Eco-friendly engineering: Geopolymer materials in marine construction.

Caroline Gonzaga de Souza [a].

[a] Departament of Material Science, Faculty of Material Engineering, Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG), Minas Gerais, Brazil; carolinesgonzaga@gmail.com, demat.cefetmg@gmail.com

Abstract. The construction industry plays a vital role in the country's economic growth but faces numerous obstacles, including environmental impact. Traditional materials, such as Portland cement, have limited applications in marine construction due to their vulnerability to corrosion attacks in harsh marine environments. Therefore, there is increasing demand for long-lasting, corrosion-resistant materials that can withstand extreme marine environment conditions. Geopolymer materials are a promising alternative as they possess mitigating properties to the shortcomings of conventional building materials and have thus been studied over the years with significant improvements since their discovery in the late 1970s. Geopolymers are inorganic, amorphous, and typically ceramic-like materials formed by the chemical reaction of source materials with alkaline activators. They have lower CO_2 emissions during production, require less water, and have superior mechanical properties superior to those of traditional cement-based materials. This literature review aims to investigate durable geopolymer materials that can be used in marine infrastructure works and their advantages over conventional materials.
The methodology involved searching major publication databases and other relevant sources to gather articles related to the topic. The risk of bias was evaluated using the ROBIS tool to ensure the review was comprehensive, systematic, and unbiased. The paper is divided into several sections after the research methodology that discuss the geopolymerization process, the characteristics of alkaline activators used in geopolymer synthesis, the properties of geopolymer materials, and case studies of geopolymer materials used and tested in marine conditions. The paper also discusses the limitations of the studies reviewed and outlines possible solutions. Finally, the review findings are summarized in the conclusion.

Keywords. Marine infrastructure, Portland cement, Geopolymer concrete, Compressive strength, Chloride resistance

1. Introduction

The construction sector is an essential industry that significantly impacts any country's economic progress and advancement. It entails planning, designing, and constructing buildings, infrastructure, and other structures required for social and economic activities. However, this industry faces several obstacles that limit its effectiveness and efficiency. The most significant challenge is the environmental impact of construction works, which includes carbon emission, waste generation, and depletion of natural resources [1,2].

Traditional construction materials such as cement and concrete have limited marine construction and building applications due to their vulnerability to corrosion attacks in harsh and unfavourable marine environments. These conditions can cause significant damage to marine infrastructure, resulting in increased maintenance costs and shortened structure lifespan. Because of these reasons, there is an increasing demand for long-lasting, corrosion-resistant materials that can withstand the harsh and corrosive conditions of the marine environment. Geopolymer materials have gained significant attention in recent years because they provide a range of advantages over traditional materials, such as having a lower carbon footprint, requiring lower temperatures during production, and using industrial waste materials as source materials [3]. They also need less water during preparation than Portland cement, reducing water consumption and making them more environmentally friendly. Furthermore, geopolymers have superior mechanical properties, such as higher compressive strength, higher resistance to acid and alkali environments, and better fire resistance.

Geopolymer materials are inorganic, amorphous, and typically ceramic-like materials formed by the chemical reaction of source materials such as fly ash, slag, kaolin, or metakaolin with alkaline activators like sodium or potassium silicates. The materials are thus also known as alkali-activated materials (AAMs) [4]. This chemical reaction, geopolymerization, results in a three-dimensional network of aluminosilicate chains like those found in natural minerals such as zeolites and feldspars.

Joseph Davidovits, a French materials scientist, in the late 1970s proposed the concept of "geopolymerization" as an alternative to the traditional use of ordinary Portland cement (OPC) in construction materials. Davidovits believed geopolymers could provide a more environmentally friendly and sustainable alternative to cement because of their lower CO_2 emissions during production and superior mechanical properties [5]. Since then, the field of geopolymer materials has grown, with research focusing more on property optimization, new formulations, and potential applications. Geopolymers have been used in various applications, including construction materials, refractories, ceramics, and composites.

The following sections will look at the potential applications of geopolymer materials in the marine construction industry and their advantages over traditional construction materials.

2. Research Methods

The present research is a literature review that investigates durable geopolymer materials that can be used in marine infrastructure works/industries, such as breakwaters and embankments. No actual experiments were carried out in this study, and the methodology is solely based on reviewing existing literature on the topic. The research methodology started with clearly defining the research question and objectives to ensure the literature review remains focused and relevant.

A comprehensive search was conducted to collect pertinent articles across several major publication databases: Google Scholar, Scopus, Microsoft Academia, Web of Science, and Elsevier. Elsevier and Scopus were chosen as the chief data sources since they offer a more comprehensive range and more relevant bibliometric data than the other databases. Supplementary data sources and databases like ACM Digital Library, Dimensions, and Wiley Online Library were also employed. The search strings used in the research were “geopolymer,” “marine infrastructure,” “erosion resistance,” and “alkali-activated materials.” A criterion was established to determine the relevant journal articles to be used.

The criteria for eligibility were set as follows: First, the article must be published in a peer-reviewed journal. Second, the article must be written in English. Third, the article must be published between 2018 and 2023. Lastly, the article must be related to the topic of research. After selecting the relevant articles that meet the inclusion criteria, the reference lists of the selected articles were reviewed to find additional relevant information. This Technique is referred to as backward citation searching.

The search process was documented throughout by keeping track of the keywords used, databases searched, and sources found. Keeping a record of the keywords helped refine the search strategy over time while keeping track of the databases searched helped identify the resources most relevant to the research topic. This helped to ensure that the review was comprehensive and that no relevant sources were missed.

The Risk of Bias in Systematic Reviews (ROBIS) tool was used to determine the trustworthiness and relevance of this review by assessing the risk of bias. This tool estimates the risk of bias across three spheres; one, study eligibility criteria; two, identification and selection of studies; and three, data collection and study assessment. Using this tool, the potential biases of the selected articles were evaluated to ensure the validity and credibility of the review.

This research methodology aimed to identify relevant articles and assess their quality to ensure the review is comprehensive, systematic, and unbiased.

3. Geopolymerization

Geopolymerization is a chemical process that involves converting aluminosilicate materials into geopolymer materials using alkaline activators. Figure 1 shows the different constituents and the geopolymer production process. Aluminosilicate materials can be found in various natural sources, such as clay minerals, volcanic ash, or industrial by-products, like fly ash and slag.

The first stage of geopolymerization is preparing raw materials, such as fly ash, slag, kaolin, or other aluminosilicate materials. These materials are ground and sieved to obtain a uniform particle size distribution. In the next stage, the raw materials are mixed with alkaline activators, usually sodium hydroxide and potassium hydroxide. Phosphoric acid is sometimes used as an alternative activator but is less preferred because the acidic medium is more hazardous and corrosive than the alkaline medium. Water is also added to the mixture to achieve the desired consistency. The mixture is then allowed to gel and harden into a solid geopolymer material by adding a setting agent such as sodium silicate. Curing is done at an elevated temperature to help achieve the desired mechanical and physical properties. The curing time and temperature vary depending on the desired geopolymer material and application. The final geopolymer product is tested to meet the required specifications and standards.

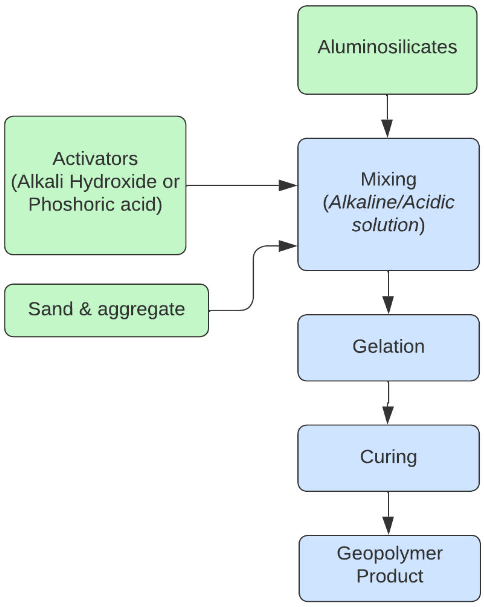

Fig. 1 – Geopolymer production process flowchart.

4. Alkaline activators

The activator's nature and amount influence the final geopolymer product's physical and chemical features.

4.1 Alkaline type

Alkaline activators play a crucial role in geopolymerization. They are responsible for initiating the chemical reaction between the raw materials. The alkaline activator typically consists of an alkali metal hydroxide, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH), or calcium hydroxide ($Ca(OH)_2$).

During geopolymer synthesis, the most employed alkaline activator is sodium hydroxide (NaOH), which is typically utilized along with sodium silicate (Na_2SiO_3). Adding sodium silicate helps reduce the amount of NaOH required and improves the success of the geopolymerization process. This mixture also produces less carbon dioxide emission.

The choice of an alkaline activator depends on various factors, including the type of precursor material used, the desired mechanical properties of the final product, the environmental impact, and the cost and availability of the activator. For example, potassium hydroxide is used when a high level of dissolution is desired. It is also often used with metakaolin as the precursor material, as it enhances the final product's mechanical properties. Calcium hydroxide is commonly used in geopolymerization processes that utilize waste materials such as slag, as it is cost-effective and readily available.

4.2 Alkaline concentration

The alkaline activator's concentration depends on the precursor aluminosilicate's nature and the curing conditions. The activator's concentration is crucial because it will affect the reaction kinetics and the properties of the final geopolymer material.

In general, the higher the concentrations of the activator, the faster the reaction rates, resulting in higher mechanical strength and denser geopolymer material. This is because the higher concentration of the activator leads to a greater concentration of hydroxyl ions (OH-) in the solution, which increases the pH and facilitates the dissolution of the aluminosilicate precursors. The high pH conditions also promote the polymerization of the geopolymeric gel, resulting in a denser material.

However, excessive concentrations of the activator can have adverse effects on the properties of the final geopolymer product. For example, a high concentration of the activator can lead to the formation of pores within the material, which decreases its mechanical properties. Several studies have shown fly-ash-based geopolymers' compressive strength generally increases as the sodium silicate to sodium hydroxide ratio rises from 0.5 to 1.5. Between 1.5 and 2.5 sodium silicate to sodium hydroxide ratios, the compressive strength of fly-ash based geopolymers decreases. This is because the high concentration of the activator results in a rapid reaction rate that generates excessive heat, leading to bubbles and voids within the material.

Additionally, high activator concentrations can cause the geopolymeric gel to polymerize too quickly, resulting in a brittle and weak material. The premature formation of geopolymeric gel can result in insufficient packing and incomplete polymerization, forming pores and cracks within the material.

Therefore, it is essential to carefully select the type and concentration of the alkaline activator during geopolymerization to ensure an optimal balance between reaction rate and mechanical properties to achieve the desired product.

5. Properties of geopolymer materials

5.1 Mechanical properties

In cement mortar, both compressive strength and flexural strength are closely related. However, due to the delicate nature of geopolymer and its strong adhesion to aggregate particles, geopolymer cement has a low compressive strength compared to flexural strength. According to research, increasing the sand concentration to 75% increases the flexural strength of a geopolymer to its maximum value. This value, however, gradually decreases due to a lack of binder to hold the grains together, resulting in the formation of large pores and increased porosity. Consequently, the type of alkali activator solution used, and the curing temperature significantly impacts the flexural strength of geopolymer concrete.

Isa and Awang [6] investigated the effects of adding granulated blast furnace slag (GGBS) to a palm oil fuel ash-based geopolymer. They found that this improved the mechanical, rheological, and durability properties of the geopolymer. The compressive and flexural strength were around 20–28 MPa and 4–4.5 MPa, respectively.

Kim et al. [7] developed a "Ca-rich slag-based Ultra-High-Performance Fiber-Reinforced Geopolymer Concrete (UHP-FRGC)" that has a high compressive strength of over 150 MPa. They used various silica sand-to-binder ratios to optimize its mechanical properties and achieved the highest compressive strength of 160.7 MPa. The best performance also resulted in a tensile strength of 10.3 MPa.

Table 1 shows a compilation of common geopolymer materials and their average compressive and tensile strengths based on various research journals.

Tab. 1 – Common geopolymer materials and their average compressive and tensile strengths.

Aluminosilicate precursor	Compressive Strength (MPa)
Fly-ash (FA)	40-80
High-calcium fly ash (HCFA)	40-60
Olive biomass fly-ash	40-50
Ground-granulated blast furnace slag (GGBS)	30-70
Metakaolin (MK)	60-80
Nano-MK	40-50
Kaolin (K)	50-60
Rice husk ash (RHA)	40-50
Red mud (RM)	30-40
Palm oil fuel ash (POFA)	20-30
Halloysite	~ 65
Activated clay (AC)	40-50
Volcanic ash (VA)	60-80
Bauxite ore tailing (BOT)	40-50
Iron ore tailing (IOT)	~110
Electrolytic manganese dioxide residue (EMDR)	~90
Ceramic grog (CEG)	~95
Silica fume (SF)	60-80
Pyroclastic flow deposit	60-80
Cassava peel ash (CPA)	20=30

5.2 Durability

Durability, in this context, broadly refers to the concrete's ability to withstand weathering, chemical attack, and abrasion. Several factors affect the durability of concrete in marine environments, including chlorine penetration and carbonation-induced corrosion.

Chloride resistance

Chloride ions are the most harmful and corrosive elements in marine environments. Chloride ingress can cause corrosion of steel reinforcement in concrete, leading to structural deterioration and reduced service life. Studies have shown that geopolymer concrete can have significantly lower chloride ion permeability and higher chloride binding capacity than OPC concrete.

Some research, however, revealed contradictory findings. Noushini et al. [8] conducted a study that extensively analyzed the impact of curing temperature and duration on the microstructure, mechanical properties, and durability of low-calcium fly ash-based geopolymer concrete. The specimens were subjected to twelve different heat curing regimes involving several temperatures and durations. The 28-day compressive strength varied between 27.4 and 62.3 MPa. The investigation discoveries showed that fly-ash (FA) based geopolymer concrete had little resistance to chloride ingress. Therefore, it is recommended for use in applications with minimal or no concerns about chloride-related durability.

Carbonation resistance

Carbonation is a process by which carbon dioxide from the atmosphere reacts with hydrated cement, thereby reducing the pH and decreasing the durability of the concrete.

While geopolymer concrete is generally believed to be more resistant to carbonation than OPC, the extent of carbonation resistance depends on the specific mix design and curing conditions. Although some studies have been conducted to test the carbonation resistance of geopolymers, they still need to be improved. Because the microstructure of geopolymers is more complex than that of OPC, it is impossible to use methods of carbonation effect testing of regular concrete to test the same in geopolymers.

Sulfate resistance

He et al. [2] found that when appropriate quantities of sodium chloride and gypsum are introduced to slag-based geopolymer concrete, the compressive strength and sulfate resistance of the concrete is enhanced. The mechanical strength increased by 90% in three days and 180% in four weeks, while sulfate corrosion resistance increased by 38% compared with ordinary Portland cement. Other areas of improvement were reduced overall cost and reduced carbon emissions by 25% and 50%, respectively.

6. Case Studies of geopolymer applications in marine-related environments

Li et al. [1] conducted a study that examined the gel evolutions of copper tailing-based green geopolymers in different environments, including air, deionized water, seawater, and under different situations, including freeze-thaw cycle and carbonization. After seven days of exposure to artificial seawater, they observed precipitation in OPC concrete sample, but no precipitation was found in the geopolymer concrete sample. They concluded chloride diffuses into the OPC concrete, resulting in portlandite solubility and decreasing strength. The strength of the geopolymer concrete sample increased slightly after being exposed to air for 28 days. The sample subjected to a cycle of freezing and thawing in seawater was extensively damaged, so a compressive strength test could not be done.

Ahmad et al. [3] c to determine the properties of geopolymer concrete made from fly ash and kaolin when exposed to salt water. They used an alkaline sodium silicate solution with a 12M sodium hydroxide activator (having two part solid to one-part liquid ratio). They managed to achieve a compressive strength of 46.71 MPa. The mixing ratio used was 2.5 sodium silicate to sodium hydroxide. However, this product showed less strength than the control geopolymer material because the salty water absorbed the strength component (calcium). The product managed, nevertheless, to pass the standard for use underwater as it retained over 90% strength compared to the control material.

Gupta et al. [9] highlight the potential of geopolymer materials for heavy metal removal from aqueous solutions. Due to their amorphous nature and porous structure, geopolymers have shown acceptable performance in heavy metal remediation processes. The researchers recommend customizing parameters, including factors such as surface consistency and area, and adjusting to the original chemistry to optimize the utilization of their full potential. They found fly ash-based geopolymers are an economical and eco-friendly solution for depolluting environmental dimensions while concurrently managing fly ash solid waste material. The article points up the need for further studies to improve the adsorption rates of geopolymer materials on multi-component industrial effluents for continuous operations.

Alzeebaree et al. [10] investigated the durability performance and mechanical properties of geopolymer concrete and standard concrete samples in their study. The research was conducted in ambient and salt-water environments, with some samples confined by carbon fiber and basalt fiber-reinforced polymer (FRP) fabric materials. The study's primary goal was to assess the durability and longevity of these hybrid materials, particularly for retrofit purposes in marine structures. The confined geopolymer demonstrated improved strength, ductility, and durability. The research also showed that carbon fiber with three layers outperformed basalt fiber with one layer in terms of mechanical and durability performance against chloride attack. Furthermore, the unconfined specimens demonstrated the worst performance.

In their research, Rahman and Al-Ameri [11] investigated the mechanical properties of self-compacting geopolymer concrete (SCGC) under ambient and saline conditions. They discovered that the SCGC mix could be effectively utilized for marine applications without experiencing any loss in mass. They also observed no cases of salt leaching during the study period. Additionally, specimens subjected to ambient curing and saltwater exposure exhibited better mechanical properties, including a 30% increase in compressive strength compared to the 4-week strength of 40 MPa. The authors established that some SCGC mixes had the potential to attain a strength of 40-50 MPa and be utilized efficiently in harsh marine environments without undergoing any deterioration over time. They concluded that warm environments with high moisture content promote the development of compressive and tensile strength of the concrete by facilitating the geopolymerization of any unreacted materials present in the concrete. Finally, the study highlights the need for further research on the long-term change in mechanical properties of geopolymers for their widespread application in marine construction.

Li et al. [12] studied the deterioration of metakaolin (MK) based geopolymers in saline conditions. They synthesized the geopolymer materials and exposed them to marine water for up to three months. They cured the geopolymer for seven days and achieved 48 MPa compressive strength. When exposed to air, the mechanical strength increased to 59MPa at three months. When exposed to saltwater, the mechanical strength decreased to 32Mpa at three months. They used a scanning electron microscope to observe the microstructure and found that the geopolymer exposed to seawater exhibited halite precipitation. Furthermore, there were cracks which may have been the reason for the low mechanical strength.

Ge et al. [13] studied the effect of casting and curing geopolymers in saline solutions of different concentrations. They mixed Class C fly ash and metakaolin (MK) as raw materials for the geopolymer synthesis with a fixed Si/Al molar ratio and varying Na/Al ratios. After curing for four weeks, they measured the microstructure, chemical, and mechanical properties. Results showed that the mechanical properties were influenced by salt concentrations and the ratio of Na/Al used. The study found that the ratio of 0.80 Na/Al was optimal for the maximum strength of geopolymers cast in saline environments. A higher ratio of up to 1.00 Na/Al resulted in a gradual decrease in the geopolymer strength.

Wu et al. [14] report on their investigation of the compressive strength and microstructure of geopolymers made using copper slag reprocessing tailings (CSRT) with varying amounts of metakaolin in a saline environment. After curing the geopolymer for seven days, the mechanical strength increased from 2.3Mpa to 15MPa when metakaolin content increased from 40% to 60%. The mechanical strength increased to 32.6MPa at 60% metakaolin content after 30 days of exposure to saltwater. In contrast, the geopolymer strength did not change when exposed to ambient air for 30 days. When exposed to seawater heat-cool cycles, the geopolymer achieved a maximum compressive strength of 23MPa at 60% metakaolin content. The results proved that marine conditions improve the compressive strength of the geopolymers while also ensuring that only a few cracks develop. The study suggests that CSRT-based geopolymers could find application for marine concrete after future improvements.

Hannanee et al. [15] investigated the durability of low calcium Class F fly-ash-based geopolymer concrete in a saline environment compared to OPC concrete. After seven days of submerging in seawater, the geopolymer samples showed no precipitation because they were well bonded. The water absorption was significantly lower in the geopolymer compared to OPC concrete. After immersion in seawater for four weeks, the geopolymer concrete showed a higher compressive strength of 56MPa against 46MPa of OPC concrete.

7. Limitations and future research work

Despite the great potential of geopolymer materials as an alternative to traditional building materials, there are still limitations to their applications in marine construction. One major shortcoming is the need for more comprehensive studies on the long-term durability of geopolymer materials in seawater. While several studies have shown promising results, more research is needed to fully understand their performance in aquatic environments and under different loading conditions before their large-scale implementation into the construction industry. This will enable engineers to design and construct geopolymer structures that can withstand the harsh marine environment.

Another area for improvement is the high variability in a geopolymer mix design and manufacturing processes, which makes it difficult to establish standard guidelines for their use in the construction industry. The lack of standardization and regulatory guidelines significantly affects their acceptance in the industry, as this can result in consistency in the quality and performance of structures built using these materials. Future research should focus on establishing standard guidelines for geopolymer mix design and geopolymerization processes to ensure uniformity in the excellence and performance of geopolymer structures.

Lastly, the cost of geopolymer materials is higher than traditional building materials, hindering wider adoption into marine construction/works. Scientists and engineers should find cost-effective ways of synthesizing and using geopolymers.

8. Conclusion

Using geopolymer materials in marine works has shown great potential in addressing the durability and sustainability challenges conventional concrete structures face in harsh marine environments. Geopolymer materials have been found to exhibit excellent mechanical and chemical properties, including high compressive strength, low permeability (low water and corrosive agent penetration), and resistance to corrosion and degradation by chlorine inhibition and carbonization. Furthermore, geopolymer materials are produced from industrial by-products and waste materials, which makes them an eco-friendly alternative to traditional materials. Using geopolymer materials in marine works also significantly reduces the carbon footprint of constructing and maintaining marine infrastructure.

Overall, the utilization and advancement of geopolymer materials in marine works present a hopeful solution to conventional concrete structures' sustainability and durability challenges. Further research and development in this field will be crucial in advancing geopolymer materials as a viable, cost-effective alternative in the marine and construction industries.

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