Chapter

The Physical and Mechanical Characteristics of Geopolymers Using Mine Tailings as Precursors

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Abstract

Mine tailings are waste materials that resulted from the extraction and processing of raw materials to form mineral products. These dusty particles present negative environmental effects after being deposited in different types of dumping areas. Based on the circular economy concepts and the presently pushing need of identifying wastes as a potential replacement for natural resources, this chapter aims to present the physical (density, microstructure) and mechanical (compressive strength, flexural strength) characteristics of different types of geopolymers which use mine tailings as precursors or blended systems (mixes of different raw materials). The main reasons of approaching this topic are the need to decrease the consumption of natural resources, reduce environmental pollution and create an economic system aimed to capitalize the mining wastes. Accordingly, this chapter includes information regarding the availability of this waste and its potential utilization as a raw material in civil engineering applications. Therefore, reports of specific agencies and multiple research studies which approach tailing based geopolymers or blended systems have been summarized.

Keywords: geopolymers, mine tailings, ecofriendly materials, fusion activation, leaching, reinforced structures, flexural strength, compressive strength

1. Introduction

Nowadays, globalization generates large amounts of waste that significantly affects the storage areas and the surrounding environment. At the same time, the civil engineering sector is experiencing an exponential development process, which increases the demand for building materials and usable space. Therefore, the need to obtain new materials with lower exploitation costs and natural resources consumption became primary. One solution that has been intensively studied in the last past year, especially in this sector, consists of the development of environmentally friendly materials through a mechanism called geopolymerisation (**Figure 1**). The resulting materials, the geopolymers, consist of a tetrahedra network of aluminates (AlO_4) and silicates (SiO_4), chemically balanced by alkali ions of K^+, Na^+ or Li^+ [1]. The geosynthesis manifests itself in nature in great abundance. The Earth consists

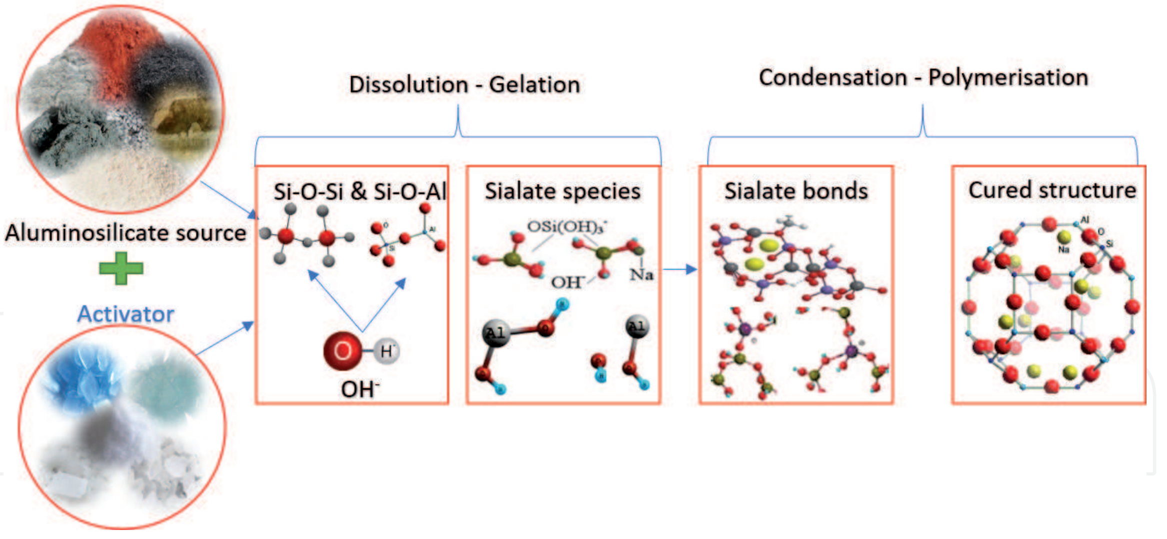

Figure 1.
Geopolymerisation process.

of 55% of volume, from siloxo-sialates and sialates, but only 12% pure silica or quartz. The geosynthesis process is based on changes induced in the crystallography of the silica backbone by the aluminum ion (6-fold or 4-fold coordination) and on the chemical changes produced by the same aluminum ion. This geosynthesis process is based on changes in crystallography of the silica backbone by the aluminum ion (VI-fold or IV-fold coordination) and the changes on the chemical part made by the same aluminum ion [2]. In this study, geopolymers refer to alkali activated materials obtained through the geopolymerisation reaction.

Currently, these materials are used in multiple industries, starting from civil engineering applications, up to medicine and spaces industry [3–5]. Therefore, there is high interest in the development of new geopolymers that possess higher properties than conventional materials (such as concretes with ordinary Portland cement or ceramics that use natural resources for their synthesis) [6]. However, the main zone of geopolymeric technology application is in the development of low CO_2 construction materials, mainly as an alternative to Portland-based (calcium silicate) cement [7, 8]. Being a performant material is not enough for the market, where it cannot go without a real demand for materials with such characteristics.

Nevertheless, the geopolymers preference over conventional materials is also supported by the soil decontamination potential of these materials, which is mainly related to the possibility to use waste as precursors or as reinforcing elements (**Figure 2**) [3, 9, 10]. Considering these characteristics, i.e. high properties and positive impact on the environment, it can be stated that this cycle is energy saving, natural resources conserver and waste-reducing [11, 12]. Continuing into this idea, using waste it's economically friendly and, first of all, cheaper. Therefore, up to now, waste such as coal ash, red mud, slags, rice husk ash etc. have been investigated as geopolymers precursors [13]. However, the possibility of using waste for geopolymers manufacturing is mainly constrained by the availability of the aluminosilicate source [14, 15]. Based on this limitation, a considerable source for geopolymerisation has been identified, i.e. mine tailings. Moreover, the use of this waste was also encouraged by the fact that mine tailings can be used in blended geopolymers (two or more types of aluminum and silicone rich powders are used for the geopolymers' synthesis). Therefore, when the properties of the final product aren't suitable for the specific application, i.e. when tailored properties are required, usually, the structure of the geopolymers must be reinforced with different types of particles which will contribute to their mechanical characteristics [16–18].

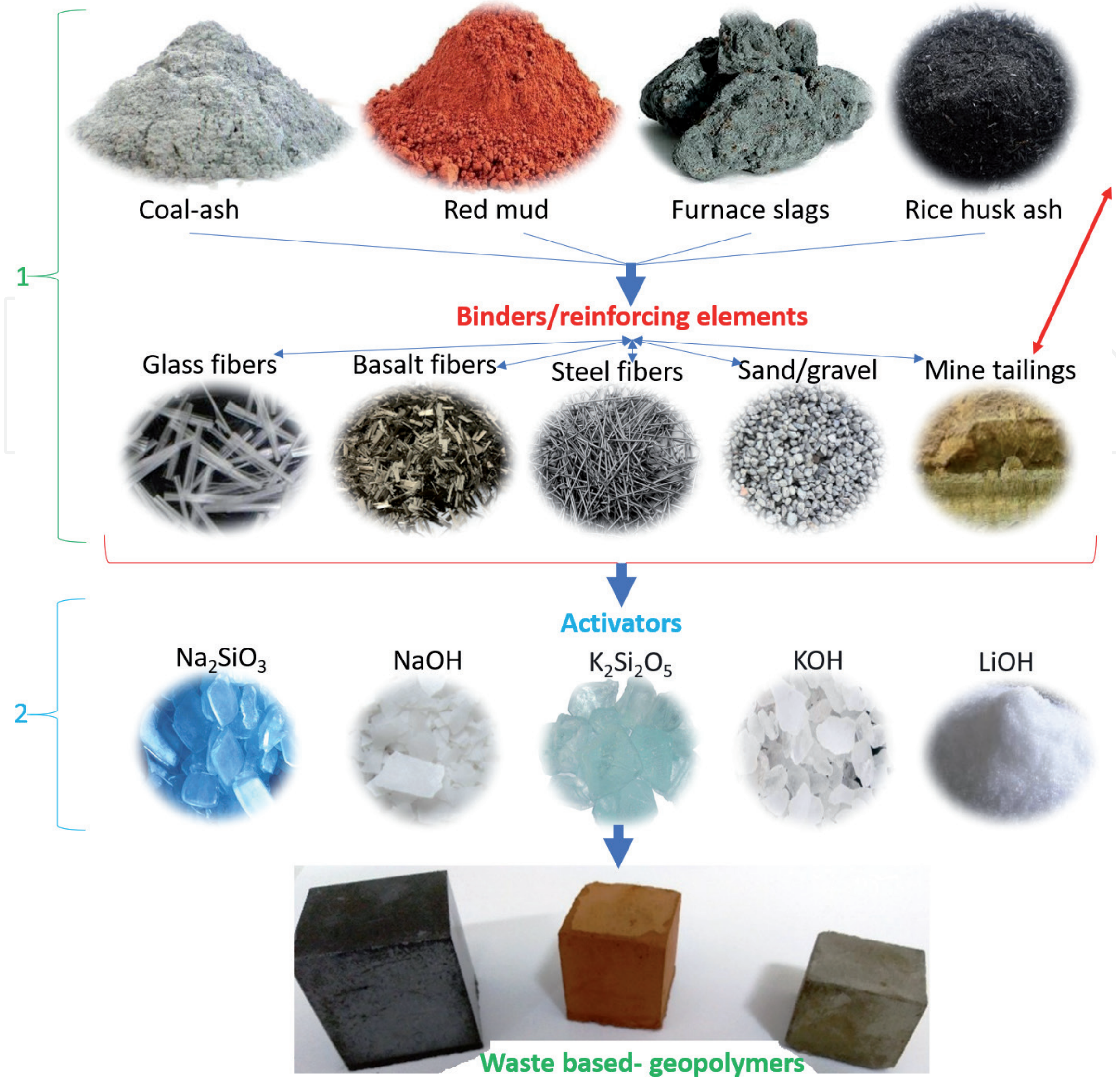

Figure 2.
The main components of waste-based geopolymers.

During the last decades, numerous studies have been focused on using mine tailings as precursors or blended component in geopolymers. Therefore, a compressive presentation of the obtained results, i.e. state-of-the-art review, could be a strong encouraging point for further research on this topic and scientific progress. Accordingly, this chapter includes information regarding the availability of this waste and its potential utilization as a raw material in civil engineering applications. Therefore, reports of specific agencies have been summarized and multiple research studies which approach tailing based geopolymers or blended systems are reviewed, and future research objectives have been presented accordingly.

2. Resources and production methods

The resources of an element consisting of the available amount in the earth's crust, the oceans and the atmosphere, which could be identified as extractible. The part of these resources, which can be exploited in economic conditions at a given time, represents the reserves. The boundary between resources and reserves varies over time depending on the economic and technological factors of exploitation and the strategy of different states and industrial groups. The average concentrations of the main elements from the earth crust are presented in **Table 1**. As can be observed,

Chemical element	O	Si	Al	Fe	Ca*	Na	K	Mg**	Oth. Elem.***
%, wt.	46.6	27.7	8.1	5.0	3.6	2.8	2.6	2.1	1.5

*Ca – calcium.
**Mg – magnesium.
***Oth. Elem.- other chemical elements.*

Table 1.
The main chemical elements from the earth crust [19].

eight elements represent almost 98.5% of the earth's crust. The base elements for geopolymerisation, i.e. oxygen (O), aluminum (Al) and silicon (Si), are situated in the first three positions and occupies almost 82% by weight from the entire earth's crust. However, because one more element (sodium (Na) and/or potassium (K) or lithium (Li)) is needed for activation, the total percentage is increased up to 88%. Moreover, considering the fact that aluminum, iron (Fe) and copper are the most extracted elements, large quantities of those goes to the mine tailing dumps, becoming a resource for geopolymers.

In order to obtain different products, the extracted resources go through a cycle of physical, chemical and mechanical processing called the circuit of materials in the production process. After extraction, the raw material undergoes a series of physical and chemical transformations until the final product is obtained (aluminum, iron, copper ingots etc.). During this transformation process, different parts from the raw material are lost, therefore, those volumes of extracted materials go to waste. Extraction, processing and manufacturing of materials require large amounts of energy and therefore production costs are highly dependent on the price of energy. From an energy point of view, organic materials are much more cost-effective, because their synthesis and shaping require much lower energy consumption than metals or ceramic materials. Therefore, to reduce the production costs, the waste can be recycled and capitalized by converting it into raw materials for other products.

In the development of one technology, one material is often substituted for another, for economic or performance reasons. Thus, the car body was originally made of wood - a light material, existing in nature. Then the wood was replaced with steel sheet, a heavier but more resistant material, with controllable properties and easy to process into complex shapes. To reduce energy consumption, we switched to lighter materials. This has led to the use of thin sheets of high-strength steel, as well as very light unidirectional composite materials made of carbon fibers embedded in organic polymers.

2.1 Recycled raw materials

Anything that is not recycled or recovered from waste represents a loss of raw materials and other production factors used in the chain, in terms of production, transport and product consumption, respectively. Therefore, the environmental impacts of these secondary products are significantly higher than those associated exclusively with the effects produced during the deposition in waste dumps.

Directly or indirectly, waste affects our health and well-being in many ways: methane gas contributes to climate change, air pollutants are released into the atmosphere, drinking water sources are contaminated, crops grow on contaminated land, and fish ingest toxic chemicals, after which they reach our plates.

2.2 Coal ash

The main waste of interest to the industry, resulting from the burning of coal in thermal power plants, is the ash from thermal power plants. The interest shown by researchers in a multitude of fields is mainly due to its hydraulic properties and chemical composition (high content of oxides of silicon, aluminum, calcium and iron). Thus, it has been shown that these pozzolanic powders can become raw materials for the manufacture of technically and economically competitive materials.

Coal-ash (fly ash and bottom ash) is a result of coal burning in thermal power plants for producing energy, which is an important polluter of the environment and lands in the close areas of power plants and coal ash store units/facilities. Since the need for energy is increasing, the power plants will produce more coal-ash which is estimated approximately to 776MT per annum [20]. Because of this enormous quantity, it is necessary to make alternative technology to reduce environmental impact.

Coal ash is a silico-aluminum or low calcium material that can be used in many applications, primarily in the construction industry, e.g. concrete, pavements, recipients for containment and immobilization of radioactive wastes, refractory ceramics and because of its elemental structure, a source of geopolymerisation reaction. Due to these properties fly ash gives great mechanical strength and a good fire and chemical resistance, which influenced the researchers to find a different application of fly ash. Coal ash, especially, fly ash has been intensively studied in the geopolymers technology, therefore, this waste already presents a high interest for the researcher, and it will not be evaluated/presented intensively here [21].

2.3 Mine tailings

The first stage of ore processing consists of hard rock blocks (ore) crushing and grinding up to particles with a diameter of a few centimeters or even micrometers. Secondly, the use phase is separated from the gangue part by specific means (depending on the type of ores and the used extraction technology). Mineral separation is achieved by various methods, namely: gravimetric; magnetic; electric. The surface properties of the mineral phases can also be used in the separation process. Accordingly, the products that resulted from ore processing are the concentrate and the tailings. The concentrate is processed further until the desired metal is obtained, while the tailings are deposited in different types of dumps/facilities.

A tailings dump can be defined as "the site of surface storage and the deposit of tailings extracted from the mine or tailings resulting from mechanical preparation operations". Accordingly, tailings ponds are excavated land surfaces in which liquid waste with a high content of suspensions is deposited, in order to sediment them, while mining tailings dumps are surfaces on which the material resulting from the excavation of non-metalliferous and metalliferous ores has been deposited.

As a result of the way the excavated and piled material is deposited, the piles are in the form of mounds with the appearance of a pyramid trunk, which have an upper part, more or less horizontal, which constitutes the plateau part and is bordered around the slopes.

The mineralogical and granulometric composition of the dumped material is strongly influenced by the dependence on the geological and lithological structure of the territory studied.

Under conditions of Neogene sedimentary formations composed of intercalations of fine sandy marls, sands, gravels, clays interspersed with bundles of layers of variable thickness, the uncovered and non-selectively deposited piled material leads to a mineralogical and granulometric structure highly variable from one pile to another and especially inside the same dump.

Mining has a strong influence on the environment, through various forms and ways affecting most environmental factors, namely: air, water, flora, fauna, landscape and human settlements, cultural heritage, population health, agriculture. Among the most important influences are [22]:

- affecting large areas of land that can no longer be used for other purposes for a very long time;
- pollution of soil, groundwater and surface water with various compounds solubilized by the action of rainwater;
- in the case of exploitation of materials containing sulfides, the phenomenon of acid drainage is amplified;
- visual impact (unattractive landscapes, dust picked up by the wind affects the traffic visibility etc.).

Waste recycling brings many benefits (**Figure 3**), the most important being: conservation of natural resources, reduction of storage space, protection of the environment and recovery of materials deposited in dumps by developing new materials.

The physical and the chemical characteristics of the tailings vary considerably, depending on the mineralogical and geochemical composition, sedimentation characteristics, specific gravity of the particles, rheology and viscosity, hydraulic permeability and conductivity, the evolution of the cementation process, the chemical composition of the water in the pores, the degree of contamination of the external

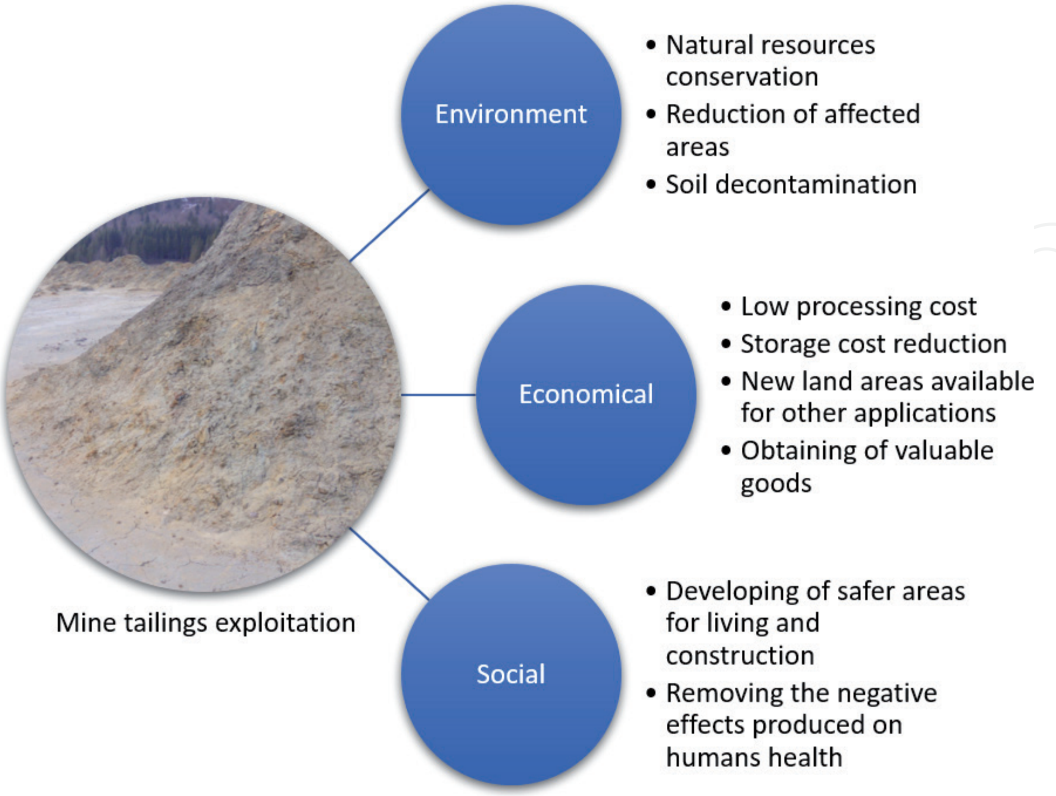

Figure 3.
Advantages of mine tailing recycling.

surface or underground environment etc. The mineralogical and geochemical composition of the solid material is strictly dependent on the paragenetic characteristics of the processed deposits. This aspect gives the tailings ponds uniqueness because there aren't two ore deposits with the same characteristics. On top of, depending on the quality and performance of the technology used in the separation process, tailings ponds can sometimes contain large amounts of metal sources.

The effects produced by the mine tailings facilities on the soil are, also, related to the raising type of storage (**Figure 4**). As can be seen, over 40% of the tailing dumps worldwide are upstream, mostly, because this is the cheapest design, unfortunately, this is also the most susceptible to failure design, which can result in huge environmental consequences [23]. Downstream is the following inline, being used at over 30% of the tailing's facilities. This design eliminates the disadvantages specific to the upstream designs, yet, the production cost is higher and the occupied space is considerably increased. Moreover, the amount of concrete building materials is significantly higher. Centerline design is a mix between upstream and downstream, this shows a lower failure coefficient than upstream and can be realized with fewer materials than downstream. The designs used in lower percentage (single-stage, dry stack, other) are usually specific to small mines, in terms of the extracted volume, while the in-pit method requires an empty/closed mine that can be filled with the resulted waste. A simplified schematic representation of the upstream, downstream and centerline design can be seen in **Figure 5**.

Although new construction designs have been developed, due to the fact that mines producing greater amounts of mine tailings, as lower grades of ore must be processed, the waste facilities are filled overcapacity, therefore, serious tailings dam failure occur (until 2027, globally, more than 15 catastrophic failures are predicted) [24]. Accordingly, by introducing and encouraging the use of mine tailings in geopolymerisation technology, a convenable source of raw materials for civil construction applications will be developed, while the requirements for a circular economy of the mining sector will be fulfilled.

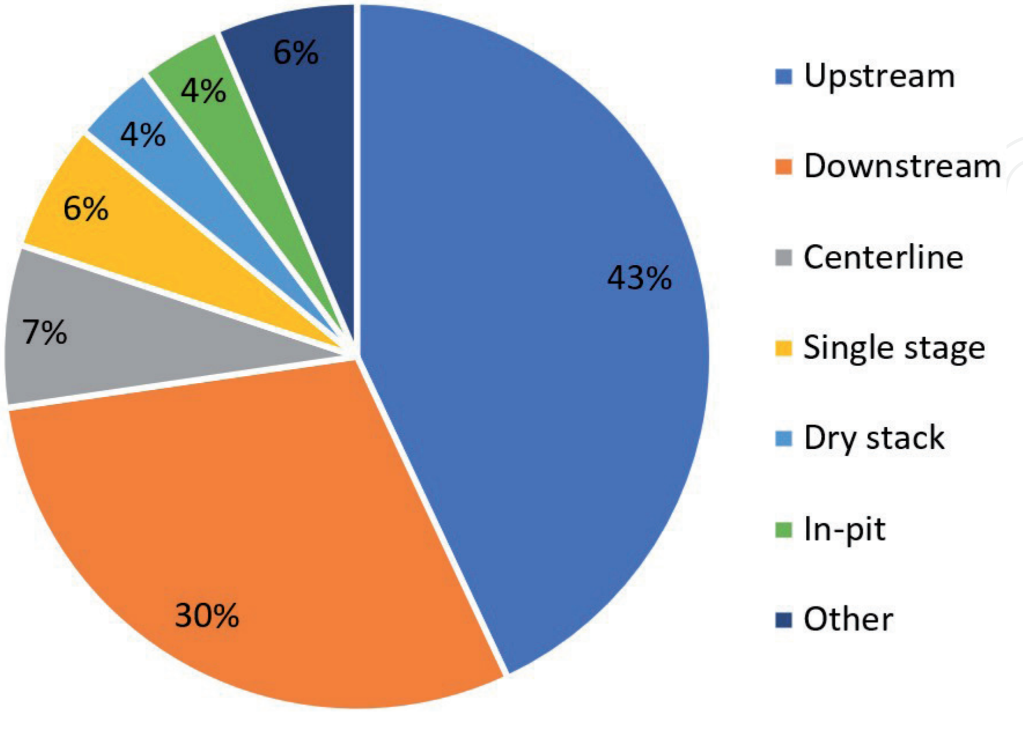

Figure 4.
Tailings storage facilities distribution, depending on the construction design type [23].

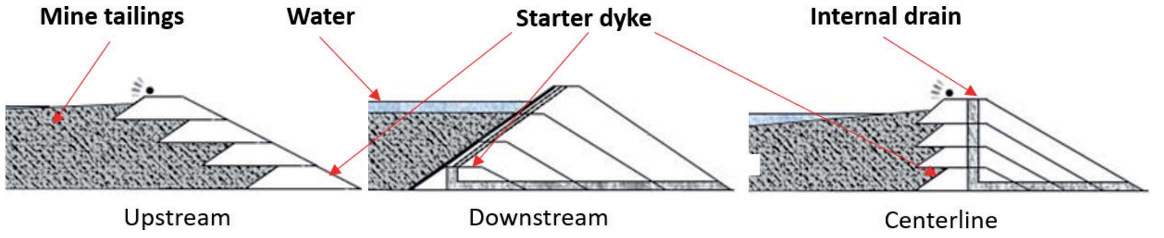

Figure 5.
Schematic representation of the construction design of tailings facilities [23].

Only in Romania, there are over 1100 tailings dumps and industrial landfills, distributed on the territory of 29 counties, respectively 13 counties for waste dumps (**Figure 6**). Of these, over 990 come from mining activities, while about 190 are located near protected areas. Moreover, more than 40 of them present serious stability problems [25]. Moreover, according to the report published by the Ministry of Economy, Romania is the country with the highest percentage (over 85%, the average in Europe being 25%) of waste resulting from the extractive industry.

Currently, the global stored volume of mine tailings is close to 55 billion cubic meters, and an increase of 23% is expected until 2025 [26]. Accordingly, the use of mine tailings in concrete can support the conservation of natural resources, specific to these activities, for 4 to 5 years [27].

2.3.1 Cooper mine tailings

Considering the fact that copper tailings are available in large volumes worldwide, and those increase considerable every day [25, 28], multiple authors focused their study on introducing these types of aluminosilicates in geopolymers technology, as precursors or partial replacements of conventional resources. Furthermore, this section aims to summarize the results obtained in this study and the main parameters that influence the feasibility of mine tailings synthetization in geopolymers.

Paiva et al. [29] developed geopolymers based on two types of metakaolin which incorporates fine particles of high-sulfidic Mine Tailings (MT) which comes from a copper and zinc mine. According to their study, the compressive strength of the geopolymers decreases with the increase of the substitution percentage despite the

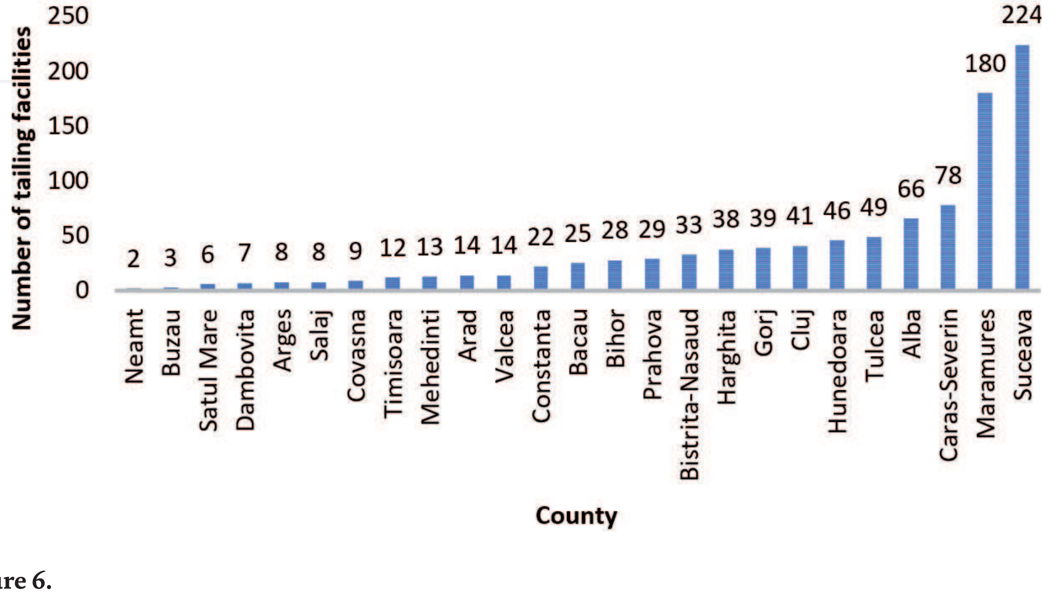

Figure 6.
Distribution of mine tailing facilities on Romania territory [25].

curing temperature. Therefore, after replacing 38% of MetaKaolin (MK) mass with mine tailings a decrease of 44% of compressive strength was obtained, while after 50% of metakaolin was replaced a decrease of 69% was observed, for the samples cured at room temperature (**Figure 7**). Based on the XRD evaluation (phases identified: Pyrite FeS_2, Anhydrite $Ca(SO_4)$, Caldecahydrite $CaAl_2O_4$ $10H_2O$, Quartz SiO_2), they stated that the analyzed mine waste cannot be used as a precursor for geopolymerisation because no reactive aluminosilicates are present in its composition. However, it can be used in blended systems, even its incorporation results in a more compact structure (bulk density increases from 1.7 to 1.9) with lower mechanical characteristics. Moreover, when Blast Furnace Slag (BFS) was used as a precursor, the bulk density decreases and so does the compressive strength, however, better values can be obtained by curing at high temperature (**Figure 8**).

The structural analysis of a cooper-barium mine tailing activated with 10 M NaOH for geopolymers synthesis exhibits a heterogeneous matrix with a partially dissolved structure, full of voids and unreacted particles (**Figure 9**).

The reactivity of mine tailings in alkaline activators was reported by Obenaus-Emler et al. [30]. According to their publication, the amount of dissolved species from metakaolin reaches 80%, for granulated furnace slag the value was close to 60%, while for copper mine tailing the dissolved amount was lower than 5%. However, better results were obtained after increasing the curing time or the NaOH concentration (**Table 2**). The compressive strength of the obtained geopolymers seems to depend on the same parameters, accordingly, an increase of 40% was obtained for samples cured at 60°C (compared with those cured at room temperature), while by increasing the concentration of water glass from 10–30%, four times higher compressive strength was obtained for room temperature cured samples, and 6 times higher for 60°C cured samples, respectively. Moreover, one more parameter that showed promising results on improving mechanical characteristics was the addition of finer particles or BFS, however, this also affects the pore size distribution of the hardened product.

In another study, Ahmari et al. [31] successfully synthesized geopolymers with copper mine tailings as precursors. According to their study, satisfying compressive strength can be obtained by customizing the curing parameters and the activator (**Figure 10**). The samples synthesized with a 15 M NaOH solution exhibit the optimum value when cured at 90 °C, while for 5 M NaOH and 10 M NaOH, 75°C was the optimum temperature.

Moreover, by introducing sodium silicate in the composition, the highest compressive strength can be obtained at SiO_2 to Na_2O equal to 1, for the geopolymer activated with 10 M NaOH and cured for 7 days at 60°C (sample 1SS). When the ratio is increased the mechanical characteristics will decrease because this solution

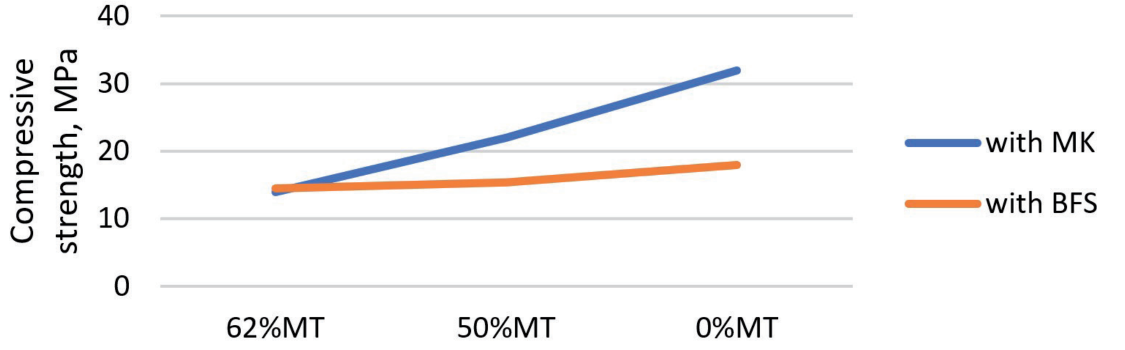

Figure 7.
The effect of precursors replacing with copper mine tailings on compressive strength (- approximate value).*

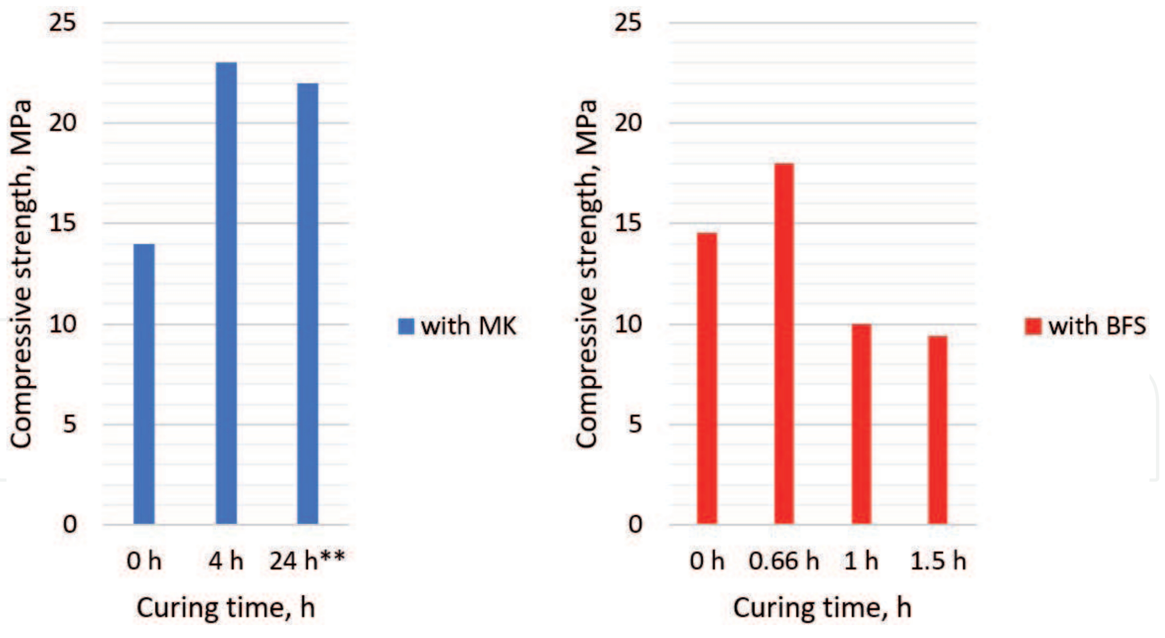

Figure 8.
*Compressive strength of 50°C cured samples for different periods (** - for sealed samples).*

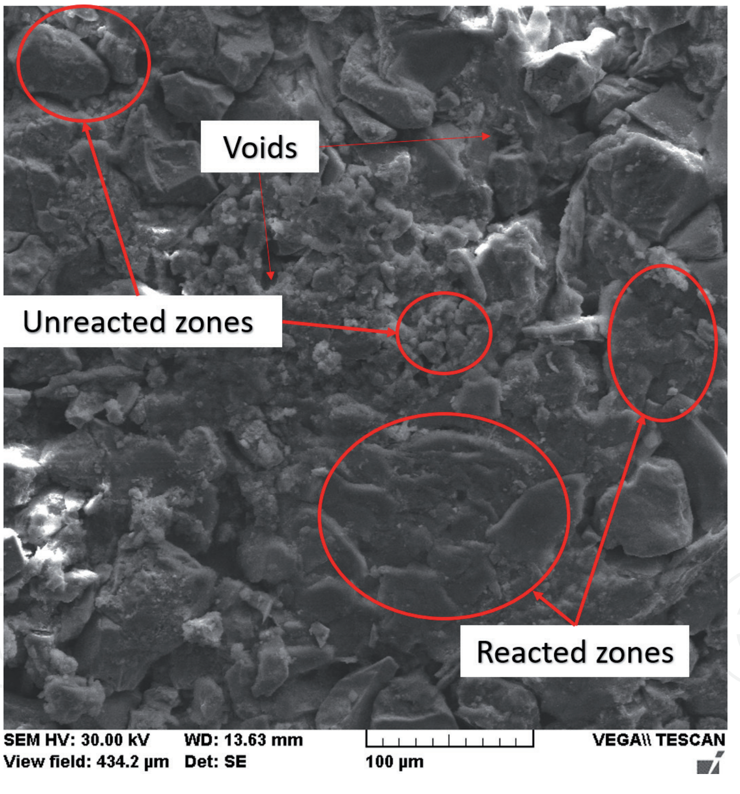

Figure 9.
The microstructure of cooper-barium mine tailing based geopolymer.

provides the amount of silicon needed in the early stages of geopolymerisation, but in too high concentrations it prevents water evaporation, while encapsulates the particles of the raw material in a film that does not allow the catalyst to advance. Also, for 10 M NaOH activate geopolymers, cured at 90°C, the addition of sodium aluminate in a mass ratio of 1.25 (sodium aluminate/NaOH solution) showed an impressive increase of compressive strength from ≈6 MPa to ≈17 MPa (sample 1SA). The activator and curing parameters also affect the microstructure of the obtained samples, consequently, a denser matrix was observed at higher NaOH concentration

Raw material	Absolute amount dissolved, mg/l					
	Ca	Mg	Al	Si	Fe	S
MT, 5 M NaOH	4.4	0.3	2.2	16	3.7	97.2
MT, 10 M NaOH	13	9.2	3.1	28	37	70
MK, 10 M NaOH	—	—	2122	3148	—	—
BFS, 10 M NaOH	21.8	2.3	603	2450	1.9	880

Table 2.
The amount of dissolved species after 24 h leaching.

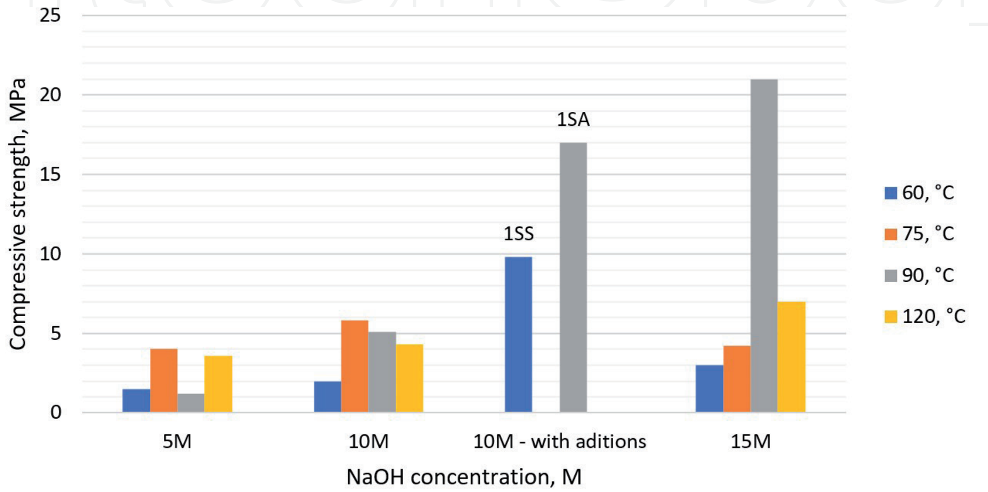

Figure 10.
Activator and curing parameters effects on compressive strength in cooper mine waste-based geopolymers.

or curing temperature. As can be seen from the graph, better results can be obtained by curing the 1SS samples at 90°C, or by increasing the molar concentration of the NaOH solution from 10 M to 15 M, in the case of geopolymers with additions.

According to another study [32], if appropriate manufacturing conditions (NaOH concentration, initial water content, forming pressure, and curing parameters) are selected, the copper mine tailings are feasible to produce eco-friendly bricks by a simple three steps method: (i) mixing the mine tailing with the activator, (ii) compress the mixture in a mold at a specific pressure, (iii) cure the products at slightly elevated temperature.

2.3.2 Tungsten mine tailings

Usually, tailings from many tungsten extraction facilities contain only small quantities of heavy metals and fatty acids, therefore, those aren't classified as class A facilities. However, due to their large amount available (the production of tungsten reached 87,000 metric tons in 2015, therefore, the amount of waste is even higher) long-term processing and managements solution must be developed [33].

Tungsten Waste-based Geopolymers (TWG) has been successfully synthesized by mixing the cementitious powder with different percentages of calcium hydroxide and mixes of NaOH and waterglass solution. According to previous studies, this type of geopolymers has good adhesion properties, low water absorption and high mechanical characteristics. In their study, Pacheco-Torgal et al. [34], evaluated the influence of aggregates (sand) and calcium hydroxide ($Ca(OH)_2$) introduction in the matrix of TWG on compressive strength evolution. The optimum $Ca(OH)_2$

concentration was 10%, while the ratio of 1 for sand to binder mass showed the most promising results. Moreover, when water to sodium hydroxide ratio was evaluated (**Figure 11a**) it was observed that higher NaOH concentrations result in better compressive strength, while higher water content badly affects the mechanical strength evolution (**Figure 11b**).

In another study [35], the authors evaluated the adhesion characteristics of tungsten-based geopolymers to the surface of pretreated OPC concrete. According to their study, the samples exhibit a high bond strength and monolithic failure even after 1 day of curing. Moreover, they stated that this type of geopolymers are three times stronger than C30/37 strength class OPC concrete, in terms of abrasion resistance, and, almost the same difference, in terms of sulfuric acid resistance. This can be related to the low unrestrained shrinkage and capillary water absorption coefficients, respectively.

2.3.3 Gold mine tailings

Considering the fact that the majority of the processed gold comes from the open querries, and their activities include substrate removal and grounding of high amounts of rock (almost 20 tones of waste is generated for a standard 18-karat ring). Gold products obtained following mining activities are through the most tailing generative.

Waste resulted from gold mining activities was also approached in geopolymers obtaining. Kiventera et al. [36] synthesized Gold Mine Tailing (GMT) based geopolymers or blended systems of GMT and BFS activated with different NaOH solutions. According to their study, due to the fact that the water quantity constrains the efficiency of the polycondensation stage, the workability was affected by the molarity of NaOH solution and solid to liquid ratio. Additionally, it was observed that a higher water quantity can result in multiples cracks and pores which

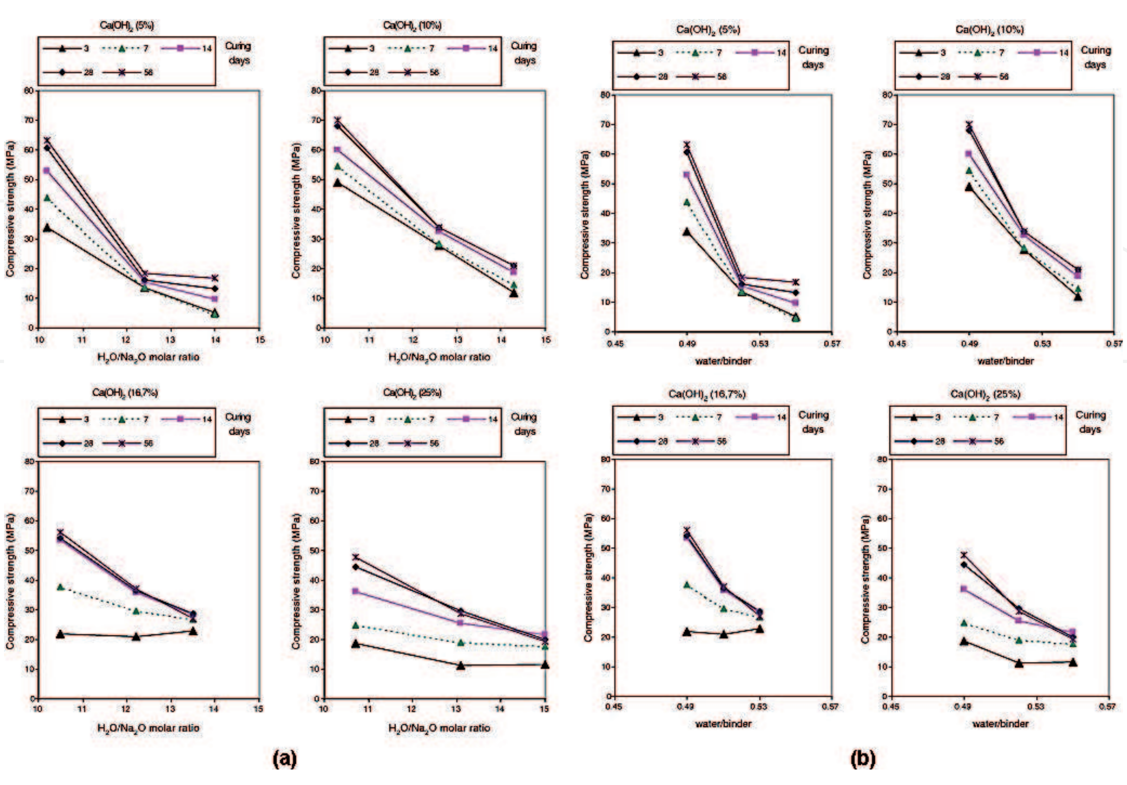

Figure 11.
The influence of different parameters on compressive strength of TWG, depending on curing time: a) water to sodium hydroxide mass ratio; b) solid to liquid ratio; [34].

significantly affects the mechanical characteristics of the samples. Therefore, for optimal properties, a high NaOH quantity must be dissolute in the binder because the Na/Al and Na/Si ratios depend on this, while the strength of the products depends on the volume of binder created during the dissolution stage. However, this need is limited by the NaOH solubility in water, previous studies [31] show that a molar concentration higher than 24 is hard to achieve.

The compressive strength of GMT bricks, measured after 28 days of curing, exhibit a 35% increase, when the NaOH concentration was changed from 5 M to 15 M, also, an even higher effect (at 5 M the compressive strength increased from 1.4 MPa to 2.2 MPa, at 10 M it increases from 2.2 MPa to 3 MPa, while at 15 M NaOH the value increases from 3 to 3.5 MPa) was observed when the liquid to solid ratio was decreased from 0.25 to 0.15 [36].

Demir et al. [37] studied the possibility of obtaining GMT geopolymers for the removal of toxic and radioactive waste by realizing tests of Pb^{2+} adsorption from aqueous solutions. Firstly, the reaction degree depending on the curing temperature and Al_2O_3 addition was analyzed, accordingly, it was observed that higher Al_2O_3 content results in better reaction degree, while curing temperature showed minimum effects. Secondly, the Langmuir isotherm model and second-order kinetic model were identified as being the most suitable to evaluate the Pb^{2+} absorption. Accordingly, they state that the highest absorption efficiency obtained was 94% for GMT geopolymers with alumina addition.

In another study [38], the author evaluated the potential of obtaining geopolymeric concrete by replacing different percentages of type I Ordinary Portland Cement (OPC). The evaluation has been performed by compressive strength test on samples with 50% by wt. GMT (50GMT), 70%, wt. GMT (70GMT), 80% wt. GMT (80GMT) and 90% by wt. GMT (90GMT), respectively. According to their results, the presence of high percentages of tailing particles significantly increases the mechanical characteristics of the concrete, in 12 h cured samples at 70°C, despite the aging time (**Figure 12**).

Moreover, when the effects of harsh environment conditions (H_2SO_4, HNO_3, $MgSO_4$, Na_2SO_4 acids attack or high-temperature exposure) was evaluated, it was concluded that the increase of GMT also has good effects on these characteristics. However, if 55 days of immersion in acids reduce the compressive value to almost half, the high-temperature exposure at 1000°C almost destroyed the structure of the samples.

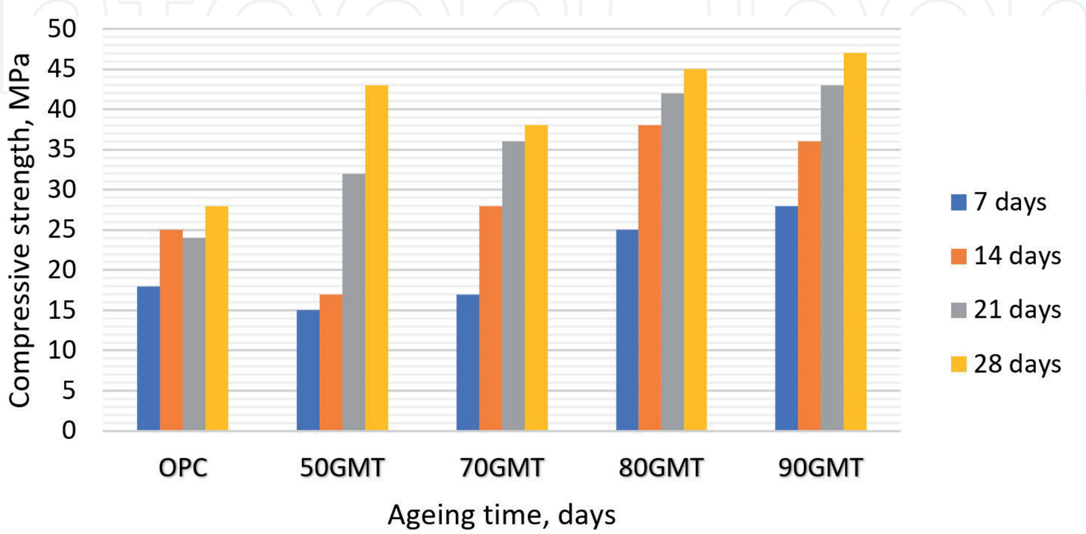

Figure 12.
Compressive strength evolution of OPC concrete with different percentages of GMT.

2.3.4 Phosphate mine tailings

The amount of tailings generated by a potassium mine depends primarily on the configuration of the potassium vein, the stability of the rocks and the mineral composition. All these are natural conditions that vary from one mine to another, from one warehouse to another and sometimes even within the same warehouse. Therefore, there is no standard model of mines in terms of processing and generation of finished products and tailings. Each mine has its specific conditions regarding the generation of liquid and solid tailings and their management. Thus, these specific conditions can vary throughout the life of a mine. However, for economic reasons, operators will seek to minimize the amount of mined tailing and processed [39].

Regarding the solid tailing facilities, waste management involves discharging it into the dump sites and refilling underground mines. The tailings from hot distillation and flotation, with sodium chloride as the main component, are dehydrated using centrifuges and filters, and then transported, employing conveyor belts, to the tailings dump. Besides, the dry process of electrostatic separation allows the dry management of the tailings at the tailings dump [40].

Regarding the liquid tailings, waste management involves discharge into groundwater (under certain geological conditions) and/or discharge into surface waters.

Fine Phosphate Sludge (PS) from the Moroccan Youssoufia plants were used for blended geopolymers obtaining by Moukannaa et al. [41]. According to their publication, PS rich in fluorapatite, quartz, calcite, dolomite, illite, palygorskite and hematite, needs supplementary aluminum content to present geopolymerisation potential, therefore, highly amorphous metakaolin was introduced in addition. Moreover, the reactivity increase was also performed by fusion activation at 550°C and 800°C, respectively. Based on the XRD analysis, it was observed that due to the presence of NaOH and high temperature, hematite decomposition occurs, while sodium aluminum silicate, sodium-calcium silicate, periclase and titanite formation is confirmed. Also, it was stated that the 550°C activations slightly reduce the content of dolomite, palygorskite, calcite and fluorapatite, while the quartz content seems to remain constant. However, at 800°C dolomite was greatly reduced, while the content of Na-rich phases significantly increases. On top of that, when the NaOH content was increased from 10–20%, the effects obtained at 800°C, were obtained at much lower fusion temperature (550°C). Surprisingly, based on the compressive strength results, the samples, cured at 28°C, made with raw materials fused at 550°C with 10% NaOH showed higher values than those with 20% NaOH or those fused at 800°C. Based on the microstructural analysis, it was stated that the poor strength, of 800°C fused samples, is related to the heterogeneous distribution of the sand particles, which acts as barriers for crack propagation in the matrix of 550°C fused samples (**Figure 13**). This phenomenon was also reported in previous studies [17, 42]. However, higher mechanical properties can be obtained by increasing the metakaolin content or by curing the samples at temperatures lower than 350°C.

The recycling possibility through geopolymerisation technology was also confirmed in [43]. According to the study, for optimum physical (low water absorption, high density etc.) and mechanical properties (compressive strength up to 62 MPa) a curing temperature of 83.33°C, a curing time of 14.50 days, and NaOH concentration of 12.5 M must be selected for phosphate sludge-based geopolymers mixed with fly ash or metakaolin.

2.3.5 Aluminum mine tailings (red mud)

Red Mud (RM) is the main secondary product (waste) that results from the Bayer process of refining bauxite to produce alumina. Generally, this process

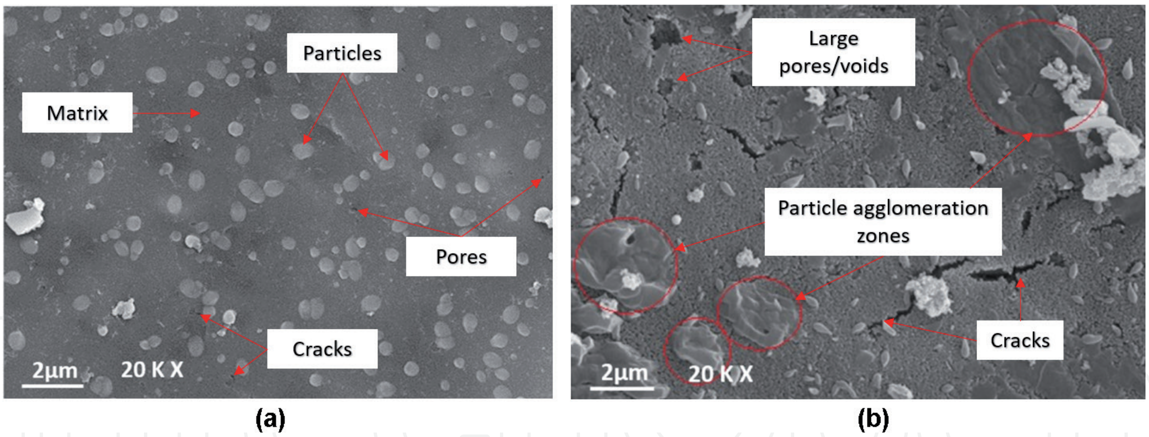

Figure 13.
Particle distribution effects on geopolymers microstructure: a) uniform distribution; b) heterogeneous distribution [41].

treats the aluminum ore (bauxite) with concentrated NaOH solutions at elevated temperature and pressure aiming to extract the gibbsite ($Al(OH)_3$), diaspore (AlO(OH)) and/or boehmite (γ-AlO(OH)). Therefore, RM is a strong alkaline waste due to the incomplete removal of NaOH. Accordingly, its composition depends on several factors but mainly on the composition of bauxite. The resulting amount of red mud also depends on the composition of the bauxite, however, it ranges from 0.33 up to 2 t of red mud per ton of alumina produced [5, 44]. Apart from the huge amount which is stored in tailing lakes, the main problem related to the environmental effects produced by this waste is its alkalinity. Moreover, considering that from Jan 1974 to Oct 2020 the global amount of extracted alumina was ≈2,814,091 thousand metric tonnes by multiplying with 1.1 (the average value of generated waste), the total amount of waste generated due to alumina extraction is ≈3,095,500 thousand metric tonnes [45]. According to the literature, only 2–3% of the produced waste is used in industrial-scale application, especially in civil engineering applications, therefore, almost 98% is being deposited [46].

Although, the methods of depositing and securing red mud facilities have been improved significantly over time, currently, worldwide more than 60 refineries extract alumina through the Bayer process depositing the waste in lakes [47, 48].

As can be seen from the literature, red mud is the most studied mine tailing for geopolymers obtaining [49, 50]. As stated in [49], Wagh et al. [51] published the most systematic study on the red mud use in alkali-activated materials. Accordingly, even from preliminary studies promising compressive strength (between 35 and 45 MPa) results have been obtained for RM as a single solid precursor. Moreover, by 15% metakaolin addition [52], RM becomes acts as a filler, and the compressive strength increase more than four times, compared with the geopolymer with RM as a single precursor. Depending on the replaced percentages, other authors obtained even better results [53, 54]. In terms of mechanical compressive, the addition of ground granulated blast furnace slag [55], rice husk ash [56] or fly ash [57] also showed significant improvements.

3. Conclusions

Based on the analyzed studies, the following conclusions can be drawn regarding the possibility to use mine tailings as precursors or components for geopolymers:

- Both mechanical and physical characteristics of geopolymers are affected by the water content introduced by the activator (NaOH concentration) and the curing parameters (time and temperature). Accordingly, higher NaOH concentrations and curing temperature results in an increase of the mine tailing reactivity.

- The introduction of aggregates in blended systems significantly influence the mechanical characteristics of geopolymers, generally, better properties are obtained. Moreover, their content can influence the dissolution degree of the matrix.

- The mine tailings can be used in multiple civil engineering applications since compressive strength up to 70 MPa can be achieved for 28 days cured samples.

- If appropriate manufacturing conditions (NaOH concentration, initial water content, forming pressure, and curing parameters) are selected, the copper mine tailings are feasible to produce eco-friendly bricks by a simple three steps method: (i) mixing the mine tailing with the activator, (ii) compress the mixture in a mold at a specific pressure, (iii) cure the products at slightly elevated temperature.

- Some types of mine tailings (especially sulphidic ones) show low interest as single precursors, generally, blast furnace slag additions are necessary to obtain suitable properties. Moreover, better results can be obtained by subjecting the mine tailing to mechanical grinding, calcination and alkali fusion.

- In corresponding conditions, gold mine tailing geopolymers are suitable for heavy metals encapsulation and immobilization.

- During the geopolymerisation, both, the crystalline and the amorphous phase from the tailings react in the alkaline environment, especially at high curing temperature. Also, higher temperature results in a denser structure.

- Thermal activation by drying or calcination removes the water content, creates many reactive phases and significantly increase the amorphous fraction of the aluminosilicate sources. Moreover, the alkaline fusion activation method significantly affects the mineralogical composition, resulting in Na-rich crystalline or amorphous phases.

- Mine tailings are available in enormous quantities worldwide (several thousand million tons per year) and can be used for cementitious application due to their high content of silicon and aluminum oxides content. Accordingly, by using them worldwide in the already developed applications and by encouraging their use in new ones, significant natural resources can be preserved.

- Five types of mine tailings have been identified and their potential use in geopolymerisation technology was evaluated.

- The main conclusion that can be drawn from this study is as follows, mine tailings can be successfully used for different application through geopolymerisation technology. The amount used currently is lower than the amount produced, therefore, the deposited quantities will increase. In order to avoid future disasters, related to tailings facilities failure, significant efforts must be made on the introduction of this waste in new, highly used goods.

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