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Geopolymers—Base Materials and Properties of Green Structural Materials †

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Abstract: Nowadays, most industrial solid waste, agriculture waste, and natural minerals are piled up, which not only occupies land resources, but also has a dangerous impact on the environment. The responsible management and recycling of these materials can have significant environmental benefits, while also providing a means of accessing raw materials for the creation of geopolymers. Geopolymers are new, environment-friendly, cementless materials and alternative construction materials to ordinary Portland cement. They not only have excellent mechanical properties, but also have valuable properties, e.g., high-temperature resistance. This paper summarizes the feasibility studies in terms of base materials and properties of today's developing geopolymers. This paper also highlights the significance of developing sustainable materials for civil engineering.

Keywords: geopolymers; precursors; activator solutions; environment

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1. Introduction

Geopolymer composites are a "green" alternative to traditional cementitious materials. It is estimated that the production of geopolymers creates four to eight times less carbon dioxide than cement production [1]. The process requires twice less energy compared to the manufacture of Portland cement [1]. It seems that geopolymers have low emissions of CO_2, SO_2, and NO_X. In spite of the mechanical resemblances, the chemical and morphological differences in this material create challenges when comparing it to ordinary Portland cement (OPC), particularly in light of the current standards.

The term "geopolymers", concerning aluminosilicate binders, was introduced in the late 1970s, and developed by the French scientist and engineering prof. Joseph Davidovits in 1978 [2]. Geopolymers are inorganic [3] and belong to the family of alkali-activated materials, which, unlike cementitious materials, require alkalis to harden. They are also amorphous aluminosilicate materials with three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra that can be produced via alkali activation even at low temperatures (20 and 120 °C, according to Davidovits [1]) and at low pressure. Geopolymers are synthesized via geopolymerization. The mineral raw materials dissolve in the alkaline environment at room temperature or higher. As a result, an amorphous phase and three-dimensional aluminosilicate structure are formed. The mechanisms of geopolymerization are not fully understood at present, but most hold that the geopolymer binding process can be presented in three main stages [4–8]:

- The dissolution of the aluminosilicate precursors to form reactive particles $Si(OH)_4$ and $Al(OH)^{4-}$.
- Restructuring and modification of aluminosilicate structures to a more stable state. The hydrolysis process leads to the release of water from the structure at this stage.

- Gelation/Polycondensation: Polymerization and precipitation of the system, i.e., the formation of a three-dimensional network of silico-aluminate that forms a geopolymer.

The production of a hard geopolymer involves mixing aluminosilicate powder that meets specific requirements for particle size distribution and specific surface area with an alkali solution (such as NaOH, KOH, or waterglass), resulting in the formation of a gel-like substance that solidifies quickly [9–11]. This alkali-activated material boasts exceptional physical, chemical, and mechanical properties, including low density, micro- and nano-porosity, high mechanical strength, thermal stability, fire resistance, and chemical resistance. Geopolymer materials allow non-polluting production and do not emit toxic gases or fumes. They can be reinforced, for example with carbon fibers, which provide excellent adhesive properties to the reinforcement.

2. Base Materials of Geopolymers

2.1. Mineral Precursors

As a geopolymer precursor, any aluminosilicate that is able to dissolve in an alkaline solution is suitable. There is a wide range of reactive products that can be used, including calcined or non-calcined clays [12], industrial or agricultural by-products [13] and artificial pozzolans [14]. However, the choice of raw material may depend on several factors, including availability, cost, and type of application. The raw materials may be distinguished as primary and secondary raw materials.

2.1.1. Primary Raw Materials

According to the literature, Geopolymer production can be achieved using raw materials with high silica and alumina content. The main sources of primary raw materials are natural minerals. [15].

➢ *Clay and clay minerals*

Through thermal treatments, clay can be transformed into various clay minerals. As an aluminosilicate salt consisting of tiny particles (less than 2 μm), clay is a pliant and cohesive earthen material [16]. It is a layered silicate that is composed of alternating silicon–oxygen tetrahedrons and alumina octahedrons, and it is an appropriate precursor for preparing geopolymers [16].

➢ *Metakaolin*

Metakaolin (MK) is a type of clay mineral known as kaolinite that has been dehydroxylated. Kaolinite is a soft, fine, white clay that exhibits excellent plasticity and fire resistance. When kaolinite is subjected to thermal treatment, typically at a temperature range of 600–800 °C, the original structure of the clay is destroyed, leading to the formation of metakaolin. This new substance is an anhydrous aluminum silicate [16]. Metakaolin is a commonly used aluminosilicate source for geopolymerization due to its purity and predictable properties. This material provides a consistent chemical composition, which makes it a preferred starting material for geopolymer research [15]. Despite its benefits, metakaolin-based geopolymers have some drawbacks, such as the need for high amounts of water and sometimes low mechanical strength, which limit their application areas [15]. As a result, the geopolymerization of various Al–Si minerals and clays, particularly kaolinite and metakaolin, has been extensively studied over the past few decades.

2.1.2. Secondary Raw Materials

Within the framework of reducing environmental impact via alternative waste management, the production of geopolymers can be envisaged using industrial and agricultural wastes as raw materials, as follows.

➢ *Fly Ash*

Coal-fired power plants generate fly ash (FA) as a byproduct, which is considered an industrial waste (Figure 1). Its main components are SiO_2 and Al_2O_3, but it can contain small components such as CaO, Fe_2O_3, MgO, etc. However, the composition of these components in this waste material is significantly variable, especially depending on the coal source and burning conditions. FA is generally divided into classes F (FFA) and C (CFF). FFA is a low calcium fly ash and is a by-product of burning bituminous coal; FFC is a high calcium fly ash and is produced by burning lignite and sub-bituminous coal [17]. Geopolymer synthesis can benefit from the unique characteristics of FA, such as its alumina-silicate composition, ability to function with minimal water, high malleability, and widespread availability. Notably, in the United States alone, an estimated 63 million tons of FA are produced annually, and Hungary generates approximately 200 million m^3 of fly ash and slag each year [15].

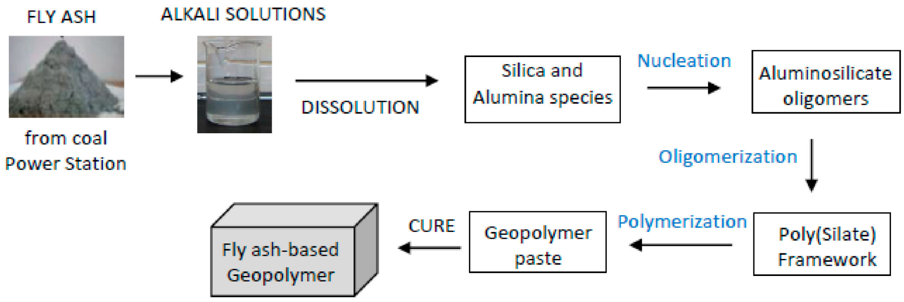

Figure 1. The transformation process of fly ash into a binder for geopolymer materials [10,11].

➢ *Granulated Blast Furnace Slag (GBFS)*

Blast furnace slag (BFS) is a by-product of iron making and is often referred to as slag. It can be obtained at approximately 1500 °C [18]. Following rapid cooling and grinding processes, a granular substance known as granulated blast furnace slag (GBFS) can be formed. This raw material (GBFS) contains S_iO_2, Al_2O_3, CaO, and MgO. GBFS is one of the common geopolymer raw materials, given its strong reactivity towards geopolymer synthesis. Additionally, it is possible to achieve an optimal reaction rate using GBFS at temperatures as low as 0 °C [19]. GBFS is known as a raw material which can reduce porosity. GBFS in geopolymer can improve reactivity of the mix, enhance mineral structure, rise long-term strength and increase resistance to sulfate. It also reduces the water demand, permeability, and hydration heat of a geopolymer.

➢ *Red Mud*

Red Mud (RD) is a by-product of processing bauxite into alumina using the Bayer process. The Bayer process dissolves the soluble part of bauxite using sodium hydroxide under high-temperature and high-pressure conditions. However, a small amount of sodium hydroxide remains in the RD after the Bayer process and allows it to have a high pH value (over 12) [20]. RD contains generally solid and metallic oxides, especially Fe_2O_3, Al_2O_3, S_iO_2, Cao, Na_2O, and TiO_2. The red color of RD comes from iron oxides, which represent more than 60% of red mud mass [21].

➢ *Rice Husk*

Fillers known as rice husk ash (RHA) are obtained by calcining rice husks, which are often considered a form of agricultural waste and a potential environmental hazard. During calcination, most rice husks components disappear, and generally an amorphous silicate remains. Research has shown that every 100 kg of husks burnt in a boiler yields approximately 25 kg of RHA [22]. The temperature of calcination must not exceed 600 °C to obtain reactive pozzolanic ashes and to avoid the risk of forming less reactive crystalline silicas. Well-burnt RHA contains 90% amorphous silica, 5% carbon and 2% K_2O [22]. However, the chemical composition of RHA depends on combustion conditions. RHA is a small, fine material; its particle size ranges from 3 to 75 μm [22]. RHA is greyish-black in color because of unburned carbon.

Some other raw materials, such as steel slag (STS), silica fume (SF), volcanic ash (VA), waste glass (WG), coal gangue (CG), high magnesium nickel slag (HMNS), etc., can be used in synthetic geopolymers because of their abundant silicate and aluminum elements and amorphous structures [16].

A variety of structures based on geopolymers can be manufactured using different precursors. For example, previous research has shown that the mechanical strength and durability of geopolymer materials based on FA can be improved by the addition of metakaolin or other wastes [15]. Geopolymer-based elements can exhibit superior properties and greater durability when compared to structures formed using interconnected Portland cement. Additionally, the microstructure of geopolymer materials is influenced by the composition of the amorphous phase, the content of oxides, and especially, the particle fineness [23].

2.2. Activator Solutions

In the geopolymerization process, the activating solution plays a fundamental role. Depending on its quantity and concentration, it will provide the necessary mixture that not only initiates the reaction, but also determines the ultimate structure of the solidified material. For geopolymerization to occur, the presence of strongly alkaline activators is essential in the solution. Indeed, they accelerate the dissolution of the aluminosilicate source, favoring the formation of stable hydrates with low solubility and the formation of a compact structure with these hydrates. The physical and chemical properties of the activating solutions play an important role in the behavior of the activated material.

2.2.1. Alkali Activators

Numerous studies have demonstrated that the activation of geopolymer materials is achieved through the use of alkali activators. Alkalinity, resistance to chemical attacks, strength development, and durability are all dependent on the type of Alkali activator used. Additionally, the selection of suitable activator solutions is based on the chemical composition and the source of raw materials. Typically, the activation of alkali materials involves the use of sodium- or potassium-based activators (e.g., hydroxides, such as NaOH and KOH), sodium- and potassium-based silicate solutions, and carbonates. Each of these activators has distinct advantages, with sodium- and potassium-based activators being the most commonly used due to their cost-effectiveness and widespread availability. Prior investigations have revealed that, in the case of FA, sodium-based activators exhibit greater activation efficiency than their potassium-based counterparts [24], despite the higher alkalinity in potassium-based solutions [25]. To produce a metakaolin-based geopolymer, sodium waterglass has been used as an activator; the research has shown a compressive strength reaching 63.8 MPa [26].

In addition to conventional activators, ash generated from the incineration of solid waste and organic material can be employed as activators. Moreover, ash sourced from olive oil biomass can serve as an alkali activator for GBFS-based geopolymer production. [16].

2.2.2. Acidic Activators

Although Alkali activators are the most commonly used means of activation in geopolymers, some compositions rely on the use of acidic activators. For instance, MK-based geopolymer has exhibited remarkable compressive strength, up to 93.8 MPa, via the implementation of phosphoric acid as an activator [26,27]. Moreover, research has indicated that acid-based geopolymers possess higher temperature resistance (up to 1450 °C) and superior mechanical properties than alkali-based geopolymers [28]. In addition, recent studies suggest that an innovative phosphoric acid-based geopolymer could function as a dependable and robust fire or heat insulator, as it has a conductivity of no more than 10^{-7} S/cm at elevated temperatures [29].

3. Properties of Geopolymers

Geopolymers are known for their exceptional fire resistance up to 1400 °C, as well as their resistance to heat and acid [30]. These materials have high early compressive strength, excellent fracture toughness, long-term durability, low apparent porosity or nano-porosity, and freeze-thaw resistance. Geopolymer composites and concrete present similar mechanical properties to OPC-based materials, or better [31]. Its Mohs hardness ranges from four to seven [30].

One of the important properties of geopolymer binders is that they can be use to immobilization toxic waste [32]. Geopolymer materials have been observed to exhibit zeolitic and feldspathoid-like behavior, which allows them to immobilize hazardous elemental wastes within their matrix. This property makes them an effective binder for converting semi-solid waste into solid adhesive materials. [32]. Moreover, geopolymers have excellent workability because of the particle shape of raw materials, which allows their fluent production [16]. Previous studies have indicated that the addition of certain materials can enhance the workability of geopolymers. For example, the inclusion of silicon powder, calcium carbonate, or specific amounts of superplasticizer have been shown to improve their workability [16].

Furthermore, a high slag content in geopolymer mixtures can accelerate the initial and final setting time. A decrease in the molar concentration of NaOH can extend the setting time of FA-based geopolymer. [16].

Geopolymers can be strengthened using various types of material, such as carbon, glass, minerals, or steel, which can be used to produce advanced composite materials with improved mechanical properties, such as flexure, tension, shear, and flexural fatigue, particularly at high temperatures. This is due to the excellent adhesive properties of geopolymer binders, making them an attractive option for reinforcement [16].

4. Conclusions

In this study, the ways geopolymer composites are designed and developed were summarized. According to the state-of-the-art, the following conclusions can be drawn:

- Many mineral raw materials can be used in geopolymer technology.
- Especially interesting is the possibility of using waste materials from the industrial, energy, and mining sectors in the geopolymer synthesis process. This solution allows the reduction of the carbon footprint of the geopolymer composite, which makes the geopolymer material more environmentally friendly.
- The most optimal solution is to use locally available waste materials. In this way, it is possible to reduce both the financial and environmental costs of producing geopolymer materials.
- The properties of geopolymer composites indicate that such materials can be an alternative to cement-based materials in some applications (Figure 2).

Geopolymers are a promising, eco-friendly alternative to ordinary Portland cement (OPC). The production of geopolymer binders is associated with lower carbon dioxide emissions compared to the production of Portland cement. [30]. Industrial solid waste and waste incineration bottom ash are commonly piled up, taking up valuable land resources and posing environmental risks. However, these wastes can be recycled and used as raw materials for geopolymer production, which presents significant potential. The possibility of using geopolymer materials as an alternative to OPC binder allows to reduce the consumption of cement, which production is associated with high CO_2 emissions.

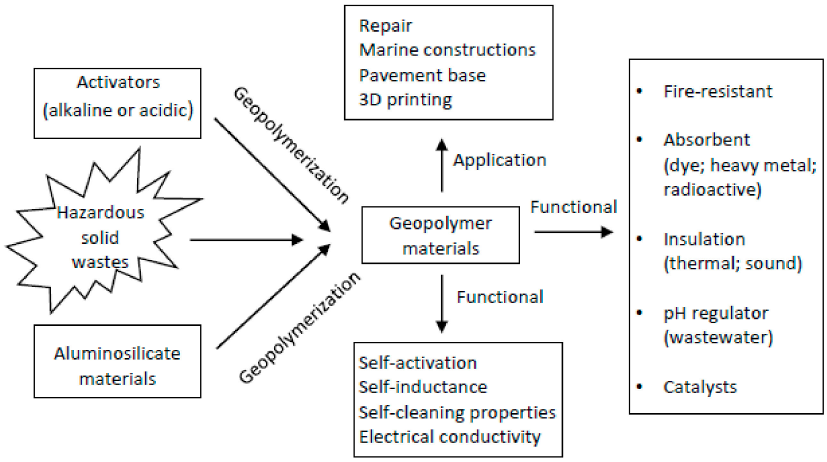

Figure 2. Geopolymerization process and geopolymers applications [16].

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