Perspective on the use of mine tailings in fly ash-based geopolymers in the South African context

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Mine tailings represent a substantial environmental and economic problem. However, they may also represent secondary mineral resources in the form of aggregates or aluminosilicate precursors for the synthesis of geopolymer materials. Geopolymers are inorganic polymeric materials that can be synthesised from aluminosilicate materials and alkaline activators. They have been used in various applications, including construction materials, coatings, and environmental remediation. Different kinds of mine tailings (e.g., barite, copper, gold, molybdenum, iron ore, lead-zinc, nickel-laterite, phosphate, sphalerite, vanadium, and kaolinite tailings) have been investigated for geopolymer synthesis. The main challenge lies in the limited reactivity exhibited by most mine tailings. Given their low reactivity, mine tailings can be effectively employed as a filling material in geopolymer mix designs when paired with an appropriate co-binder. Alternatively, their reactivity can be enhanced through, for example, mechanical activation (such as grinding), thermal treatment (calcination), and alkaline fusion, although this incurs a cost penalty.

INTRODUCTION

Geopolymers are a class of inorganic polymeric materials or binders consisting of repeating units, chains or networks of mineral aluminosilicate molecules linked with covalent bonds, such as silico-oxide (Si-O-Si-O-), silico-aluminate (Si-O-Al-O-) or ferro-silico-aluminate (Fe-O-Si-O-Al-O-), created through a chemical process of geopolymerisation (Davidovits, 2020). During this process, aluminosilicate materials are typically reacted with alkaline activators, which break down the existing Si-O and Al-O bonds and subsequently form new Si-O-Al bonds, creating a three-dimensional, polymer-like structure. The source of aluminosilicate can be obtained from various materials, such as coal fly ash, metakaolin, blast furnace slag, and mine tailings. The alkaline activators can be e.g., sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate ($Na_2O.(SiO_2)_x$ where x is the silica-to-alkali SiO_2/Na_2O weight ratio), potassium silicate ($K_2O.(SiO_2)_x$ where x is the silica-to-alkali SiO_2/K_2O weight ratio), used either on their own or in combination with one or more activators. Geopolymers can typically be used in various applications, including construction materials (Giacobello *et al.*, 2022), coatings applied in surface protection of concrete, steel or wood structural elements (Jiang *et al.*, 2020), and environmental remediation (Adewuyi, 2021; Elgarahy *et al.*, 2023).

In South Africa, the most widely used source of aluminosilicate for geopolymer synthesis is coal fly ash (e.g., Dludlu *et al.*, 2017; Temuujin *et al.*, 2018). However, coal fly ash cannot be used as a generic material term because variations between ashes can lead to substantial differences in the microstructural and mechanical properties of geopolymers (Zhang *et al.*, 2016). Given the wide range of ashes available in South Africa, it is necessary to highlight their properties and how these properties could influence geopolymer characteristics.

FLY ASH_BASED GEOPOLYMERS

Availability of South African coal fly ash

Fresh coal fly ash

Coal fly ash (CFA) is the solid, light- to dark-grey, incombustible residue generated in large quantities during the direct combustion of pulverised coal in thermoelectric power stations (Toporov, 2014). It is formed from the lighter particles that rise with the flue gases during coal burning and is collected using electrostatic precipitators or bag filter systems. Once collected, CFA is typically disposed of and managed on large ash dumps or slurry dams, except for about 7% which is mostly reused in the construction industry (Reynolds-Clausen and Singh, 2019). In South Africa, most pulverised CFA is sourced from coal-fired power stations operated by Eskom (Figure 1). Other organisations such as Kelvin Power, Sappi and Sasol are also producers of CFA (SACAA, 2021).

About 35 million tons (Mt) of CFA are generated in South Africa per annum (Eskom, 2015; Reynolds-Clausen and Singh, 2019), mostly in the Gauteng, Mpumalanga and the Free State Provinces (Figure 1; Doucet *et al.*, 2021). However, when it comes to the re-use and/or sale of freshly generated CFA, this quantity may be misleading since only a fraction of it is made available by Eskom. This is because Eskom uses 74% of its fresh CFA (i.e., ca. 26.7 Mt) for effluent treatment (Eskom, 2016) – as part of its Zero Liquid Effluent Discharge policy and in order to preserve and protect South Africa's water resources, Eskom disposes of all its saline effluents generated at its power stations at the CFA-handling facilities, where CFA acts as a salt sink for the effluents. As a result, only 26% of the fresh ash produced is available for reuse, which amounts to about 9.5 Mt, of which 2.5 Mt is already sold to the construction sector. These circumstances bring the total amount of fresh CFA available for resale down to about 7.0 Mt per annum, which is distributed between several power stations (Table 1) (Reynolds-Clausen and Singh, 2019). The latter figure may bear significant importance if CFA-based geopolymers are developed commercially on a large scale in this country in the future. The significance of this consideration holds even truer if one considers the 'Just Transition' movement and the anticipated low carbon economy that will eventually follow in South Africa and globally, which will reduce the volumes of CFA produced considerably.

In addition, a number of power stations make use of blended coal (Eskom, 2016). This production process results in the generation of CFA with an inconsistent composition that varies in quality (Reynolds-Clausen and Singh, 2019). For these reasons, CFA from some power stations is not widely used or accessible for re-use in the ash market (Table 1). The most promising opportunities for further sale of CFA from Eskom are the Arnot, Duvha, Hendrina, Kendal, Kriel, Lethabo, Majuba and Matimba power stations. Ash Resources (Pty) Ltd operates CFA manufacturing sites next to the Lethabo, Matla, Kendal and Matimba power stations (Ash Resources, 2021a). Ulula Ash operates CFA manufacturing sites next to the Kriel power station (Ulula Ash, 2009). In addition, the most limiting factor in using CFA in geopolymers is transport cost (EPRI, 2016), which means that large scale use of fly ash-based geopolymers may be limited to the Gauteng, Mpumalanga and the Free State Provinces for economic reasons.

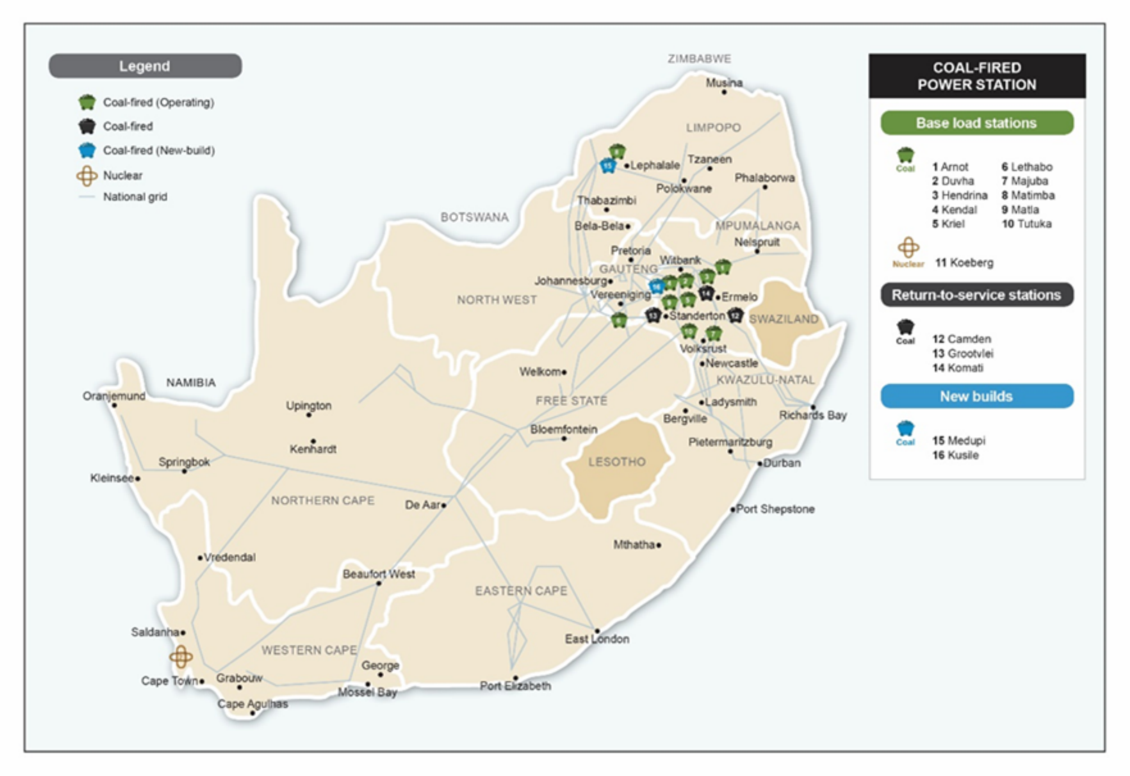

Figure 1. Map illustrating the locations of South African coal-fired power stations as main generators of coal fly ash (adapted from Eskom; Doucet et al.*, 2021).*

Table 1. Estimated ash volumes produced and available for sale per power station in South Africa (Reynolds-Clausen and Singh 2019)

Power station	Produced (Mt)	Ash used for effluent sink (Mt)	Saleable (Mt)	Ash sold (Mt)	Opportunity for further sale (Mt)
Arnot	1.65	1.25	0.40	0.00	0.40
Camden	1.07	1.07	0.00	0.00	0.00
Duvha	2.51	2.31	0.20	0.00	0.20
Grootvlei	1.00	1.00	0.00	0.00	0.00
Hendrina	1.82	1.62	0.20	0.00	0.20
Kendal	4.91	1.91	3.00	0.54	2.46
Komati	0.32	0.32	0.00	0.00	0.00
Kriel	2.30	1.30	1.00	0.31	0.69
Lethabo	6.48	5.18	1.30	1.23	0.07
Majumba	3.43	2.43	1.00	0.04	0.96
Matimba	4.75	2.75	2.00	0.01	1.99
Matla	3.04	2.64	0.40	0.40	0.00
Tutuka	2.93	2.93	0.00	0.00	0.00

Fresh fly ash can be categorised into unclassified ash and classified ash. The unclassified ash is the raw form of fly ash that can be collected directly from the hoppers at coal-fired power stations. It has not undergone any specific processing or treatment and might have varying properties and impurities. These impurities may limit its use in some applications due to potential environmental and technical concerns. More specifically, it may not be suitable for certain applications that demand specific performance criteria because it lacks the controlled characteristics of classified ash. On the other hand, classified ash refers to CFA that has undergone physical processing such as selection and classification, sieving, drying, blending, grinding or carbon reduction to optimise its fineness, reduce its water demand and obtain high uniformity and consistency and meets certain quality standards (Ripfumelo, 2012; Longarini, 2014). For instance, Ash Resources uses an air-stream classification process that separates the heavy and light particles in order to select the required particle size range. Other grades are conditioned by washing.

Commercial classified CFA is mainly produced and supplied by Ash Resources and Ulula Ash in South Africa. Trade names include Durapozz, DurapozzPro, SuperPozz, SuperPozzPro, and Class S (CFA). Typical chemical compositions of some classified CFA are summarised in Table 2.

Table 2. Typical chemical composition of some commercial South African classified coal fly ash (%)

Chemical composition (% oxide)	Durapozz	SuperPozz	Class S (CFA)
SiO_2	47.0–55.0	53.5	50.0–52.5
Al_2O_3	25.0–35.0	34.3	28.5–30.5
Fe_2O_3	3.0–4.0	3.6	2.0–3.0
Mn_2O_3	0.1–0.2		
CaO	4.0–10.0	4.4	6.0–9.5
MgO	1.0–2.5		2.0–2.5
P_2O_5	0.5–1.0		
K_2O	0.5–1.0		< 1.0
Na_2O	0.2–0.8		< 1.5
TiO_2	1.0–2.0		1.5–2.0
SO_3	0.1–0.5		0.8–1.2
LOI	0.5–2.0		0.8–1.6
SiO_2:Al_2O_3 ratio	**1:0.5–1:0.6**	**1:0.6**	**1:0.6**
Source	Ash Resources, 2011	Ash Resources, 2021b	Ulula Ash, 2016a

Commercial unclassified CFA is also produced and supplied by Ash Resources and Ulula Ash. Trade names include PozzSand, PozzFill and Class N (NFA). Typical chemical compositions of unclassified CFA are summarised in Table 3.

Table 3. Typical chemical composition of some commercial South African unclassified coal fly ash (%)

Chemical composition (% oxide)	PozzSand	PozzFill	Class N (CFA)
SiO_2	53.8	51.0–65.0	51.5–56.0
Al_2O_3	34.3	25.0–35.0	27.5–30.0
Fe_2O_3	3.6	3.0–8.5	3.0–4.0
Mn_2O_3	0.1	0.1–2.0	
CaO	4.4	1.0–8.0	6.5–10.0
MgO	1.1	0.5–2.0	1.5–2.0
P_2O_5	0.3	0.3–0.7	
K_2O	0.5	0.1–1.0	< 1.0
Na_2O	0.4	0.1–0.6	< 1.2
TiO_2	1.6	1.0–2.0	1.5–1.8
SO_3	0.1	0.1–1.0	0.5–0.9
LOI	1.2	< 3.0	1.0–2.0
SiO_2:Al_2O_3 ratio	**1:0.6**	**1:0.5**	**1:0.5**
Source	Ash Resources, 2021c	Ash Resources, 2021d	Ulula Ash, 2016b

Coal fly ash tailings dams

Once CFA is disposed of at an ash pond or dam, it undergoes weathering as it gets continuously exposed to fluctuating environmental conditions. The weathering of CFA results in changes in its physical, chemical and mineralogical properties such as the formation of secondary mineral phases, decrease in the pH and electrical conductivity of the pore water in the CFA and reduction of soluble salt content. This may have a significant effect on the leaching and mobilisation of the CFA species (Eze *et al.*, 2013; and reference therein). For instance, Eze *et al.*, (2013) showed morphological changes in CFA from spherical particles with smooth outer surfaces for the fresh CFA to agglomerated, irregular particles with encrusted, etched and corroded appearances for weathered CFA. Ash dumps are also typically water-logged, which creates favourable conditions for leaching of species. Figure 2 illustrates the spatial variation in resistivity, and hence heterogeneity, of a wet disposed ash dump (Eze *et al.*, 2013).

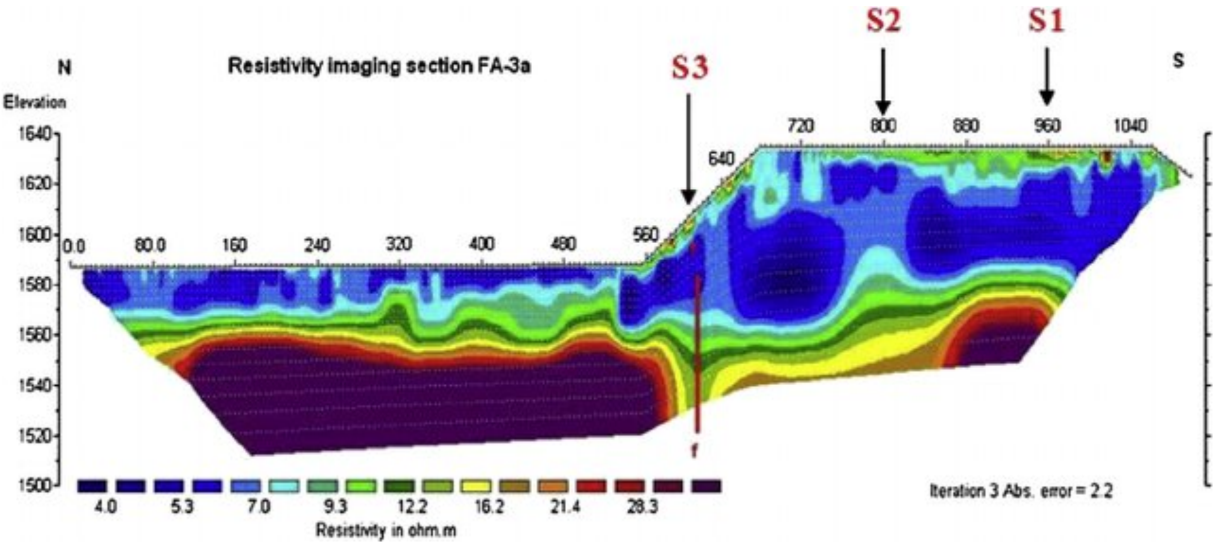

Figure 2. Resistivity profile of a wet disposed coal fly ash dump (Eze et al.*, 2013).*

Understanding the changes in and the distribution of the chemical, physical, morphological properties and phase transformation of CFA due to weathering across tailings dams is vital in predicting the impact associated with the use of weathered CFA on the properties and performance of geopolymers. Blending CFA from different dams according to a consistent methodology and good quality control may assist in producing fairly homogeneous CFA feeds to geopolymer processing plants. In this instance, the purpose would be to build a CFA product stockpile with a more consistent chemical and mineralogical composition and particle distribution, although the issue of changed morphology in weathered ash would be unresolved.

Physicochemical considerations

Both classified and unclassified fly ashes are therefore available commercially in South Africa, and very large volumes of weathered unclassified fly ashes are scattered across several power stations. It is recommended to use commercially available fly ash for geopolymer preparation because they are manufactured and sold with known and controlled specifications. This will ensure the use of raw materials with consistency in specifications and quality. Classified fly ashes are finer than their unclassified counterparts. They are therefore expected to be more reactive with activators and contribute to the geopolymerisation process more efficiently.

The use of non-commercial, unclassified, weathered ash from dumps is not recommended, although it is a cheaper raw material than commercial ones. The reason is that such ashes are highly heterogeneous in terms of particle size and chemical and mineralogical compositions. Their use is likely to have an adverse effect on the geopolymerisation process and the physicochemical and mechanical properties of the produced geopolymers, which can be problematic for some applications.

Ash legislation

CFA is classified as hazardous waste by the National Environmental Waste Management Act (NEMWA), 2008 (Act 59 of 2008) because of its heavy metal content (Reynolds-Clausen and Singh, 2019). However, since 2020, fresh and weathered CFA from Eskom's power stations has been excluded from the definition of waste in terms of regulation 5 and 6 of the waste exclusion regulations, on the condition that CFA is used for specific applications, including the preparation of geopolymers.

Because of the exemption of Eskom's CFA from the regulation of hazardous waste, CFA from these power stations can now be used in geopolymer applications as stipulated in the Department of Forestry, Fisheries and the Environment (DFFE) gazette dated 3 February 2020. The exclusion of Eskom's ash from the definition of waste for the application of geopolymers provides a regulatory framework that will regulate the use of ash in geopolymer applications. According to the requirements of the exclusion, Eskom is nevertheless required to keep records of all aspects of beneficial use as per the requirements of regulation 9 and to further report the uses of ash to the DFFE in terms of regulation 10. Moreover, the DFFE remains within its rights to periodically review the generator's compliance with the exclusion to prevent environmental degradation that might emanate from the implementation of the exclusion. Failure to comply with this regulation may constitute an offence in terms of NEMWA, 2008, and will be liable for any environmental damage. Furthermore, Eskom had to submit a risk management plan in terms of regulation 10 of the waste exclusion regulations to show the risks on the use of CFA and management programme thereof.

POTENTIAL USES OF MINE TAILINGS FOR GEOPOLYMER PRODUCTION

The utilisation potential of mine tailings for geopolymer production is an emerging field of study and has been the subject of several recent reviews (Krishna *et al.*, 2021; Lazorenko *et al.*, 2021; Xiaolong *et al.*, 2021; He *et al.*, 2022; Qaidi *et al.*, 2022). Tailings from various commodities have been considered (Table 4). Depending on their reactivity under alkaline conditions, they can act as either reactive aluminosilicate precursors or inert aggregate substitutes and fillers.

Table 4. Sources of mine tailings from various commodities used in geopolymer production

Source of mine tailings	References
Barite mine tailings	Nergis *et al.*, (2021)
Copper mine tailings	Zhang *et al.*, (2011); Tian *et al.*, 2020; Ahmari and Zhang (2012, 2013)
Copper and nickel mine tailings	Blanc *et al.*, (2020)
Copper and zinc mine tailings	Paiva *et al.*, (2019)
Copper sulfide flotation tailings	Morales-Aranibar *et al.*, (2021)
Gold mine tailings	Wan *et al.*, (2017); Demir and Derun (2019); Falayi (2020); Falayi and Ikotun (2021); Zhang *et al.*, (2021a,b)
Iron ore mine tailings	Duan *et al.*, (2016a,b); Kuranchie *et al.*, (2016); Almada *et al.*, (2022); Ferreira *et al,*. (2022)
Lead-zing mine tailings	Bah *et al.*, (2022); Dai *et al.*, (2023)
Molybdenum-derived garnet mine tailings	Muttashar *et al.*, (2018); Wang *et al.*, (2019); Zhang *et al.*, (2023)
Nickel-laterite mine tailings	Longos Jr *et al.*, (2020)
Phosphate mine tailings	Moukannaa *et al.*, (2018)
Sphalerite flotation mine tailings	Wan *et al.*, (2018)
Vanadium mine tailings	Jiao *et al.*, (2013); Wei *et al.*, (2017)
Multiple mine tailings	Perumal *et al.*, (2019)

Mine tailings as aluminosilicate precursors

The structure and properties of geopolymers depend on the reactivity of the mineral components of mine tailings used as precursors with alkalis, which vary from minerals to minerals. Alkaline reactivity of mine tailings is generally considered as low. In order to make a preliminary assessment of the geopolymerisation potential of a mine's tailings, its mineralogical characterisation must be assessed and compared with the geopolymerisation behaviour of natural aluminosilicate minerals as ranked by Xu and van Deventer (2000; 2002) and Komnitsas and Zahakari (2007) (Figure 3). The higher the dissolution of Si and Al from minerals contained in mine tailings, the higher the suitability of the tailings for the production of geopolymer with good mechanical properties.

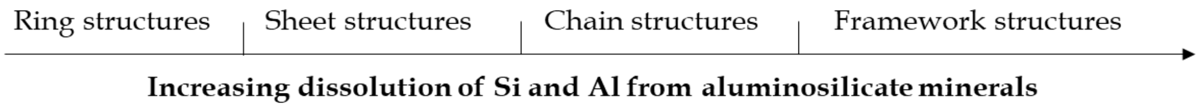

Figure 3. Pattern of geopolymerisation behaviour of natural aluminosilicate minerals under alkaline conditions.

The reactivity of mine tailings can be increased via pre-treatment methods such as mechanical, thermal, or thermochemical activation methods. This enhanced reactivity increases the specific surface areas of particles, and in turn the initial rate of geopolymerisation and the mechanical properties of cured geopolymers (e.g., Marjanovic *et al*., 2014).

Mine tailings are typically characterised by a high content of silica when compared to CFA. This increases the SiO_2/Al_2O_3 molar ratio in geopolymers, which negatively impacts the geopolymerisation process. This issue can be overcome by addition of, for example, metakaolin as a source of Al (Moukannaa *et al*., 2018).

Mine tailings as sand or aggregate substitutes and fillers

Mine tailings that have little or no chemical reactivity with alkaline reagents during the geopolymerisation process may be incorporated as a filler (sand replacement) or aggregate materials in geopolymer mix designs (Wan *et al*., 2017; Muttashar *et al*., 2018; Lazorenko *et al*., 2021). In order to be used for this purpose, mine tailings must also demonstrate other important physicochemical properties. These properties include:

- Particle size distribution – The particle size distribution of mine tailings is crucial for achieving a suitable packing and interlocking of particles in the geopolymer matrix. A well-graded distribution with a range of particles sizes is therefore desirable.
- Chemical composition – The chemical composition of mine tailings should be assessed to determine the presence of potentially harmful substances such as heavy metals or other contaminants. Low levels of harmful elements are preferred to ensure the safety and stability of the resulting geopolymer, although geopolymer matrices can also encapsulate them with reduced leachability. Low-reactivity mine tailings that could be used as fillers or aggregates will typically be finely-dispersed silica-containing wastes. Their reuse would assist in cutting the cost of geopolymers and preserving natural mineral resources (Lazorenko *et al*., 2021).
- Surface area – Mine tailings with a high surface area provide more reactive sites for geopolymerisation reactions to occur. A larger surface area allows for better bonding between the tailings and the geopolymer binder.
- Water absorption – The water absorption capacity of mine tailings is important to consider as it affects the workability of the geopolymer mixture. Tailings with high water absorption may require adjustments in the activator concentration or additional water to achieve the desired consistency.

Before mine tailings can be used as aggregates in geopolymer formulation, it is imperative to conduct thorough testing and analysis of the tailings to ensure their suitability for geopolymer production.

SOUTH AFRICAN CONTEXT

River sand is a natural fine aggregate commonly used as a filler in construction materials. It can represent up to a quarter of the cost of raw materials in the mix design of geopolymers. It is also a scarce natural resource, harvesting of which can cause damage to river systems. Materials that could potentially replace river sand, in part or full, in geopolymer mix designs in view of improving the cost-effectiveness of geopolymers are quartz-based gold mine tailings. Gold mine tailings were tested as fine aggregates to partially replace CEN (the European Committee for Standardisation) standard sand in geopolymers, where addition of up to 12.5 % of the tailings did not affect the mechanical properties of geopolymers (Barrie *et al*., 2015). Quartz sand, which makes up many South African gold mine tailings, was also successfully used as a filler in the production of metakaolin geopolymers with compressive strength up to 56 MPa (Wan *et al*., 2017). Quartz mill tailings were also used to replace up to 20% of metakaolin in geopolymer preparation without a negative impact on mechanical properties (Song *et al*., 2016). In South Africa, about 6 billion tons of silica-rich gold mine tailings are scattered across the West Rand, East Rand, and the Central Gauteng region. These tailings should be tested in geopolymer mix designs to ascertain their suitability as river sand substitutes without compromising the performance of the geopolymers. Further research (as in laboratory and field trials using tailings) with different fines contents should be carried out so that proper or optimum grading and proportioning of particles for geopolymers can be tentatively set as general guidelines for aggregate suppliers to follow.

The range of mine tailings that may be suitable as aluminosilicate precursor needs to be assessed.

FUTURE RESEARCH NEEDS, CHALLENGES, AND OPPORTUNITIES

Mine tailings have the potential to be utilised as a source of aluminosilicate material for the production of geopolymers. They are rich in silica and alumina, essential components for geopolymerisation. The sentiment around their utilisation in this context is generally positive, emphasising their potential environmental, economic, and material benefits. However, further research is needed to fully understand the properties and behaviour of mine tailings-based geopolymer composites. Addressing the technical challenges associated with their utilisation and establishing supportive frameworks are crucial for their successful implementation and widespread use in various industries. While the utilisation of mine tailings for geopolymers holds promise, several challenges and limitations exist. These include the variability in tailings composition, which affects the properties of the resulting geopolymers. Tailings from different mines may require specific processing techniques to optimise their reactivity and performance. Furthermore, market acceptance, standardisation, and regulatory frameworks for tailings-based geopolymers may still be under development, posing obstacles to widespread adoption.

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