

THE POSSIBILITY OF USING WASTE MATERIALS AS RAW MATERIALS FOR THE PRODUCTION OF GEOPOLYMERS

Beata Figiela

Institute of Material Engineering, Faculty of Material Engineering and Physics
Cracow University of Technology, Jana Pawła II 37, 31-864 Cracow, Poland, beata.figiela@pk.edu.pl

 <https://orcid.org/0000-0001-5493-0914>

Kinga Korniejenko

Institute of Material Engineering, Faculty of Material Engineering and Physics
Cracow University of Technology, Jana Pawła II 37, 31-864 Cracow, Poland, kinga.korniejenko@pk.edu.pl

 <https://orcid.org/0000-0002-8265-3982>

Abstract

This article shows the possibility of using industrial and mining waste for creating new eco-friendly materials – geopolymers. The main objective of the article is to analyze the possibilities of using new composite received from waste materials from mining industry in practical applications, especially in construction industry. The article presents benefits and potential threats for using wastes for production of geopolymers from gangue, waste from iron processing, waste from copper mining and processing, waste from chromium processing and so-called red mud from aluminum production. Research methods applied in the article are: critical analysis of literature sources, including comparison new material with other materials used in similar applications.

Keywords

geopolymer; mining waste; environmental protection; mine tailing

Introduction

The European Union's policy regarding the production and use of waste from all walks of life aims to reduce its impact on the environment and health. As Eurostat data shows, waste from mining and extraction of minerals is second in the European Union and represents 25.3% of waste generated by the economy [1]. According to the Polish Geological Institute in Poland, this waste constitutes about 55% [2]. The mining industry in Poland and the European Union generates a large percentage of waste that is not properly managed. Identifying new possibilities for their application is an important and current topic of research around the world. Estimates say that only 55.2% of the generated carbon combustion residues are reused, largely by the cement and mining industries, however, these solutions do not use all the waste generated, therefore there is still a need for solutions to remove carbon residues that are also friendly the environment [3].

Limiting the consumption of mineral and natural resources in the world for building materials leads to the search for alternative solutions of the main sources of raw materials. The reuse of industrial waste is just such a strategy. Research is carried out with different types of waste, among others bottom ash and marble powder, which are used in red clay mixtures for the production of ceramic materials. The addition of marble residue allowed to observe a decrease in mechanical properties and an increase in porosity. In turn, the addition of bottom ash did not affect the mechanical properties, while it improved the porous properties, compared to traditional samples [3].

Alkali-activated materials e.g. waste sludge from tungsten mining. They are used in research to replace Portland cement and potentially thermal insulation materials. They reduce CO₂ emissions and thus global warming. Reuse of some mineral wastes using the alkaline activation process technology is done by mixing precursors, i.e. mineral wastes, with alkaline solutions. Research on this material as an alkali-activated binder proves that, in combination with red clay waste or polished blast furnace slag, compressive strength and critical pore size are reduced. In the second case, the tests are carried out with aluminum powder as a foaming agent [4].

Data from the United Nations Food and Agriculture Organization show that around 700 million tons of rice are harvested worldwide every year. Residues in the form of rice husk are burned to generate electricity and reduce waste [5]. Rice husk is a hard protective cover for grain, its components are: cellulose (50%), lignin (25% -30%),

silica (15%-20%), water (10% - 15%). Combustion under controlled conditions removes cellulose and lignin and leads to the formation of ash, which consists of amorphous silica with a cell structure [6]. Rice husk ash (RHA) is used in construction as a partial replacement for cement and such use requires its specific properties. Cement substitution improves concrete strength from 1-3 days of maturing, and ensures the availability of concrete in developing countries, thanks to low ash costs [6].

The American manufacturer Goodyear Tire and Rubber Company specializing in the automotive industry, mainly in the production of tires and rubbers, is conducting tests on the production of tires from silica obtained from rice husk ash. This application provides an alternative source of silica and is environmentally friendly [7].

The term "geopolymers" was proposed by the French scientist Davidovits, who discovered that the strength of ancient concrete is due to the presence of alkaline aluminosilicates in the structure. The aluminosilicate cement has high mechanical strength [8].

Geopolymers are inorganic polymers produced at low temperatures not exceeding 100 °C [9], resulting from the synthesis of silicon and aluminum and obtained geologically from minerals. They can be produced on the basis of both natural raw materials and waste materials [10]. Metakaolin is the most commonly used material for the synthesis of geopolymers. Its main advantage is the constant and repeatable composition, while the disadvantage is that it is very expensive, which limits the development of geopolymers [11]. Slags and ashes are the second most commonly used raw material in the production of geopolymer materials. Slags are used both as a basic raw material for synthesis and as an addition to other raw materials [12]. The production of geopolymers based on rice husk ashes or palm oil [12] is less popular. These ashes come from burning products of plant origin. They are rich in silicon, but poor in aluminum, which is why they usually require the use of additives for the synthesis process [13].

Minerals used in the synthesis of geopolymers also include materials of volcanic origin, in particular volcanic tuffs. Tuffs are pyroclastic rocks that were formed by cementing various material fractions with clay or silica binder [14].

Methods

The aim of the article is to show the possibilities of using waste materials from the mining industry as structural elements made of geopolymer materials. The research method used in the article is a critical analysis of literature sources. Examples from world literature are analyzed showing the possibilities of using mining waste, in particular from the extraction of hard coal and metal ores, as well as from the processing of mineral resources as a material for the production of environmentally friendly composites.

Literature databases such as ScienceDirect, ResearchGate and Google Scholar were used for the analysis. The review was based on the search for articles based on the terms gangue, waste from the mining industry, i.e. iron ore, copper ore, chromite ore and red mud in combination with the term geopolymer.

Results and discussion

Coal gangue

Coal gangue is a byproduct of hard coal mining around the world. It is a material whose quantity increases rapidly with energy consumption. In China, annual coal production is over 70 million tons, which gives over 500 million tons of deposited gangue [15]. Its use is used to a small extent, namely for the production of aggregates, reclamation of degraded areas, as a component of energy mixtures for combustion processes [16]. The main components of gangue associated with coal mining are illite, quartz and kaolinite, which contain a large amount of silicon oxide and aluminum oxide. Their chemical composition makes them potentially a good raw material in the process of alkaline activation [17]. In order to improve the reactivity of gangue to be used as a cement substitute, its activation is needed due to the relatively stable chemical structure. The main activation methods: thermal, mechanical, microwave and compound activation are studied in detail for gangue interaction. It is possible to use only one of these processes for material activation, however, optimal properties are obtained by mechanical activation - milling (fine particles show higher reactivity) and thermal activation in the calcining process [17]. Noteworthy is the fact that the best material properties are characterized by gangue-based components that have a high content of amorphous aluminosilicate [18]. The next important elements are the content of aluminum and active silicon, i.e. reactive components [19].

Research on the use of gangue for the production of geopolymers was carried out in Chinese centers on samples where it was used as an addition to blast furnace slag, slaked lime and gangue itself as the basic raw material [11]. Sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) were used for the alkaline activation process [19]. The lowest strength properties were obtained by samples based on the gangue alone. Samples reached 20.19 MPa after 28 days and 2331 MPa after 60 days. These values are significantly lower than in the case of Portland cement, which strength after 28 days is about 42.5 MPa, but they are comparable with lower grade concretes [19].

Materials with the addition of blast furnace slag had higher mechanical properties than the materials from the first group [19]. The best results were obtained for 40% and 50% of the slag addition, obtaining values of 40.18 MPa after 28 days and 43.22 after 60 days for samples with 40% slag content [19]. The obtained properties are comparable to the mechanical strength of Portland cement. A third group of samples was prepared based on 60% gangue and 40% slag compositions [19]. Slaked lime was added to the mixture in these proportions as 2,5-20% by weight of the composition. In this case, the compressive strength was: 60.24 MPa after 28 days and 63.38 MPa after 60 days. These values significantly exceed the properties obtained for Portland cement and give wide possibilities of using the new material. Phases specific to structural concrete are obtained for this kind of samples, not geopolymers [19].

Researchers are also investigating the impact of gangue activation on the properties of geopolymers based on it. The macromechanical and microstructural changes of geopolymers based on gangue rock, activated by mechanical and thermal methods were examined. The effects that have been observed in the case of thermal activation show that the optimal temperature is 800 °C and then the structure of active metakaolinite is formed and the value of uniaxial compressive strength of geopolymers is the highest. At a temperature of 900°C, this structure is destroyed, which is unfavorable for geopolymerization and thus reduces compressive strength. Activation of gangue at 700 °C showed similar conclusions [20].

Research on gangue is carried out mainly in China and focuses on its use as a material for structural use [21]. Mechanical properties and durability of building materials based on gangue are important. Already a small addition as a cement substitute, in the amount of 10% -20% by weight, becomes a sustainable and ecological approach [15].

Iron ore waste

Research on the use of iron ore waste (IOT) for the production of geopolymer materials, among others, is carried out with pure waste and in mixtures with glass wool residues replacing 10%, 20%, 30% by mass of iron ore waste. Compression and bending strength tests were conducted after 7 days on prismatic samples. Compressive values above 100 MPa and 20 MPa bending strength were achieved [22]. Iron ore wastes require pre-treatment in several stages because they contain elements harmful to health. As a rule, this raw material in the geopolymer production process is combined with other materials, e.g. fly ash [23].

India has been among the largest raw steel producers on the world market since 2017. The large development of this country causes an increase in the steel and iron industry, which is also associated with an increase in the production of waste from this extraction. Research was conducted on the use of iron ore waste from two different mines to produce geopolymer materials [24].

The first waste material was from the Bellary mining area (BMM Ispat). The first mixture with BMM mine waste was prepared with the addition of blast furnace slag (GGBS) and slaked lime. The iron ore waste was mixed in an amount of 30-50% with blast furnace slag in an amount of 25-45%, so that the total for each composition was 75%. Lime was added in a constant amount of 5%, as was the concentration of sodium silicate solution as 20%. The resulting paste was made of 230x115x75 mm brick. It was observed that at increased iron ore content, compressive strength increased [24]. A second mix was prepared with iron ore waste, fly ash, slag sand (admixed with blast furnace slag and other aluminosilicate compounds from Jindal Steel LTD., Karnataka in India), blast furnace slag and sodium silicate solution. It has been observed that the increase in iron ore waste worsens the compressive strength. The best strength values were obtained for 20% IOT, 15% GGBS, 15% fly ash, and 40% slag sand samples [24].

Copper ore waste

Research on the use of copper ore waste is conducted on materials from various regions of the world. Scientists

are conducting research on the production of ecological bricks that are formed in the process of geopolymerization. The production of these materials is based on mixing an alkaline solution with copper ore waste, then forming the resulting mass by pressing under a certain pressure in a mold at a slightly elevated temperature. The tests cover physical and mechanical properties by means of water absorption and compression tests, microstructure testing on a scanning electron microscope and X-ray diffraction analysis. The obtained results show that this waste can be used as materials for the production of geopolymers [25].

The development of new technologies affects the search for alternative experimental solutions for geopolymer binder. Research is conducted not only in relation to building materials but also materials used in road construction. The literature gives examples of tests of copper ore waste mixtures and low calcium slag. Research is often based on the influence of the content of individual components and the development of mechanical properties. An experimental study was carried out on a geopolymer binder based on copper mine waste, low calcium slag and sodium silicate solution. Variable values of individual components and solution concentration allowed to obtain the highest compressive strength 23.5 MPa, for 50% blast furnace slag, 10 molar NaOH concentration and curing at 60 °C for seven days. These studies allow further development of the use of copper ore waste as a geopolymer binder [26].

Chromite ore

Chromite ore is industrial waste produced during the production of chromium salts. Due to leaching, Cr (VI) is considered toxic and very dangerous. Further processing of this material involves the neutralization and protection of Cr in the ore. Despite this, scientists are attempting to use this waste in the production of geopolymers, which is associated with the neutralization of chromite ore. This is done on the basis of blast furnace slag, obtaining material that can potentially be used construction [27].

Literature analysis has shown an example of waste testing for use in the production of geopolymers, carried out with sodium sulfate and a geopolymer based on metakaolin, which may dispose of the residue after processing. Concentrated Cr leaching from the resulting samples was used, followed by X-ray / dispersion X-ray (SEM / EDX) scanning spectroscopy and X-ray photoelectron spectroscopy (XPS), which showed a reduction of CR (VI) to CR (III). The compressive strength of the obtained samples was higher than 42 MPa [28].

Another example of the study is an attempt to neutralize waste from chromite ore using composite materials, namely fly ash, blast furnace slag and metakaolin, based on a geopolymer correlated with zero-valent iron. X-ray diffraction studies and observations on a scanning electron microscope with an energy dispersion spectrometer showed effective immobilization of the chromite ore [29].

Red mud from aluminum production

This material is becoming a big problem for the environment and the degree of its use is negligible. In the production of 1 ton of aluminum, about 2 tons of red mud is generated [30]. It has a complex chemical composition, among which you can mention: iron, aluminum, silicon, calcium, sodium with the highest concentrations.

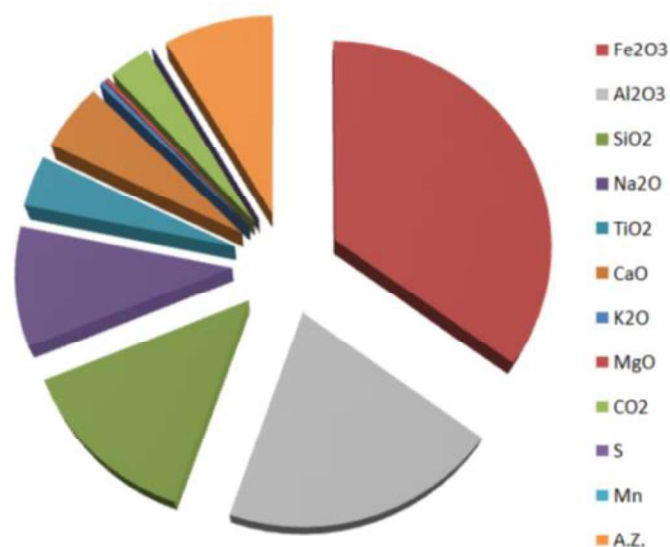


Fig. 2. Red mud chemical composition. Source: [30].

One of the modern applications of red sludge is its implementation as a raw material for the production of geopolymer cements [31]. An additional advantage of this waste is the fact that it is many times cheaper than e.g. metakaolin [11]. Research on the use of this material for the production of geopolymers mainly concerns its combination with other components, i.e. fly ash [32] or slag [33], as well as gangue from hard coal mining [11] [34], although it is possible to make geopolymer cement from red mud only. The production of alkali-activated material takes place with a pre-treatment process followed by activation, which is possible both through thermal activation - calcination and mechanical activation - grinding the raw material. Both processes are characterized by energy consumption, resulting in increased costs and a negative impact on the environment [33] [34]. After adding fly ash, the geopolymer prepared with the use of gangue, red mud with a sodium silicate solution can achieve a compressive strength of 7.3 MPa [35].

The compressive strength of geopolymers based on waste materials are summarized in Table 1.

Table 1. Compressive strength of geopolymers based on waste materials.

Kind of waste	Compressive strength [MPa]	Source
Coal gangue, sodium silicate	20.19	[18]
60% coal gangue, 40% blast furnace slag, sodium silicate	40.18	[18]
60% coal gangue, 40% blast furnace slag, 2,5-20% slaked lime, sodium silicate	60.24	[18]
Iron ore waste, glass wool	>100	[22]
30-50% iron ore waste, 25-45% blast furnace slag, 5% slaked lime, sodium silicate	N/A	[24]
Iron ore waste, fly ash, slag sand, blast furnace slag, sodium silicate	N/A	[24]
Copper ore waste, slag with calcium content, sodium silicate	23.5	[26]
Chromite ore, metakaolin, sodium sulfate	>42	[28]
Chromite ore, fly ash, blast furnace slag, metakaolin	N/A	[29]
Red mud, coal gangue, fly ash, sodium silicate	7.3	[35]

The best properties from the given measurable values are characterized by geopolymers based on iron ore with glass wool, which achieve the required compressive forces above 100 MPa. A set of high temperature properties of marked materials in which the composition includes gangue with slag and lime dependence - 60.24 MPa, or gangue with 40.18 slag alone. The lowest available number of samples from the last group of commonly discussed and nominated sludge, gangue, fly ash - 7.3 MPa.

There are many advantages for which it is worth becoming interested in the topic of replacing traditional natural materials with mining waste. The table shows both the pros and cons of using these raw materials

Table 2. Advantages and disadvantages of using waste materials for the production of geopolymers.

Advantages	Disadvantages
Reducing the amount of waste in landfills [16]	Coal gangue requires proper activation [17]
Saving natural resources [3]	Several-stage pre-treatment of iron ore waste required due to the content of elements harmful to health [23]
Availability of raw materials and their lower cost [12]	The use of chromite ore before application involves the neutralization and protection of Cr in the ore [27]
Binding of heavy metal elements [23, 27]	The use of red sludge is energy intensive and expensive due to pre-treatment processes and alkali activation [34]
Elimination of the risk to the soil and water environment [16]	The properties of the obtained material depend on the base material

The research on the use of waste materials as raw materials for the production of geopolymers presented in this article requires large financial contributions for further development and adaptation to the regional conditions of individual countries. The search for appropriate technologies and implementation to domestic markets is associated with the strengthening of cooperation between research and development centers and enterprises from the industrial sector. Undoubtedly, the advantages that may encourage the implementation of such projects are the measurable benefits for the environment, as well as the implementation of innovations, which may become the main factor of competitiveness on the economic market. Preparation and application of a technological solution requires a number of requirements specified by the legal regulations of a given country. Hence, the strategy of managing the technological process and favorable system conditions (regulations and legal acts) is important. From the point of view of implementing the selected solution, it is important to choose the right raw material, because the properties of the final product are strongly dependent on the chemical stability and appropriately used additives. The analysis of the economic sector and the demand will allow to assess the choice of the market (local, national, international), where, when exporting items, the determinant will be transport costs and the so-called "Carbon footprint".

Geopolymerization process with the use of waste materials is a method of neutralizing hazardous substances in post-process materials. This allows for economic and ecological efficiency at the same time. On the one hand, the obtained product can replace traditional Portland cement, and on the other hand, it can be used to secure landfills [36].

Geopolymers based on waste materials can be used in the production of heat-resistant materials, thermal insulation, protective coatings for industrial pipelines and chimneys, or load-bearing materials for the stabilization of toxic waste [37] [38]. The increasing technological progress in the use of these raw materials will allow for the development of more and more modern courses for their management, which over time becomes a necessity [39].

Impact

The dynamic development of the construction, mining and processing market forces the search for new solutions and technologies to combine these areas in the field of the circular economy. Sustainability and circular economy policy are main factor for the development of sustainable construction materials for decreasing environmental impact of construction industry. They are also main motivators to research works on new, innovative materials' solutions for replacement traditional Portland cement technology [40]. Contemporary, the technology of Portland cement is widely used, but it has many disadvantages such as [41] [42]:

- energy- and non-renewable natural resource-intensity
- intolerable volume of CO₂ emissions
- and questionable durability.

Geopolymerization seems to be most promise alternative solutions are traditional technologies used in cement industry [40]. The processes of pretreatment, alkaline activation and heat curing influence the total GHG emissions in the production of geopolymers. However, this area is still under investigation and depends on the location of the experiments carried out. Research is also carried out in terms of the optimization of greenhouse gas emissions, costs, availability and strength properties, so that the solutions found are sustainable in their use in terms of economy, environment and durability. The data that were obtained and which compare the CO₂ emissions in the production of Portland cement with the production of geopolymer cement show that the production of 1 ton of geopolymer material emits 0.184 tons of CO₂ from the combustion of coal fuel, compared to 1 ton of CO₂ for Portland cement. [43]. These technologies have much lower carbon footprint than traditional construction materials. It is estimated that the manufacturing of geopolymers produced 6 times less CO₂ than Portland cement [44].

The challenge in the production of geopolymers is the replacement of natural resources (metakaolin, slag, fly ash from coal combustion, volcanic tuff), mining waste and thus their management going hand in hand with environmental protection. From an economic point of view, the replacement of the above materials leads to the development of geopolymers due to cheaper waste raw materials. Geopolymerization is also an exciting technology that allows the use of different wastes streams (hazardous and non-hazardous) in geopolymer production [27] [34]. The presented article presents the possibilities of using waste materials from hard coal and metal ores mining, as well as from the process of processing mineral resources as a material for the production

of environmentally friendly composites. The growing importance of sustainable development of materials intended for buildings with low environmental impact and greater environmental awareness are the main determinants mobilizing research on the use of recyclable materials [45].

Nowadays, the replacement of metakaolin and fly ash by waste materials are important factor for possibilities geopolymer implementation. The high quality fly ash, especially class F, become valuable raw material for concrete industry. Because of that the process of this by product become higher and higher. There is a need investigation the new raw materials for that purpose. Moreover, this kind of approach is in line with the Strategic Implementation Plan of the European Innovation Partnership on Raw Materials [46], especially by ensuring the sustainable supply of raw materials to the European economy whilst increasing benefits for society as a whole. The additional value for this approach is to change the way of thinking about these waste materials and, by recycling, those complex products that contain many valuable raw materials create a more sustainable future. Through the use of waste and by-products the geopolymers could help reducing import dependency by improving supply conditions from EU, especially diversifying raw materials sourcing and improving resource efficiency (including recycling) and finding alternative raw materials came from wastes [47] [48].

The other important aspect is economic feasibility. In case of geopolymer it is quite complex problem. The price of material is dependent of such factor as:

- Used raw material, including cost of transportation [48]
- Used alkali activator; nowadays, this is the most unpredictable factor for long-term investments, because of huge changes [48]
- Price of energy
- Local regulations “greenhouse gas”, including “environmental” fees connected with waste management and greenhouse gas emission.

Conclusions

Geopolymers can be called "green material" because of the possibility of producing them with waste depending on the mining and mining industries. An additional advantage is the low CO₂ emissions when used for port cement.

Within the article, the technical solutions for reuse and recycling of mine tailings, as well as process for other types of waste aim to integrate them in building products was explored. The analysis carried out in the article shows the possibilities of mineral waste management from mining and processing into materials that can be used in the wider construction industry. Materials obtained in the geopolymerization process are characterized not only by proper mechanical properties, but also by a number of features, i.e. binding of heavy metal elements or fire resistance. Such properties predestine the obtained product also for applications as so-called special materials. Examples of possible applications are landfill protection. Where materials often have corrosive effects. Refractory properties suggest that this material may also be used in mining. The solutions presented are currently at the prototype stage. The technologies developed require significant expenditure on their development and adaptation to local conditions prior to their application. The analyzed examples of using waste materials as raw materials to create new materials for construction and transport are a promising future perspective.

Conflict of interest

There are no conflicts to declare.

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