyl glucoside (DG) and cetyltrimethylammonium bromide (CTAB), are then embedded in a geopolymer matrix. The synthesis of these particles is confirmed using various characterization methods. With the primary goal of characterizing the solid/liquid interactions between the target oil for immobilization and the synthesized particles, wettability of the particles and leaching tests are performed. Finally, immobilization in a geopolymer matrix is carried out to confirm the advantages of solid impregnation.

Methods

TGA measurements

Thermogravimetric analysis was performed using a Q500 thermogravimetric analyser (TA Instruments). Each sample was heated from 25 to 900 °C at a rate of 10 °C.min^{-1} under nitrogen, with a 5-minute isotherm at 120 °C to ensure complete removal of water.

Washburn characterization

Washburn tests are carried out using a Krüss Force Tensiometer - K100 with the Krüss Windows-based Laboratory Desktop software, specifically in sorption mode. The process involves placing 1.0 g of powder, whether in its natural or hydrophobically modified form, into a suitable sample holder. The sample is then compressed for 30 seconds using a 2 kg weight. Afterward, the sample is suspended from the balance within the tensiometer. The liquid is gradually raised until it lightly touches the bottom of the porous sample (Figure 1). Throughout this process, data is collected, measuring squared mass (m^2) against time (t). This data collection occurs as the liquid permeates into the solid sample, allowing for the investigation of sorption phenomena and the characterization of the material's wettability and sorption properties. All experiments are repeated three times.

Figure 1. Illustration of a Washburn test: packing of particles in a capillary tube and immersion of particles in a given solvent

Formulation of geopolymers

Geopolymers were formulated with a final molar composition $SiO_2/Al_2O_3 = 3.5$, $K_2O/SiO_2 = 0.29$, and $H_2O/K_2O = 10$ (liquid/solid ratio of 1.41). he activating solution, composed of potassium silicate solutions, is initially prepared by dissolving 11.08 g of sodium hydroxide pellets in 72.39 g of aqueous silicate (Betol® K 5020 T) along with 4.35 g of deionized water under magnetic stirring at 500 rpm. Due to the exothermic nature of this dissolution process, the solution must be allowed to return to room temperature before further use. Subsequently, 62.18 g of metakaolin is introduced into the activating solution and stirred at 800 rpm using a Heidolph RZR 2051 stirrer for 5 minutes. To ensure thorough mixing, the blend of powder/oil is then incorporated into the geopolymer paste for 7 minutes at 1000 rpm. Torque measurements are recorded during stirring at various rates (ranging from 100 to 1,000 rpm) using the same apparatus, and data is captured using dedicated software (Watch/Control 200) provided by Heidolph. The resulting mixture is shaped using a silicon mold and left to age at room temperature under 100% relative humidity until the structure is fully consolidated.

Results

Characterization of functionalized particles

The TGA study was carried out to verify the successful grafting of surfactants onto the surface of the particles. Figure 2 displays the thermograms of surfactant-grafted particles. If the entire surfactant amount is adsorbed onto the powder, the maximum yield is estimated at 4%. While challenging to quantify precisely with TGA, this method reveals slope changes indicating the impact of the grafting protocol on the particles. Observing water content initially, a decrease is noticeable in grafted particles, especially in sepiolite. After the final step of drying at 80°C overnight, a significant amount of water is removed. Since sepiolite and diatomaceous earth particles contain inherent water, they experience more mass loss compared to others. In terms of grafting, distinct slope changes are seen for surfactant degradation temperatures in sepiolite particles. For metakaolin, CTAB degradation occurs around 250°C, while DG grafting is less evident. Diatomaceous earth shows slope changes between 200 and 300°C for both grafted particles, indicating possible surfactant degradation, though with minimal mass loss due to low surfactant concentration relative to clays.

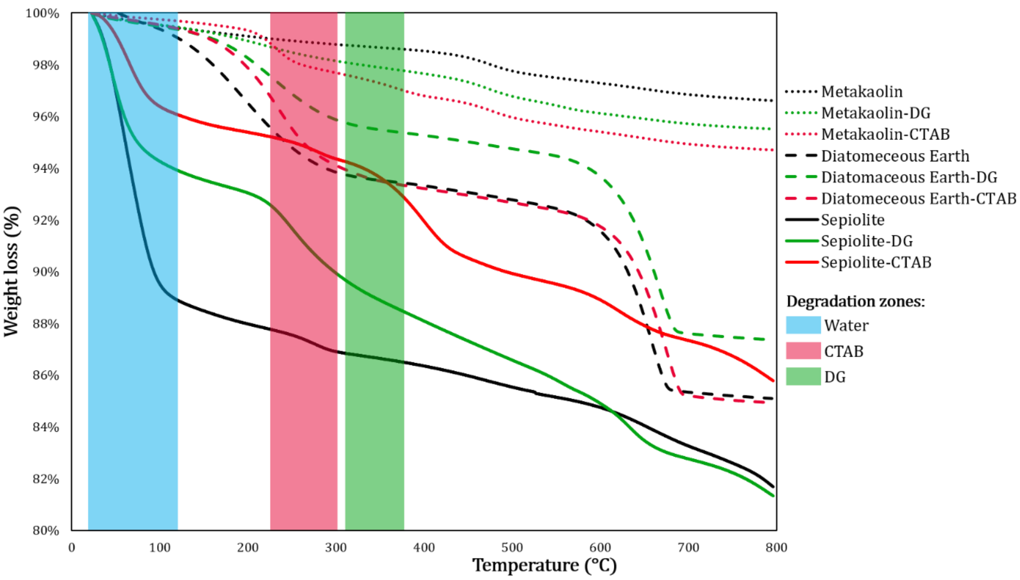

Figure 2. Thermogravimetric plots of the powders grafted with Decyl Glucoside (DG) and CetylTrimethylAmmonium Bromide (CTAB)

Due to the porous nature of the particles, the measurement of contact angles using the drop deposition method was rendered infeasible. Even though solid and smooth surfaces were achieved using a uniaxial compression press, the liquids were promptly absorbed into the material upon deposition. Consequently, the Washburn method was employed to investigate the wettability of the powders. Capillary rise occurs as the liquid is drawn into the porous material due to capillary forces. The rise of the liquid is monitored over time, and the rate of capillary rise varies depending on the characteristics of the powder. The Washburn equation, utilized to analyze the data and determine relevant parameters, is as follows [6]:

$$m^2 = A.t \text{ and } A = \frac{\rho^2.\gamma.C.\cos(\theta)}{\eta} \quad (1)$$

where m (kg) is the mass of liquid adsorbed on solid; t (s) is the time of contact of the experiment; ρ (kg.m^{-3}), γ (mN.m^{-1}) and η (Pa.s) are the density, the surface tension and the viscosity of the liquid, respectively; C (m^5) is the capillary constant associated with the material measured; and θ (°) is the contact angle between the liquid and the solid.

The evaluation of surfactant grafting effects on powder will specifically target sepiolite. *Figure 3* illustrates all Washburn curves related to sepiolite, both grafted and ungrafted. When comparing water measurements, raw sepiolite displays higher hydrophilicity than sepiolite-CTAB, with sepiolite-DG being the least hydrophilic. Grafting thus enhances particle hydrophobicity, a trait observed across all powder types.

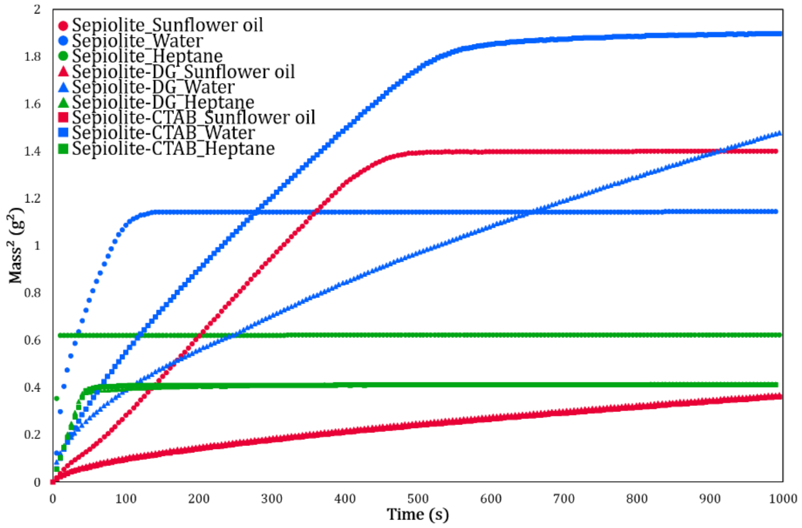

Figure 3. Impact of functionalization with surfactants (cationic CTAB or non-ionic DG) on the wettability characteristics of particles

Immobilization in geopolymer matrix.

The CTAB-grafted sepiolite demonstrates superior performance in terms of physicochemical properties, particularly in the context of the vegetable oil absorption test where no oil release occurs upon contact with demineralized water. This sepiolite-CTAB was consequently employed to impregnate 20 % v/v (128 g geopolymer paste, 18.4 g vegetable oil, and 23.5 g CTAB-sepiolite particles) of oil. Following a 28-day curing period in an environment maintained at 100 % relative humidity, the formulated geopolymers undergo leaching tests. These tests entail immersing the geopolymer in demineralized water to examine any observable oil release. No macroscopic oil expulsion is observed. At the microscopic level, there are no discernible oil droplets.

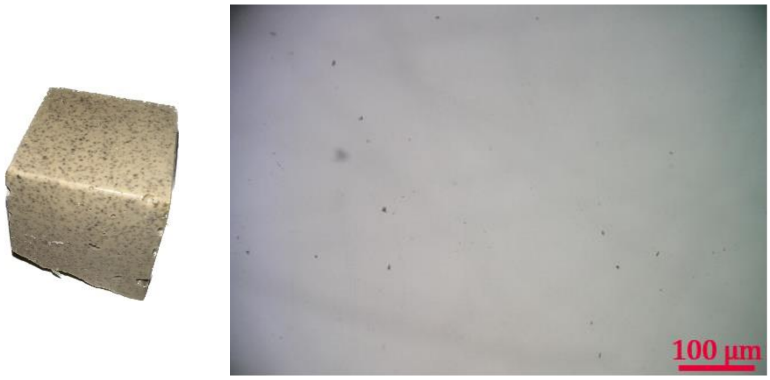

Figure 4. Macroscopic and microscopic photographs of geopolymer (20 % v/v vegetable oil + sepiolite-CTAB). Microscopic images were captured at a magnification of x500 under non-polarized light.

Conclusion

In summary, this study provides valuable insights into treating hydrolysable nuclear organic liquids by impregnation onto particles functionalized with surfactants, before immobilization in a geopolymer matrix. The results highlight the effectiveness of this two-step process, involving impregnation followed by conditioning into mineral binders like geopolymers. Particularly noteworthy is the superior performance of sepiolite-CTAB in oil absorption, capable of immobilizing 20% v/v of vegetable oil in a geopolymer matrix without detectable oil after 90 days. Successful surfactant grafting onto clay surfaces, confirmed through various characterization methods, significantly enhances adsorption efficiency and alters physicochemical properties, making these clays more suitable for nuclear waste management. The comparative analysis of different clay and surfactant combinations reveals the nuanced relationship between clay type, surfactant choice, and resulting oil absorption and immobilization capabilities. This underscores the potential for customized solutions tailored to specific waste management needs.

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