

Structure, Design and Applications of Geopolymeric Materials

Ioanna Giannopoulou^{1,a} and Dimitrios Panias^{1,b}

¹National Technical University of Athens, School of Mining and Metallurgical Engineering, Laboratory of Metallurgy, 9 Heroon Polytechniou str., Zografos Campus, 15780, Athens – Greece.

^a mmpgi@central.ntua.gr, ^b panias@metal.ntua.gr

Keywords: Geopolymerization, Inorganic Polymers

Abstract. The term “geopolymer” was firstly applied to describe a family of alkaline aluminosilicate binders formed by the alkali activation of aluminosilicate minerals. The formation of geopolymeric materials is the result of a complicated heterogeneous chemical reaction occurring between Al-Si solid materials and strongly alkaline silicate solutions. The geopolymerization reaction is exothermic and takes place under atmospheric pressure at temperatures below 100°C. Despite of the intense research on the geopolymerization of different aluminosilicate materials and the development of a wide range of geopolymeric materials, the exact mechanism that takes place during geopolymerization is not fully understood. The most proposed mechanism for geopolymerization includes the following four stages, which proceed in parallel and thus, it is impossible to be distinguished:

- (i) Dissolution of Si and Al from the solid aluminosilicate materials in the strongly alkaline aqueous solution.
- (ii) Formation of Si and / or Si-Al oligomers in the aqueous phase.
- (iii) Polycondensation of the oligomers to form a three-dimensional aluminosilicate framework.
- (iv) Bonding of the solid particles into the geopolymeric framework and hardening of the whole system into a final solid polymeric structure.

This paper will describe in detail the structure of the geopolymeric materials, the parameters that has to be taken into consideration for their designing and their potential applications.

Introduction

Geopolymers is a new family of synthetic aluminosilicate materials formed by alkali activation of solid aluminosilicate raw materials [1]. The term “alkali activation” refers to the chemical dissolution of aluminosilicate raw materials in a strongly alkaline environment caused by an aqueous solution of sodium or potassium hydroxide. Geopolymers belong to the family of inorganic polymers, which are macromolecules linked by covalent bonds and having -Si-O-M-O- backbone, where M denotes principally aluminum and secondarily other metals such as iron [1,2]. The difference between geopolymers and the other inorganic polymers lies in the kind of silicon and aluminum precursors used for their synthesis. Normal inorganic polymers are synthesized with the sol – gel process, which employs silicon and aluminum alkoxides in alcohol–water solution as precursors. In such systems the alkoxide groups are removed stepwise by hydrolysis under acidic or basic catalysis and replaced by hydroxyl groups, which then form -M-O-M- linkages, where M denotes Si or Al. Thus, branched polymeric chains grow and interconnect and through the gelation process form a network that spans the entire solution volume. Inorganic polymers, such as Poly(aluminosiloxanes), are polymers containing an -Si-O-Al-O- backbone synthesized by the sodium salt of a poly(dimethylsiloxane) and aluminium chloride as Si and Al precursors, respectively. Geopolymers, on the other hand, are synthesized by alkali activation of solid aluminosilicate raw materials utilizing as activator a strong alkaline aqueous solution of sodium or potassium silicate and sodium or potassium hydroxide [3]. In this case the Si precursor is the sodium or potassium silicate solution as well as the dissolved silicon from the aluminosilicate raw

material. The Al precursor is only the dissolved aluminum from the aluminosilicate raw material, although in some cases the aqueous activator phase is doped with aluminum cations [4,5]. Therefore, the synthesis systems of geopolymers are composed only from pure inorganic chemicals in contrast with the synthesis systems of typical inorganic polymers that are composed primarily from organometallic compounds.

The geopolymeric systems have gained the scientific interest during the last two decades. This is attributed to the large variety of solid aluminosilicate raw materials that can be used for the synthesis of geopolymers. Among the potential solid aluminosilicate raw materials, industrial minerals, such as kaoline, feldspars, bentonite, perlite, etc. [6-8], as well as solid industrial by-products, such as fired-coal fly ash, alumina red mud, tailings from bentonite and perlite exploitation, metallurgical slag, building demolition materials, etc. [9-13], are the most important raw materials. The latter class of potential raw materials is extremely attractive, mainly for environmental reasons. Indeed, the European Union has identified the harmful effects caused by industrial wastes and promotes in the Member States the establishment of a legal framework to protect the human health and the environment against these effects. Through that framework, the European Union among the others encourages the recovery and re-use of waste in order to conserve natural resources. The geopolymerization technology has the potential to utilize the solid industrial aluminosilicate wastes as raw materials for the production of alternative construction materials with excellent mechanical properties and unique thermal properties.

Structure of geopolymeric materials

The most proposed mechanism for the synthesis of geopolymers includes the following four stages [2,7,11,14], which proceed in parallel and thus, it is impossible to be distinguished:

- (i) *Dissolution of Si and Al from the solid aluminosilicate materials in the strongly alkaline aqueous solution.*

In the presence of water the surface metal ions of the aluminosilicate oxides may coordinate H₂O molecules and form hydroxylated surface sites that are well known as Silanol (>Si-OH) and Aluminol (>Al-OH) groups. These groups comprise the surface active sites, where the hydroxide ions of the alkaline solution act chemically to form surface chemical species. Under a complicated mechanism, silicon and aluminium ions are released from the surface species into solution, where they form aqueous species through the complexing action of hydroxide ions completing in this way the dissolution process. The Si and Al dissolution from the starting materials can be described by the chemical Equation (1).



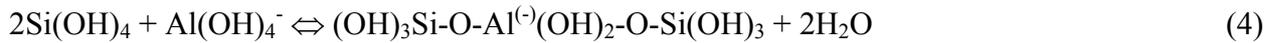
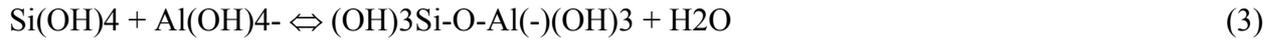
Where *M* denotes Na or K.

In aqueous solutions, the chemical dissolution of Al-Si minerals and generally of materials of aluminosilicate composition is favoured in the range of high pH values, given that the dissolution rate of these materials increases significantly as the solution pH is increased. Moreover, the dissolution rate of Al-Si solid materials is strongly depended on the size and the specific surface area of particles, as it concerns for a typical heterogeneous chemical reaction.

- (ii) *Formation of Si and / or Si-Al oligomers in the aqueous phase.*

As Si and Al concentrations in the aqueous phase increase gradually, certain chemical reactions take place between the formed hydroxy-complexes. Reactions result in the formation of the geopolymers precursors that are oligomer species (polynuclear hydroxy-complexes) consisting of polymeric bonds of Si-O-Si and Si-O-Al type, as is described by chemical Equations (2) - (4).

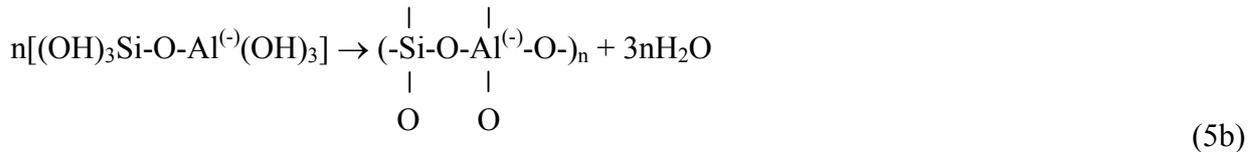
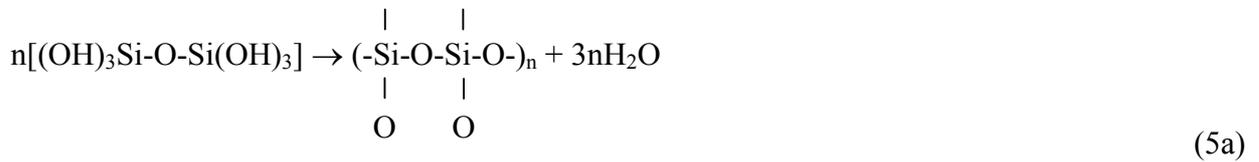




The existence of soluble silicates in the alkaline aqueous phase of the geopolymeric system enhances the formation of oligomer species. Soluble silicates in the aqueous phase increase essentially the concentration of Si, shifting mainly Equation (2) to the direction of Si-O-Si species formation, as well as Equations (3) and (4) to the direction of Si-O-Al oligomers formation. Thus, alkaline silicate solutions used in the synthesis of geopolymers provide the system with the necessary silicate oligomers for the development of the geopolymeric framework.

(iii) *Polycondensation of the oligomers to form a three-dimensional aluminosilicate framework.*

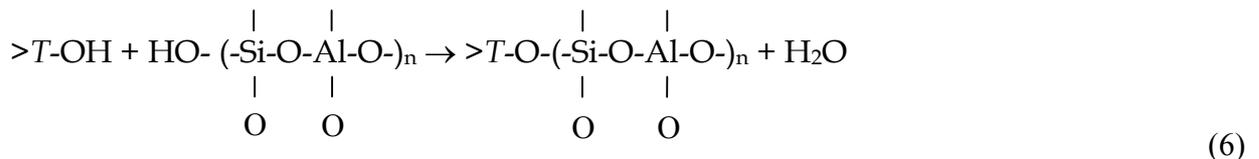
The increase of oligomers concentration in the aqueous phase involves their polycondensation, which in turn lead to the development of a three dimensional framework consisted of SiO_4 and / or AlO_4 tetrahedra linked alternately by sharing common oxygen ions, as it is presented by chemical Equations (5a) and (5b).



Polycondensation reaction involves the chemical bonding of geopolymers precursors (oligomers) by simultaneous removal of water molecules. This procedure is well known as polymerization. Oligomers may react in every hydroxyl ion site, forming macromolecular chains and /or rings that result in a three dimensional framework. As long as aluminum ion Al^{3+} participates into the geopolymeric framework in IV-fold coordination with respect to oxygen (Equations (3) – (5)), a negative charge imbalance is created and therefore, the adsorption of diluted cations (Na^+ , K^+ , Li^+ , Ca^{++} , Ba^{++} , NH_4^+ , H_3O^+ , etc.) in the framework cavities, near the sites of aluminum ions, is essential to maintain the electric neutrality in the matrix.

(iv) *Bonding of the solid particles into the geopolymeric framework and hardening of the whole system into a final solid polymeric structure.*

Since the geopolymeric framework is developed in the aqueous phase, it comes across the active surface sites of the solid particles, where it is possible to react bonding the undissolved particles in the final geopolymeric structure, according to the chemical Equation (6).



Where $>\text{T}$ denotes surface Si or Al sites.

The active surface sites of the solid particles, which are presented as $>\text{T-OH}$ in Equation (6), are the silanol ($>\text{Si-OH}$) and aluminol ($>\text{Al-OH}$) groups. It is possible for a macromolecular chain or a ring of the geopolymeric framework to create a bond of $>\text{Si-O-Si}$ and $>\text{Al-O-Si}$ type on these sites, bonding in this way the undissolved particles in the polymeric framework. Thereinafter, hardening

of the polymeric matrix, which occurs as the excess of water is removed from the geopolymeric matrices during the curing procedure, may lead to durable and tough materials.

The geopolymeric materials are composite materials. Their typical microstructure, as it has been observed by Scanning Electron Microscopy, is depicted in Figure 1.

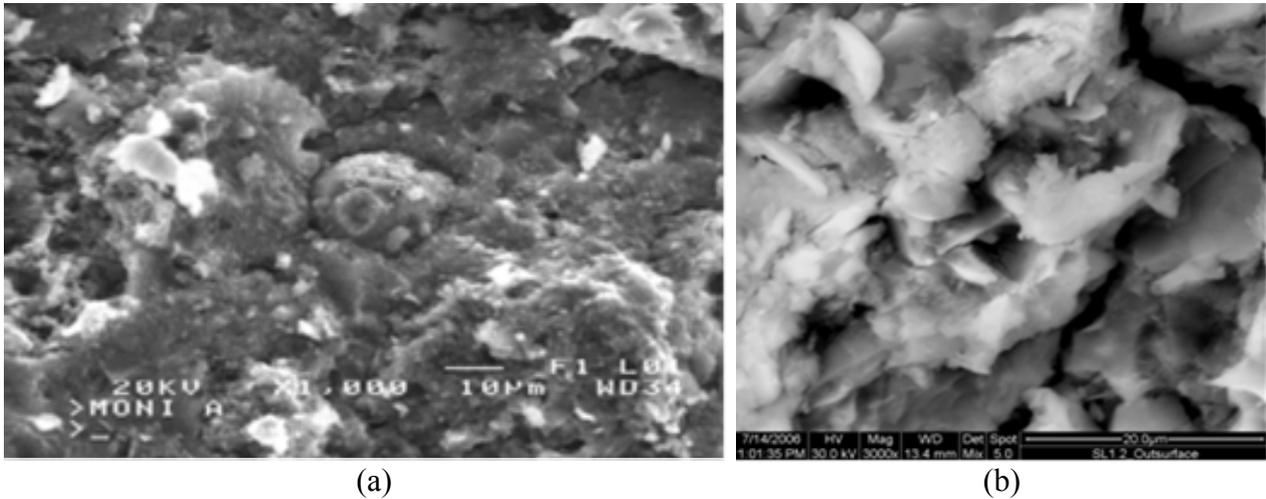


Fig. 1. Typical microstructure of geopolymeric material as it is seen by SEM. (a) Geopolymer produced from fired coal fly ash (b) Geopolymer produced from ultrafine perlite.

It is clearly observed that non-dissolved spherical fly ash particles (Fig. 1a) or elongated perlite particles (Fig. 1b) are enclosed within an amorphous aluminosilicate matrix acting as a binder. Therefore, the geopolymeric materials are composed from solid particles chemically connected with an inorganic polymeric binder formed during the geopolymerization process. The mechanical strength of materials is strongly related to the strength of the chemical bonds formed on the interface solid particle / inorganic polymer. This interface is normally the surface where the geopolymeric materials fail.

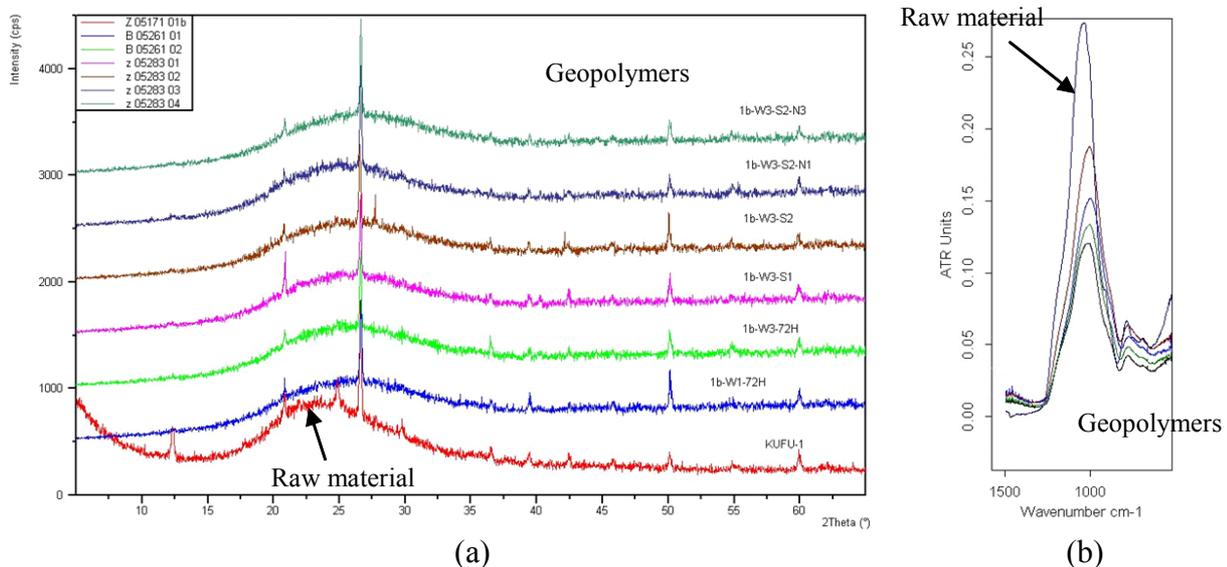


Fig. 2. (a) Typical XRD diagrams and (b) FTIR diagrams of geopolymers synthesized from an aluminosilicate by-product produced during the exploitation of Greek bentonites.

The inorganic polymeric binder has primarily an aluminosilicate chemical composition, although impurities such as calcium and iron oxides are the most usually occurring chemical constituents of geopolymeric systems. The polymeric binder is normally amorphous or semi-crystalline, as it is clearly seen in Figure 2. Figure 2(a) shows typical XRD diagrams of geopolymeric materials as well

as of an aluminosilicate raw material used for the formation of these materials. It can be observed the slight shift of the broad hump registered between $2\theta=20^\circ$ and 30° , attributed to the amorphous phase of the raw material, towards higher values $2\theta=25^\circ-35^\circ$.

This typical shift indicates the dissolution of the primary amorphous phase and the formation of a new amorphous phase in the geopolymeric material. The formation of this new amorphous phase is also observed in Figure 2(b), where the typical FTIR spectrums of geopolymeric materials, as well as of the raw material used for their formation, are shown. The most characteristic FTIR band in the geopolymeric systems appears in the wavenumbers region $990-1090\text{cm}^{-1}$ and is attributed to the asymmetric stretching vibration of T-O-Si, where T denotes Si or Al [11]. The shift of this peak towards lower wavenumbers indicates the dissolution of the amorphous aluminosilicate phase of the raw material and the formation of a new amorphous gel in which the backbone is consisting of polymeric chains with smaller length in relation to the ones of the raw material.

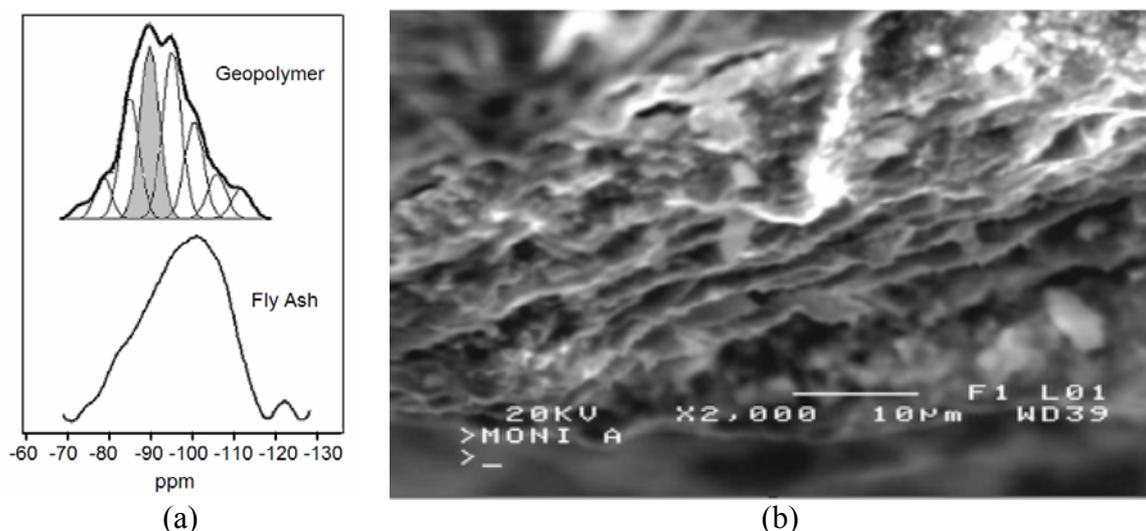


Fig. 3. (a) ^{29}Si MAS-NMR spectrum for a geopolymeric system based on fired coal fly ash. (b) 2D structure in a geopolymeric system based on red mud and metakaoline.

The structure of the new amorphous aluminosilicate gel formed during the geopolymerization can be revealed with the application of ^{29}Si Nuclear Magnetic Resonance spectroscopy as it is seen in Figure 3(a). The ^{29}Si MAS-NMR spectrum reveals the degree of structural order in geopolymers [15]. In Figure 3(a), it is seen the ^{29}Si MAS-NMR spectrum and its deconvolution, which means the analysis of spectrum in several component peaks. The most intense peaks are located at around -88ppm and -94ppm. The first one denotes the existence of an $\text{Q}^4(4\text{Al})$ aluminosilicate backbone having as structural unit silicon tetrahedra $[\text{SiO}_4]^{4-}$ surrounded by four aluminum tetrahedra $[\text{AlO}_4]^{5-}$. The latter peak denotes the existence of an $\text{Q}^4(3\text{Al})$ aluminosilicate backbone. The peaks at around -99ppm, -105ppm and -110ppm denote the presence of $\text{Q}^4(2\text{Al})$, $\text{Q}^4(1\text{Al})$ and $\text{Q}^4(0\text{Al})$ structural units in the aluminosilicate gel formed during geopolymerization. Peaks at less than -84ppm are normally attributed to monomeric or oligomeric units consisting of silanol groups. The general conclusion is that the backbone of the geopolymeric materials is consisting of silicon tetrahedra surrounded by four, three, two, one or zero aluminum tetrahedra. The relative amount of $\text{Q}^4(4\text{Al})$, $\text{Q}^4(3\text{Al})$, $\text{Q}^4(2\text{Al})$, $\text{Q}^4(1\text{Al})$ and $\text{Q}^4(0\text{Al})$ structural units is strongly dependent on the Si:Al molar ratio in the gel, which in turn is dependent on the amount of easily dissolved aluminum in the utilized solid raw materials as well as on the chemical activity of NaOH in the initial strong alkaline aqueous solution of the geopolymeric synthesis. Increased aluminum content in the aluminosilicate gel, which means low Si:Al molar ratio, improves the cross-linking of the growing polymers having as a result the formation of a three-dimensional structure. High Si:Al molar ratio in the gel promotes the formation of a two-dimensional structure with the form of layers interconnected imperfectly with cross-linking, as it is seen in Figure 3(b).

Design of geopolymeric materials

The geopolymeric systems are composed from two phases, the solid one and the aqueous one which is called activator. The solid phase is an aluminosilicate material, which contains easily dissolved silicon and aluminum in a strongly alkaline aqueous solution. This material could be a typical aluminosilicate industrial mineral, such as kaoline, feldspars, bentonite, perlite, etc. or a solid industrial by-product, such as fired-coal fly ash, alumina red mud, tailings from bentonite and perlite exploitation, metallurgical slags, building demolition materials, etc. The aqueous phase is a strong alkaline sodium hydroxide and sodium silicate solution. The sodium hydroxide concentration in the aqueous phase has to be high enough so that the hydroxide promoted dissolution of the solid phase to take place under substantially high rates. This value can be obtained experimentally by performing specifically designed dissolution's tests. On the other hand, the sodium silicate concentration in the activator must be high enough so that the mass ratio $\text{SiO}_2:\text{Na}_2\text{O}$ to be higher than 1 accelerating with this way the polycondensation phenomena (Figure 4) and forming larger rings, complex structures and at the end polymers [11].

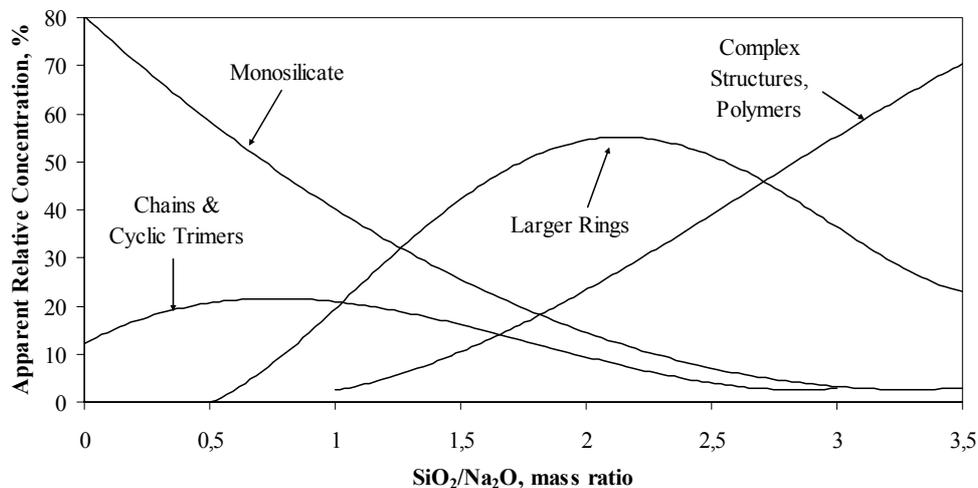


Fig. 4. Soluble silicate species equilibria in 1M aqueous silicate solution.

The solid and aqueous phases are mixed together in the highest allowable Solid:Liquid ratio so that the obtained viscous paste to have good workability and therefore to be easily molded in plastic molds. The molded materials are vibrated in a vibration table in order for the entrapped air bubbles to be efficiently removed and then are cured under low temperatures ($<100^{\circ}\text{C}$) in a controlled humidity environment. The curing duration is strongly depended on the curing temperature and varies normally from some hours to some days. In general, the higher the curing temperature, the lower the curing duration.

Properties and applications of geopolymeric materials

Although some factors governing the formation of geopolymers are still not completely understood, the physical, chemical and mechanical properties of these materials indicate that they offer attractive options towards a wide range of industrial applications. The Si:Al molar ratio in the geopolymeric structures determines essentially the properties and therefore, the application fields of geopolymers. Depending on the Si:Al ratio, it is possible to obtain products with different characteristics and consequently, for different industrial applications [16], as they are summarized in Table 1.

Geopolymers with three-dimensional structure can substitute ceramic, cement and concrete products. They present excellent mechanical properties concerning mainly to the compressive strength that, in certain cases, overcomes largely the respective one of the Portland cement, the tensile strength, which is twice to three times that of Portland cement and the Mohs hardness that ranges from 4 to 7. Additionally, they have normally low apparent porosity or nano-porosity, which

gives them very low water permeability ranging between 10^{-9} - 10^{-12} cm/s and thus, very good resistance in freezing-thawing cycles. Moreover, geopolymers are exceptional fire resistant, heat resistant, endothermic materials that can be used for the fire protection of constructions from steel reinforced concrete, such as buildings and road tunnels. Recently, geopolymers are examined as potential technological solutions for the management of toxic and radioactive waste materials. Extent laboratory and pilot-plant researches suggest that geopolymeric composites are well suited for the disposal of toxic and radioactive wastes (mine tailings, slugs, etc.) offering a safe chemical encapsulation of the contaminants and presenting structural long-term stability with respect to adverse environmental conditions. Properties, such as low water permeability, small shrinkage, good resistance to freezing-thawing cycles and high resistance to acid attack, favor the use of geopolymeric materials as solidification and immobilization systems for toxic and radioactive wastes.

Table 1. Dependence of the geopolymers structure and applications on the molar ratio Si:Al

Si:Al ratio	Polymeric character	Applications	
		Low technology	High technology
Si:Al=1:1	3D Network	- Tiles - Ceramics - Fire protection	
Si:Al=2:1		- Cements - Concretes - Radioactive and toxic wastes management	
Si:Al=3:1	2D Cross-link	- Foundry equipment - Fire resistant fiber glass composites	- Tooling for aeronautics - Heat resistant composites
Si:Al>3:1		- Sealants for industry	- Tooling for aeronautics
20:1<Si:Al and Si:Al>35:1			- Fire and heat resistant fiber composites

Geopolymers with two-dimensional cross-linking structure poses even better heat and fire resistant properties in relation to the three-dimensional structure materials. This is attributed to their unique structure that allows physically and chemically bonded water to migrate and evaporate without damaging the material. In order for their mechanical properties to be improved, 2D cross-linked geopolymers are reinforced by different types of fibers (carbon, glass, minerals or steel) to produce advanced composite materials. Provided that geopolymeric composites are able to withstand at high temperatures exhibiting refractory properties, they can find specific applications in high technology industrial areas. The fiber reinforced geopolymeric materials can be used as fire safety advanced materials into the transportation (air, sea, rail, car, etc.), nuclear and pharmaceutical industrial areas as well as for the production of moulds for thermoplastic materials and metals casting, containers for hazardous chemicals and radioactive wastes, components for high performance engines, lightweight materials and prototype automobile components.

As it is evident from the aforementioned applications, geopolymers gain increasingly attention as viable alternative to conventional materials in numerous industrial areas. The most important advantages that render them attractive are related mainly to:

- (i) The low production cost, considering that they are based on aluminosilicate materials, which both, occur naturally in abundance on the crust of the Earth as clay minerals and derive from industrial wastes as fly ash, blast-furnace slag, red mud etc.

- (ii) The energy-effectiveness of the production procedure, since geopolymers are cured and hardened at relatively low temperature. As it is documented, the energy consumed for geopolymeric tiles fabrication is less than 16% of that of conventional ceramic bodies.
- (iii) The environmental contribution provided that: (a) a number of waste materials can be transferred into added value innovative products, (b) greenhouse gas emissions are essentially reduced during geopolymeric materials production (the geopolymeric materials manufacture emits 80% less CO₂ than that of Portland cement) (c) geopolymeric composites can be utilized for safe stabilization and immobilization of radioactive and toxic wastes.

Conclusions

Geopolymers are novel materials, which are rapidly developed during the last decades. They are produced by geosynthesis that involves the alkali activation of solid aluminosilicate raw material. Geopolymers belong to the family of inorganic polymers, which are macromolecules linked by covalent bonds and having -Si-O-Al-O- backbone. Factors such as the molar ratio Si/Al of the starting materials, the concentration of the alkali metal silicate solution, the water content in the synthesis and the extent of Si and Al dissolution have a significant correlation with the structure and consequently, with the properties of the resulted geopolymeric materials. Despite that the geopolymerisation chemistry and mechanism have not yet clearly understood, geopolymers have gained increasingly attention as viable alternative to conventional materials in numerous industrial areas. Their most important potential applications are the substitution of ceramic, cement and concrete products in construction industry, the fire protection of buildings and road tunnels, the management of toxic and radioactive wastes and the production of advanced composite materials for high technology applications into transportation, nuclear, pharmaceutical and aeronautic industrial areas. The main advantages of geopolymeric materials are their low production cost, the energy-effective production procedure and their environmental friendly character.

References

- [1] J. Davidovits in: "Geopolymer '99" Proc. of the 2nd International Conference (1999), p. 9.
- [2] J. Davidovits in: "Geopolymer '88" Proc. of the 1st International Conference (1988), p. 25.
- [3] V.F.F. Barbosa, K.J.D. Mackenzie and C. Thaumaturgo in: "Geopolymer '99", Proc. of the 2nd International Conference (1999), p. 65.
- [4] L. Weng, K. Sagoe-Crenstil, T. Brown and S. Song: Mater. Sci. and Eng. B, Vol. 117 (2005), p. 163.
- [5] J. W. Pair and J. S. J. van Deventer: Ind. Eng. Chem. Res. Vol. 41 (2002), p. 4242.
- [6] R. Cioffi, L. Maffucci and L. Santoro: Res. Cons. Rec. Vol. 40 (2003), p. 27.
- [7] H. Xu and J.S.J. van Deventer: Int. J. Miner. Proc. Vol. 59 (2000), p. 247.
- [8] H. Wang, H. Li and F. Yan: Colloids and Surfaces A: Physicochem. Eng. Aspects, Vol. 168 (2005), p. 1.
- [9] J. C. Swanepoel and C.A. Strydom: Appl. Geochem., Vol. 17 (2002), p. 1143.
- [10] H. C. Wu and P. Sun: Con. Build. Mater., Vol. 21 (2007), p. 211.
- [11] D. Papias, I. Giannopoulou and T. Perraki: Colloids and Surfaces A: Physicochem. Eng. Aspects, Vol. 301 (2007) p. 246.
- [12] J. G. S. van Jaarsveld, J. S. J. van Deventer, G. C. Lukey: Chem. Eng. J., Vol. 89 (2002), p. 63.
- [13] T. W. Cheng and J.P. Chiu: Miner. Eng., Vol. 16 (2003), p. 205-210.
- [14] J. G. S. van Jaarsveld, J. S. J. van Jaarsveld and L. Lorenzen: *Min. Eng.*, vol. 10 (1997), p. 659.
- [15] G. Kovalchuk, A. Fernandez-Jimenez, A. Palomo: Fuel, Vol. 86 (2007), p. 315.
- [16] D. Papias and I. Giannopoulou in: "AMIREG 2004", Proc. of the 1st International Conference on Advanced in Minerals Resources Management and Environmental Geotechnology, (2004), p. 407.