Incorporation of organic liquids into geopolymer materials - A review of processing, properties and applications

Charles Reeb, Christel Pierlot, Catherine Davy, David Lambertin

Review article

Incorporation of organic liquids into geopolymer materials - A review of processing, properties and applications

Charles Reeb [a,b], Christel Pierlot [a], Catherine Davy [a,*], David Lambertin [b]

[a] *Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ, Artois, UMR 8181-UCCS-Unité de Catalyse et de Chimie Du Solide, F-59000, Lille, France*
[b] *CEA, DES, ISEC, DE2D, SEAD, LCBC, Univ Montpellier, Marcoule, France*

ARTICLE INFO

ABSTRACT

Geopolymers, composed of an amorphous three-dimensional inorganic network and synthesized by the activation of a solid alumino-silicate precursor with an alkaline activating solution, have attracted increasing attention because of their environmental benefits and favorable characteristics. This review deals with the development of organic/inorganic composite materials made by adding organic liquids into inorganic geopolymer matrices. Firstly, the incorporation processing approaches are presented and are divided into three categories: (i) Direct incorporation, (ii) Pre-emulsification (iii) Solid impregnation. Their main advantages and drawbacks are discussed in relation to the aimed properties. Secondly, this review highlights that geopolymers are low-cost candidates allowing technologically significant applications, through the incorporation of various organic liquids. Aside from the well-studied immobilization of industrial waste streams commonly known as stabilization/solidification (S/S), the development of highly porous geopolymer foams and the design of reinforced organic/inorganic composite matrices are being notably investigated. This review aims at summarizing the main published results, and fostering further investigations into innovative uses of organic liquids incorporated into geopolymers for a wide range of applications.

1. Introduction

Nowadays, the world production of Portland cement has reached about 4 billion tons [1], being one of the most produced merchandise worldwide (in volume). Such a significant production induces a high environmental impact; the production of Portland cement is responsible for about 0.8 tons of CO_2 equivalent per ton produced and contributes to about 8% of anthropogenic CO_2 emissions [2]. Therefore, there is an urgent need for alternatives to Portland cement, which are able to handle the increasing demand for infrastructure building while reducing the CO_2 emissions.

In the late 1970s, J. Davidovits drew the attention to Alkali Activated Materials (AAM) based on low calcium precursors, and named these materials geopolymers by analogy to their organic counterparts [3,4]. Geopolymers can be made from natural alumino-silicate minerals or industrial alumino-silicate wastes such as metakaolin, fly ash, blast furnace slag, rice husk ash, etc. mixed with aqueous solutions containing reactive ingredients (potassium/sodium hydroxide, phosphoric acid, potassium/sodium silicates, etc.) [5]. With a life cycle analysis

approach, the reductions in CO_2 emissions by replacing Portland cement with geopolymers strongly vary, but they are estimated to be of 30% at least [6], and can be as high as 80% [7]. Nowadays, geopolymers are one of the most promising material to replace Portland cement, because of their powerful characteristics including good mechanical properties, low permeability to liquids, resistance to high temperatures and acidic attack, etc. [8]. There has been a series of reviews related to geopolymer in the past few years testifying of the increasing interest for this material [8–18].

Incorporation of industrial wastes into cementing materials (by Stabilization and Solidification i.e. S/S[1]) is well known, because it offers assurance of chemical stabilization of many compounds and produces a mechanically stable waste form [19–21]. However, the stabilization of organic liquids (OL) in Ordinary Portland Cement (OPC) strongly retards and interferes with cement setting, and organic liquids usually do not form strong chemical bonds within the cement as some inorganics do [22–24]. Due to these issues, geopolymers have been proposed instead of OPC for the treatment of OL wastes; the influence of OL on geopolymer properties has been observed as less important [25,26].

Hydration of OPC is based on dissolution-precipitation reactions. The

---

* Corresponding author.
  E-mail address: catherine.davy@centralelille.fr (C. Davy).
  [1] Stabilization and solidification (S/S) is a process by which contaminants are immobilized and rendered immobile.

Glossary

AAF	Alkali-activated Fly ash
AAM	Alkali-activated material
CTAB	Cetyl Trimethyl Ammonium Bromide or Cetrimonium bromide
EDS	Energy-Dispersive X-ray Spectroscopy
GEOIL	Composite made of Geopolymer and OIL, i.e. Oil-containing geopolymer
GP	GeoPolymer
IAEA	International Atomic Energy Agency
FT-IR	Fourier Transform Infrared Spectroscopy
MK	MetaKaolin
NAF	Non-Aqueous drilling Fluid
OBM	Oil-Based Mud
OK	Odorless Kerosene
OL	Organic Liquid
OPC	Ordinary Portland Cement
PCM	Phase Changing Material
PEG	Polyethylene Glycol
QAS	Quaternary Ammonium Salt
SBM	Synthetic-Based Mud
SEM	Scanning Electron Microscopy
S/S	Stabilization/Solidification
TBP	TriButyl Phosphate

anhydrous phases dissolve in water until saturation at which the hydrates precipitate through a nucleation process. The main reacting phases in OPC[2] are Alite (C_3S), Belite (C_2S) and Celite (C_3A and C_4AF), which dissolution-precipitation reactions provide Calcium Aluminate and Silicate Hydrates (C-A-S-H); C-A-S-H are amorphous, with an atomic structure arrangement based on lamellar tobermorite models [27,28].

Geopolymers belong to alkali-activated materials (AAM). Unlike OPC, AAM (and geopolymers) require a strong alkaline (e.g. NaOH) source to accelerate the dissolution of various inorganic precursors [29]. Theoretically, any material composed of reactive silicates and aluminates can be alkali-activated. Two main types of AAM can be distinguished, depending on the amount of Ca present in the raw materials[3] [12,30,31]. C-(N)-A-S-H type gels are formed in Ca-rich systems through hydration mechanisms similar to the formation of C-A-S-H in Portland cements [32]. N-A-S-(H) type gels are formed in Ca-poor systems through polycondensation reactions, also called geopolymerization [33]. It is noted that water is part of C-A-S-H structures (through hydration reactions). On the opposite, for N-A-S-(H) tridimensional aluminosilicate networks, water is only required as a dissolution medium and is released upon gel formation (i.e. after poly-condensation). These fundamental differences in raw materials, reactivity or structures are starting points to understand the distinct behavior of both systems in the presence of liquid organic species.

In this review, three methods for the incorporation of OL into cementing materials, and more specifically into geopolymers, are distinguished (Fig. 1):

(i) Direct incorporation into the reactive slurry, (ii) Pre-emulsification prior to the addition of the solid precursor, (iii) Solid impregnation prior to the addition into the reactive mixture. In the following, the processing features of these methods will be discussed and compared depending on the properties required for the end applications.

Aside from the S/S of industrial waste, the significant efficiency of geopolymers to incorporate OL offers the possibility to expand the use of these composite materials to a number of applications. Two of the main applications already under strong investigation (apart from S/S) will be presented in this paper. These are the preparation of geopolymer foams by emulsion templating of vegetable oils, and the incorporation of organic polymers to design composite materials with reinforced or emerging properties.

2. Processing routes

This section describes the main processing routes to introduce OL into cementing materials (OPC and AAM[4]). Usually, Portland cement powder is mixed with water, whereas AAM powders are activated with an alkaline silicate aqueous solution (or with water, in the case of "one part geopolymers" [30]). Therefore, the addition of an extra liquid (OL) which is non-miscible with water is adding complexity to the system, because it will be made up of two distinct liquid phases and of a high amount of solid particles. Contrarily to the obvious, the OL is not necessarily incorporated at the end of the process, i.e. directly into the reactive cement slurry, but it can be introduced at different stages of the composite manufacturing, using different approaches. Fig. 1 presents a simplified schematic description of the three main processing routes for the incorporation of OL into cementing materials:

- Route 1 represents the *direct* process. First, the cement paste slurry is produced by dispersing the solid precursors in the aqueous solution. The OL is then directly incorporated into the slurry under strong mechanical mixing before the cement hardens.
- Route 2 represents the *pre-emulsification* process. First, the OL is emulsified in the activating solution still free from any solid precursor. As soon as a stable emulsion of the OL in the aqueous activating solution (O/W[5]) is obtained, the solid precursor is added to the emulsion to initiate cement hardening.
- Route 3 represents the *solid impregnation* process. This process consists of impregnating the OL on a solid powder. It can be divided into two distinct paths depending on the type of powder that is impregnated:
  - 3.1: The OL is impregnated on the cementing precursor itself and then mixed with the activating solution.
  - 3.2: The organic liquid is impregnated on a dedicated adsorbing powder before being added to the cement slurry.

2.1. Direct incorporation

The direct incorporation is a common procedure because of its simplicity (Fig. 1, route 1). All the components are successively introduced into a single container, which is also called "one pot" mixing [34]; the order of addition is very important. As mentioned earlier, the reactive slurries leading to the formation of cementing materials are in fact aqueous solutions, highly loaded with solid particles. In such instance, the addition of a water-immiscible liquid (the OL) into the reactive

---

[2] The cementing nomenclature consists of abbreviating the oxides and to replace them by the following capital letters: $CaO = C$; $SiO_2 = S$; $Al_2O_3 = A$; $Fe_2O_3 = F$; $H_2O = H$; $Na_2O_3 = N$.

[3] Systems for which the molar ratio $Ca/(Si + Al)$ is higher than 1 are considered rich in Ca.

[4] In order to simplify, OPC and AAM will be referred as cement throughout this document, unless stated otherwise.
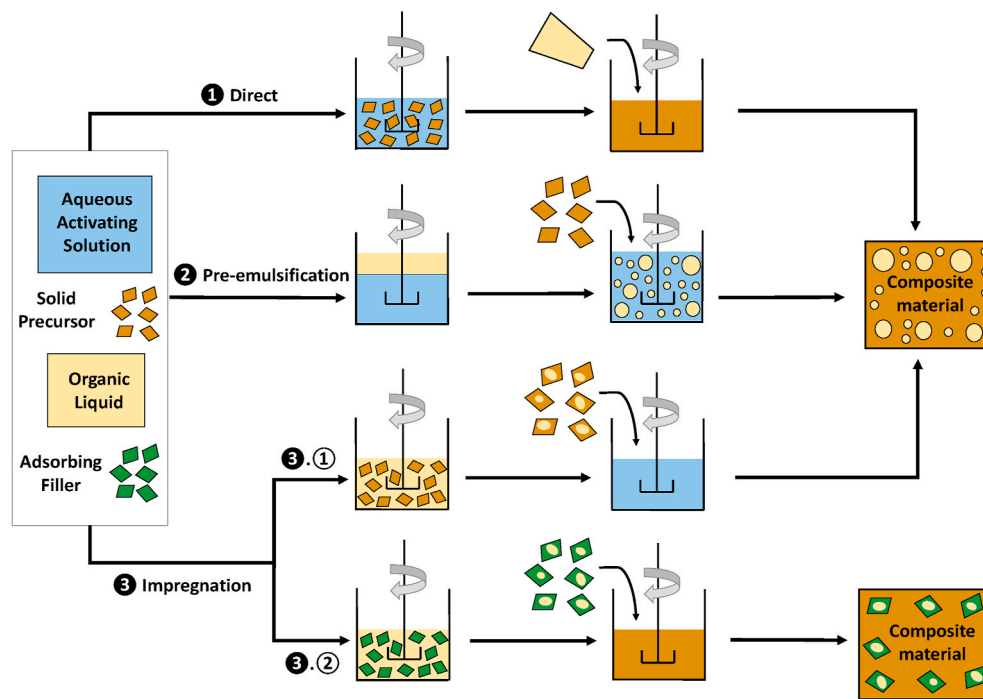
[5] W = Water and O = Oil.

Fig. 1. Simplified schematic representation of the three main processing routes of incorporation of OL into Portland cement or alkali-activated materials. The sizes of the components are not scaled.

aqueous slurry resembles the formulation of an emulsion, in which the dispersed liquid is likely to undergo spontaneous coalescence to minimize the overall Gibbs free energy of the liquid-liquid interface [35]. An advantage of the direct route is the intrinsic high viscosity of the cement slurry, which increases the shear stress applied to the dispersed liquid, thus promoting the creation of smaller droplets. Viscosities of cementing slurries (OPC and AAM) are hundreds of times higher than that of water, depending on the formulation parameters [36,37]. In her study on emulsion fragmentation [38], Mabille studied the influence of viscosity (η) of the continuous phase on the droplet size distribution. Keeping the fraction of dispersed phase (2.5 wt%) and the shear rate constant ($\gamma = 500$ s^{-1}), the author played with the viscous shear stress ($\sigma = \eta\gamma$) by changing the viscosity of the continuous phase. The viscosity ratio between continuous and dispersed phase and the interfacial tension, both having an impact on emulsion formulation where also kept constant at 1.0 and 6.0 mN m^{-1} respectively. It was observed that the higher the viscosity of the continuous phase (i.e. the higher the viscous shear stress), the smaller and the more homogeneous the droplet size distribution. A gradually increasing shear stress (from 170 to 475 Pa) creates gradually decreasing droplet size distributions from 10 to 5 μm. This was demonstrated for concentrated emulsions up to 75 wt% of the dispersed phase. Another advantage of having a higher viscosity of the continuous phase is that it hinders the coalescence of the formed droplets. To illustrate this latter point, sedimentation or creaming may occur over time, and are indirectly responsible for droplets coalescence. The velocity of coalescence and creaming is driven by several parameters, in particular the viscosity of the continuous phase. It is described using the Stokes equation [39]:

$$v = \frac{2(\rho_p - \rho_f)gr^2}{9\mu} \tag{1}$$

where **v, ρ_p, ρ_f, g, r, μ** are respectively the droplet velocity (m/s), the droplet density (kg/m^3), the density of the dispersing phase (kg/m^3), the gravity field (m/s^2), the spherical droplet radius (m) and the dynamic viscosity of the medium (Pa.s). This relationship shows that sedimentation or creaming are slowed down as the viscosity of the dispersing phase increases, therefore decreasing flocculation and hence coalescence.

Several types of OL have been incorporated through the direct route. Masrullita et al. [40] incorporated 10 wt% of paraffin oil into OPC that way. Several works describe the easy direct incorporation of vegetable oils into geopolymer materials, even at high oil amounts [41–43]. Davy et al. [44] directly immobilized a mineral oil in geopolymer up to 60 vol %. Despite the viscosity of the geopolymer suspension, the phases can undergo separation, especially when the amount of incorporated liquid is high [45,46].

Another concern appears when the viscosity difference is high, i.e. for organic liquids with low viscosity [38]. If the viscosity difference is too pronounced, the droplets maintain an equilibrium state upon shearing and do not break [38], therefore keeping a broad size more likely to undergo coalescence. Grace [47] evidenced that the closer the viscosity ratio is to 1, the easier the incorporation of the second liquid; the incorporation becomes more difficult as the viscosity ratio diverges from 1 in either directions (bigger or smaller than 1). Composite organic/inorganic materials have been prepared through the direct route by mixing geopolymer slurries with curable epoxy resins by hand mixing only, hence testifying of the easiness of incorporation [45]. In this process, the key step is to perform the incorporation of the curable resin at the adequate polymerization rate in order to avoid phase separation. As an explanation, several authors mention a better chemical compatibility between the organic and the inorganic phases at an early stage of resin polymerization, but there may be a viscosity effect as well. The resin is initially very fluid and becomes more viscous over time (with the progression of its hardening), hence decreasing the viscosity difference between the two liquid phases.

Finally, it is worth noting that for most of the direct incorporation processes presented in this section, no additives (e.g. surfactants) have been necessary to reduce the interfacial tension and promote the OL incorporation, even at high amounts (up to 60 vol%). However, the counterpart of not adding any surfactant is the lack of control over droplet size distributions and homogeneity [44].

2.2. Pre-emulsification

When manufacturing OL/cement composites, it is crucial to avoid phase separation between the OL and the slurry until hardening of the cementing material. The higher the amount of OL, the most likely the emulsion is to undergo phase separation. Even if the OL incorporation is achieved, the droplet size distribution may be large and inhomogeneous [44]. To avoid these issues, the pre-emulsification process (Fig. 1, Route 2) was developed. It consists in emulsifying the OL into the activating solution (and make an oil-in-water system O/W) prior to the addition of solid precursors and fillers. It is reasonably assumed that if the emulsion shows a good stability over time, the cement material will have sufficient time to set before the system goes back to its thermodynamically most stable state, the latter being reached when the two liquids are separated. In addition, by proceeding that way, it is also easier to control the droplet size distribution and homogeneity. In return, that process requires an extra step and the use of additives promoting the stability of the emulsion (e.g. surfactants or polymers). Surfactants are required to both decrease the interfacial tension between the two liquids and stabilize the droplets. Without surfactant, the viscosity of the aqueous activating solution is not high enough to stabilize the emulsion for a sufficient time. However, during the emulsion step, the system is still free from any solid particles that might act as Pickering stabilizers as described by Cantarel et al. [25].

The International Atomic Energy Agency (IAEA) mentioned a significant increase in the waste proportion which can be incorporated when using the pre-emulsification technique [48]. In Ref. [48], only 12 vol% of waste could be incorporated using the direct route, whereas up to 35 vol% could be incorporated using the pre-emulsification technique, although the latter requires a huge amount of surfactant (30 vol %).

In particular, Zhang et al. [49] solidified a spent radioactive organic solvent (by about 10 wt%), namely Tri-Butyl Phosphate/Odorless Kerosene (TBP/OK), in Portland cement added with Zeolite, calcium hydroxide or non ionic MR-1 type emulsifier; they named this technique emulsification-solidification by analogy to the stabilization-solidification (S/S) process. Dong et al. [50] successfully immobilized up to 18 wt% of TBP/OK using 4 wt% of Tween 80 (i.e. Polyethylene glycol sorbitan monooleate, CAS Number: 9005-65-6) as an emulsifier in a phosphate acid-based geopolymer. Cantarel et al. [25, 36,51] stabilized various organic liquids in geopolymer materials up to 70 vol% by using different surfactants; for instance, for highly fluid hexadecane, a CetylTrimethylAmonium Bromide (CTAB) cationic surfactant is essential. Cantarel et al. focused on the incorporation of 20 vol % OL, and were able to obtain a small and homogeneous distribution of oil droplets ranging from a few micrometers to about 50 μm [36]. Although replacing OL by air, Glad and Kriven were able to synthetize highly porous geopolymers with tailored pore sizes ranging from 200 nm to 10 μm using hydrophobic polymers, i.e. alkoxysilanes such as dimethyldiethoxysilane (DIDE) [(CH$_3$)2(OCH$_2$CH$_3$)2Si] [52].

Smitha et al. [53] went a step further, and prepared an emulsion of industrial lubricating oil by phase inversion in OPC. In practice, the aqueous solution is progressively added under strong mechanical stirring to the oil until a creamy emulsion is obtained; the optimal formulation is of 25%wt oil to cement ratio, i.e. about 10%vol; NaOH serves as both emulsifier and setting accelerator. Preparing an emulsion by catastrophic inversion (W/O to O/W or vice versa) is known to provide high stability because the droplets formed are very small. This is due to the fact that, at the point of phase inversion, the curvature radius of oil and water are equal to zero, allowing the formation of very small droplets (as small as 200 nm [54]); these are significantly more stable than bigger ones.

Skalle et al. [55] worked on an interesting hybrid mechanism combining both the direct and the pre-emulsification processing routes. First, a W/O emulsion is created (Fig. 1, Route 2) before being directly added to a reactive cement slurry (O/W) (Fig. 1, Route 1), providing a double emulsion.

As mentioned earlier in this section, the use of surfactant is most of the time mandatory to create the emulsions in the presented examples, but by proceeding that way, the incorporation is controlled throughout the process.

2.3. Solid impregnation

Among the three main processing routes, the solid impregnation process (Fig. 1, Route 3) is not as obvious as the direct and preemulsification routes. The amount of OL that can be incorporated is low in comparison with the two aforementioned routes, i.e. generally not exceeding a few percent. The advantage of using this route lies in the fact that the organic liquid is adsorbed onto a solid material early in the process and it is added in the form of a solid in the cement slurry; additives such as surfactants are generally omitted. Therefore, there is no emulsion to be considered, and no risk of phase separation that may occur in the course of cementation. The incorporation of a solid in a cement material is easier than the incorporation of a liquid, and the properties of the final composites, especially mechanical performance, are expected to be less impacted.

Some authors are using the impregnation route in order to mimic oil polluted sands, and to understand in what conditions they can be used as fillers to produce concretes in particular areas of the world [56]. It has been evidenced that a quantity of diesel oil contamination as little as 2%, fixed to sand, causes a significant decrease in compressive strength of the resulting cement materials. Moreover, when following the evolution of compressive strength over time, the impact of contaminated sand is especially observed in the late hardening phase of the material, and less in the initial setting phase.

Other studies evidenced that hydration reactions of OPC are strongly affected by the addition of small amounts of organic compounds, leading to setting and hardening issues [20,57–59]. However, by using the impregnation route, Almabrok et al. [60] successfully stabilized industrial 10 W mineral oil up to 10 wt% in OPC. They compared the preliminary wetting of the cement precursor or of the sand by the oil before adding water, but there was no significant difference; the compressive strength is divided by a factor 3 in both cases. By adding non swelling kaolinite clay, which acts as an oil adsorbent, the authors were able to lower the impact on mechanical properties to a factor of 2.5.

The IAEA studied the impregnation process of turbine and pump oils, and described it as the conversion of OL into dry particles prior to cementation in Portland cement, using a variety of adsorbents (e.g. natural or synthetic fibers, vermiculite, clays, diatomeous earth, alkyl styrene polymer beads) [48]. According to the authors, this technique is more tolerant of batch-to-batch waste variability and higher waste incorporation of up to 56 vol% could be attained; this contrasts with other studies using the impregnation process, which generally allow the incorporation of a lower amount of liquid (below 10% and often at a few percent only). However, the IAEA also recognizes that a number of factors affect the efficiency of the process, including the OL viscosity. The associated mechanical performance of the composites is not provided.

The OL waste needing stabilization in cementing materials often contains toxic species, which must not leach out of the solidified material. Therefore, the oil impregnation on an appropriate adsorbent is helpful to avoid leaching and immobilize the toxic species. For instance, Sazonov et al. [61] decreased the tritium leaching rate by adsorbing tritiated oil on various adsorbents (zeolites, active alumina, activated carbon); the best results are achieved with activated carbon. Montgomery et al. [24] used a commercially available QAS-clay[6] prior to

---

[6] QAS-clay: Quaternary Ammonium Salt exchanged clay. These clays are modified beforehand in order to adsorb organic compounds, e.g. by being added with CTAB (CTAB: CetylTrimethylAmmonium Bromide).

incorporation. QAS-clays are specifically designed to strongly adsorb organic compounds. In Ref. [24], the cement-based solidification of organic effluent waste adsorbed on QAS-clays provides solid bodies, with unconfined compressive strength significantly higher than the standard requirement of 350 kPa. Moreover, due to the strong binding of organics to QAS-clay, their leaching from the stabilized products is very low. The total organic carbon (TOC) is reduced by over 90% for each of the tested waste compared with unsolidified ones; the release of heavy metals is similarly reduced.

El-Naggar et al. [62] impregnated an organic solvent extraction liquid (2 hydroxy-5-nonylacetophenon) on metakaolin, before adding the activating solution to achieve a geopolymer-solvent composite (Fig. 1, 3.1). Leaching tests, and other characterizations, of the formulations containing the solvent extraction liquid proved that the solvent did not move out of the solidified cement composite, even under severe acidic attack. The compressive strength was slightly impacted, as shown by the formulation containing 8%vol of solvent (28 MPa), only experimenting a 4 MPa decrease in comparison with the reference material (32 MPa). The strength of formulations containing 8%vol solvent could be further improved from 28 MPa to 54 MPa by increasing the SiO$_2$/-Na$_2$O molar ratio. The authors evidenced the good compatibility of the solvent with the geopolymer network and its low impact on the hardened material, which contrasts with OPC.

Cuccia et al. [63,64] immobilized radioactive waste oils in geopolymers, by preliminary adsorbing the oil on a commercial polymer. The resulting composite material complies with local leaching rate regulations but does not fulfill mechanical strength criteria (its compressive strength is lower than 10 MPa). However, the compressive strength of the pure geopolymer formulation is of only about 19 MPa. This means that the poor mechanical properties of the waste containing sample is not necessarily attributed to a bad oil/geopolymer compatibility but rather to the low mechanical properties of the pure geopolymer formulation. Formulation parameters (especially the Si/Al molar ratio) have a strong impact on the connectivity of the aluminosilicate network formed during geopolymerization, and hence, on the mechanical properties of the geopolymer materials [65].

2.4. Summary

Although possible, the addition of an extra immiscible liquid into a cementing material generally increases the setting time, lowers the mechanical properties, disturbs the flow of reactive slurries, may induce leaching of the OL, etc. However, by using the most appropriate incorporation process in accordance with the end applications, these issues can be overcome. Unfortunately, studies comparing the different processing routes at the same time are scarce [66]. Table 1 compares the processing routes and aims to summarize the advantages and drawbacks of using one or another, in order to guide the decision of the most appropriate path for a specific application. Moreover, all the examples discussed in this section are generally at a laboratory scale. At the industrial scale, the pre-emulsification and impregnation processes would be more challenging because they involve an additional step, which, in some cases (e.g. when dealing with radioactive waste), might be an issue. Moreover, these two processing routes require the addition of costly surfactants or adsorbents, which might be a limiting factor as well. Other incorporation techniques exist, such as the incorporation through diffusion of the OL into the cement pore network after cement hardening, but they are less commonly used [67].

3. Aimed applications

In the past few years, an increasing interest for the incorporation of OL into inorganic geopolymers has been observed, because if offers a wide variety of unique applications. This section aims at presenting the three main applications of the incorporation of OL into geopolymers, as summarized in Fig. 2. The OL is introduced in the fresh geopolymer

mortar following one of the processes described previously (Fig. 1). Interestingly, the type of oil appears to dictate the corresponding application, as follows:

- Mineral oils → Immobilization of industrial waste by S/S
- Vegetable oils → Production of highly porous materials
- Organic polymers → Production of materials with improved and/or emerging properties

3.1. Immobilization of waste OL (mineral oils)

3.1.1. Background on oil immobilization into Ordinary Portland Cement (OPC)

Before detailing the immobilization of OL waste into geopolymers, it is useful to recall the use of Portland cement for that purpose, because it has been widely and successfully used for the immobilization of many compounds.

As detailed earlier, according to IAEA, the direct immobilization of radioactive OL waste by cementation (i.e. S/S) is one of the best options because it is simple and cost effective [48]. It offers assurance of chemical stabilization of many compounds by producing a mechanically stable waste form, and OPC has been widely studied for that purpose [68]. A varied but non-exhaustive list of examples is presented below.

Early studies on that topic were presented by Clark et al. [66]. Their work aimed to determine the most suitable solidification agent for the disposal of radioactively contaminated OL wastes. Initially, the immobilization of a lubricating oil (mineral oil) in pure OPC from 12 to 50 vol % was performed using the direct process (Fig. 1, Route 1). All the samples ended in soft appearing materials, indicating that OPC alone is not a very effective media to solidify oily wastes. Then, vermiculite, an adsorbent clay that can retain liquids within the pores of its particle aggregates, as well as between the clay particles themselves, was used to adsorb the oil prior to solidification in OPC (Fig. 1, Route 3). OPC samples prepared with oil-saturated vermiculite set in about three days, which provided convenient monolithic solids; however, all had an initial oily appearance on the surface with traces of free liquid, and were not considered suitable. This is why a third technique, developed by the Nuclear Technology Corporation (NUTEK) was used. It consists of a chemical process to solidify radioactive waste oils, by combining an emulsifying agent (Fig. 1, Route 2) and a setting time accelerator, both aiming at preventing coalescence of the liquid before solidification. Adequate solid monoliths were obtained with this procedure, and no free liquid was observed at oil incorporation rates up to 30 vol%. Being the best option for the lubricating oil, the NUTEK technology was then used in the same way to solidify a complex mixture of organic liquids, but it was not very efficient. The only acceptable sample contained only 6 wt% of the liquid mixture, and even at this low proportion, the smell of organic vapors was strong. The conclusion of this research is that the pre-emulsification process using the NUTEK procedure is the best option for stabilizing lubricating oil, but in the case of an organic mixture, OPC is not a suitable option.

Masrulita et al. [40] stabilized paraffin oil in OPC and observed that the more paraffin is added, the lower the compressive strength. According to the authors, this is because the cement cannot efficiently coalesce with the added hydrocarbon; instead, cavities are formed in the composite materials, resulting in lower densities and therefore lower compressive strength.

OPC has often been used for S/S of TBP/OK, which is a common mixture for extraction of radioactive waste [34,69]. However, the addition of TBP strongly decreases the compressive strength of the resulting solid materials [70]. In a recent study [49], about 10 wt% of simulated radioactive spent organic solvent (TBP/OK) was solidified with OPC by the emulsification–solidification method (Fig. 1, Route 2). X-Ray Diffraction (XRD) analysis illustrated that the incorporation of both TBP/OK and the emulsifier did not change the cement hydration

Table 1
Summary of advantages and drawbacks of the main incorporation processing routes.

|	Advantages	Drawbacks
Direct	o Easy incorporation in one step o High amount of oil o No extra additives required	o Phase separation before setting might occur
Pre-emulsification	o High amount of oil o Phase separation controlled by preliminary emulsification o Controlled size of oils droplets	o Two steps process o Addition of surfactants required
Impregnation	o Useful for high leachable toxic compounds (adsorption on solid particles) o No phase separation because the liquid is solidified beforehand	o Low amount of oil incorporated o Two step process o Requires the addition of a solid adsorbent (if not impregnated on the cementing precursor) o Cost of solid adsorbent
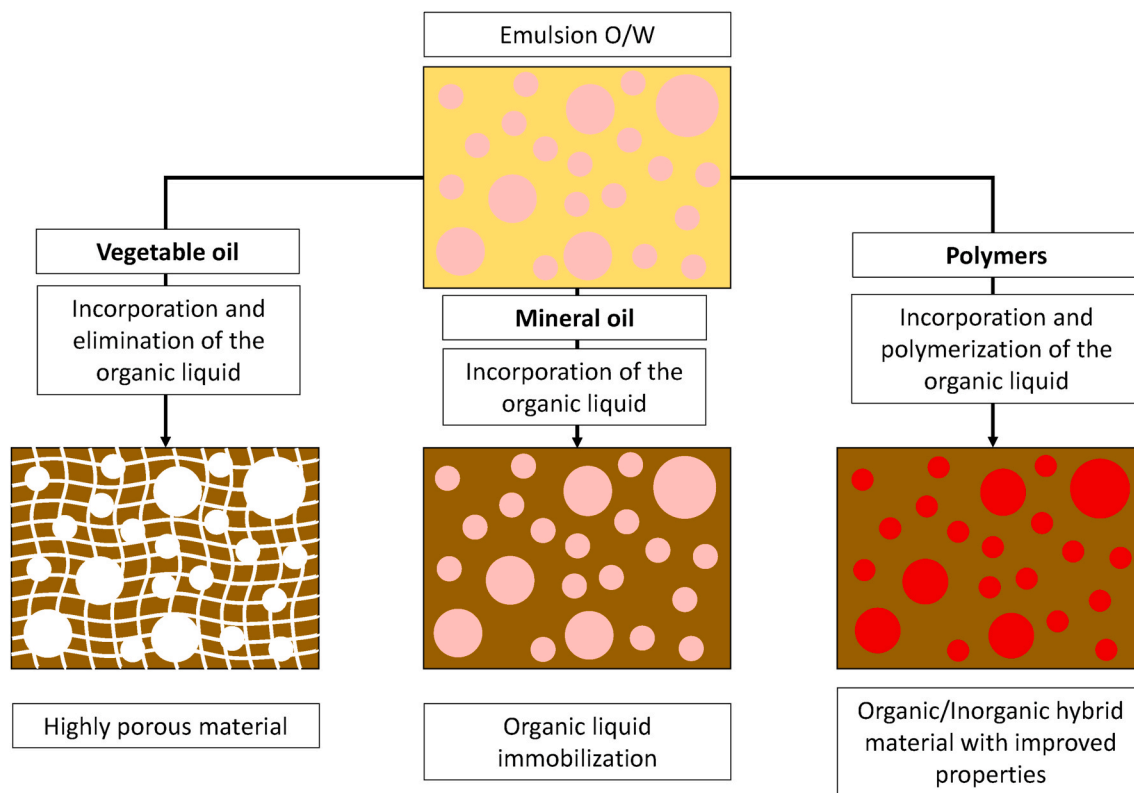
Fig. 2. Schematic representation of the three main application of incorporating OL into geopolymer materials: Incorporation of vegetable oil to produce geopolymer foams (left), stabilization of mineral waste oils (middle), addition of organic polymers to design reinforced materials (right).

products. The resulting compressive strength of the composite material is of about 19 MPa. Unfortunately, no comparison of mechanical properties with a liquid free cement was performed.

Several authors presented the impact of crude oil on compressive strength [71–73]. As discussed earlier, oil-contaminated sands used as additives in cement manufacturing strongly reduces the compressive strength of concretes. For instance, sands contaminated with crude oil at only 5 wt% reduces the compressive strength at 28 days of concretes by almost 50% (32–18 MPa) [71].

Almabrok et al. [60,74,75] studied the incorporation of various OL in Portland cement using the impregnation route (Fig. 1, Route 3), in order to avoid side effects on setting time and strength development. Despite impregnation, the addition of oil strongly affected cement setting and strength development, largely due to the perturbation of cement hydration. The addition of more than 10% of mineral oil led to unacceptable materials (compressive strength < 20 MPa) [60]. The addition of contaminated aggregates at 10 wt% with canola oil, refined mineral oil or crude oil, decreased the 28-day compressive strength by 71%, 75%

and 50%, respectively [74]. Moreover, calorimetric measurements highlight that the hydration of C_3S and C_3A is inhibited by the addition of oil, despite their adsorption prior to solidification. Hydration reactions are differently impacted by the type of oil; mineral oil is the most influencing one, whereas crude oil has only a slight impact. This testifies that inhibition is not due to the addition of oil-contaminated aggregates but rather to an interaction between the oils and the hydrating phases [74].

A recent study summarizes the issues faced by the use of Portland cement for gas well cementing, because of the intermixing of cement slurry and drilling mud[7] that will almost inevitably occur [37]. In most

---

[7] In wellbore processes, drilling muds cool the drill bit and carries the rock cuttings along back to the surface. Most of the muds are oil-based, using direct products of petroleum refining such as diesel oil or mineral oil. Sometimes, synthetic-based muds are prepared using highly refined fluid compounds that are more adapted to property specifications than traditional petroleum-based oils.

cases, the mud-contaminated cement undergoes failure, because it does not harden properly. As the cement slurry becomes more contaminated, it strongly thickens until it cannot flow anymore, which is also a major issue. According to the authors, a mud-to-cement conversion technique has not been successfully developed and applied for NAFs[8] (Non-Aqueous drilling Fluids) so far. Contamination by NAFs is for instance detrimental to the strength development of Portland cement slurries, with as strong a drop as of 50% of the original compressive strength at 15 vol% of contamination [76]. Comparatively, alkali-activated fly ash (AAF) slurries exhibit superior performances against NAFs contamination compared to Portland cement [37]. According to the authors, this could be due to the breakdown of NAF emulsions, releasing an excess amount of water. In AAF containing a low Ca amount, water is not chemically bound to the N-A-S-(H) gel formed, i. e. it is only acting as the reaction medium, whereas in Portland cement water is part of the C-A-S-H structure. Therefore, changes in water amount might have less effect on the strength development of AAF than Portland cement. Unlike Portland cement slurries, AAF slurries develop sufficient compressive strength for cementation purposes at high levels of mud contamination. An incorporation rate of up to 40 vol% of Synthetic Based Mud (SBM)[9] in AAF leads to materials with measurable compressive strength, while Porltand cement loses the ability to harden with 30 vol% SBM contamination. Moreover, the incorporation of SBM into AAF provides flowable slurries (even at 40 vol%), whereas Portland cement slurries become too viscous. As for strength development, the excess of water released by the breakdown of the SBM emulsion could explain the decrease in viscosity observed in AAF slurries. On the contrary, the thickening of Portland cement slurries could be explained by capillary forces, which depend on the affinity of particles for both liquids [77–79]. In liquid-liquid-particle ternary systems, the addition of the second immiscible liquid to the particles suspension in the first liquid results in an increase in viscosity. In such systems driven by capillary forces, the second liquid stands between the particles leading to agglomerate formation, which is characterized by an increase in viscosity. Finally, AAF could efficiently solidify two types of SBMs and two types of Oil-Based Muds (OBMs)[10], meaning that the mud-to-cement conversion in AAF is a versatile method. Likewise, AAF materials are more resistant than Porltand cement to a contamination by water-based drilling [80]. The AAF solid precursor used in that study is class F[11] fly ash, containing a low amount of Ca, leading to the formation of N-A-S-H i.e. to a geopolymer.

3.1.2. Geopolymers: emerging materials as alternatives for OL immobilization

Table 2 below summarizes a number of works performed on the immobilization of OL into geopolymer materials and published in the recent years.

3.1.2.1. Waste immobilization. The immobilization of radioactive mineral oils in geopolymer materials, also named GEOIL (for **GE**opolymer/ **OIL**) composites, has been extensively studied in the recent years [25, 36,44,51]. First, the feasibility of incorporating up to 70 vol% of a mineral oil in geopolymers was demonstrated, while maintaining the formation of strong monolithic solids [51]. Then, the influence of oil addition on the mechanical performance and leaching rate of GEOIL has

been studied [36]. For oils of viscosity on the order of 0.1–2 Pa s, an easy incorporation of up to 20 vol% in a geopolymer matrix was demonstrated, where the oil takes the form of an emulsion made of homogeneous and spherical droplets. The droplet size ranges from a few μm to 50 μm, with the diameter of the main population being about 5 μm, showing the good dispersion of the oil in the geopolymer material. As expected, the compressive strength decreases when the oil content increases, but the effect is not as pronounced as in OPC matrices. In particular, at 30 days, the decrease in compressive strength for GEOIL containing 20 vol% oil is about 35% (32–22 MPa) compared to the geopolymer without oil (reference GP); with 14 vol% oil, the compressive strength of GEOIL is smaller by only 12.5% when compared to the reference GP (32–28 MPa) [36]. Moreover, the cumulative quantity of oil compounds released in the leachate at 30 days does not exceed 0.19% of the organic material initially encapsulated in the sample, demonstrating the efficiency of the oil encapsulation in GEOIL composite. Unlike for Portland cement, rheological measurements and Fourier Transform InfraRed spectroscopy (FT-IR) have shown that there is no change in the geopolymerization kinetics (in particular in the setting time) [25]. The reason probably lies in the fact that geopolymers undergo polycondensation reactions to build their gel network, whereas Portland cement undergoes hydration mechanisms, which is fundamentally different.

Despite the fact that highly fluid OL (such as hexadecane) can be efficiently stabilized into geopolymer matrices, the addition of surfactants can be of use to better control the droplet size distribution, improve the incorporation quality and the rheology of the paste. In Ref. [25], CTAB and Pluronic L35[12] surfactants have been tested (respectively cationic and nonionic surfactant). Both surfactants provide GEOILs with rather homogeneous size distributions of oil droplets in the range of 10–100 μm (Fig. 3 [25]). Using surfactants also results in composite pastes with different rheological behaviors, thanks to the effect of the surfactant molecules at the intermolecular level.

At such scale, surfactants have the ability to position themselves at the surface of oil droplets through their polar head, leading to the formation of hydrophobic forces between droplets; the repulsive forces between these hydrophobically modified droplets are due to the interaction of the nonpolar tails of the surfactant molecules attached to the oil surface. The resulting system consists of a "shell" around each oil droplet, and induces an increase in viscosity. Several authors observed this phenomenon with cationic surfactants (for which it is strongest, owing to the strong adsorption on negatively charged particles) [83–85] and nonionic surfactants [86–88]. Cantarel et al. [25] also concluded that metakaolin particles surrounded oil droplets and acted as Pickering stabilizers (Fig. 4). Without mentioning the Pickering effect, Glad and Kriven present a similar behavior for metakaolin around oil droplets [52].

However, the quantity and type of surfactant should be chosen carefully when incorporating OL in geopolymers, particularly for systems with a high volume fraction of dispersed phase. In such context, 3D X-Ray micro-computed tomography quantifies the spatial distribution of the oil droplets in GEOIL (Fig. 5 [44]) and provides a connectivity analysis of the 3D oil emulsion. This allows to analyze whether the oil emulsion percolates (and may leach out of GEOIL). With an industrial gear oil immobilized at up to 60 vol%, the oil percolation threshold is reached from 27 vol% incorporation.

In order to overcome the undesirable leaching of OL with the direct immobilization technique as with Portland cement [89], El-Naggar et al. [62] have investigated geopolymers as an alternative to immobilize a solvent extraction liquid of interest in the nuclear industry, loaded with Cu^{2+} beforehand (LIX-84, made up of 2-hydroxy-5-nonylacetophenon). FT-IR analyses were performed after leaching tests to verify that the solvent was still present in the materials and proved the compatibility

---

[8] NAFs are invert emulsions (water in oil) containing solids including organophilic clays, viscosity modifying polymers and dispersing agents.

[9] SBM (Synthetic-Based Mud): Invert emulsion where synthetic oil (based on C_{16}–C_{18} internal olefins) is the continuous phase and $CaCl_2$ brine is the dispersed phase. Also contains various additives.

[10] OBM (Oil-Based Mud): Mineral oil-based mud.

[11] Several types of fly ashes exist and are classified according to their oxide contents. Class F fly ash is poor in CaO and contains a significant amount of Al_2O_3.

[12] Pluronic L35: Commercial nonionic surfactant.

Table 2

Immobilization of mineral waste oils in geopolymer materials; MK = Metakaolin, FA = Fly ash, vol% = volume percentage, wt.% = weight percentage, CTAB = CetylTrimethylAmmonium Bromide (cationic surfactant), SBM = Synthetic Based Mud, OBM = Oil Based Mud. Pluronic L35 and Tween 80 are non-ionic surfactants.

Alumino-silicates sources	Activating solution	Oil type	Amount	Surfactant	Incorporation process (Fig. 1)	Ref.
MK	Acid: H_3PO_4	TriButyl Phosphate/odorless kerosene (TBP/OK)	6-18 wt%	Tween 80	❷ Pre-emulsification	[50]
FA	Alkaline: NaOH	Paraffin wax	8-15 wt%	None	❸.②. Impregnation on lightweight coarse aggregates	[81]
MK	NaOH	Dodecanol	About 3.5 wt%	CTAB	Impregnation after GP set[a]	[67]
MK	NaOH	Motor oil	5-60 vol%	None	❶ Direct	[44]
MK	NaOH	Motor oil (aliphatic compounds)	7-20 vol%	None	❷ Pre-emulsification	[36]
MK	NaOH	Hexadecane	20 vol%	CTAB or Pluronic L35>	❷ Pre-emulsification	[25]
MK	NaOH	Lubricating oils	10 wt%	None	❸.② Impregnation on commercial polymer	[63]
MK	NaOH	LIX84 (commercial solvent extraction liquid)	0–15%	None	❸. Impregnation on MK	[62]
MK	NaOH	Dimethyldiethoxysilane (DIDE)	About 10 wt%	None	❶ Direct	[60]
FA	NaOH	SBM and OBM	10-40 vol%	None	❶ Direct	[37]
MK	NaOH, KOH	Hexadecane	20-70 wt%	None	❶ Direct	[82]

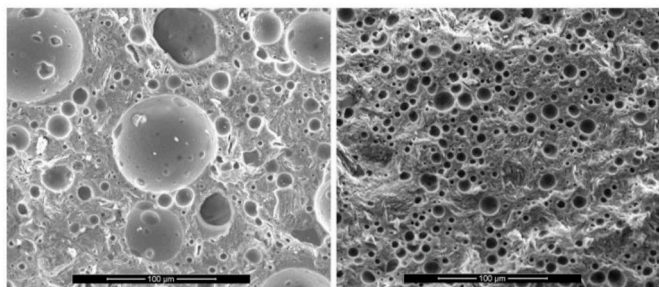[a] The solid geopolymer is left in touch with an excess of dodecanol at 60 °C for 30 min.

Fig. 3. Scanning electron micrograph of a calcinated GEOIL composite containing 20 vol% of hexadecane with CTAB (left) or L35 (right) surfactants [25].
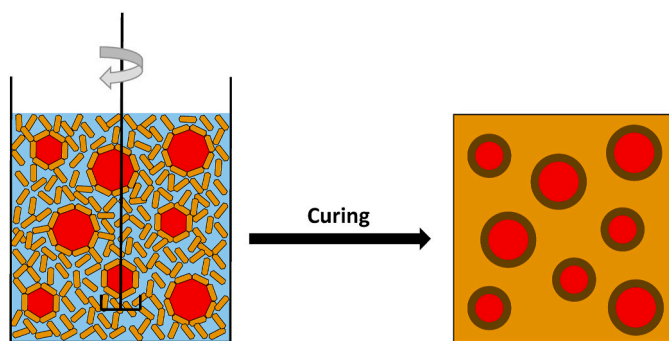

Fig. 4. Pickering-type stabilization of oil droplets in a fresh geopolymer mortar (left) providing encapsulated oil droplets after curing (right).

between geopolymers and LIX-84. Indeed, leaching experiments indicated that the formulations performed well, because most of the Cu^{2+} remained in the geopolymer material, even under severe acidic conditions (less than 5% of the total Cu^{2+} leached out).

Cuccia et al. [63] have studied the immobilization of radioactive waste oil in geopolymer materials with the impregnation process (Fig. 1, 3.2). They used two different types of adsorbents prior to solidification, i.e. bentonite and a commercial polymer (NOCHAR). For both kinds of adsorbents, the authors obtained geopolymer matrices with homogeneously distributed waste and leaching rates at 150 days compliant with local regulations.

Apart from alkaline activating conditions, geopolymers can also be

activated in acidic conditions. This is a valuable asset in specific applications where alkaline conditions are deleterious. In a recent study, phosphate acid-based geopolymers were investigated as a solidification technology for TBP/OK [50]. These acidic-synthesized geopolymers have reputed to have higher strength, durability, and thermal stability than alkali silicate-metakaolin geopolymers [90–93]. This is explained by the formation of berlinite ($AlPO_4$) resulting from the combination of Al^{3+} (from metakaolin) and PO_4^{3-} (from phosphoric acid). The presence of this crystalline phase reinforces the structure of geopolymers by filling air voids (porosity) [92,93]. In Ref. [50], the phosphate acid-based geopolymer has a high compressive strength of about 79 MPa, and that of solidified TBP/OK forms is up to 59 MPa. The compressive strength does not decrease drastically with increasing TBP/OK content. With 18 wt% of TBP/OK, the decrease in compressive strength is about 25%, which is significant but still more than acceptable considering the initial high value. Leaching tests demonstrate that a very limited amount of solidified TBP/OK is released from phosphate acid-based geopolymers, meaning that TBP/OK is physically well encapsulated within the solid body. The only drawback is with setting time, which significantly increases with the addition of TBP/OK.

3.1.2.2. Phase changing materials (PCM). The incorporation of phase changing materials (PCM) into geopolymers aims to produce smart materials, able to mitigate temperature changes in their vicinity. PCM are capable of changing phase from solid to liquid at a specific melting temperature (or vice versa), and it is usually low (i.e. below 100 °C). During the phase changing process, a certain amount of energy (i.e. heat) is captured from or released into the surrounding environment [94], retarding the change in temperature. Several studies have investigated the immobilization of PCM in building materials, such as thermal regulating panels [95]. More precisely, OL such as paraffin [81,96,97] or dodecanol [67], were incorporated into geopolymers to produce materials with smart thermal properties. A wall made-up of this type of material would be able to keep comfortable temperatures inside a building during daytime (by the endothermic melting of the PCM) and night-time (through the exothermic solidification of the PCM).

Using the direct incorporation (Fig. 1, Route 1), paraffin is distributed homogeneously in a geopolymer concrete, among voids and aggregates. However, after a number of temperature change cycles, a leakage of paraffin to the material surface is often encountered. In order to overcome that issue, paraffin can be pre-encapsulated or stored into small (inert and stable) closed polymer capsules to prevent leakage, before being mixed with concrete [96,97]. Shadnia et al. [97] studied
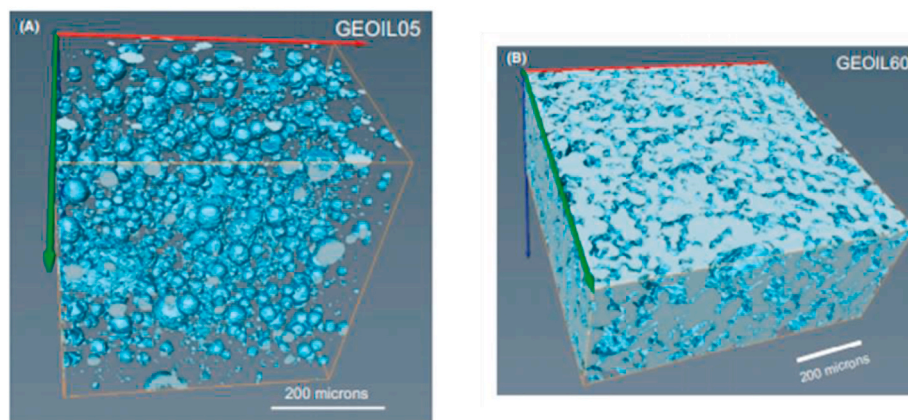
Fig. 5. Spatial representation obtained by X-ray micro-CT of the oil distribution (in light blue) in GEOIL composites containing 5 vol% (left) and 60 vol% (right) of oil. The oil volume is either not-percolating (left) or percolating (right) [44]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the incorporation of commercial micro-encapsulated PCM (paraffin) powder into geopolymer mortar. A decrease in mechanical properties is observed, but geopolymers with up to 20 vol% PCM incorporation are still convenient with compressive strength exceeding 15 MPa. The heat capacity curves of geopolymers added with PCM display endothermic peaks between 20 °C and 30 °C. This corresponds to the melting temperature range of the PCM material, which contrasts with the straight heat curve of the pure geopolymer material. The higher the amount of PCM, the higher the amplitude of the endothermic peak, meaning that incorporated PCM can effectively reduce the transport of heat through geopolymer bodies.

In a study by Sukontasukkul et al. [81], the PCM is impregnated on porous lightweight aggregates (Fig. 1, 3.2), which are then used as coarse aggregates in a geopolymer concrete mixture. The maximum incorporation is 60 vol% (40 vol% of PCM and 20 vol% of aggregates). As expected, the compressive strength decreases with the addition of pure lightweight aggregates (15–5 MPa with 60 vol% of aggregates), but it increases with the presence of paraffin in the aggregates, due to void filling by paraffin (5 MPa–7 MPa with aggregates loaded at 65 vol% of paraffin). The presence of paraffin significantly improves both thermal storage and heat insulation of geopolymer panels, as shown by the time delay of 22 min to reach the peak temperature (65 °C) and the ability to maintain the temperature higher than 55 °C inside the panel for more than 180 min after the end of heating.

Gasca-Tirado et al. [67] studied the use of dodecanol as PCM in geopolymers. The incorporation was performed after solidification of the geopolymer material, which is different from the incorporation routes presented earlier in this paper (Fig. 1). The solid bodies were immersed in an excess of liquid dodecanol at 60 °C, which then diffused into the material through its pore network. The effectiveness of CTAB is shown as a coupling agent between dodecanol and geopolymer; a surface treatment increases the maximum amount of incorporated dodecanol. However, the highest amount of dodecanol remains low (about 3 wt%) and further studies are needed to increase the incorporation capacity, in particular by modifying the geopolymer porosity. With the process involved, this method provides a percolating (connected) OL system.

3.2. Development of highly porous materials (mainly with vegetable oils)

Nowadays, porous geopolymers, also referred to as geopolymer foams, are becoming of interest because of their unique combination of properties, i.e. good thermal and chemical stability [15,98,99], high mechanical strength [100,101], low CO_2 emission and low energy use during their manufacture. They have been studied for a variety of applications, including membrane and membrane supports [102,103],

adsorbents and filters [104–109], catalysts [94,110–112] and acoustic and thermal insulators [17,18,113–115].

Over the last 10 years, the number of publications concerning geopolymer foams has increased significantly, bringing forth several reviews related to that topic [17,18,116]. For many of these applications, the porosity of geopolymer foams needs to be as high as possible and as open as possible, i.e. the porous network needs to be connected (or percolating) as much as possible to allow external species to flow in and out. A significant amount of meso- and macro-porosity[13] is intrinsically present in geopolymers [117–119] and can be optimized simply by regulating the formulation and processing parameters of its bulk components [120,121]. The focus of the following studies is to promote the introduction of interconnected ultra-macro-porosity[14] in addition to the meso- and macroporosity of geopolymers by combining a vegetable oil and a blowing agent, in general oxygen peroxide H_2O_2.

In pioneering studies [43,122,123], vegetable oils were used to produce highly porous and open geopolymers by emulsion templating (Fig. 6, Red pathway). First, vegetable oils are easily incorporated in the geopolymer slurries following the direct route (Fig. 1, route 1). Vegetable oils, mainly triglycerides, then undergo saponification in alkaline conditions [78], leading to water-soluble soap and glycerol species, which are easily extracted after GP curing; after removal, these species leave a large and connected pore network.[15] The extraction is usually done by hot water exchange. In addition, the extraction allows to check the completion of geopolymerization, since non-fully condensed geopolymer materials are sensitive to water, would swell and disaggregate [41,42]. A very recent study [124] has investigated the influence of various surfactants on sunflower oil emulsification. It has highlighted that the pore network could be sized by the use of specific surfactants. However, vegetable oils mainly allow the formation of meso- or small macro-pores [125]. It is not the most efficient way to increase total porosity, but the advantage of vegetable oils is their ability to promote the connectivity of the pore network. Table 3 summarizes the main

---

[13] In the IUPAC classification of pore sizes, the micropore width does not exceed 2 nm, the mesopore width is in the range 2–50 nm and the macropore width is above 50 nm (0.05 μm) [160].

[14] The term "ultramacroporosity" refers to pores displaying a width of hundreds of microns, and generated on purpose by the use of a blowing agent, in contrast with macropores intrinsically present in geopolymers and generally having a width lower than 100 μm.

[15] Portland cements could not be considered in this application because they are water-activated and would not provide the required alkalinity. Despite this drawback, some studies on the incorporation of vegetable oils in OPC for the purpose of making lightweight concrete have been performed [161].
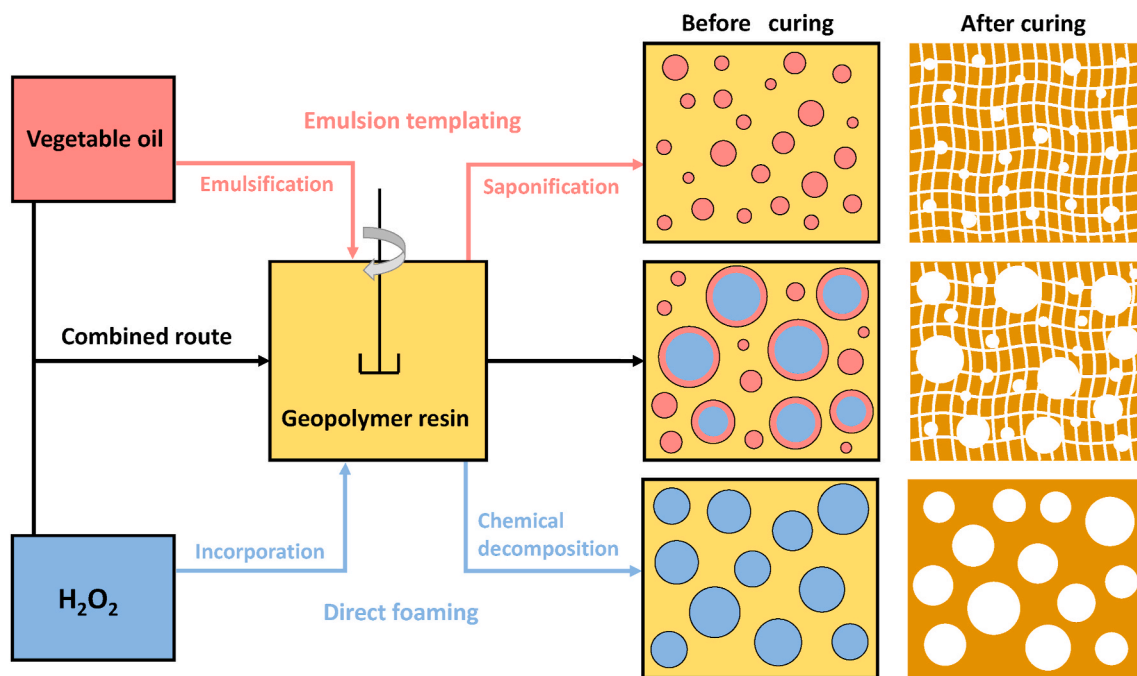
Fig. 6. Simplified schematic representation of synthetic routes to porous geopolymer, by emulsion templating of vegetable oils (red pathway), by direct foaming using H_2O_2 as a blowing agent (blue pathway), or through the combined route (black pathway). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
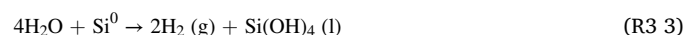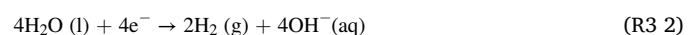
Table 3
Processing of highly porous geopolymers using vegetable oils; MK = Metakaolin, FA = Fly ash, vol% = volume percentage, wt.% = weight percentage.

Alumino -silicate sources	Alkali ions	Oil type	Amount incorporated	Amount of H_2O_2	Process of incorporation (Fig. 1)	Reference
FA	NaOH	Corn, Palm	4-12 wt%	/	❶ Direct	[43]
MK	KOH	Canola, Biodiesel, Paraffin	1:1 oil-to-water volume fraction	/	❶ Direct	[125]
MK	KOH	Olive	20-45 wt%	5-15 wt%	❶ Direct	[126]
MK	KOH	Sunflower, Canola, Olive	20-70 wt%	0-20 wt%	❶ Direct	[41]
MK	KOH	Sunflower, Canola, Olive	0-10 wt%	0-20 wt%	❶ Direct	[127]
MK	NaOH	Soy bean	20 wt%	About 6 wt%	❷ Pre-emulsification	[128]
MK and FA	KOH	Coconut, Babassu, Palm Stearin, Beef tallow, Olive, Castor, Sunflower, Soybean, Biodiesel	25 wt%	6 wt%	❶ Direct	[129]
MK	NaOH	Canola	2-6 wt%	0,5-1,5 wt%	❶ Direct	[130]
MK and FA	KOH	Sunflower	25 wt%	6 wt%	❶ Direct	[131]
MK	NaOH	Sunflower	20 wt%	/	❷ Pre-emulsification	[124]

research works on the development of highly porous geopolymers using vegetable oils for emulsion templating, with saponification reactions.

Without involving OL, the direct foaming processing route is the most widely used technique for producing highly porous geopolymers [17,132] (Fig. 6, Blue pathway). With this method, wet geopolymer foams are produced by incorporating air or gas into the homogeneous slurry, which sets subsequently by curing at a given temperature to obtain consolidated porous materials. To develop alkali-activated foams, several frequently selected blowing agents are H_2O_2 [42,101] (Equation R1), aluminum powder [133,134] (Equation R2), or silica fume [114,135,136] (Equations R3). These agents decompose in alkaline conditions and react inside the cement matrix, generating gas and resulting in the creation of macropores of different sizes and shapes, through the following decomposition reactions:

$$H_2O_2 \text{ (l)} \rightarrow 2H_2O \text{ (l)} + O_2 \text{ (g)} \tag{R1}$$

$$Al \text{ (s)} + 3H_2O \text{ (l)} + OH^- \text{(aq)} \rightarrow Al(OH)^{4-} \text{ (aq)} + 3/2H_2 \text{ (g)} \tag{R2}$$

$$Si^0 \text{ (s)} \rightarrow Si^{4+} \text{ (aq)} + 4e^- \tag{R3 1}$$

$$4H_2O \text{ (l)} + 4e^- \rightarrow 2H_2 \text{ (g)} + 4OH^- \text{(aq)} \tag{R3 2}$$

$$4H_2O + Si^0 \rightarrow 2H_2 \text{ (g)} + Si(OH)_4 \text{ (l)} \tag{R3 3}$$

These foaming agents are very efficient in drastically increasing the total porosity, but they mainly form a closed pore network [101,133, 131]. This is a drawback for a number of potential applications of geopolymer foams. Moreover, despite the high viscosity of geopolymer slurries, foaming is a thermodynamically unstable process, as the gas bubbles in the wet foams are likely to undergo spontaneous drainage, continuous Ostwald ripening and coalescence for minimizing the overall Gibbs free energy of the slurry/air system. Due to the instability of wet foams, large pores (of hundreds of micron size) and a wide range of pore sizes are typically present in the final foam. In order to avoid this phenomenon, the most frequently used approach is to add stabilizing agents such as surfactants, particles or fibers to the suspension or to the liquid

medium [103,131,137].

Several authors [41,42,127,128] have proposed to combine H_2O_2 (as a blowing agent) and vegetable oils, in order to benefit from both the high porosity generated by O_2 production (Equation (1)) and from the capacity of the oils to build connection between pores. The soap molecules generated through the oil saponification are in fact anionic surfactants, able to stabilize both the gas bubbles produced by the decomposition of H_2O_2 and the oil droplets (Fig. 6, Black pathway). For instance, Bai et al. [41] were able to produce a geopolymer foam with a total volume porosity of 89%, of which 86% is open. However, these highly porous materials have low compressive strengths, of less than 1.0 MPa.

Further studies have been dedicated to improving the mechanical strength of geopolymer foams by varying several parameters, such as vegetable oil and H_2O_2 contents [41,127] or the type of oil [129], while keeping a highly interconnected ultra-macro-porosity. Moreover, several authors [132,129,126] proposed a heat treatment up to 1200 °C once the material has hardened. In general, such heat treatment significantly increases the mechanical compressive strength while maintaining a highly interconnected ultra-macro-porosity. Heating above 1000 °C leads to the formation of crystalline phases (ceramic glasses) while samples heated below 800 °C remain amorphous (i.e. geopolymer) [138]. Table 4 summarizes the porous and mechanical properties of ultra-porous geopolymers synthesized with various processing parameters. It is observed that total porosity is generally very close to open porosity; this means that the porosity of these foams is almost fully interconnected. According to Bai et al. [41], 10 wt% H_2O_2 and 20 wt% olive oil is a favorable combination regarding final porosity and strength. As for the heat treatment, an optimal temperature is about 800 °C in order to avoid extensive dimensional changes [138]. Finally, in order to increase mechanical strength, composite materials are also added with ceramic particles (silicon carbide) or polyurethane resins in the geopolymer, as a complement to H_2O_2 and vegetable oils [126,130].

3.3. Improvement of existing properties or promotion of emerging ones (organic polymers)

Geopolymers, as ceramics, display a typical brittle mechanical behavior with low ductility and low fracture toughness. These properties might represent significant limits for structural applications. A number of studies aimed at overcoming this drawback by producing geopolymer composites, improved by the addition of liquid organic polymer compounds, such as water-soluble polymers, polymer emulsions, or water-immiscible (epoxy or polysiloxane) resins. Table 5 summarizes a number of research works performed to develop such composites.

3.3.1. Water-soluble organic polymers

The incorporation of functional organic polymers containing carboxyl groups, amino groups or hydroxide radicals into geopolymers increases the compatibility between organic and inorganic phases, due to their interactions with the polar SiOH or Si–O- functions of the geopolymer N-A-S-H structure. For this reason, polyacrylic acid, sodium polyacrylate, polyethylene glycol (PEG), polyvinyl alcohol and polyacrylamide have been used as water-soluble polymer reactants into metakaolin-based concretes. High quantities of water-soluble polymers could probably be incorporated into fresh geopolymers. However, since the incorporation of only 1% of such polymer is already leading to a significant improvement (29%) of compressive strength, these polymers have not been tested at higher concentrations [144,145].

In [147], the addition of up to 6 wt% of polyethylene glycol (PEG) in metakaolin-based geopolymers shows a global increase in elastic strain, associated to a decrease in flexural and compressive strengths. Porosity increases as the percentage of PEG increases, due to cavities formed after removal of the polymer particles ranging from 1 to 10 μm and having a spherical shape. Others authors have studied the effect of PEG molecular weights. As observed in Ref. [146], the lowest compressive strengths are observed with the heaviest PEG (20 000 g mol^{-1}). Low molecular weights PEGs (400 g mol^{-1}), incorporated at up to 10 wt% contribute to an important increase in compressive strength, probably due to lower porosity [146].

Composites made of geopolymer and alginate spheres have been developed through ionotropic gelation [154,155]. Ionotropic gelation is based on the capability of polyelectrolytes to crosslink in the presence of multivalent counter ions, to form hydrogels [156]. Sodium alginate is dissolved in water and then directly added to the fresh geopolymer; the mix is added with $CaCl_2$ (Ca^{2+}) to initiate the ionotropic gelation [154]. Alginate is a natural anionic polysaccharide containing many carboxyl groups, which are effective for binding metallic ions. However, the mechanical properties of alginate alone are insufficient and its range of application is therefore limited. The combination of alginate with a strong geopolymer network leads to the development of composite materials capable of adsorbing heavy metals, and useable for wastewater treatment. In Ge et al. [154], composite spheres with a geopolymer/alginate mass ratio of 1:(0.10–0.18) were developed; the sample at 1:0.16 displayed the highest efficiency for Cu(II) removal from water, with a value of about 70%.

3.3.2. Polymers in emulsions

To avoid the incompatibility between aqueous and organic phases, some authors [152] have used a resin emulsion of butyl acrylate and acrylic acid, which can be easily diluted with metakaolin in the activating solution. Even if the highest compressive and flexural strengths are obtained for geopolymer composites reinforced with only 1 wt% of organic resin, this pathway allows an incorporation up to 5 wt% of organic materials. Good compatibility between the two phases is ensured by the polycondensation reaction between carboxylic acid functions and hydroxyl groups from the aluminosilicate source, which creates an organic/inorganic continuous gel. Moreover, the water

Table 4
Porosity and mechanical strength of various geopolymers for different processing parameters.

Sample label and Ref.	Oil type	Oil wt%	H_2O_2 wt%	Heat treatment	Total porosity[a] (vol%)	Open porosity[b] (vol%)	Compressive strength (MPa)
1 [41]	Olive	20	10	none	81.4	79.5	3.11
2 [41]	Olive	53	10	none	70.3	68.4	2.38
3 [41]	Olive	20	15	none	86.3	84.0	0.78
4 [41]	Sunflower	20	10	none	77.0	75.0	2.00
5 [131]	Sunflower	25	6	none	83.5	66.4	0.45
6 [129]	Sunflower	25	6	900 °C	81.0	73.0	0.60
7 [129]	Coconut	25	6	900 °C	82.0	79.0	0.70
8 [129]	Olive	25	6	900 °C	80.0	77.0	1.50
9 [129]	Olive	25	6	600 °C	86.0	80.0	0.50
10 [129]	Olive	25	6	1200 °C	76.0	73.0	1.90

[a] The total porosity (TP) was obtained based on the relation TP = 100 x (1 - ρ/ρ_0), where ρ is the bulk density obtained by the ratio of weight over the geometrical volume and ρ_0 is the true density of the pore-free solid material, measured with a helium pycnometer.
[b] The open porosity was estimated by the Archimedes principle using distillated water.

Table 5

Processing of reinforced hybrid organic/inorganic geopolymers using organic polymers; MK = Metakaolin, FA = Fly ash, BFS = Blast furnace slag, * = dry extract of 50%.

Alumino -silicate sources	Alkali ions	Organic polymer	Incorporated amount (%)	Incorporation process (Fig. 1)	Ref.
MK	NaOH	Epoxy resin	30	❶ Direct	[139]
FA	NaOH	Epoxy resin	20	❶ Direct	[140]
MK	NaOH	Epoxy resin	20	❷ Pre-emulsification	[38]
MK	NaOH	Epoxy resin	20	❷ Pre-emulsification	[39]
MK	NaOH	Epoxy resin	25	❷ Pre-emulsification	[141]
MK	NaOH	Epoxy resin	25	❷ Pre-emulsification	[142]
MK	NaOH	Polydimethylsiloxane	15	❷ Pre-emulsification	[143]
MK, K	NaOH	Sodium polyacrylate (PAANa),polyacrylamide (PAm), polyethylene glycol (PEG), polyvinyl alcohol (PVA)	1	❶ Direct	[144]
MK	NaOH	Sodium polyacrylate	1.2	❶ Direct	[145]
MK	NaOH	Polyethylene glycol	10	❶ Direct	[146]
MK	NaOH	Polyethylene glycol	6	❶ Direct	[147]
MK, BFS	NaOH	Waterborne bisphenol-A epoxy resin	25*	❶ Direct	[148]
MK, FA	NaOH	Waterborne bisphenol-A epoxy resin	4*	❶ Direct	[149]
FA, BFS	NaOH	Styrene-butadiene emulsion	10*	❶ Direct	[150]
MK, BFS	NaOH	Acrylic acid/butyl acrylate emulsion and ethylene-vinyl acetate copolymer (powder)	7.5*	❶ Direct	[151]
MK, BFS	NaOH	Acrylic acid/butyl acrylate emulsion and ethylene-vinyl acetate copolymer (powder)	2.5*	❶ Direct	[152]
BFS	NaOH	Acrylic emulsion	2.5*	❶ Direct	[153]

molecules generated by these reactions are stabilized by hydrogen bonding with acrylate ester groups, and their evaporation is inhibited in favor of the geopolymerization reaction [151].

Geopolymer samples have been synthesized with an incorporation rate from 0 to 5 wt% of polyacrylic resin emulsion [153]. The results show that an increase in polyacrylic resin content up to 1 wt% has a positive impact on compressive strength (it is increased by 36,3%) and flexural toughness (increased by 104.6%); beyond this concentration the mechanical properties decline. Further studies confirmed an increase by 50% in the flexural toughness coefficient of geopolymer with the incorporation of only 0.8 wt% of polyacrylate [145].

Finally, the dilution of Styrene-butadiene latex (as an emulsion) has been carried out into mixed fly ash/slag based geopolymers. This increases the flexural strength of geopolymer mortars thanks to the enhanced bonding interactions in the geopolymer cement [150].

3.3.3. Epoxy resins

The first blending tests between water-immiscible organic polymers and geopolymers have been carried out with an epoxy resin from diglycidyl ether of bisphenol-A (DGEBA) and diethyltoluene-diamine as a curing agent [157,158]. A 20 wt% aqueous suspension of kaolin mixed with potassium silicate and potassium hydroxide was simply added to a mixture of DGEBA and diamine. After simultaneous curing of both organic and inorganic parts, epoxy matrices with homogeneously distributed geopolymer parts were obtained. A composite epoxy material containing 20 wt% of dispersed geopolymer has shown improved thermal stability compared to epoxy alone. These first composite matrices have highlighted the possibility of combining organic epoxy resins and inorganic geopolymer cements.

Following these research, composite materials have been synthesized by dispersing fresh epoxy resins within geopolymers. By playing with the chemical composition of the components in the mixture, several types of materials have been developed. They present varied properties and their applications often depend on the ratio between organic and inorganic phases.

The first attempts to prepare composite materials with geopolymer as the continuous phase consisted in reversing the process developed by Hussain [157,158]. In other words, the organic epoxy phase (epoxypolyol and polyamine) is directly introduced into the geopolymer suspension but phase segregation is observed [142]. The issue was solved by modifying the process, so as to mix the epoxypolyol and the polyamine prior to their addition into the geopolymer suspension, to

initiate the polymerization of the epoxy resin. With that method, the partially cross-linked epoxy resin is efficiently added to the geopolymeric suspension without phase segregation. According to the authors, this is due to an improved compatibility between the organic and the aqueous inorganic phases, leading to a homogeneous and stable dispersion of organic micro domains into the inorganic continuous phase. The large number of hydroxyl tails formed during the epoxy ring opening reaction makes the organic phase "temporarily hydrophilic", and hence increasing the compatibility with the aqueous inorganic phase [141]. If mixing is delayed, the compatibility between the phases reduces because the dispersed phase recovers its hydrophobic nature over time. By correctly monitoring the process, 25 wt% of epoxy resin can be mixed with the geopolymer suspension without needing external additives. Epoxy resins are easily observed by Scanning Electron Microscopy (SEM) in hardened geopolymers, in order to analyze their dispersion state. They are generally incorporated in well-defined
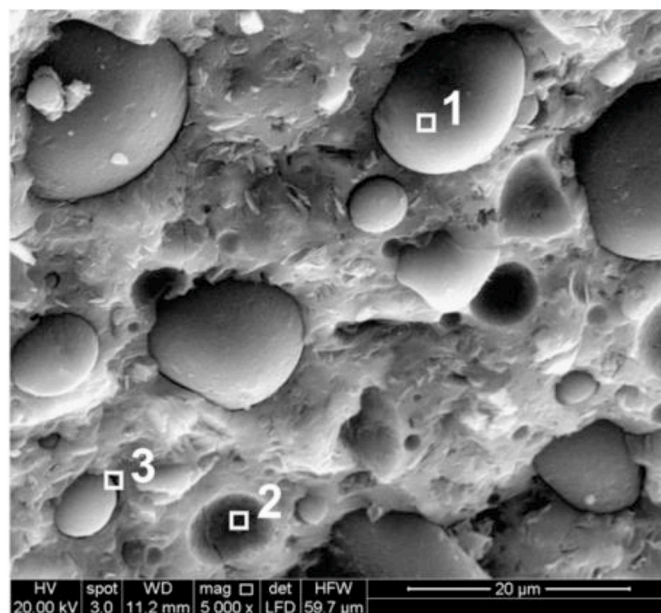

Fig. 7. SEM micrographs of a composite geopolymer material containing 20 wt% of epoxy resin cured at room temperature for 24 h [45].

microspheres with diameters in the range of 1–20 μm (Fig. 7 [45]). In order to evidence the organic-inorganic compatibility, Energy Dispersive Spectrometry (EDS) measurements have been performed at the organic-inorganic interface (Fig. 7, 3), showing the significant presence of both the elements of the inorganic phase (Na, Si, Al) and the organic phase (C,O) [45]. In contrast, EDS measurements on areas representing pure inorganic or organic phases (Fig. 7, 1 and 2 respectively) only present the respective elements of the phases. Such composite materials have been developed for different systems, namely the combination of N,N-diglycidyl-4-glycidyl-oxyaniline, bis-(2-aminoethyl)amine and 2, 4-diamino-toluene [45] and several two-components commercial mixtures named Epojet®epoxy [142], Epojet® and EpojetLV® [46,141]. Both two-components Epojet® and EpojetLV® resins contain an aromatic amine that contributes to improve the thermal stability of the geopolymer [141]. Whatever the epoxy resin used, the highest amount that could be incorporated into the geopolymer without phase separation is about 25 wt% [141]. The main advantage of adding epoxy resins in geopolymer materials is the significant enhancement of their compressive strength and toughness compared to pure geopolymers.

Recently, Roviello et al. [143] have proposed a new class of epoxy resin, using both melamine as curing agent and aminopropyltrimethoxysilane as silicon source, to be introduced into geopolymers. The advantage of using melamine is the assurance of high thermal stability and fire resistance due to the presence of an azacyclic ring. Aminopropyltrimethoxysilane, which can be fixed to the organic resin via covalent bonds, ensure a high compatibility with the inorganic silicate matrix thanks to the silane groups. Such composite materials based on geopolymers are able to contain up to 25 wt% of epoxy melamine resin. They are particularly attractive for designing thermo-resistant and thermo-insulating wall panels.

Waterborne bisphenol-A epoxy resins have been used to formulate geopolymers by mold pressing [149]. The authors obtain an optimal compressive strength of 116 MPa at a molding pressure of 200 MPa. With an increasing epoxy resin content from 0 to 8 wt%, porosity gradually increases while the pore size distribution initially reduces and then increases. Waterborne bisphenol-A epoxy resin and waterborne polyamine epoxy curing agent have been used together to formulate geopolymers for in deep water oil well cementation applications [148]. The mixing of epoxy resin and curing agent with geopolymer needs to be performed after the initiation of both polymerization reactions. During the cross-linking process of the resin, the epoxy opening ring reaction initially makes the resin phase hydrophilic and compatible with the aqueous geopolymer suspension. The amount of organic phase could be as high as 50% while presenting an excellent dispersion quality up to a micrometric scale.

Epoxy resin has also been used without amino-organic curing agent. Direct mixing of 30 wt% of epoxy resin in a geopolymer solution was carried out in Ref. [139], in order to reduce drying shrinkage and easy cracking of green anti-corrosion coating applications. The compressive strength decreased at earlier age with an increasing amount of epoxy resin due to polycondensation slowdown, but after 28 days, the compressive strength of samples containing epoxy resin was almost as high as the resin-free reference. In Ref. [140], up to 20 wt% of epoxy resin have been added into fly ash based geopolymer suspensions in order to reinforce thermal and microstructural properties. Composites containing 5 to 10 wt% of epoxy resins are suitable as geothermal pipes because of enhanced fire resistance. This is especially the case of the formulation containing 5 wt% epoxy, which also has the highest tensile strength (3.33 MPa compared to 2.56 MPa for resin-free GP).

3.3.4. Polysiloxane resins

In order to obtain a closer interaction between organic and inorganic components within a geopolymer-based material, some authors exploited the chemical similarity between polysiloxanes and polysialates [142]. Polysiloxanes are inorganic polymers based on Si–O chains, containing alkyl or aryl groups bonded to Si atoms, therefore possessing a backbone very similar to those characterizing geopolymers (polysialates).

In Roviello et al. [142], composite polysiloxane-geopolymer samples have been prepared by incorporating 15 wt% of a commercial oligomeric dimethylsiloxane resin into a freshly prepared geopolymeric suspension under mechanical stirring. Prior to the addition into the geopolymeric suspension, a Sn (IV) catalyst is added to initiate the organic polymerization. With this method, by mixing both organic and aqueous phases, the polycondensation reactions of geopolymer and dimethylsiloxane are already initiated, improving the compatibility between both phases. After the full curing of the two, the combination of SEM and EDS shows that the siloxane phase is well dispersed in the GP down to a nanometric scale (Fig. 8 [142]). This indicates a very close interaction between the phases, characterized by the scattered mapping of carbon. An interpenetrated network between geopolymeric and siloxane components is probably formed, in which chemical bonds between aluminosilicate and siloxane species could be present. The enhanced mechanical properties, along with the high fire resistance of the resulting composite materials, suggest their usefulness for building applications and for the production of heat-resistant protective coatings and adhesives.

4. Summary

Driven by the need for low-cost, eco-friendly engineering parts, tremendous efforts have been recently devoted to develop varied and novel processing technologies for the design of geopolymers. More specifically, the incorporation of OL into geopolymers to create composite organic/inorganic materials has gained significant interest in the past few years, with a range of possible applications depending on the type of organic liquid incorporated:

- Mineral oils are efficiently immobilized in geopolymers to treat various OL waste streams or to produce materials with improved thermal properties (PCM). The durability of these systems over a long period is still under investigation, because they are quite recent in the field when compared to traditional Portland cements, for which a number of durability studies has been reported.
- Vegetable oils, mainly made up of triglycerides, are used as such or in combination with blowing agents to produce geopolymer foams with better understanding and control of the pore network design (pore size distribution and connectivity/percolation).
- The possibility of blending organic polymers and inorganic geopolymer materials is used for the development of composite materials with improved or emerging properties.

Unfortunately, studies dealing with the direct comparison between geopolymers and Portland cements regarding the incorporation of organic liquids are still scarce, so that it may be difficult to fully testify of the technical benefits of using geopolymers instead of traditional Portland cements.

This review also aimed at highlighting that the method of OL incorporation into geopolymers needs to be carefully chosen depending on the end application, which determines the required properties of the resulting materials. In addition, the industrial feasibility of these processes has to be taken into account. In particular, the cost of additives (e. g. surfactants, adsorbents) or the extra handling of toxic OL may be practical issues. Following research on S/S of OL in inorganic geopolymers, the favorable compatibility between inorganic and organic phases can be used to broaden the application range of these composite materials. Among them, this review presents both the production of highly porous geopolymer foams and the development of polymer-reinforced materials, which have already been widely investigated. In the future, other types of OL could be stabilized in geopolymers in order to develop geopolymer composite materials with emerging properties, such as geopolymer composites with high corrosion resistance [139] or
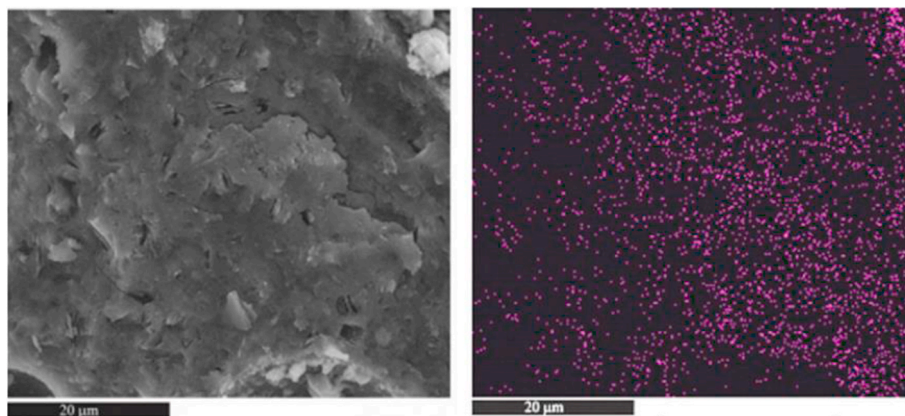
Fig. 8. SEM micrograph at 5000 magnification (left) and EDS mapping at the same magnification of carbon (right) of a geopolymer composite material containing 10 wt% of dimethylsiloxane [142].

biomimetic properties [159], besides possessing a reasonable carbon footprint.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

References

[1] A. Naqi, J. Jang, Recent progress in green cement technology utilizing low-carbon emission fuels and raw materials: a review, Sustainability-Basel 11 (2) (2019) 537, https://doi.org/10.3390/su11020537.

[2] R.M. Andrew, Global CO2 emissions from cement production, 1928–2018, Earth Syst. Sci. Data 11 (4) (2019) 1675–1710, https://doi.org/10.5194/essd-11-1675-2019.

[3] J. Davidovits, Geopolymers of the first generation: SILIFACE -process, in: Proceedings of the Geopolymer '88 First International Conference on Soft Mineralurgy, vol. 1, 1988, pp. 49–67.

[4] J. Davidovits, Geopolymer Chemistry and Applications, fifth ed., GEOPOLYMER Institute, 2020, ISBN 978-2-9544531-1-8.

[5] J.L. Provis, J.S.J. van Deventer, Geopolymers: Structure, Processing, Properties and Industrial Applications, 2009, ISBN 978-1-4398-0970-9.

[6] B. Tempest, O. Sanusi, J. Gergely, V. Ogunro, D. Weggel, 'Compressive Strength and Embodied Energy Optimization of Fly Ash Based Geopolymer Concrete', Presented at the World of Coal Ash, WOCA, 2009 ([Online access]).

[7] U. Ernst, von Weizsäcker, Factor five: transforming the global economy through 80% improvements in resource productivity, Earthscan/The Natural Edge Project, 2009.

[8] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. van Deventer, Geopolymer technology: the current state of the art, J. Mater. Sci. 42 (9) (May 2007) 2917–2933, https://doi.org/10.1007/s10853-006-0637-z.

[9] D. Khale, R. Chaudhary, Mechanism of geopolymerization and factors influencing its development: a review, J. Mater. Sci. 42 (3) (Feb. 2007) 729–746, https://doi.org/10.1007/s10853-006-0401-4.

[10] J.L. Provis, G.C. Lukey, J.S.J. van Deventer, Do geopolymers actually contain nanocrystalline zeolites? A Reexamination of Existing Results', Chem. Mater. 17 (12) (Jun. 2005) 3075–3085, https://doi.org/10.1021/cm050230i.

[11] K. Komnitsas, D. Zaharaki, Geopolymerisation: a review and prospects for the minerals industry, Miner. Eng. 20 (14) (Nov. 2007) 1261–1277, https://doi.org/10.1016/j.mineng.2007.07.011.

[12] J.L. Provis, S.A. Bernal, Geopolymers and related alkali-activated materials, Annu. Rev. Mater. Res. 44 (1) (2014) 299–327, https://doi.org/10.1146/annurev-matsci-070813-113515.

[13] P.N. Lemougna, K. Wang, Q. Tang, U.C. Melo, X. Cui, Recent developments on inorganic polymers synthesis and applications, Ceram. Int. 42 (14) (Nov. 2016) 15142–15159, https://doi.org/10.1016/j.ceramint.2016.07.027.

[14] Y.-M. Liew, C.-Y. Heah, A.B. Mohd Mustafa, H. Kamarudin, Structure and properties of clay-based geopolymer cements: a review, Prog. Mater. Sci. 83 (Oct. 2016) 595–629, https://doi.org/10.1016/j.pmatsci.2016.08.002.

[15] B. Singh, G. Ishwarya, M. Gupta, S.K. Bhattacharyya, Geopolymer concrete: a review of some recent developments, Constr. Build. Mater. 85 (Jun. 2015) 78–90, https://doi.org/10.1016/j.conbuildmat.2015.03.036.

[16] Y.H.M. Amran, N. Farzadnia, A.A. Abang Ali, Properties and applications of foamed concrete; a review, Constr. Build. Mater. 101 (Dec. 2015) 990–1005, https://doi.org/10.1016/j.conbuildmat.2015.10.112.

[17] C. Bai, P. Colombo, Processing, properties and applications of highly porous geopolymers: a review, Ceram. Int. 44 (14) (Oct. 2018) 16103–16118, https://doi.org/10.1016/j.ceramint.2018.05.219.

[18] Z. Zhang, J.L. Provis, A. Reid, H. Wang, Geopolymer foam concrete: an emerging material for sustainable construction, Constr. Build. Mater. 56 (Apr. 2014) 113–127, https://doi.org/10.1016/j.conbuildmat.2014.01.081.

[19] A.K. Karamalidis, E.A. Voudrias, Cement-based stabilization/solidification of oil refinery sludge: leaching behavior of alkanes and PAHs, J. Hazard Mater. 148 (1–2) (Sep. 2007) 122–135, https://doi.org/10.1016/j.jhazmat.2007.02.032.

[20] S. Trussell, R.D. Spence, A review of solidification/stabilization interferences, Waste Manag. 14 (6) (1994) 507–519.

[21] S. Paria, P.K. Yuet, 'Solidification–stabilization of organic and inorganic contaminants using portland cement: a literature review', Environ. Rev. 14 (4) (Dec. 2006) 217–255, https://doi.org/10.1139/a06-004.

[22] N. Nestle, C. Zimmermann, M. Dakkouri, R. Niessner, Action and distribution of organic solvent contaminations in hydrating cement: time-resolved insights into solidification of organic waste, Environ. Sci. Technol. 35 (24) (Dec. 2001) 4953–4956, https://doi.org/10.1021/es015528y.

[23] S.J.T. Pollard, D.M. Montgomery, C.J. Sollars, R. Perry, 'Organic compounds in the cement-based stabilisation/solidification of hazardous mixed wastes—mechanistic and process considerations', J. Hazard Mater. 28 (3) (Nov. 1991) 313–327, https://doi.org/10.1016/0304-3894(91)87082-D.

[24] D.M. Montgomery, C.J. Sollars, R. Perry, Optimization of cement-based S/S of organic-containing industrial wastes using organophilic clays.pdf, Waste Manag. 9 (1991) 21–34.

[25] V. Cantarel, D. Lambertin, A. Poulesquen, F. Leroux, G. Renaudin, F. Frizon, Geopolymer assembly by emulsion templating: emulsion stability and hardening mechanisms, Ceram. Int. 44 (9) (Jun. 2018) 10558–10568, https://doi.org/10.1016/j.ceramint.2018.03.079.

[26] C. Shi, A. Fernández-Jiménez, Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements, J. Hazard Mater. 137 (3) (Oct. 2006) 1656–1663, https://doi.org/10.1016/j.jhazmat.2006.05.008.

[27] I.G. Richardson, The calcium silicate hydrates, Cem. Concr. Res. 38 (2) (Feb. 2008) 137–158, https://doi.org/10.1016/j.cemconres.2007.11.005.

[28] R.J. Myers, S.A. Bernal, R. San Nicolas, J.L. Provis, 'Generalized structural description of calcium–sodium aluminosilicate hydrate gels: the cross-linked substituted tobermorite model', Langmuir 29 (17) (Apr. 2013) 5294–5306, https://doi.org/10.1021/la4000473.

[29] J.L. Provis, Activating solution chemistry for geopolymers, in: Geopolymers, Structures, Processing, Properties and Industrial Applications, Elsevier, 2009, ISBN 978-1-84569-449-4, pp. 50–71.

[30] C. Shi, B. Qu, J.L. Provis, Recent progress in low-carbon binders, Cem. Concr. Res. 122 (2019) 227–250, https://doi.org/10.1016/j.cemconres.2019.05.009.

[31] C. Li, H. Sun, L. Li, A review: the comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements, Cem. Concr. Res. 40 (9) (Sep. 2010) 1341–1349, https://doi.org/10.1016/j.cemconres.2010.03.020.

[32] F. Puertas, M. Palacios, H. Manzano, J.S. Dolado, A. Rico, J. Rodríguez, A model for the C-A-S-H gel formed in alkali-activated slag cements, J. Eur. Ceram. Soc. 31

(12) (Oct. 2011) 2043–2056, https://doi.org/10.1016/j.jeurceramsoc.2011.04.036.

[33] V.F.F. Barbosa, K.J.D. MacKenzie, C. Thaumaturgo, Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers, Int. J. Inorg. Mater. 2 (4) (Sep. 2000) 309–317, https://doi.org/10.1016/S1466-6049(00)00041-6.

[34] W.O. Greenhalgh, The Immobilization of organic liquid wastes, in: Presented at the Waste Management '86, 1986 ([Online access]).

[35] C. Costa, Emulsion formation and stabilization by biomolecules: the leading role of cellulose, Polymers 11 (10) (2019) 1570, https://doi.org/10.3390/polym11101570, al.

[36] V. Cantarel, F. Nouaille, A. Rooses, D. Lambertin, A. Poulesquen, F. Frizon, Solidification/stabilisation of liquid oil waste in metakaolin-based geopolymer, J. Nucl. Mater. 464 (Sep. 2015) 16–19, https://doi.org/10.1016/j.jnucmat.2015.04.036.

[37] X. Liu, S. Nair, K. Aughenbaugh, E. van Oort, Mud-to-cement conversion of non-aqueous drilling fluids using alkali-activated fly ash, J. Pet. Sci. Eng. 182 (Nov. 2019) 106242, https://doi.org/10.1016/j.petrol.2019.106242.

[38] C. Mabille, Fragmentation of Emulsions in a Simple Shear Stress Flow, PhD, University of Bordeaux, France, 2013.

[39] G. G. Stokes, 'On the Effect of the Internal Friction of Fluids on the Motion of Pendulums', Cambridge Philosophical Society, vol. vol. 9, 1850.

[40] M. Masrulita, P. Burhan, Y. Trihadiningrum, Stabilization/solidification of waste containing heavy metals and hydrocarbons using OPC and land tras cement, J. Ecol. Eng. 19 (6) (Nov. 2018) 88–96, https://doi.org/10.12911/22998993/92926.

[41] C. Bai, G. Franchin, H. Elsayed, A. Conte, P. Colombo, High strength metakaolin-based geopolymer foams with variable macroporous structure, J. Eur. Ceram. Soc. 36 (16) (Dec. 2016) 4243–4249, https://doi.org/10.1016/j.jeurceramsoc.2016.06.045.

[42] M.S. Cilla, M.R. Morelli, P. Colombo, Open cell geopolymer foams by a novel saponification/peroxide/gelcasting combined route, J. Eur. Ceram. Soc. 34 (12) (Oct. 2014) 3133–3137, https://doi.org/10.1016/j.jeurceramsoc.2014.04.001.

[43] S.K. Kaliappan, A.A. Siyal, Z. Man, M. Lay, R. Shamsuddin, Effect of pore forming agents on geopolymer porosity and mechanical properties, in: Presented at the 3rd International Conference on Applied Science and Technology, Penang, Malaysia, 2018, https://doi.org/10.1063/1.5055468.

[44] C.A. Davy, G. Hauss, B. Planel, D. Lambertin, 3D structure of oil droplets in hardened geopolymer emulsions, J. Am. Ceram. Soc., p. jace (Oct. 2018) 16142, https://doi.org/10.1111/jace.16142.

[45] C. Ferone, G. Roviello, F. Colangelo, R. Cioffi, O. Tarallo, Novel hybrid organic-geopolymer materials, Appl. Clay Sci. 73 (Mar. 2013) 42–50, https://doi.org/10.1016/j.clay.2012.11.001.

[46] F. Colangelo, G. Roviello, L. Ricciotti, C. Ferone, R. Cioffi, Preparation and characterization of new geopolymer-epoxy resin hybrid mortars, Materials 6 (7) (Jul. 2013) 2989–3006, https://doi.org/10.3390/ma6072989.

[47] H.P. Grace, Dispersion phenomena in high viscosity immiscible fluid systems and applications of static mixers as dispersion devices in such systems, Chem. Eng. Commun. 14 (3–6) (Mar. 1982) 225–277, https://doi.org/10.1080/00986448208911047.

[48] International Atomic Energy Agency (IAEA), Treatment and Conditioning of Radioactive Organic Liquids, 1992. Accessed: May 05, 2020. [Online]. Available: https://www-pub.iaea.org/MTCD/publications/pdf/te_656_web.pdf.

[49] W. Zhang, J. Li, J. Wang, Solidification of spent radioactive organic solvent by sulfoaluminate and Portland cements, J. Nucl. Sci. Technol. 52 (11) (Nov. 2015) 1362–1368, https://doi.org/10.1080/00223131.2015.1076747.

[50] T. Dong, S. Xie, J. Wang, G. Zhao, Q. Song, Solidification and stabilization of spent TBP/OK organic liquids in a phosphate acid-based geopolymer, Sci. Technol. Nucl. Install. 2020 (Jan. 2020) 1–7, https://doi.org/10.1155/2020/8094205.

[51] D. Lambertin, A. Rooses, F. Frizon, Process for Preparing a Composite Material from an Organic Liquid and Resulting Material, 2014 patent n°WO2014/044776 A1.

[52] B.E. Glad, W.M. Kriven, Highly porous geopolymers through templating and surface interactions, J. Am. Ceram. Soc. 98 (7) (Jul. 2015) 2052–2059, https://doi.org/10.1111/jace.13584.

[53] M. Smitha, N. Sathi Sasidharan, P.K. Wattal, Immobilisation of Alpha Contamined Lubricating Oils in Cement Matrix, Technical report, Atomic research center, Mumbai, India, 2000.

[54] C. Pierlot, J.F. Ontiveros, M. Royer, M. Catté, J.-L. Salager, Emulsification of viscous alkyd resin by catastrophic phase inversion with nonionic surfactant, Colloids Surf. Physicochem. Eng. Asp. 536 (Jan. 2018) 113–124, https://doi.org/10.1016/j.colsurfa.2017.07.030.

[55] P. Skalle, J. Sveen, Emulsion cement, Technical report, in: Presented at the Offshore Europe Conference, 1991.

[56] G.M. Ayininuola, Influence of diesel oil and bitumen on compressive strength of concrete, J. Civ. Eng. 37 (2009) 65–71.

[57] D.M. Montgomery, C.J. Sollars, R. Perry, S.E. Tariingt, P. Barnes, E. Henderson, Treatment of organic-contamined industrial wastes using cement-based S/S - I. Microstructural analysis of cement-organic interactions, Waste Manag. Res. 9 (1991) 103–111.

[58] S.A. Wilson, N.J. Langdon, P.J. Walden, The effects of hydrocarbon contamination on concrete strength, Geotech. Eng. (3) (2001) 189–193.

[59] S. Chandra, P. Flodin, Interactions of polymers and organic admixtures on portland cement hydration, Cem. Concr. Res. 17 (6) (1987) 875–890, https://doi.org/10.1016/0008-8846(87)90076-7.

[60] M.H. Almabrok, R. McLaughlan, K. Vessalas, Investigation of oil solidification using direct immobilization method, in: Presented at the Environmental Research Event, Sydney, Australia, 2011 ([Online access]).

[61] A.B. Sazonov, A.V. Aleshina, E.P. Magomedbekov, Immobilization of tritium-containing oil wastes by their incorporation in a cement matrix, Radiochemistry 51 (4) (2009) 412–414, https://doi.org/10.1134/S106636220904016X.

[62] M.R. El-Naggar, E.A. El-Sherief, H.S. Mekhemar, Performance of geopolymers for direct immobilization of solvent extraction liquids: metakaolin/LIX-84 formulations, J. Hazard Mater. 360 (Oct. 2018) 670–680, https://doi.org/10.1016/j.jhazmat.2018.08.057.

[63] V. Cuccia, C.B. Freire, A.C.Q. Ladeira, Radwaste oil immobilization in geopolymer after non-destructive treatment, Prog. Nucl. Energy 122 (Apr. 2020) 103246, https://doi.org/10.1016/j.pnucene.2020.103246.

[64] Y Tech Tech, Fiche technique NOCHAR [Online]. Available at: https://www.tech-y-tech.fr/nochar/.

[65] P. Duxson, J.L. Provis, G.C. Lukey, S.W. Mallicoat, W.M. Kriven, J.S.J. van Deventer, Understanding the relationship between geopolymer composition, microstructure and mechanical properties, Colloids Surf. Physicochem. Eng. Asp. 269 (1–3) (2005) 47–58, https://doi.org/10.1016/j.colsurfa.2005.06.060.

[66] D.E. Clark, P. Colombo, R.M. Neilson Jr., Solidification of Oils and Organic Liquids, BNL-51612, Nuclear Waste Management, 1982, https://doi.org/10.2172/6462993.

[67] J.R. Gasca-Tirado, Porous geopolymer as a possible template for a phase change material, Mater. Chem. Phys. 236 (2019) 121785, https://doi.org/10.1016/j.matchemphys.2019.121785.

[68] J.R. Conner, S.L. Hoeffner, A critical review of stabilisation/solidification technology, Crit Rev Env. Sci Technol 28 (1998) 397–462, https://doi.org/10.1080/10643389891254250.

[69] C. Zhuying, W. Huang, G. Zhang, Y. Zhang, J. Zhang, Study on the formulation of cement solidification of 30% TBP- OK organic liquid waste, At. Energy Sci. Technol. 2 (4) (1991) 74–78.

[70] Z.Z. Hua Rong Liu Shu-juan, Luo Ming-biao, Solidification of spent TBP by alkali-activated slag, At. Energy Sci. Technol. 47 (2013) 11, https://doi.org/10.7538/yzk.2013.47.11.1956.

[71] W.O. Ajagbe, O.S. Omokehinde, G.A. Alade, O.A. Agbede, Effect of crude oil impacted sand on compressive strength of concrete, Constr. Build. Mater. 26 (1) (2012) 9–12, https://doi.org/10.1016/j.conbuildmat.2011.06.028.

[72] R.B. Abdul-Ahad, A.A. Mohammed, Compressive and tensile strength of concrete loaded and soaked in crude oil, Eng. J. Univ. Qatar 13 (2000).

[73] S.P. Ejeh, O.A.U. Uche, Effect of crude oil spill on compressive strength of concrete materials, J. Appl. Sci. Res. 5 (10) (2009) 1756–1761.

[74] M.H. Almabrok, R.G. McLaughlan, K. Vessalas, P. Thomas, Effect of oil contaminated aggregates on cement hydration, Am. J. Eng. Res. 8 (5) (2019) 81–89.

[75] Characterisation of cement mortar containing oil-contaminated aggregates, in: C.M.H. Almabrok, R.G. McLaughlan, K. Vessalas (Eds.), From Materials to Structures: Advancement through Innovation, 2013, ISBN 978-0-415-63318-5, pp. 1091–1096.

[76] K. Aughenbaugh, S.D. Nair, K. Cowan, E. van Oort, Contamination of Deepwater Well Cementations by Synthetic-Based Drilling Fluids, Galveston, Texas, USA, 2014, https://doi.org/10.2118/170325-MS.

[77] E. Koos, J. Johannsmeier, L. Schwebler, N. Willenbacher, Tuning suspension rheology using capillary forces, Soft Matter 8 (24) (2012) 6620, https://doi.org/10.1039/c2sm25681a.

[78] F. Bossler, E. Koos, Structure of particle networks in capillary suspensions with wetting and nonwetting fluids, Langmuir 32 (6) (Feb. 2016) 1489–1501, https://doi.org/10.1021/acs.langmuir.5b04246.

[79] F. Bossler, L. Weyrauch, R. Schmidt, E. Koos, Influence of mixing conditions on the rheological properties and structure of capillary suspensions, Colloids Surf. Physicochem. Eng. Asp. 518 (Apr. 2017) 85–97, https://doi.org/10.1016/j.colsurfa.2017.01.026.

[80] M. Ahdaya, A. Imqam, Investigating geopolymer cement performance in presence of water based drilling fluid, J. Pet. Sci. Eng. 176 (May 2019) 934–942, https://doi.org/10.1016/j.petrol.2019.02.010.

[81] P. Sukontasukkul, N. Nontiyutsirikul, S. Songpiriyakij, K. Sakai, P. Chindaprasirt, Use of phase change material to improve thermal properties of lightweight geopolymer panel, Mater. Struct. 49 (11) (Nov. 2016) 4637–4645, https://doi.org/10.1617/s11527-016-0812-x.

[82] A. Barneoud-Chapelier, J. Causse, A. Poulesquen, Synthesis of geopolymer emulsions, Mater. Lett. 276 (Oct. 2020) 128188, https://doi.org/10.1016/j.matlet.2020.128188.

[83] P. Panya, E.J. Wanless, O. Arquero, G.V. Franks, The effect of ionic surfactant adsorption on the rheology of ceramic glaze suspensions, J. Am. Ceram. Soc. 88 (3) (Mar. 2005) 540–546, https://doi.org/10.1111/j.1551-2916.2005.00121.x.

[84] Y.K. Leong, D.V. Boger, P.J. Scales, T.W. Healy, Interparticle forces arising from adsorbed surfactants in colloidal suspensions: an additional attractive force, J. Colloid Interface Sci. 181 (2) (Aug. 1996) 605–612, https://doi.org/10.1006/jcis.1996.0418.

[85] M. Sakamoto, Y. Kanda, M. Miyahara, K. Higashitani, Origin of long-range attractive force between surfaces hydrophobized by surfactant adsorption, Langmuir 18 (15) (Jul. 2002) 5713–5719, https://doi.org/10.1021/la025701j.

[86] A. Suzzoni, L. Barre, E. Kohler, P. Levitz, L.J. Michot, J. M'Hamdi, Interactions between kaolinite clay and AOT, Colloids Surf. Physicochem. Eng. Asp. 556 (Nov. 2018) 309–315, https://doi.org/10.1016/j.colsurfa.2018.07.049.

[87] Y. Deng, J.B. Dixon, G.N. White, Bonding mechanisms and conformation of poly (ethylene oxide)-based surfactants in interlayer of smectite, Colloid Polym. Sci. 284 (4) (Jan. 2006) 347–356, https://doi.org/10.1007/s00396-005-1388-0.

[88] R.A. Kennedy, M.L. Kennedy, Effect of selected non-ionic surfactants on the flow behavior of aqueous veegum suspensions, AAPS PharmSciTech 8 (1) (Mar. 2007) E171–E176, https://doi.org/10.1208/pt0801025.

[89] I. Natali Sora, R. Pelosato, D. Botta, G. Dotelli, Chemistry and microstructure of cement pastes admixed with organic liquids, J. Eur. Ceram. Soc. 22 (9–10) (2002) 1463–1473, https://doi.org/10.1016/S0955-2219(01)00473-3.

[90] D.S. Perera, Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials, J. Mater. Sci. 43 (19) (Oct. 2008) 6562–6566, https://doi.org/10.1007/s10853-008-2913-6.

[91] M. Sellami, M. Barre, M. Toumi, Synthesis, thermal properties and electrical conductivity of phosphoric acid-based geopolymer with metakaolin, Appl. Clay Sci. 180 (Nov. 2019) 105192, https://doi.org/10.1016/j.clay.2019.105192.

[92] H.K. Tchakouté, C.H. Rüscher, E. Kamseu, F. Andreola, C. Leonelli, Influence of the molar concentration of phosphoric acid solution on the properties of metakaolin-phosphate-based geopolymer cements, Appl. Clay Sci. 147 (Oct. 2017) 184–194, https://doi.org/10.1016/j.clay.2017.07.036.

[93] H.K. Tchakouté, C.H. Rüscher, Mechanical and microstructural properties of metakaolin-based geopolymer cements from sodium waterglass and phosphoric acid solution as hardeners: a comparative study, Appl. Clay Sci. 140 (May 2017) 81–87, https://doi.org/10.1016/j.clay.2017.02.002.

[94] S. Sharma, D. Medpelli, S. Chen, D.-K. Seo, Calcium-modified hierarchically porous aluminosilicate geopolymer as a highly efficient regenerable catalyst for biodiesel production, RSC Adv. 5 (80) (2015) 65454–65461, https://doi.org/10.1039/C5RA01823D.

[95] A. Marani, M.L. Nehdi, Integrating phase change materials in construction materials: critical review, Constr. Build. Mater. 217 (Aug. 2019) 36–49, https://doi.org/10.1016/j.conbuildmat.2019.05.064.

[96] D. Frattini, G. Roviello, L. Ricciotti, C. Ferone, F. Colangelo, O. Tarallo, Geopolymer-based composite materials containing pcm for thermal energy storage, Cem. Concr. Compos. 59 (May 2015) 89–99, https://doi.org/10.1016/j.cemconcomp.2015.03.007.

[97] R. Shadnia, L. Zhang, P. Li, Experimental study of geopolymer mortar with incorporated PCM, Constr. Build. Mater. 84 (Jun. 2015) 95–102, https://doi.org/10.1016/j.conbuildmat.2015.03.066.

[98] W.D.A. Rickard, A. van Riessen, Performance of solid and cellular structured fly ash geopolymers exposed to a simulated fire, Cem. Concr. Compos. 48 (Apr. 2014) 75–82, https://doi.org/10.1016/j.cemconcomp.2013.09.002.

[99] T. Bakharev, Resistance of geopolymer materials to acid attack, Cem. Concr. Res. 35 (4) (Apr. 2005) 658–670, https://doi.org/10.1016/j.cemconres.2004.06.005.

[100] P. Palmero, A. Formia, P. Antonaci, S. Brini, J.-M. Tulliani, Geopolymer technology for application-oriented dense and lightened materials, Elaboration and characterization', Ceram. Int. 41 (10) (Dec. 2015) 12967–12979, https://doi.org/10.1016/j.ceramint.2015.06.140.

[101] R.M. Novais, L.H. Buruberri, G. Ascensão, M.P. Seabra, J.A. Labrincha, Porous biomass fly ash-based geopolymers with tailored thermal conductivity, J. Clean. Prod. 119 (Apr. 2016) 99–107, https://doi.org/10.1016/j.jclepro.2016.01.083.

[102] Y. Ge, Y. Yuan, K. Wang, Y. He, X. Cui, Preparation of geopolymer-based inorganic membrane for removing Ni2+ from wastewater, J. Hazard Mater. 299 (Dec. 2015) 711–718, https://doi.org/10.1016/j.jhazmat.2015.08.006.

[103] C. Bai, High-porosity geopolymer foams with tailored porosity for thermal insulation and wastewater treatment, J. Mater. Res. 32 (17) (Sep. 2017) 3251–3259, https://doi.org/10.1557/jmr.2017.127.

[104] M. Minelli, V. Medri, E. Papa, F. Miccio, E. Landi, F. Doghieri, Geopolymers as solid adsorbent for CO2 capture, Chem. Eng. Sci. 148 (Jul. 2016) 267–274, https://doi.org/10.1016/j.ces.2016.04.013.

[105] M. Minelli, 'Characterization of novel geopolymer – Zeolite composites as solid adsorbents for CO2 capture', Chem. Eng. J. 341 (Jun. 2018) 505–515, https://doi.org/10.1016/j.cej.2018.02.050.

[106] R.M. Novais, L.H. Buruberri, M.P. Seabra, J.A. Labrincha, Novel porous fly-ash containing geopolymer monoliths for lead adsorption from wastewaters, J. Hazard Mater. 318 (Nov. 2016) 631–640, https://doi.org/10.1016/j.jhazmat.2016.07.059.

[107] Y. Ge, X. Cui, Y. Kong, Z. Li, Y. He, Q. Zhou, Porous geopolymeric spheres for removal of Cu(II) from aqueous solution: synthesis and evaluation, J. Hazard Mater. 283 (Feb. 2015) 244–251, https://doi.org/10.1016/j.jhazmat.2014.09.038.

[108] D. Medpelli, R. Sandoval, L. Sherrill, K. Hristovski, D.-K. Seo, Iron oxide-modified nanoporous geopolymers for arsenic removal from ground water, Resour.-Effic. Technol. 1 (1) (Jul. 2015) 19–27, https://doi.org/10.1016/j.reffit.2015.06.007.

[109] K. Okada, A. Ooyama, T. Isobe, Y. Kameshima, A. Nakajima, K.J.D. MacKenzie, Water retention properties of porous geopolymers for use in cooling applications, J. Eur. Ceram. Soc. 29 (10) (Jul. 2009) 1917–1923, https://doi.org/10.1016/j.jeurceramsoc.2008.11.006.

[110] M.I.M. Alzeer, K.J.D. MacKenzie, R.A. Keyzers, Facile synthesis of new hierarchical aluminosilicate inorganic polymer solid acids and their catalytic performance in alkylation reactions, Microporous Mesoporous Mater. 241 (Mar. 2017) 316–325, https://doi.org/10.1016/j.micromeso.2016.12.018.

[111] P. Sazama, O. Bortnovsky, J. Dědeček, Z. Tvarůžková, Z. Sobalík, 'Geopolymer based catalysts—new group of catalytic materials', Catal. Today 164 (1) (Apr. 2011) 92–99, https://doi.org/10.1016/j.cattod.2010.09.008.

[112] M.I.M. Al-Zeer, K.J.D. MacKenzie, Fly ash-based geopolymers as sustainable bifunctional heterogeneous catalysts and their reactivity in friedel-crafts acylation reactions, Catalysts 9 (4) (Apr. 2019) 372, https://doi.org/10.3390/catal9040372.

[113] Z. Zhang, J.L. Provis, A. Reid, H. Wang, Mechanical, thermal insulation, thermal resistance and acoustic absorption properties of geopolymer foam concrete, Cem. Concr. Compos. 62 (Sep. 2015) 97–105, https://doi.org/10.1016/j.cemconcomp.2015.03.013.

[114] Y. Luna-Galiano, C. Leiva, C. Arenas, C. Fernández-Pereira, Fly ash based geopolymeric foams using silica fume as pore generation agent. Physical, mechanical and acoustic properties, J. Non-Cryst. Solids 500 (Nov. 2018) 196–204, https://doi.org/10.1016/j.jnoncrysol.2018.07.069.

[115] J. Feng, R. Zhang, L. Gong, Y. Li, W. Cao, X. Cheng, Development of porous fly ash-based geopolymer with low thermal conductivity, Mater. Des. 1980-2015 65 (Jan. 2015) 529–533, https://doi.org/10.1016/j.matdes.2014.09.024.

[116] R.M. Novais, Robert C. Pullar, J.A. Labrincha, Geopolymer foams: an overview of recent advancements, Prog. Mater. Sci. 109 (Apr. 2020) 100621, https://doi.org/10.1016/j.pmatsci.2019.100621.

[117] F.G.M. Aredes, T.M.B. Campos, J.P.B. Machado, K.K. Sakane, G.P. Thim, D.D. Brunelli, Effect of cure temperature on the formation of metakaolinite-based geopolymer, Ceram. Int. (2015) 10, https://doi.org/10.1016/j.ceramint.2015.02.022.

[118] P. Risdanareni, J.J. Ekaputri, M.M.A.B. Abdullah, Effect of alkaline activator ratio to mechanical properties of geopolymer concrete with trass as filler, Appl. Mech. Mater. 754–755 (2015). https://doi.org/10.4028/www.scientific.net/AMM.754-755.406.

[119] V. Benavent, F. Frizon, A. Poulesquen, Effect of composition and aging on the porous structure of metakaolin-based geopolymers, J. Appl. Crystallogr. 49 (6) (Dec. 2016) 2116–2128, https://doi.org/10.1107/S1600576716014618.

[120] Y. Ma, J. Hu, G. Ye, The pore structure and permeability of alkali activated fly ash, Fuel 104 (Feb. 2013) 771–780, https://doi.org/10.1016/j.fuel.2012.05.034.

[121] E. Jämstorp, M. Strømme, G. Frenning, 'Modeling structure–function relationships for diffusive drug transport in inert porous geopolymer matrices', J. Pharm. Sci. 100 (10) (Oct. 2011) 4338–4348, https://doi.org/10.1002/jps.22636.

[122] D.K. Seo, D. Medpelli, J. Seo, Porous Geopolymer Materials, 2013. Patent n°US 2013/0055924 A1.

[123] A. Thomas, Fats and fatty oils, in: Ullmann's Encyclopedia of Industrial Chemistry, 2000.

[124] Z. Wang, D. Lu, Study on the effect of emulsifiers on the pore structures of geopolymer prepared by emulsion templating, Mater. Res. Express (May 2020), https://doi.org/10.1088/2053-1591/ab94f9.

[125] D. Medpelli, J.-M. Seo, D.-K. Seo, Geopolymer with hierarchical meso-/macroporous structures from reactive emulsion templating, J. Am. Ceram. Soc. 97 (1) (Jan. 2014) 70–73, https://doi.org/10.1111/jace.12724.

[126] C. Bai, J. Zheng, G.A. Rizzi, P. Colombo, Low-temperature fabrication of SiC/geopolymer cellular composites, Compos. Part B Eng. 137 (Mar. 2018) 23–30, https://doi.org/10.1016/j.compositesb.2017.11.013.

[127] C. Bai, T. Ni, Q. Wang, H. Li, P. Colombo, Porosity, mechanical and insulating properties of geopolymer foams using vegetable oil as the stabilizing agent, J. Eur. Ceram. Soc. 38 (2) (Feb. 2018) 799–805, https://doi.org/10.1016/j.jeurceramsoc.2017.09.021.

[128] P. Hua, Adsorption of acid green and procion red on a magnetic geopolymer based adsorbent: experiments, characterization and theoretical treatment, Chem. Eng. J. 383 (Mar. 2020) 123113, https://doi.org/10.1016/j.cej.2019.123113.

[129] M.S. Cilla, M.D. de Mello Innocentini, M.R. Morelli, P. Colombo, Geopolymer foams obtained by the saponification/peroxide/gelcasting combined route using different soap foam precursors, J. Am. Ceram. Soc. 100 (8) (Aug. 2017) 3440–3450, https://doi.org/10.1111/jace.14902.

[130] J. Fiset, M. Cellier, P.Y. Vuillaume, Macroporous geopolymers designed for facile polymers post-infusion, Cem. Concr. Compos. 110 (Jul. 2020) 103591, https://doi.org/10.1016/j.cemconcomp.2020.103591.

[131] M. Strozi Cilla, M. Raymundo Morelli, P. Colombo, Effect of process parameters on the physical properties of porous geopolymers obtained by gelcasting, Ceram. Int. 40 (8) (Sep. 2014) 13585–13590, https://doi.org/10.1016/j.ceramint.2014.05.074.

[132] E. Landi, Alkali-bonded ceramics with hierarchical tailored porosity, Appl. Clay Sci. 73 (Mar. 2013) 56–64, https://doi.org/10.1016/j.clay.2012.09.027.

[133] P. Hlaváček, V. Šmilauer, F. Škvárab, L. Kopecký, R. Šulc, Inorganic foams made from alkali-activated fly ash: mechanical, chemical and physical properties, J. Eur. Ceram. Soc. (2015), https://doi.org/10.1016/j.jeurceramsoc.2014.08.024.

[134] R. Arellano Aguilar, O. Burciaga Díaz, J.I. Escalante García, Lightweight concretes of activated metakaolin-fly ash binders, with blast furnace slag aggregates, Constr. Build. Mater. 24 (7) (Jul. 2010) 1166–1175, https://doi.org/10.1016/j.conbuildmat.2009.12.024.

[135] E. Prud'homme, Silica fume as porogent agent in geo-materials at low temperature, J. Eur. Ceram. Soc. (2010), https://doi.org/10.1016/j.jeurceramsoc.2010.01.014.

[136] E. Prud'homme, P. Michaud, E. Joussein, C. Peyratout, A. Smith, S. Rossignol, In situ inorganic foams prepared from various clays at low temperature, Appl. Clay Sci. 51 (1–2) (Jan. 2011) 15–22, https://doi.org/10.1016/j.clay.2010.10.016.

[137] L. Korat, V. Ducman, The influence of the stabilizing agent SDS on porosity development in alkali-activated fly-ash based foams, Cem. Concr. Compos. 80 (Jul. 2017) 168–174, https://doi.org/10.1016/j.cemconcomp.2017.03.010.

[138] C. Bai, P. Colombo, High-porosity geopolymer membrane supports by peroxide route with the addition of egg white as surfactant, Ceram. Int. 43 (2) (Feb. 2017) 2267–2273, https://doi.org/10.1016/j.ceramint.2016.10.205.

[139] W. Bian, Z. Wang, M. Zhang, 'Epoxy resin's influence in metakaolin-based geopolymer's antiseawater corrosion performance', Int. J. Corros. 2019 (Jul. 2019) 1–7, https://doi.org/10.1155/2019/5470646.

[140] I. Firawati, Jasruddin, Subaer, On the physico-mechanics, thermal and microstructure properties of hybrid composite epoxy-geopolymer for geothermal pipe application, MATEC Web Conf 97 (2017), https://doi.org/10.1051/matecconf/20179701007, 01007.

[141] G. Roviello, L. Ricciotti, C. Ferone, F. Colangelo, R. Cioffi, O. Tarallo, Synthesis and characterization of novel epoxy geopolymer hybrid composites, Materials 6 (9) (Sep. 2013) 3943–3962, https://doi.org/10.3390/ma6093943.

[142] G. Roviello, Preparation, structure and properties of hybrid materials based on geopolymers and polysiloxanes, Mater. Des. 87 (Dec. 2015) 82–94, https://doi.org/10.1016/j.matdes.2015.08.006.

[143] G. Roviello, L. Ricciotti, C. Ferone, F. Colangelo, O. Tarallo, Fire resistant melamine based organic-geopolymer hybrid composites, Cem. Concr. Compos. 59 (May 2015) 89–99, https://doi.org/10.1016/j.cemconcomp.2015.03.007.

[144] S. Zhang, K. Gong, J. Lu, Novel modification method for inorganic geopolymer by using water soluble organic polymers, Mater. Lett. 58 (7–8) (Mar. 2004) 1292–1296, https://doi.org/10.1016/j.matlet.2003.07.051.

[145] X. Chen, M. Zhou, X. Ge, Z. Niu, Y. Guo, Study on the microstructure of metakaolin-based geopolymer enhanced by polyacrylate, J. Ceram. Soc. Jpn. 127 (3) (Mar. 2019) 165–172, https://doi.org/10.2109/jcersj2.18186.

[146] O. Mikhailova, P. Rovnaník, Effect of polyethylene glycol addition on metakaolin-based geopolymer, Procedia Eng 151 (2016) 222–228, https://doi.org/10.1016/j.proeng.2016.07.379.

[147] M. Catauro, F. Papale, G. Lamanna, F. Bollino, Geopolymer/PEG hybrid materials synthesis and investigation of the polymer influence on microstructure and mechanical behavior, Mater. Res. 18 (4) (Aug. 2015) 698–705, https://doi.org/10.1590/1516-1439.342814.

[148] J. Du, Y. Bu, Z. Shen, X. Hou, C. Huang, Effects of epoxy resin on the mechanical performance and thickening properties of geopolymer cured at low temperature, Mater. Des. 109 (Nov. 2016) 133–145, https://doi.org/10.1016/j.matdes.2016.07.003.

[149] S. Wang, X. Ma, L. He, Z. Zhang, L. Li, Y. Li, High strength inorganic-organic polymer composites (IOPC) manufactured by mold pressing of geopolymers, Constr. Build. Mater. 198 (Feb. 2019) 501–511, https://doi.org/10.1016/j.conbuildmat.2018.11.281.

[150] N.K. Lee, E.M. Kim, H.K. Lee, Mechanical properties and setting characteristics of geopolymer mortar using styrene-butadiene (SB) latex, Constr. Build. Mater. 113 (Jun. 2016) 264–272, https://doi.org/10.1016/j.conbuildmat.2016.03.055.

[151] Y.J. Zhang, Y.C. Wang, D.L. Xu, S. Li, Mechanical performance and hydration mechanism of geopolymer composite reinforced by resin, Mater. Sci. Eng. A 527 (24–25) (Sep. 2010) 6574–6580, https://doi.org/10.1016/j.msea.2010.06.069.

[152] Y.J. Zhang, S. Li, Y.C. Wang, D.L. Xu, Microstructural and strength evolutions of geopolymer composite reinforced by resin exposed to elevated temperature, J. Non-Cryst. Solids 358 (3) (Feb. 2012) 620–624, https://doi.org/10.1016/j.jnoncrysol.2011.11.006.

[153] X. Chen, G.R. Zhu, J. Wang, Q. Chen, Effect of polyacrylic resin on mechanical properties of granulated blast furnace slag based geopolymer, J. Non-Cryst. Solids 481 (Feb. 2018) 4–9, https://doi.org/10.1016/j.jnoncrysol.2017.07.003.

[154] Y. Ge, X. Cui, C. Liao, Z. Li, Facile fabrication of green geopolymer/alginate hybrid spheres for efficient removal of Cu(II) in water: batch and column studies, Chem. Eng. J. 311 (Mar. 2017) 126–134, https://doi.org/10.1016/j.cej.2016.11.079.

[155] V. Medri, E. Papa, J. Lizion, E. Landi, Metakaolin-based geopolymer beads: production methods and characterization, J. Clean. Prod. 244 (Jan. 2020) 118844, https://doi.org/10.1016/j.jclepro.2019.118844.

[156] P. Patil, D. Chavanke, M. Wagh, A review on ionotropic gelation method: novel approach for controlled gastroretentive gelishperes, Int. J. Pharm. Pharm. Sci. 4 (2012).

[157] M. Hussain, R. Varely, Y.B. Cheng, Z. Mathys, G.P. Simon, Synthesis and thermal behavior of inorganic-organic hybrid geopolymer composites, J. Appl. Polym. Sci. 96 (1) (Apr. 2005) 112–121, https://doi.org/10.1002/app.21413.

[158] M. Hussain, R.J. Varely, Y.B. Cheng, G.P. Simon, Investigation of thermal and fire performance of novel hybrid geopolymer composites, J. Mater. Sci. 39 (14) (Jul. 2004) 4721–4726, https://doi.org/10.1023/B:JMSC.0000034180.35216.ba.

[159] X. Chen, S.K.J. Lim, Y.N. Liang, L. Zhang, X. Hu, Large toughening effect in biomimetic geopolymer composites via interface engineered 3D skeleton, ACS Sustain. Chem. Eng. 7 (1) (Jan. 2019) 105–110, https://doi.org/10.1021/acssuschemeng.8b05090.

[160] K.S.W. Sing, Characterization of porous solids: an introductory survey, in: Studies in Surface Science and Catalysis, vol. 62, Elsevier, 1991, pp. 1–9.

[161] M.M.A. Hafiz, A.R.M. Ridzuan, A.M. Faiza, M.F. Arshad, J. Nurliza, Morphology of formulated used cooking oil foam (FUSCOF) created for lightweight greencrete, Adv. Mater. Res. 701 (May 2013) 270–274. https://doi.org/10.4028/www.scientific.net/AMR.701.270.