



# Military and Civilian Applications of Geopolymers

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## Abstract:

*In this article, various geopolymer applications in the context of both existing and potential future military applications are summarized. Geopolymers are a type of alkaline activated concrete binder with many advantageous properties over ordinary Portland cement based materials. Geopolymers are first compared to ordinary Portland cement based materials in regards to their mechanical properties, thermal properties, chemical resistance and CO<sub>2</sub> emissions during manufacturing. History of geopolymer applications and research is also discussed. Then, various geopolymer applications are summarized, including their use as a passive fire protection, material for general construction, “ink” for 3D printing. These types of applications are also discussed in the context of existing and potential military applications of geopolymers, including their use by U.S. armed forces and U.S. military research. Superior geopolymer resistance to explosions is also presented.*

## Keywords:

*application, geopolymer, 3D printing, military, portland cement*

## 1 Introduction

Geopolymers are inorganic polymers formed by polycondensation of various precursor materials [1], including metakaolin [2], fly ash [3] and granulated blast furnace slag [4], in strongly alkaline environment, by using special activator solutions, usually water solutions of hydroxides or silicates [5]. During geopolymerization process, a zeolitic, microporous structure, similar to natural zeolites, is formed [6]. They may be used as an alternative to ordinary Portland cement (OPC) as binders for concrete production [7], with geopolymer concrete having multiple advantages over OPC-based materials. As a binder material for concrete, geopolymers have many applications, such as in construction industry, passive protection against fire, deterioration etc., or as ink for 3D printing. Like standard concrete, geopolymer properties may also be

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enhanced by various aggregates, usually silica sand [8], additives, such as silica fumes [9] or antimicrobial nanoparticles [10], and reinforcement, usually various types of fibers, including carbon [11] and basalt fibers [12].

This article summarizes geopolymer advantages over OPC-based concrete, history of their use and their various applications in the context of their existing and potential future applications in the military, especially for the purposes of infrastructure construction and military engineering. For this purpose, various documents, including scientific articles, historical records, declassified and non-classified military documents or media articles, are reviewed and summarized. Additional potential applications and possibilities of future military geopolymer uses, based on their various advantageous properties and their modification by various additives, are also presented.

## 2 Advantages of Geopolymers Over Ordinary Portland Cement Concrete

Geopolymers and geopolymer-based concretes have many advantages over concrete based on OPC, the most widely used type of concrete [13]. Geopolymers have excellent mechanical properties, especially compressive strength [14], which may reach over 100 MPa [15]. And while tensile and flexural strength of pure geopolymer is very low, it may be significantly increased by using various types of reinforcements, especially fibers [16]. Fiber reinforcement may also be used to improve geopolymer compressive strength [17] and various types of fibers are therefore commonly used as reinforcement for geopolymers. Other commonly used aggregates or additives include sand and silica fumes, which are likewise used to improve mechanical properties of geopolymers [15, 18].

Geopolymers also have higher resistance to elevated temperatures, being able to withstand temperatures over 1 000 °C or more and unlike OPC-based concrete, they do not decompose with elevated temperatures, although they undergo structural changes, including loss of porosity due to internal sintering and breakdown of certain chemical bonds, which may lead to partial loss of mechanical properties [19]. OPC-based concrete starts to degrade when temperature exceeds 400 °C, due to decomposition of calcium hydroxide (its main component formed by hydration of calcium oxide), calcium carbonate and other components, which leads to quick deterioration and loss of mechanical properties [20]. In general, geopolymers withstand the temperatures higher than OPC-based concrete and their mechanical properties degrade less at elevated temperature. It is also possible to improve geopolymer heat resistance by using special additives or aggregates, such as chamotte (fireclay), which causes the geopolymer to counter mechanical properties deterioration by partially sintering in the contact zone between geopolymer matrix and chamotte aggregate contact zone [21]. For other types of concrete to become heat resistant, OPC usually has to be replaced with another type of binder, such as calcium aluminate cement [22], although this type of cement cannot be used for general construction, as it is prone to crystalline rearrangement, which causes deterioration of mechanical properties and vulnerability to chemicals and water exposure. This may subsequently cause structural collapse when used as a construction material. For these reasons, high-alumina cement is no longer used for construction [23].

Along with high thermal resistance, thermal conductivity of geopolymers is very low, making geopolymers an excellent material for heat insulation or passive fire protection, especially in foamed form (achieved by foaming agents, such as powdered aluminum or hydrogen peroxide) [24, 25].

In addition, geopolymers are much more resistant to chemical influences, which makes them suitable for the use in aggressive environments, such as acid rain, sewage treatment plants, sewers or chimneys. Furthermore, they also exhibit significant adsorption capabilities, making them potentially useful, for example, in wastewater treatment itself, where they can serve as adsorbents or filter media. For this purpose, they can also be functionalized with antibacterial agents such as metal nanoparticles [10]. Moreover, they are also capable of encapsulating various particles, including numerous types of hazardous waste. Industrial by-products or construction waste materials may also serve as geopolymer aggregates or even base materials (especially fly ash or granulated blast furnace slag [26]).

Geopolymers are also an environmentally friendly material, especially regarding lower CO<sub>2</sub> emissions and lower energy consumption during their manufacturing. OPC manufacturing includes heating limestone to make burnt lime (calcium oxide, the main component of OPC), which produces CO<sub>2</sub> directly and consumes a lot of energy. Commonly used rebar for reinforced concrete, usually iron or steel rods, also require a lot of energy for manufacturing and cause high CO<sub>2</sub> emissions. On the other hand, geopolymer manufacturing both requires less energy and causes lower CO<sub>2</sub> emissions. Various waste materials, especially fly ash and furnace slag, may also be used as a geopolymer base. In one project, it was discovered that geopolymers made with metakaolin (made by heat treatment of kaolinite or other minerals), water glass, silica fumes, carbon fibers, sand, aluminum powder and fly ash additive, has 72.05 % lower CO<sub>2</sub> emissions compared to common reinforced concrete, made with Portland cement, sand, water, additives and steel rebar. Geopolymers do not require metal rebar, as using fibers (carbon, basalt etc.) provides sufficient reinforcement and flexural/tensile strength increase [27].

The disadvantages of geopolymers include the necessity to use caustic activators (hydroxides or silicates), which presents work safety and logistical challenge, while OPC-based cement/concrete mix has to be mixed just with water, as instead of polycondensation, the calcium oxide (burnt lime) in OPC is hydrated to form calcium hydroxide (slaked lime), which serves as binder. Another big disadvantage is the absence of standardization of geopolymer mixtures/bases, which may lead to differences in properties of geopolymers from various base materials. For example, geopolymers based on granulated blast furnace slag usually has better mechanical properties due to presence of iron ions in geopolymer structure [28]. OPC and concrete mixes based on it are highly standardized and properties of resulting concrete are therefore highly predictable. However, the lack of standardization may be resolved by creating standards for geopolymer base materials, activators, mixtures etc.

### 3 History of Geopolymer Use

Historically, material similar to geopolymers was used by Romans. So-called “Roman concrete” (opus caementicium) was manufactured by mixing burnt lime, seawater, pozzolana (aluminosilicate fine volcanic ash) and crushed rocks as aggregates. Pozzolana reacts with alkaline environment formed by burnt lime and creates a specific structure. The main advantage of Roman concrete is its durability, especially when exposed to seawater, which further reinforces it by reacting with its components and forming a lattice of various hard minerals, including aluminum tobermorite and phillipsite. This also gave it a limited self-repair capability [29]. Significant development of geopolymer research and use took place in Ukraine (Ukrainian SSR) in 1950s, by

Viktor Glukhovskiy, who also discovered their zeolitic structure. He called the new material “gruntocements” (meaning “soil cements”, also called “gruntosilicates”) and described them in his publication “Gruntosilikaty” [30]. Geopolymers were used in USSR for building railway sleepers, sewers, buildings etc., as seen in Fig. 1.



Рис. 13. Фрагмент стены жилого дома из грунтосиликатных блоков.

Рис. 14. Строительство жилого дома из грунтосиликатных блоков.

*Fig. 1 Gruntocement construction (photo from original “Gruntosilicates” publication from 1959) [30]*

The term “geopolymer” was coined by French scientist Joseph Davidovits in 1980s, first as a material formed by inorganic polymerization, later as a material formed by alkaline activation of aluminosilicates, as the former definition may be used for any inorganic polymer [1].

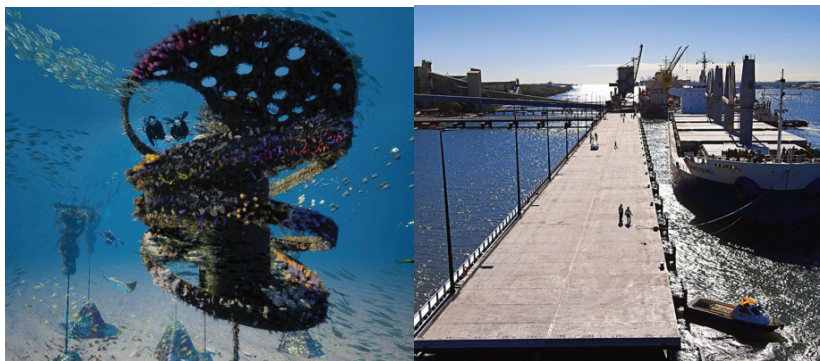
## 4 Geopolymer Applications in the Context of Military Use

### 4.1 General Construction/Infrastructure Use

Geopolymers are suitable for use in construction industry, due to their superior compressive strength, durability, low dry shrinkage and low permeability by liquids. In Australia, geopolymers are used for various applications as a construction material. In 2014, geopolymer concrete was used to build a runway and other areas at Brisbane West Wellcamp airport. In total, 40 000 m<sup>3</sup> of geopolymer-based concrete was used there [31]. Geopolymers were also used for the construction of Global Change Institute at the University of Queensland. It fulfilled all norms for standard concrete and had half the shrinkage and 30 % higher tensile strength [32]. An Australia based company, named Earth-friendly concrete, develops geopolymers as an environmentally friendly construction material to be used in infrastructure (airports, bridges, dams, railroads), building construction (houses, multistore buildings etc.) and manufacturing prefabricated components (tunnel components, sewer pipes etc.) [33]. Geopolymers are also suitable for marine or coastal applications, due to their high resistance to seawater [34]. Examples of buildings made by Earth-friendly concrete company are shown in Fig. 2.

The excellent mechanical, thermal and chemical properties of geopolymers make them a suitable material for military infrastructure construction, including applications exposing geopolymers to mechanical stress or high temperatures. In 1985, Geotechnical laboratory at Vicksburg, Mississippi, a part of US Army Corps of Engineers, investigated potential uses for “alkaline activated binders” (geopolymers) for military

purposes. This analysis considers geopolymers to be a suitable material for military applications, especially due to their mechanical properties and resistance to sulfur-based compounds (such as sulfane produced by sulfur oxidizing bacteria). Geopolymers are considered to be especially suitable for repairing infrastructure structures, such as runways, bridgeheads or roads. Quick-setting geopolymer mixtures are also considered suitable to reinforce soft soils, beaches and other unstable environment to allow transport of heavy machinery or combat vehicles. As a test, geopolymer was used to repair pavement and was able to withstand 12.2 metric tons after 4 hours. Geopolymer was also tested as a potential method for stabilization of loose soils (such as beach sand) for the purposes of military engineering, to allow safe transport of military vehicles and cargo. For this application, geopolymer is sufficient both in terms of hardening speed (in matter of hours) and mechanical properties. This analysis was declassified in 2010 as a part of USA automatic declassification procedure [35].



*Fig. 2 Underwater artificial coral reef (left) and Pikenda wharf (right) [33]*

In 1985, Joseph Davidovits and James L. Sawyer registered a US Patent no. 4,509,985 “Early high-strength mineral polymer” for Pyrament company [36]. This was later developed into a special type of geopolymer-portland based cement (trade-marked as Pyrament) for use to repair runways, roads and other concrete based structures. It is a quick setting concrete (roughly 4 hours) made from 80 % OPC and 20 % of geopolymer base (usually fly ash) and special additives. As of fall 1993, PYRAMENT concrete was listed for over 50 industrial facilities in the USA, 57 military installations in the USA, and 7 in other countries, and for non-military airports. [37]. In 1994, US army corps of engineers performed a study about this type of cement [38].

Although current development of geopolymer technology in the United States armed forces geopolymer technology cannot be fully determined due to classification, ERDC (Engineer Research and Development Center), a research organization for U.S Army Corps of Engineers is performing research of geopolymer materials and applications and publishes some of its findings. These research projects include development of soil-stabilized geopolymer platforms as a base for construction of storage sites for valuable assets (vehicles, aircraft etc.) and their protection against corrosive environment [39]. Another ERDC research project investigated using geopolymer nanoceramic mortar liner system for corrosion protection and rehabilitation of storm-water piping, which is another potential application of geopolymers, thanks to their high chemical resistance and durability [40].

Geopolymers are also a viable material for underground construction, especially due to their higher chemical resistance and compressive strength when compared to

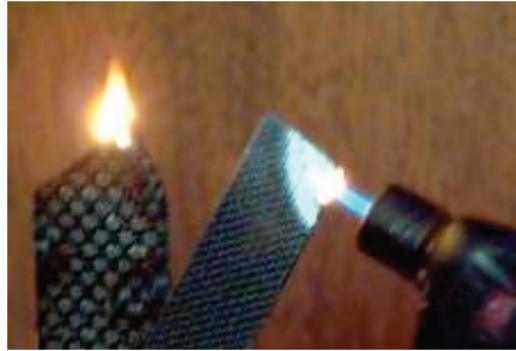
OPC-based concrete. High chemical resistance is necessary for underground construction due to possible presence of acidic groundwaters. Geopolymers are also resistant against cold and changes in temperature, which makes them useful for tunnels construction (as underground temperature is usually stable, but tunnels may be frozen by cold wind blowing through them, for example) [41]. Geopolymers are therefore feasible for construction of underground military facilities, bunkers etc. as well.

Geopolymer is also an appropriate material for manufacturing Ultra-high performance concrete (UHPC), a type of enhanced fibrous and cementitious concrete with high compressive strength (up to 250 MPa, sixteen times the compressive strength of regular concrete) and tensile strength (15-20 MPa). This type of concrete is applicable in infrastructure, marine facilities, military facilities (both general and defensive structures) and for other applications [42]. A study investigating the possibility of applying geopolymer technology for UHPC manufacturing discovered that geopolymers may make the UHPC manufacturing more sustainable by utilizing industrial byproducts in the manufacturing process and lowering energy requirements and CO<sub>2</sub> emissions. According to the study, high content of quartz powder and silica fumes, as well as inclusion of steel fibers, significantly improves geopolymer UHPC compressive strength [43].

#### ***4.2 Passive Fire Protection***

Foamed geopolymers have a very low thermal conductivity. This makes them, along with their high thermal resistance and low density, an ideal material for manufacturing passive fire protection and thermal isolation of internal structures and exteriors of buildings. Various additives may also be used to improve their properties for this application, including basalt fibers, basalt grids, hollow glass microspheres or technical garnet. For example, geopolymer material with 50 vol. % of glass microspheres and 5 % of hydrogen peroxide as foaming agent reached thermal conductivity of 0.068 W/m · K. One-hundred mm thick slabs made from this material also withstood temperature of 1 100 °C for over 2 hours while the temperature on the other side did not reach 100 °C. Spraying geopolymer coatings on OSB boards improves their durability in fire (by tens of minutes at minimum), which gives more time to extinguish the fire or evacuate people from the building. Geopolymer foams may also be used to protect internal steel beams from losing their mechanical properties and collapsing [24, 25, 44].

Geopolymer thermal resistance and low thermal conductivity may similarly be used for military applications as a passive fire protection. A 1994 study investigated foamed geopolymer-carbon composite as a fire protection for aircrafts, for the purpose of allowing crew to escape after an emergency landing and fire aboard. This composite is resistant to temperatures up to 1 200 °C (at this temperature, aviation composites are usually already burning and releasing toxic fumes). Fig. 3 shows the geopolymer-carbon composite exposed to flame. Geopolymer may likewise be potentially used on military (and civilian) ships, submarines, vehicles and military structures. All of these applications make furthermore use of low foamed geopolymers density [37]. Geopolymer-based resins or foams are considered a possible protective material for aviation industry, including aircraft construction (interior panel lining, for example), by both Federal Aviation Administration (USA) [45] and Future Sky Safety (EU-funded aviation safety research program) [46]. An example of geopolymer composite from this research is shown in Fig. 4.



*Fig. 3 Burning aviation composite (left) and geopolymer-carbon composite withstanding 1 200 °C [37]*



*Fig. 4 Geopolymer/recycled carbon fiber composite for aviation industry after flexural strength test [46]*

### **4.3 3D printing**

Like concrete, geopolymers are a viable “ink” for 3D printing of prefabricated components or even whole buildings. They may be used on their own or as a hybrid or geopolymer and common concrete. Using concrete-geopolymer hybrids leads to smaller compressive strength loss for 3D printed material when compared to casting, as geopolymer polycondensation leads to stronger bonds between printed layers. The carbon footprint of geopolymer-based 3D printing materials is also lowered compared to materials based solely on OPC [47].

Using geopolymers themselves as 3D “ink” is also possible. For example, university at Padova, Italy, in cooperation with various other organizations, developed a special granulation technique to manufacture special geopolymer base for 3D printing. In short, it is made by coating grains of sand with metakaolin. This geopolymer base produces layers without defects, has good compressive strength when 3D printed (20 MPa at 30 % porosity) and is not weakened by water exposure. This allows for variable ratios of sand and metakaolin and 3D printed geopolymer does not “melt” before hardening [48].

Italian-Russian company Renca develops and manufactures both geopolymer “3D ink” and develops various other systems for geopolymer 3D printing, such as automatic mixing system compatible with commercially available 3D printers. Their 3D ink is compatible with construction 3D printer of all sizes, including the largest ones (gantry 3D printers) [49].

Although 3D printed geopolymers are less suitable for military use, due to their lower compressive strength compared to cast geopolymers, they may still be used for construction of many types of structures, including Barracks huts or Jersey barriers. 3D printing of concrete is used by US Armed forces as part of ACES program (Automated Construction of Expeditionary Structures), developed by U.S. Army Engineer Research and Development Center, together with NASA’s Marshall Space Flight Center, Kennedy Space Center, and Caterpillar, Inc., which uses mobile 3D printers (gantry printers) to construct these types of structures in the field environment with minimum personnel requirements [50]. U.S Department of defense has also used 3D printing to construct multiple training barracks [51]. ERDC has performed research of geopolymer 4D printing (special type of 3D printing creating objects, which may further change their shape in responses to various environmental stimuli, such as being submerged in water, the 4<sup>th</sup> dimension being time after printing) [52].

#### ***4.4 Geopolymers as Explosion Proof Materials?***

Although not many studies have investigated the resistance of geopolymers to explosions, they seem to be significantly more explosion-proof than concrete (including reinforced concrete). In 2019 study, geopolymer reinforced by steel fiber mesh and reinforced concrete (Steel rebar), in the form of 1 300 × 1 300 × 100 mm cuboids in steel frames, exposed to explosion of 200 kg of TNT at 3, 5 and 7 meters. Geopolymer samples have shown higher resistance to explosions when compared to reinforced concrete, as a concrete sample positioned at 3 meters from explosion was completely blown apart, while a geopolymer sample was shattered, but not blown apart. The concrete sample positioned at 5 meters from explosion was likewise completely blown apart, unlike the geopolymer one, which was merely cracked [53]. Samples are shown in Fig. 5.

This superior blast resistance makes geopolymer a potential material for construction of defensive structures (which might be hit by explosions), such as fortifications or bunkers, although thorough testing would be needed to determine the exact geopolymer structure resistance to explosions from artillery shells, guided missiles, drone strikes etc.

#### ***4.5 Geopolymers for Electromagnetic Field and Radiation Shielding***

Geopolymers may be used for shielding electromagnetic phenomenon, including electromagnetic fields (EMF) and electromagnetic radiation. Electromagnetic fields and non-ionizing radiation, such as microwaves or radio waves generated by high-power transmitters or radar arrays, may present a health risk. For example, strong RF (radio-frequency) or microwave electromagnetic fields heat up tissues and long-term exposure to such fields may be carcinogenic. The risks of EMF exposure have been a subject of many studies, and various safety standards and guidelines are in place, usually set by the International Commission on Non-Ionizing Radiation Protection (ICNIRP), an organization recognized by World Health Organization [54]. Electromagnetic shielding is usually composed from metal sheets or grids, which are heavy and may corrode



in time, limiting their applications. For these reasons, various shielding materials are developed, including geopolymer-based materials [55]. While having low shielding capability by themselves (due to their relatively low conductivity), geopolymers may serve as a matrix for electromagnetic shielding composites. In addition to metal grids, various other types of conductive materials may be used, including carbon and basalt grids, which are also significantly lighter than metal sheets or grids. Geopolymers may also be foamed, which further reduces their density, making them an ideal material for electromagnetic shielding composite manufacturing, as they do not significantly increase the weight of whole structures, while creating Faraday cage [56]. Military applications of EMF shielding include the protection of personnel in the vicinity of strong sources of electromagnetic fields (radars, transmitters, jammers etc.), protection of equipment or structures against EMI (Electromagnetic interference) or even defense against electromagnetic (electronic) warfare, which may disrupt the function of complex electronics, block transmissions etc. [57].



*Fig. 5 Remnants of (a) concrete 3 m from explosion, (b) concrete 5 m from explosion, (c) geopolymer 3 m from explosion and (d) geopolymer 5 m from explosion [53]*

Geopolymers may also serve as shielding against ionizing radiation, especially gamma rays and neutron radiation (as alpha and beta particles are unable to penetrate most materials). While geopolymers and geopolymer based concrete have better gamma rays/neutron radiation shielding (attenuation) capabilities than OPC based concrete [58], they may be enhanced by additives of heavy metals or their oxides. A utility model registered by Technical University of Liberec uses geopolymer composite with various content of lead or lead oxide microparticles (up to 50 % of weight of geopolymer base used). The composite also uses carbon grids to both reinforce the geopolymer and to provide EMF shielding properties [59]. Geopolymers and geopolymer shielding composites are therefore a potential material for construction of nuclear reactor shielding, fallout shelters, hospitals with x-ray machines and other structures, civilian and military alike, with the risk of exposure to ionizing radiation.

## 5 Conclusion

This article reviews the geopolymer properties in comparison to OPC-based concrete and their applications in context of existing and potential military applications. Geopolymers are an alternative binder for concrete manufacturing, with many advantages over commonly used OPC, such as higher compressive strength, higher resistance to high temperatures, lower thermal conductivity etc. These properties make geopolymers a potential material for various military applications, including infrastructure construction, underground construction, military engineering or 3D printing, but also aviation safety (as passive fire protection) or material for fortification construction, due to their higher resistance to explosions when compared to OPC-based concrete. Geopolymers are used by US Armed forces, while U.S military laboratories, such as ERDC, are further researching their applications, although not all information has been released to the public, due to U.S classification policy on military research.

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