RAW MATERIALS FOR GEOPOLYMERISATION

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ABSTRACT

Geopolymers are inorganic alumina-silicate materials with excellent physical and chemical properties. Despite being a rather recent research topic, many papers and books have been published focusing on various aspects of geopolymerisation: the history, properties, production, raw materials, applications and development of geopolymers. A brief overview of geopolymer technology is presented in the article, emphasising the great variety of raw materials that can be used for geopolymer production. Considering the variety of the origin of these materials, three categories are distinguished: primary raw materials which consist of natural minerals, secondary raw materials which are industrial wastes and by-products, and wastes and by-products of natural origin. In spite of not being widely accepted by the industry yet, geopolymerisation has the potential to become a valuable waste-recycling technology in the future.

INTRODUCTION

Geopolymers are inorganic polymers created through the process of geopolymerisation. Geopolymer production involves chemical reactions between solid alumina-silicate oxides and alkali silicates under alkaline conditions at ambient or elevated temperatures – 30-100°C. The result of this reaction is a three dimensional amorphous to semi-crystalline polymer structure with Si^{4+} and Al^{3+} in IV-fold coordination with oxygen [1, 2, 3, 4].
Various materials with high silicon and aluminium content can be used for geopolymer production. The possible raw materials include natural minerals, calcined clays, industrial wastes and by-products, such as fly ash, slag, red mud or waste glass, or the mixture of these materials. The selection and preparation of raw materials determines the properties of the final geopolymer products. These characteristics may include good mechanical properties, high compressive strength, low shrinkage, low thermal conductivity and acid resistance [3, 5, 6, 7, 8].
Due to their numerous beneficial properties, there are many possible applications of geopolymers. Geopolymers can be used to immobilize and encapsulate hazardous elemental wastes within the geopolymeric matrix. They are suitable for the production of ceramics, adhesives, binders in the pre-cast industry, coatings and construction materials [1, 6].
Thus, the building industry is one of the main users of geopolymer technology in the form of geopolymer cement, a “green” cement alternative, and concrete. While the performance of these materials are comparable to ordinary Portland cement and OPC-based concrete, the production of both materials are cheaper and lessen

environmental impact because of their energy-efficiency and decreased CO_2 emission – by 95% in case of cement and 90% in case of concrete [9, 10, 11, 12].
The aim of the article is to provide a literature overview about geopolymers and geopolymerisation with special focus on the classification of the possible raw materials.

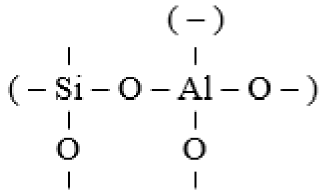
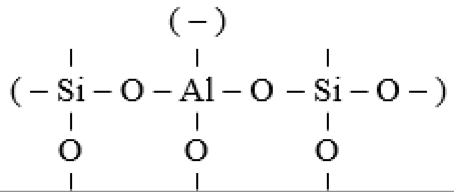
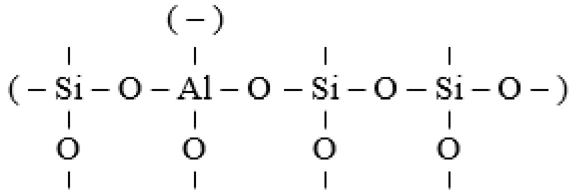
THE FUNDAMENTAL STRUCTURES OF GEOPOLYMERS

Geopolymers are produced by the reaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution. In order to describe geopolymers based on their chemical structure, the nomenclature poly(sialate) was suggested by Davidovits. Sialate is an abbreviation for silicon-oxo-aluminate whose network consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all the oxygens. The negative charge of the AlO_4 has to be balanced by alkali cations (typically Na^+ and/or K^+).

$$M_n(-(SiO_2)_z - AlO_2)_n \; wH_2O \qquad (1)$$

In the empirical formula (1) for poly(sialates), *M* stands for a cation that must be present in the structure to maintain electroneutrality, such as Na^+, K^+ or Ca^{++}, 'n' is the degree of polycondensation and 'z' is 1, 2, 3. The numbers represented by 'z' describe the Si/Al ratio, based on which three types can be distinguished: poly(sialate) with 1:1 Si/Al ratio, poly(sialate-siloxo) with 2:1 Si/Al ratio and poly(sialate-disiloxo) with 3:1 Si/Al ratio [1, 13]. The basic structures of the three types of poly(sialates) are represented in Table 1.

Table 1.
The three types of poly(sialates)

Poly(sialate)	
Poly(sialate-siloxo)	
Poly(sialate-disiloxo)	

Some limitations to the usage of these types, pointed out by Provis and van Deventer, reside in the theoretical aspect of Davidovits' system of nomenclature. As only integer Si/Al ratios are presumed and only one-dimensional description is provided to three-dimensional structures, the applicability of such classification is rather restricted [9].

CLASSIFICATION OF RAW MATERIALS FOR GEOPOLYMERISATION

Primary raw materials

Materials containing silica and alumina bearing phases are suitable for geopolymer production. The primary raw material sources are natural minerals. As more than 65% of the crust of the earth is made up of Al–Si materials, there is a large number and variety of useable resources [3, 14]. Thus, the geopolymerisation of various Al–Si minerals [3, 15, 16, 17] and clays, mostly kaolinite and metakaolin [18, 19, 20] has been examined during the past decades.

The thermal treatment of kaolinite at around 600–800°C, depending on the purity and crystallinity of the kaolinite, leads to the collapse of the original clay structure and the formation of metakaolin. The dihydroxylation of kaolin to metakaolin is represented in equation (2).

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \tag{2}$$

Using metakaolin as an aluminosilicate source provides a purer, more readily characterized starting material for geopolymerisation. Also, because of its consistent chemical composition and predictable properties, metakaolin-based geopolymers are widely used for both industrial and research purposes. On the negative side, metakaolin-based geopolymers require too much water and are too soft to be of much practical importance in construction applications [5, 18, 20, 21, 22].

However, the reactivity of kaolin can be improved not only with thermal but mechanical treatment, as well. By mechanical activation, that is prolonged grinding in case of kaolin, the crystallinity degree can be decreased, while the surface energy and hence the chemical reactivity can be increased. As greenhouse gases and air pollutants, such as CO_2, NO_x and SO_x gases, are produced during heat treatment, the mechanical treatment of kaolin with optimised parameters can be a suitable and valuable method for kaolin activation [18, 20, 21].

Secondary raw materials

In order to make the production of geopolymers more environmentally friendly and to preserve natural resources, industrial wastes and by-products can also be used as raw materials, including fly ash, blast furnace slag, red mud and waste glass. Among the secondary raw materials, fly ash and slag are the most widely used and examined materials. Secondary raw materials are inevitably heterogeneous and the inclusion of impurities, such as calcium and iron in fly ash and blast furnace slag, has the effect of adding reaction pathways during geopolymerisation. This can result in changes in the setting times, slump, strength and the shrinkage of the final product [2, 5, 6].

Fly ash is an industrial waste produced by coal-fired power plants. Its main constituents are SiO_2 and Al_2O_3 and some further minor components can be CaO, Fe_2O_3, MgO etc. Fly ash has become a material of interest for geopolymer synthesis because of its alumino–silicate content, low water demand, high workability and easy availability. For example, approximately 63 million tons of fly ash is produced in the USA and about 200 million m^3 fly ash and slag are produced in Hungary annually. Although it is available worldwide, its utilisation is rather limited. Thus, geopolymerisation can be an effective method to put this waste material to use [7, 8, 23, 25]. During geopolymer production not only the heterogeneous nature of the base material has to be taken into consideration but the low reactivity of fly ash as well. The reactivity of fly ash depends on its particle size distribution and the reactive SiO_2 and Al_2O_3 contents. Previous researches proved mechanical activation and addition of metakaolin or other wastes to be suitable methods to make fly ash an appropriate base material to produce geopolymers with high mechanical strength and enhanced durability [5, 6, 14, 24]. Figure 1 illustrates that beside the environmental benefits of these geopolymer-based building materials, they can be comparable to Portland-cement based materials not only in performance but in appearance as well.

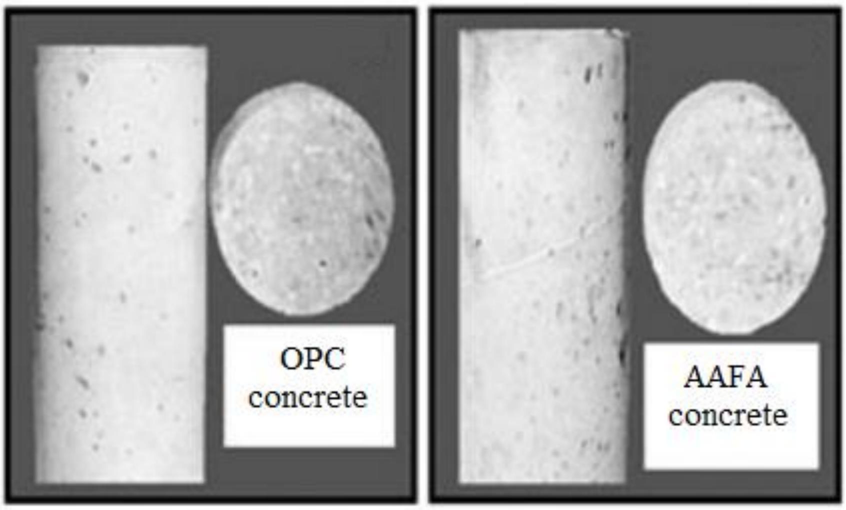


Figure 1.
Concrete samples from ordinary Portland cement and alkali-activated fly ash [26]

Blast furnace slag is a liquid by-product of iron making. After rapid cooling and grinding, a glassy, granular material with higher reactivity can be produced which is called granulated blast furnace slag (GBFS). GBFS consists of SiO_2, CaO, Al_2O_3 and MgO. Even though slags from particular blast furnaces are reasonably consistent in chemical and physical properties, slag compositions vary between specific furnaces and ores. Alkali-activated blast-furnace slags has been used as an alternative material for cement production for over 75 years and slags are often used as a component of geopolymeric systems, as well. As the reactions of slag are dominated by its small particles, the strength development of slag-based geopolymers can be controlled by careful control of particle size distribution. Furthermore, GBFS addition to other raw materials may also have beneficial effects on the strength development of geopolymers [5, 8, 25, 27].

As geopolymers are effective binders for the stabilization of toxic materials, the technology can be utilised to minimise the leaching of metals from another industrial waste, red mud. Red mud contains important constituents such as Al_2O_3, SiO_2 and caustic soda, that is sodium hydroxide, and it is produced during the extraction of alumina from bauxite ores. Due to its high alkalinity and the presence of alumina, it is suitable for geopolymer production. However, as reactive silica is absent from red mud, it is usually used in combination with other alumino-silicate materials, like metakaolin or fly ash. Beside reducing the damaging effects of the waste on the environment and human health, red mud geopolymers can be viable cementitious materials for roadway construction, as illustrated in Figure 2 [28, 29].

Figure 2.
Paving blocks made out of geopolymerised fly ash and red mud mixtures [28]

Wastes and by-products of mineral origin

As all kinds of aluminosilicates are suitable for geopolymer production, some of the possible raw materials, which had been already examined by various authors, cannot be classified as neither natural minerals nor industrial wastes or by-products. Such materials are of natural origin but arise as wastes during manufacturing processes.

Perlite is an amorphous volcanic glass rich in SiO_2 and Al_2O_3 which also contains some crystalline phases. After size reduction and heating to create a porous product, it is used as a water absorbent in agricultural applications. The perlite whose particle size or final porosity is not adequate for further utilisation, for example it is extremely fine, is considered waste. Geopolymerised perlite waste can be used by itself to produce good thermal insulating materials or in conjunction with fly ash or other waste aluminosilicates for the production of construction materials and the immobilisation of hazardous wastes [30, 31, 32, 33, 34].

SUMMARY

Some of the most important information on geopolymers and geopolymerisation are summarised in the article, focusing on the classification of the usable raw materials. Having many advantageous properties and environmental benefits, i.e. being a prosperous technology for waste management, the further examination and utilisation of geopolymers seems inevitable in order to guarantee sustainable development in the future.

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