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Functionalized geopolymers - a review

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ABSTRACT

The geopolymer technology provides an alternative good solution for the utilization of industrial waste and the preservation of primary minerals to produce an economically valuable product that can be used for several purposes. This review summarizes the preparation, the structure modifications and functionalization of geopolymers for adsorbing purposes. The mechanical performances of the geopolymers (compressive strength, flexural strength, durability such as resistance to sulfate, acid, thermal effect) are the primary concerns that depend on the chemical composition.

1. Introduction

Geopolymers are amorhpous aluminosilicate materials with three dimensional frameworks of SiO_4 and AlO_4 tetrahedra that can be produced by alkali activation even at ambient temperature and low pressure. It was first developed by Davidovits in 1978 (Davidovits, 1989). After the mechanical activation (Kumar et al., 2017; Mucsi et al., 2015; Temuujin et al., 2017) of the aluminosilicate powder with appropriate parameters (particle size distribution, specific surface area) it has to be mixed with alkali solution (NaOH, KOH, water glass) to produce amorphous gel-like substance that quickly solidifie into hard geopolymer (Barbsa et al., 1999). This alkali activated material possess excellent physical, chemical and mechanical attribution such as low density, micro and nanoporosity, high mechanical strength, heat stability, fire resistance and chemical resistance.

Geopolymers can be prepared from reactive industrial by-products: granulated blast furnace slag, iron ore tailing, power station fly ash, slag, red mud and agricultural waste (rice husk ash, palm fuel ash), from primary raw material such as kaolin. After the suitable geopolymer structure is balanced, geolopolymer foam can be produced by adding foaming agent to the geopolymeric gel (Kumar et al., 2017; Mucsi et al., 2015; Temuujin et al., 2017), that can be used for various purposes such as heat insulator material or adsorbing material. The produced highly porous gepolymer foam structure ensures active surfaces for adsorption of heavy metals from aqueous solution due to the high specific surface area and the surface bonded hydroxyl-groups due to the alkali activation. This high specific surface area can be chemically modified to produce more adsorption site.

2. Functionalization

2.1. Factors influencing the mechanical properties

The quality of the geopolymers is influenced by the amorphous nature of geopolymers (amount of geopolymer gel), the type and concentration of alkali activating solution, the ratio of the NaOH/ Na_2SiO_3, Si/Al

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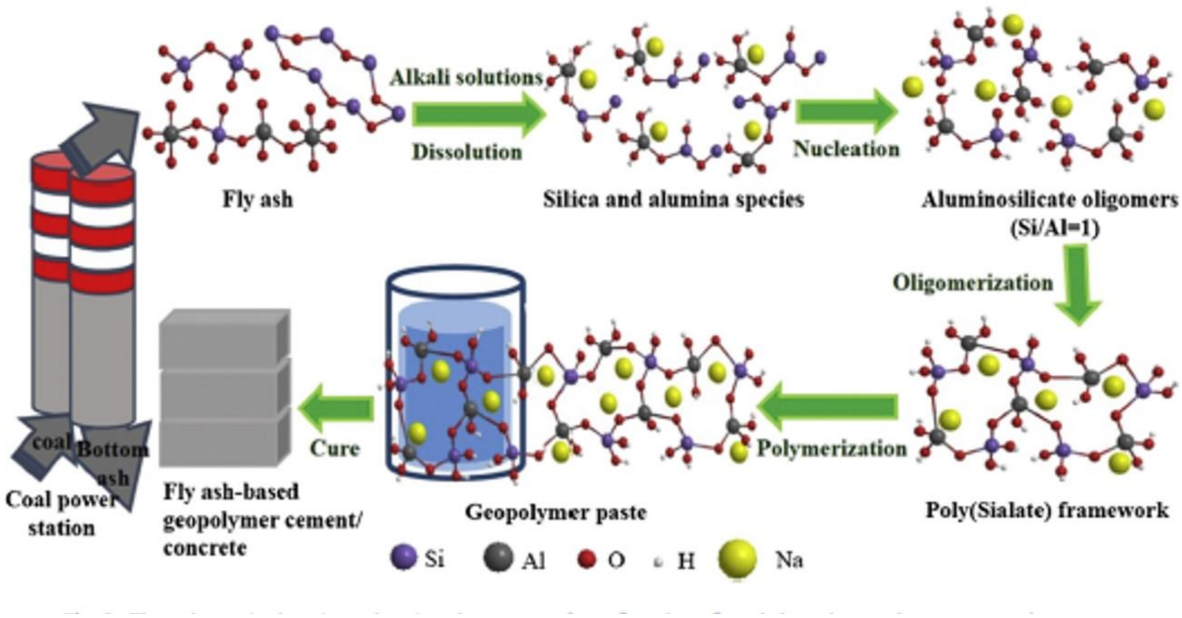

Figure 1. Geopolymer synthesis (Zhuang, 2016)

ratio, water content in the mixture, the curing time and temperature, the initial solid/liquid ratio, and the CaO content of the raw material (Barbsa et al., 1999).

The final structure of the geopolymer is influenced by the porosity depend on the composition of geopolymer. The high Si/Al ratio increases the compressive strength of the geopolymer that can be reached by adding Na_2SiO_3, slag, rice husk ash and red mud. The addition of water glass results in finer pore structure and lower porosity. The silica fume makes the geopolymerisation faster, decrease the porosity and increase the compressive strength.

After the formation of geopolymer structure (Xu and Van Deventer, 2000) having the appropriate mechanical properties and a stable structure, the use of a special chemical foaming agent can be used to produce a porous geopolymer foam suitable for further use, which have a high physical, chemical and mechanical properties to ensure low density, high strength, heat stability, depending on the parameters used in the production. To produce macroporous geopolymer aluminium powder, silicium powder (FeSi, SiC), sodium-perborat, sodium hypochlorit (NaOCl) or hydrogen-peroxid react with the alkali solution in which oxygen gas is formed.

The foam formation is based on the fact that H_2O_2 is thermodynamically unstable and easily separates into water and oxygen gas (Szabó et al., 2017). Increasing H_2O_2 concentration increases the amount of oxygen resulting in increased bubble formation, which is greatly influenced by the pH of the solution. The pore size distribution of the geopolymers depends on the hydrogen peroxide separation reaction and the geopolymerization reaction. Narrow pore size distribution improves insulating ability, while the wider pore size interval leads to complex air conduction channels and improves the acoustic resistance of the foams. Varying amount of foaming agent (1, 2, 4, 6 wt %) produces geopolymers with varying pore size. The addition of 6 % H_2O_2 seems to be an upper limit since H_2O_2 above this amount cause the very porous structure to collapse (Palmero et al., 2015). The created geopolymer foams can reach relatively high compressive strength values 5.5 to 10.9 MPa, which is highly dependent on the liquid/solid ratio and the added foaming agents, the increase of which reduces the strength values, with lower density (0.4-1.2 g/cm^3). Increasing H_2O_2 leads to decrease in density, thermal conductivity, increase in macroporosity, decrease in flexural and compressive strength values.

The porosity and specific surface of the geopolymer foams can be increased by using the combined method of saponification/peroxide/gelcasting (Cilla et al., 2014), which is nowadays increasingly used for the production and development of micro and mesoporous geopolymers with high specific surface. According to the saponification method sunflower oil react with the alkaline geopolymer and results in the formation of carboxylate surfactant (soap) molecules. This combined method produces high porosity with open pores and with regular morphology and spherical cells. Saponification leads to the formation of smaller cells with fewer open pores, while the use of peroxide leads to the formation of large but predominantly closed cells. The advantage of these method is that the open porosity can be increased by approximately 10 %. The open pore morphology play a significant role on the thermal conductivity and water absorption of geopolymers.

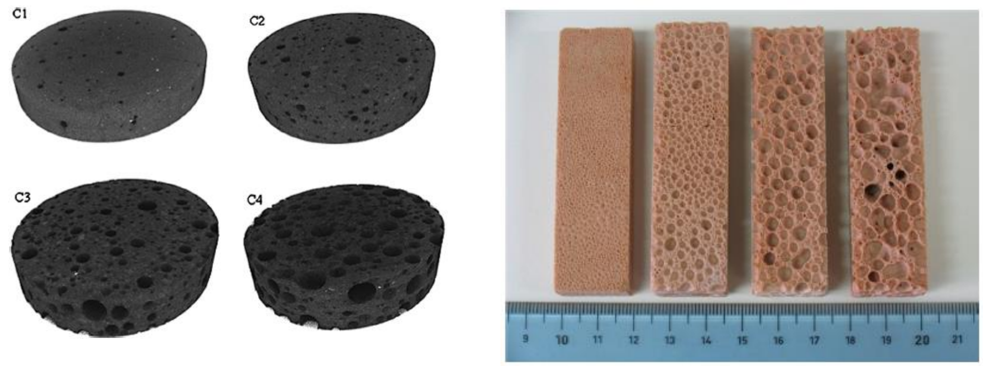

Figure 2. Geopolymer foams with different a) Al content c1-c4=5, 10, 15, 20 mg Al powder, 100 ml alkali solution, c4=70 % porosity (Zhang et al., 2014), b) H_2O_2 content, 1,2,4,6 wt %, H_2O/Na_2O=13 (Palmero et al., 2015)

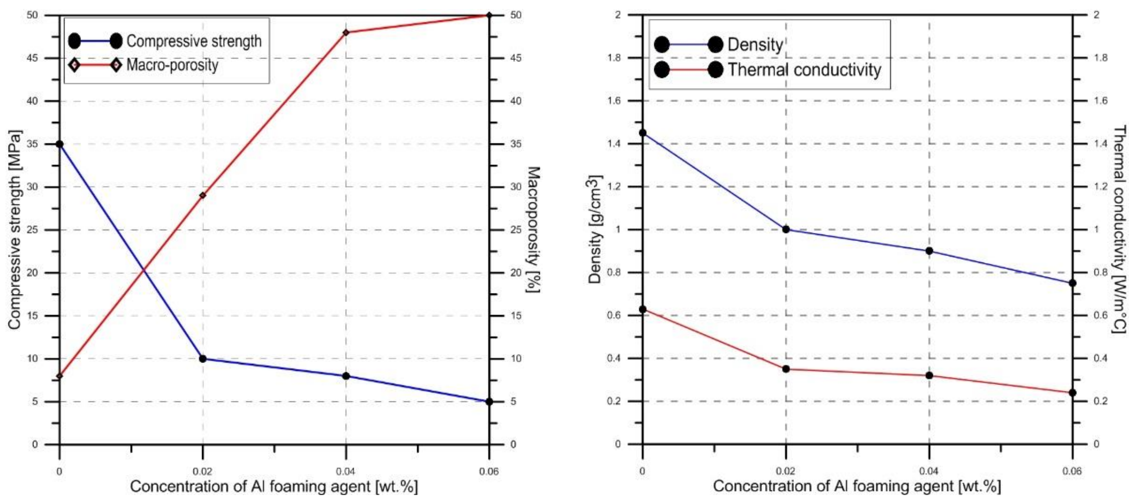

Figure 3. The relation of the compressive strength, density, heat conductivity, macroporosity and the added Al powder (based on Rickard, 2013)

After the formation of a stable foam structure, the surface of the pores can be modified with various chemical compounds, which gives the properties of the geopolymer matrix better. Previous studies have put great emphasis on modifying the geopolymer matrix with various organic compounds (Zhang et al., 2009; Ricciotti et al., 2013) such as polyvinyl acetate, polypropylene, polyvinyl alcohol or water soluble organic compounds. In the geopolymerization process, the added organic material interacts chemically with the geopolymer gel, during which hydroxyl groups develop.

2.2. Heavy metal ion adsorption of the functionalized geopolymer

Geopolymer preparation is a new technology for the removal of heavy metal ions from contaminated water. Different natural minerals normally have lower adsorption capability that can be increased by surface treatment due to the hydroxylation of the waste (for example fly ash) that transforms the non-porous hydrophobic material into mesoporous hydrophilic material with a large number of ion exchange sites. The heavy metal ion adsorption is performed on the functionalized material through ion exchange and physisorption processes due to the difference in chemical potential between the light and heavy metal ions. One of the most characteristic features of the inorganic polymers is the exchangeable K^+ and Ca^{2+} cations in the structure that can be subsituted with heavy metal ions and can migrate in the mesoporous structure of the aluminosilicate material.

2.3. Metakaolin based geopolymer

Svingala and Varela (2009) used a mixture of metakaolin and slag for geopolymer synthesis reaching 2.9-9.5 MPa compressive strength and 1.2 g/cm^3 specimen density. The mechanical properties of the geopolymers can be enhanced with chitosan and fibers, such ash polypropylene, which improves the dehydration resistance of the material at high temperature due to the formation of hydrogen bonds that connects the formed microcracks and delay the formation of them and fibers can increase the permeability of the material at high temperature. The foam structure was made from a geopolymer matrix having an average compressive strength of 54 MPa and a specimen density of 1.61 g/cm^3. The polypropylene fiber (1 wt %) was added to the geopolymer with these parameters reduces the compressive strength to 36 MPa. The addition of foam-forming aluminium powder (Rickard et al., 2013) (0.02, 0.04, and 0.06 wt. %) changed the compressive strength to 9.5 MPa, 7.9 MPa and 4.4 MPa with increasing porosity and decreasing densities between 0.7 and 1 g/cm^3. The higher amount of aluminium powder caused increased presence of large pores. Without fibres the pore structure was significantly unstable leading to pore collapse after foam formation.

In metakaolin based geopolymers the evaporation of large volumes of water added to the activating solution leads to the formation of micro cracks, that can be delayed by adding resin to the gel. The resin of 20 wt % can increase the compressive strength up to 60 MPa.

Autef et al., (2012) investigated the source of silicon and its effect on the formation of mechanical properties (quartz or amorphous silicon) in the geopolymerization process, according to which the growing amount of amorphous material increases the formation of well-consolidated geopolymer. The addition of amorphous nano grain sized (0.5-2 wt %) SiO_2 with 670 m^2/g specific surface area covered with hydroxyl surface (Autef et al., 2012) to the metakaolin increased the compressive strength from 58.9 MPa up to 71.1 MPa after 56 days.

Adsorbent material can be prepared from a mixture of organic and inorganic substances where the linkage between the organic sodium alginate and the inorganic metakolin was ensured by Ca^{2+} with soaking the sample into $CaCl_2$ solution. The beneficial physical and chemical properties of the organic material serve to improve the adsorption capacity while the inorganic phase increases the mechanical strength and heat stability. The adsorption capacity of the produced blended material is 60.8 mg/g (Yuanyuan et al., 2017).

Porous metakaolin (9.56 m^2/g specific surface area) based inorganic spheres can be formed by adding sodium dodecyl suplhate and (K12) foaming agent (1.5 wt %). According to the pore structure studies, BET indicates a high specific surface area with mesoporous property (53.95 m^2/g), low density (0.79 g/cm^3), 60 % porosity that serves as an active surface for binding Cu^{2+}, Pb^{2+}, Ca^{2+} and other ions. The adsorbed Cu(II) with the increase the contact time reached a maximum of 34.5 mg/g.

Metakaolin-based geopolymer is also effective in the removing of Ni^{2+} from aqueous solution (Yuanyuan et al., 2015). The BET specific surface area is the highest at H_2O/Na_2O=19 with 39.66 m^2/g adsorption capacity and 18.67 MPa compressive strength. López et al., (2014) produced metakaolin and rice husk based geopolymer foams with 50.8 mg/g adsorption capacity.

Yousef et al., (2009) prepared metakaolin based geopolymers with the addition of zeolitic tuff. The resulting geopolymer has good mechanical properties and adsorption capability for methylene-blue and Cu^{2+}. The affinity, the attractive force between the hydrated ion and the metal is affected by the size of the hydrated cation, the lower the hydrated radius, the greater the affinity. According to the heavy metal adsorption studies, the results are: Pb^{2+}=86.2 mg/g, Cu^{2+}=40.9 mg/g, Cr^{3+}=9.8 mg/g and Cd^{2+} =68.9 mg/g.

2.4. Fly ash based geopolymer

Yang et al., (2014) examined a mixture of fly ash and high magnesium nickel slag (HMNS) with the activation of Na_2SiO_3 (water glass), and stated that the HMNS was functionalized as micro aggregate making smaller the pores. Using 20 % HMNS results in 60 MPa compressive strength. The results indicate that the higher the amount of slag the higher the compressive strength that lead to the formation of cracks due to the shrinkage of the slag.

By activating the mixture of fly ash and iron ore tailing (30 wt % iron ore tailing) with multi-component alkali solution, higher compressive strength values can be achieved compared with the activation only in NaOH solution. The result after the addition of H_2O_2 foaming agent is a highly porous geopolymer foam showing 113.41 mg/g Cu^{2+} adsorption capacity at 40 °C and pH=6 (Duan et al., 2016).

According to recent researches, the geopolymer made from rice husk ash and fly ash mixture can be widely used as a functional material with compressive strength of 15-20 MPa after 7 days. Organic melamine resin given to the geopolymer shows a good incorporation in the inorganic geopolymer frame in nanometric scale, improving the mechanical properties and thermal stability. The organic phase provides physical reinforcement to the geopolymer, improving mechanical stability and reducing fracture. The silane-derived APTES also improves the interaction between organic and inorganic material, which in small amounts, also serves a significant structural improvement of the substance, because resin-containing panels are less rigid, thus reduce the chance of fracture.

Al-Zboon et al., (2011) investigated the Pb^{2+} adsorption capacity of the fly ash based geopolymer that produced 90.6 % removal efficiency compared to the raw fly ash with 39.87 %. Lee et al., (2017) used a fly ash/slag mixture with nano-crystalline zeolite to investigate the cezium-adsorption capacity that reach 15.24 mg/g. This material possess high compressive strength (16.57 MPa) and high specific surface area (114.16 m^2/g).

Fly ash based geopolymer (Javadian et al., 2015) can be applied for removing cadmium nitrate from water. For comparison, the adsorption capacity of Cd^{2+} by the raw fly ash at pH=5 was 7 mg/g, while the fly ash based geopolymer is 14.431 mg/g.

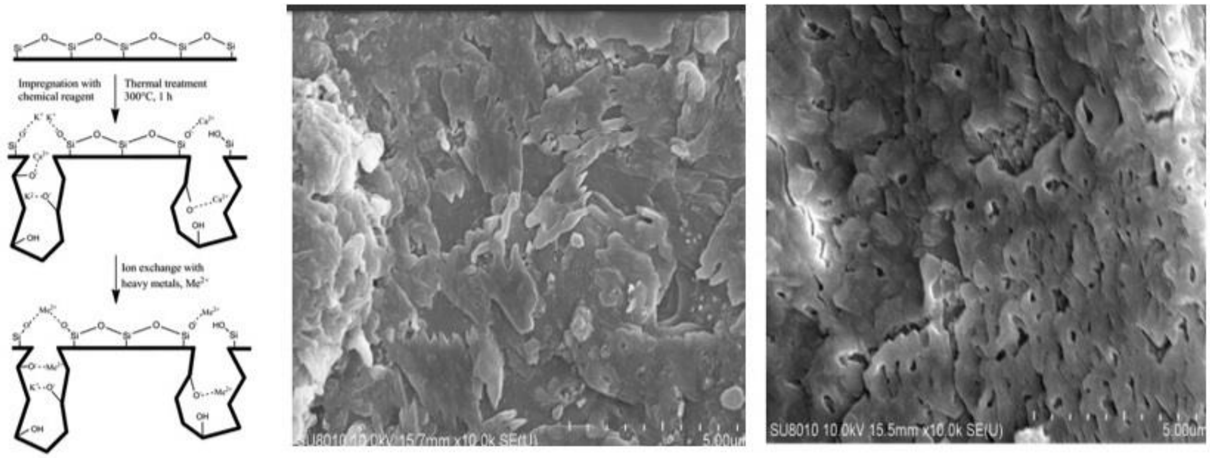

Figure 4. Surface functionalization (Hadi et al., 2016), fly ash and iron ore tailing without and with H_2O_2 (Duan et al., 2016)

2.5. Zeolite

For the construction of water storage facilities, functionalized geopolymer can be prepared from the mixture of zeolite tuff and kaolinite (Alshaaer et al., 2016). The kaolinite-based geopolymer mixed with zeolite tuff has high compressive strength, density and adsoption capacity for cadmium. Zeolite as reactive filler material may be involved in the geopolymerization process as functional reactive fillers, so it is important to properly investigate the geopolymers. The most important test is to determine the optimal amount of water to produce the geopolymer which provides adequate mechanical properties for water retention and high adsorption capacity for water purification. Zeolite tuff increased the adsorption capacity of metakaolin towards micro contaminants as a reactive filler. The optimal amount of water is close to the plasticity limit for high quality building materials.

After hydrothermal treatment, the geopolymer can be transformed into faujasite, which has a nano-sized pore structure and good heavy metal ion adsorption capability. Zeolite consists of pores of a given size that pass through certain metals, which allows for selective separation. The Pb^{2+} at pH=3-6 adsorbed is 74.83 mg/g. The adsorption capacity of faujasite (pH=3) is 143.3 mg/g, for geopolymer is 118.6 mg/g. The increase in pH increases the amount of adsorbed heavy metal ion. The best adsorption capability was reached at pH=6 is 45 °C 152 mg/g.

Zeolite has a good adsorption ability to remove metals, phosphates, ammonium and petroleum derivatives, which can be enhanced by various modifications. The adsorption nature of chitosan (Li et al., 2013) in removing heavy metals and dyes is that the amino and hydroxyl groups serve as active surfaces for heavy metal ions. In the presence of higher amounts of H^+ the surface of the adsorbent is covered with protons, the decrease in electrostatic attraction results in less adsorption.

Mesoporous silica modifies (Pizarro et al., 2015) the surface properties of raw fly ash that can be functionalized with 3-aminopropyl-triethoxysilane to achieve better adsorption capacity of Cu^{2+}. The specific surface area of mesoporous silica modified and APTS - functionalized fly ash is 415.25 m^2/g.

According to the results (Duan et al., 2016) the porous geopolymer Cu^{2+} removal efficiency is 90.7 %, while for the reference geopolymer is only 33.9 % depending on the pH. It ranges from pH=1 is 4.95 % to pH=5 is 93.5 %. Compared to the reference geopolymer and the porous geopolymer, the adsorption trend is similar, but the porous geopolymer exhibits higher values due to the increased number of active surfaces.

3. Summary

Geopolymers can be prepared from different aluminosilicate materials by alkali activation. The mechanical properties of the geopolymers depend on the chemical composition but it can be increased by mixing different materials with different nature. When compared with the initial raw material, the synthesized geopolymer foams showed a great number of active sites with large specific surface area due to the porous structure. The geopolyemer with appropriate attribution can be functionalized as a highly porous geopolymer foam structure for which its high specific surface area can be increased by adding nano-silica or after chemical modifications. The adsorption can be enhanced by modifications. The so-produced geopolymer foams with large specific surface area are suitable for the adsorption of heavy metals from aqueous solution. The produced geopolymer foams are not flammable and possess low thermal conductivity.

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Funkcionalizovani geopolimeri - pregled

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INFORMACIJE O RADU

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Geopolimerna pena
Funkcionalizacija površina

I Z V O D

Tehnologija geopolimera predstavlja alternativno dobro rešenje za proizvodnju ekonomsko isplativog i višenamenski primenljivog proizvoda korišćenjem industrijskog otpada, doprinoseći ujedno i očuvanju primarnih minerala. U radu su dati postupci pripreme, strukturne modifikacije i funkcionalizacije geopolimera u svrhu adsorbovanja. Mehaničke karakteristike geopolimera (dinamička čvrstoća - otpornost na savijanje, otpornost na pritisak, dinamička izdržljivost - otpornost na sulfate, kiseline, termalni efekat) zavise od hemijskog sastava i igraju veoma važnu ulogu u oceni kvaliteta geopolimera.