Development of Geopolymers for 3D Printing Applications on Mars

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ABSTRACT

Geopolymers have been established as a promising material option for in-situ construction on Mars due to their inherent material properties and availability of raw materials across the globally consistent basaltic composition of Martian regolith. This paper presents the current state-of-the-art geopolymer research, which primarily investigates the various base compositions of geopolymers, the factors influencing the geopolymerization process, as well as the 3D printing process. The subsequent research aims to extend current understanding by conducting material experiments and testing real-scale prototypes in controlled environments, which includes the exploration of various material compositions for geopolymer synthesis without the aid of high temperature curing. Further testing with 1:1 scale aggregates and fibres will be crucial to optimize the composition ratio, while material characterization will provide insights into enhancing the performance and durability of geopolymers in extraterrestrial environments. The aim is to contribute to the development of resource-efficient construction practices through working prototypes and material characterization for future Martian exploration and habitation.

KEYWORDS: Off-earth habitats; In-situ resource utilization; Geopolymer; 3D Printing

1 INTRODUCTION

Geopolymers have emerged in the last few decades as a cementitious material seen as an alternative to concrete. On Earth, the material is composed of recycled industrial waste and fly ash and has significantly reduced greenhouse emissions, but it is also a promising material option for in-situ construction on Mars. This is due to the material properties and the availability of raw materials found in the globally consistent largely basaltic composition of Martian regolith (Fackrell et al., 2021). Using these in-situ sourced materials minimizes transporting construction materials from Earth to extraterrestrial environments (Ma et al., 2022).

The presented study is part of the research project *Rhizome 2.0: Scaling-up Capability of Human-Robot Interaction Supported Approaches for Robotically 3D-printing Extraterrestrial Habitats*, implemented in the Robotic Building (RB) lab at TU Delft. By reviewing existing material explorations, large-scale cementitious 3D printing considerations, and conducting three rounds of experiments, the aim of the study is to identify the main parameters in material composition and the synthesis process specific to Mars, taking into account the requirements of low-temperature curing, material adaptability, and in-situ resource utilization (ISRU). By optimizing mixture ratios and evaluating mechanical performance, the research aims to contribute to the existing knowledge on geopolymer-based construction for off-world environments and serve as a basis for future testing at a 1:1 scale with aggregates and fibres to optimize construction and improve performance.

The project builds upon Calabrese et al.'s review of cementless materials for 3d printing arguing for geopolymers as a viable material option (2024). The research results in the production of a geopolymer recipe using Mars simulant regolith, which can be robotically 3D printed in conditions replicated on Mars. The geopolymer material acts as a method of testing the 1:1 constructible scale of the architectural shelters for the empty lava tubes on Mars, as developed previously in Rhizome 1.0 (Bier et al., 2024).

Methodology

The research methodology will follow a three-phase approach to develop and assess geopolymer materials for potential use in Martian construction. These steps include a comprehensive literature review, initial material experimentation, and the application of optimized recipes using Martian regolith simulants.

The study starts with the state-of-the-art review of geopolymer research encompassing the background and composition of geopolymers, their chemical and physical properties, and the methodologies used in geopolymerization. This review informs the material synthesis process, identifying key variables that influence geopolymer performance within the context of 3D printing applications. This involves factors affecting the workability, setting time, and mechanical properties of geopolymers in relation to their potential use in extraterrestrial construction.

The review is followed by initial material experiments, which will test both an alkaline-activated metakaolin geopolymer, as well as an acid-activated geopolymer, referencing existing geopolymer recipes and toolkits. These experiments will involve testing the ratios and combinations to optimize key properties such as workability for 3D printing, setting time, and compressive strength. Through this iterative testing, the key observations and considerations in the process will be identified for further application with Martian regolith simulants.

The final experimental phase involves substituting the regolith in the optimized recipe with Mars Global Hydrated Clay (MGS-1C) and Mars Global Polyhydrated Sulfate (MGS-1S) to assess the adaptability of this method of geopolymer synthesis under conditions that closely mimic Martian soil composition. The focus is on verifying the considerations made during the experimentation and analyzing the impact of regolith composition on the geopolymerization process.

The optimized recipes can then be used as a foundation for future steps in robotic 3D printing experiments with industry partners such as Vertico and Concrefy, refining scalable methods for fabricating structural components with precision and consistency in Mars-like environments.

2 STATE-OF-THE-ART

The literature review primarily investigates the various base compositions of geopolymers, and factors influencing the geopolymerization process. Sources include both research and experiments made for on-Earth applications, and those using Martian or Lunar stimulants, as well as environmental factors that reflect those extra-terrestrial conditions. These investigations encompass considerations such as binder options, water availability, energy requirement, aggregate options, structural requirements, and durability concerns, pivotal for evaluating the efficacy of geopolymer materials in Martian conditions (Reches, 2019).

Geopolymer Composition

Geopolymers are inorganic polymeric materials formed through geosynthesis, comprising chains or networks of mineral molecules linked by covalent bonds (Davidovits, 1994). Two primary synthesis routes exist: (a) alkaline activation using hydroxides and alkali silicates to produce silicate- or silico-aluminate-based networks, and (b) acidic activation using phosphoric acid to create phosphate-based geopolymers. In terms of geopolymer composition, the globally consistent composition of Martian regolith, predominantly basaltic in nature, provides a reliable source of materials for geopolymerization (Fackrell et al., 2021). The primary constituents of geopolymer, including Al-Si-O-containing minerals, can be readily obtained through the ball-milling of local rocks and regolith, which has been confirmed to have reliable sources of aluminum and silicon necessary for the formation of amorphous aluminosilicate networks (Ma et al, 2022).

The mapping of geological types and elements across Mars is used to access and address the resource management for ISRU (Appendix A,B,C). Aluminum, silicate, and olivine are three resources that play a role in geopolymer composition, and through their comparative mapping, geopolymer production sites can be chosen closer to resource-rich regions to minimize the cost and energy required for material transportation. A clear understanding of the distribution of these resources informs how sustainable and scalable geopolymer production would be for long-term Martian colonization efforts.

Aluminum is a critical component for phosphoric acid-activated geopolymers, forming the backbone of the alumino-phosphate matrix. Mapping aluminum-rich minerals, such as kaolinite, feldspar, and other aluminosilicate deposits, commonly found in volcanic and sedimentary contexts, would determine optimal sites for geopolymer production facilities. Silicates, primarily in the form of silica (SiO_2) or silicate minerals like quartz and feldspar, enhance the structural strength of geopolymers as a filler, and can be found as amorphous silica in dust and basalts in the Martian regolith. They not only contribute to geopolymer performance but also offer flexibility for tailoring recipes to specific construction needs, such as compressive strength or thermal resistance (Castillo et al., 2021). Olivine ($(Mg,Fe)_2SiO_4$) serves as a secondary material in geopolymer synthesis, contributing magnesium and iron to the composition and can enhance the thermal and mechanical properties. It is also a material that has higher reactivity in acidic environments (Olsson et al., 2012), which can be leveraged in phosphoric acid-based geopolymer recipes if combined with an alumina-rich material. Mapping olivine-rich regions on Mars, such as basaltic terrains and volcanic deposits, identifies sites where this abundant mineral can be utilized as a filler or an aggregate additive.

To achieve geopolymerization while using Martian and Lunar simulants, various approaches to material composition have been proposed and tested. The most popular is using a ready base, such as fly ash or volcanic tuff or other raw materials and supplementing it with proper metal oxides. For the alkaline synthesis method, the geopolymer reaction consists of an aqueous hydroxide or silicate alkaline medium (generally 30-35%), and a solid component that includes aluminates and silicates (generally 65-70%). A selected number of material recipes have been studied from the literature to gain an understanding of their composition, additives, and performance (Appendix D). Most state-of-the-art geopolymer developments for Martian and Lunar construction follow the alkaline synthesis method. Of the alkaline-activated geopolymer recipes that have been published, the binder solution generally falls under either hydroxide-based or silicate-based activators, which can be compared based on various factors used to assess suitability for the geopolymerization and 3D printing process (Appendix E). Acid-activated geopolymers, on the other hand, have seen less exploration but pose a similar potential as a construction material. One key advantage of phosphate-based geopolymerization is that it does not require high-temperature curing, which is a critical consideration for in-situ manufacturing where thermal energy resources are limited. Given these considerations, the subsequent material experiments within this study will focus on phosphate-based geopolymers and those forming aluminum phosphate ($AlPO_4$) networks.

For Martian applications, research indicates that phosphate-based geopolymers ($AlPO_4$) are particularly suitable due to the compatibility of phosphoric acid with the diverse mineral substrates found in Martian regolith (Buchner et al., 2018). As such, phosphoric acid is selected as the binding agent for the geopolymerization material experiments in this study. Phosphates, such as apatite identified on Mars, could serve as a local source of phosphoric acid, enabling the synthesis of durable materials for construction in extraterrestrial environments (Yen et al., 2014). The synthesis is not selective towards the planetary regolith composition, allowing its application on a wide variety of extraterrestrial sites. As part of this study, there will be the testing of this consistent method on a selection of regolith simulants, including generic lava flour, volcanic ash from Sicily, as well as high-fidelity Mars regolith simulant, which will also serve to verify the consistency of the results from this methodology.

Geopolymerization Process

An important factor to consider for 3D printing on Mars is the atmosphere. Mars has large temperature fluctuations during the day/night cycles. Martian surface experiences a swing from -153° to $+20^{\circ}$ near the equator, and the average surface pressure on Mars is also about 0.6% that of Earth's (Reches, 2019). Although the atmospheric pressure and temperature inside lava tubes will be slightly different from the surface pressure, it would still be significantly lower than Earth's atmospheric pressure. Experiments completed by Hedayati and Stulova (2023) highlight the effects of temperature and pressure on the geopolymerization process. Most experiments have been completed at ambient temperature (~23C), but due to the fact that most full geopolymerization processes take over 24 hours, meaning it will experience a full day cycle on Mars, it will also be important to look at the effect of temperature and temperature fluctuations on the curing process.

The curing time is crucial in the experiments to understand printability and avoid clogging the extruder. Curing also is dependent on the size/thickness and material composition. Based on the procedures in the referenced previous experiments regarding cementitious and geopolymer testing, casting the material in a square mould can be used to monitor and check the curing time before 3D printing, and differential scanning calorimetry (DSC) analysis is used for evaluation of the material. Although pressure is said to not affect the curing time, the porosity of the specimens was directly related to the curing pressure of the specimens (Hedayati and Stulova, 2023). It was found that curing completed at atmospheric pressure did not induce any visible porosity in the specimens, while those cured at 0.01 bar had several large pores, lowering their structural capability.

Physical Properties

When looking at the physical properties of 3D-printed geopolymers, some variables to consider are particle size, particle morphology, and the extrusion size of the print. The particle size of Martian simulants influences the viability of geopolymerization, with smaller particle sizes promoting faster activation and material strength (Tchakoute et al., 2013). For the study with the finest particle size for volcanic ash, the particle size distribution ranges from 0.23 to 80µm, with the average being 10.68 µm, while other studies show particle sizes closer to 125µm. Martian regolith contains morphological forms that do not exist on Earth; these are spherical lunar chondrules, with dimensions from a few microns to 0.5 mm (Korniejenko et al., 2022).

The particles used are predominantly angular with smooth facets. However, the commercially available regolith simulants have sharp facets because they are made by crushing and milling. Another variable found in the studies, both cast and 3D printed, was the thickness or diameter of the geopolymer. Most 3D printed versions were described as GP ink, and are extruded from diameters of 0.8mm - 7mm. To simulate the thickness of desired 3D prints for construction, moulds were often used, which will result in a difference in pressure experienced by the material.

Mechanical Properties

To evaluate the success of the geopolymer experiments that have been performed and the results, several mechanical properties are tested, primarily consisting of compression strength and tensile/ flexural strength through the addition of fibres. Compressive strength results as high as 23–50 MPa were found to be exhibited by geopolymers after 28 days, under optimal conditions, while other results have shown closer to 10MPa. Greater compressive strength values may be expected from volcanic ash-based geopolymers via a slight increase in curing temperature (Tchakoute et al, 2013). The presence of basalt deposits on Mars also offers the potential for in-situ production of basalt fibres, which can serve as reinforcing phases for fabricating geopolymer composites. Experiments by Ma et al., 2022 have demonstrated that the addition of short basalt fibres (BAsf) to the GP matrix can significantly increase the maximum flexural strength and work of fracture by a factor of 5 and two orders of magnitude. An overview of the additives used to optimize the material composition and recipes can be referenced in Appendix F. These additions to manipulate the strength and rheology of the geopolymer during and after 3-D printing will also be investigated in subsequent research.

3 MATERIAL EXPERIMENTS

The experimental phase of this research focuses on identifying the variables and considerations for the development and refinement of the geopolymerization process for 3D printing. This is done through a series of material tests, first with existing recipes, which will then be modified and tested according to the different factors that define its curing and performance. The variables that are adjusted will not only be the material composition, but also the refinement of the procedure. Two main criteria will be used to evaluate the geopolymer specimens – mechanical performance which indicates its structural capability, and rheology which indicates its printability for robotic additive manufacturing on site. Figure 3 outlines the general experimental procedure that will guide the three main rounds of material exploration.

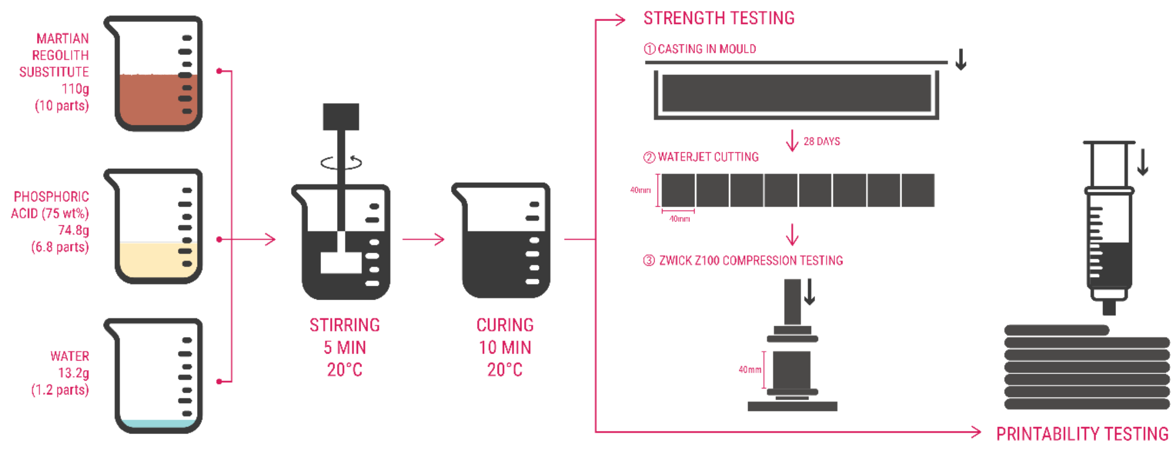

Figure 1_ Geopolymer Experimental Procedure and Testing (Source: author)

Initial Material Tests with Metakaolin-Based Geopolymer

The first set of experiments utilized a simple alkaline-activated recipe comprising metakaolin, sodium silicate, water, bentonite, and sand. One control composition, consisting solely of metakaolin and sodium silicate, was prepared alongside four variations incorporating different additives. The primary objective was to initiate the geopolymerization process without requiring high-temperature curing, replicating conditions similar to those on Mars. A rudimentary extrusion test using a syringe was conducted to evaluate the material's hardening speed, rheology, and layer buildability for 3D printing.

Unexpectedly, the setting time exceeded initial expectations. While literature suggests that extruded geopolymers should harden within 24 hours, specimens from this test series required over 48 hours to harden completely. The next steps to address this slower reaction rate will be in the material composition as well as the curing environment to achieve faster setting times under ambient conditions rather than the controlled higher-temperature environments often used in geopolymer synthesis.

RECIPE VARIATIONS	Metakaolin (g)	Sodium Silicate (g)	Water (g)	Bentonite (g)	Sand (g)
Basic Geopolymer	65	35	~20	0	0
Variation 1 (5% Bentonite)	65	35	~20	5	0
Variation 2 (1:1 Sand Ratio)	65	35	~20	0	100
Variation 3 (1.5:1 Sand Ratio)	65	35	~20	0	150
Variation 4 (Bentonite + Sand)	65	35	~20	5	100

Table 1_Inital Metakaolin Material Test Recipe Variations

Material Test with Basaltic Volcanic Ash and Phosphoric Acid

The second phase of testing involved materials more chemically aligned with Martian regolith, as well as the use of an acidic activator solution to address the ambient temperature curing conditions that are present. Lava flour, a fine volcanic ash, was paired with phosphoric acid to simulate a composition closer to Martian substrates, although not an exact match to Martian regolith. This aimed to evaluate the interaction between lava flour and phosphoric acid while exploring its behaviour under extrusion and casting conditions. Three cubic specimens were cast for preliminary compressive strength testing, and additional manual printability tests were performed. The resulting material demonstrated promising rheological properties in terms of texture and printability.

Following the initial experiments, a material recipe is prepared with basaltic volcanic ash (Table 4), and 75% phosphoric acid as the binder for the purpose of compression strength testing. Beams were cast from the mixture and subsequently cut into eight uniform cubes and edges were trimmed using a waterjet cutter. Following the optimal ratio outlined in previous research (Buchner et al., 2018), a single beam was cast to produce nine cubes. Initial observations revealed significant bubbling during the curing process, resulting in a porous and less compact final product. Additionally, after 48 hours, the material had not fully hardened, indicating a potential issue with the reaction process or mixture preparation. From these observations, 3 adjustments needed to be made to the process: controlled particle size, the deaeration of the mixture, and controlled curing conditions.

To address the porosity and delayed hardening, a second mixture was prepared by filtering the volcanic ash to a particle size of 425 µm, which resulted in a more uniform and workable consistency. As such, in this second round additional beams were cast using ash with particle sizes of 1 mm and below, as well as 425 µm and below, in addition to the unfiltered control grains. Initial observations suggest that the particle size significantly influences the reaction rate and curing process. Larger particles likely contributed to the porosity observed in the first sample, as insufficient reaction time and poor air bubble release led to voids in the material. This step will also serve to investigate whether sifting or grinding processes would be necessary for Martian regolith, which might impact the production workflows on Mars.

RECIPE VARIATIONS	Particle Size	Volcanic Ash (g)	Phosphoric Acid (g)	Water (g)
1 (control)	Unfiltered	150	102	18
2	1 mm	150	102	18
3	425 µm	150	102	18

Table 2_Basaltic Volcanic Ash Material Test Recipe Variations

The revised process incorporated a longer initial curing time of 10 minutes before stirring, tamping, and pouring, allowing the chemical reaction to stabilize and air bubbles to escape. The samples were also enclosed during curing to retain moisture and aim to improve the consistency of hardening. This adjustment resulted in a less porous material when finer particle sizes were used. However, the tacky surface of some samples raises questions about whether this is an inherent material property or a sign of an incomplete setting, requiring further investigation.

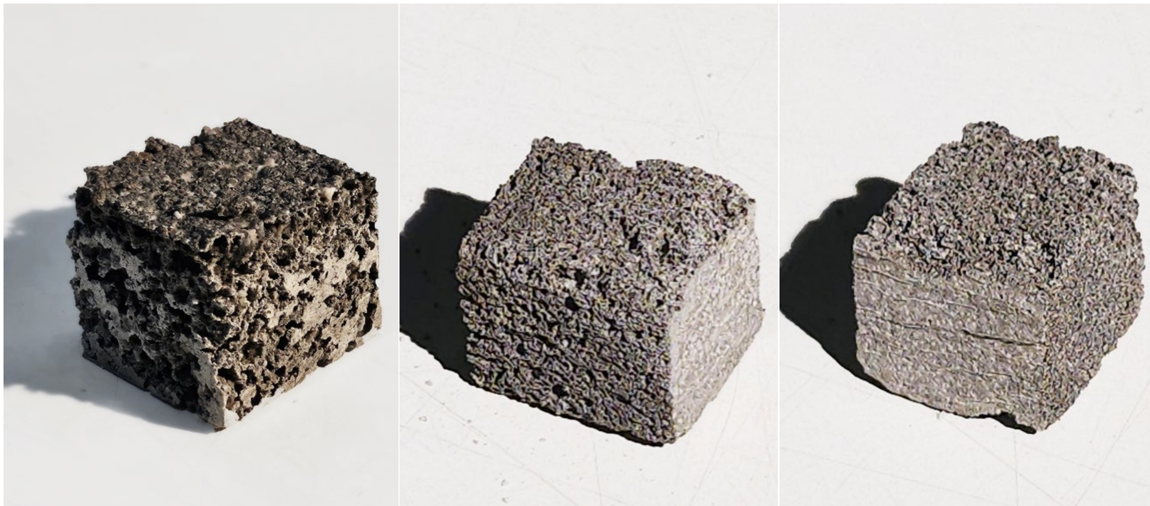

Figure 2_(a) All particle size specimen; (b) 1mm particle size specimen; (c) 425 μm particle size specimen. (Source: author)

After 28 days of curing, the compression test results from the Zwick z100 machine revealed significantly lower strength than anticipated, as shown in Figure 8, which illustrates the comparison of the 3 types of specimens made with varying particle sizes. Among the three variations of specimens, the mix without a restriction on particle size exhibited the highest compressive strength, despite being the most porous initially. Although the initial observation showed that the specimen with the smallest particle size of 425μm displayed the best consistency and least amount of bubbling and porosity immediately after mixing and setting, the results indicate that the initial workability of the mixture did not translate to a strong final product. This unexpected result may be attributed to smaller particles settling into voids over time, partially compensating for the material's porosity. However, the maximum strength achieved was only 0.2 kN, far below the target of 12 kN cited in the literature. Based on these results, further optimization of key variables will be required, including particle size distribution, mixture ratios, curing conditions, and air bubble mitigation, to achieve the desired strength for practical applications.

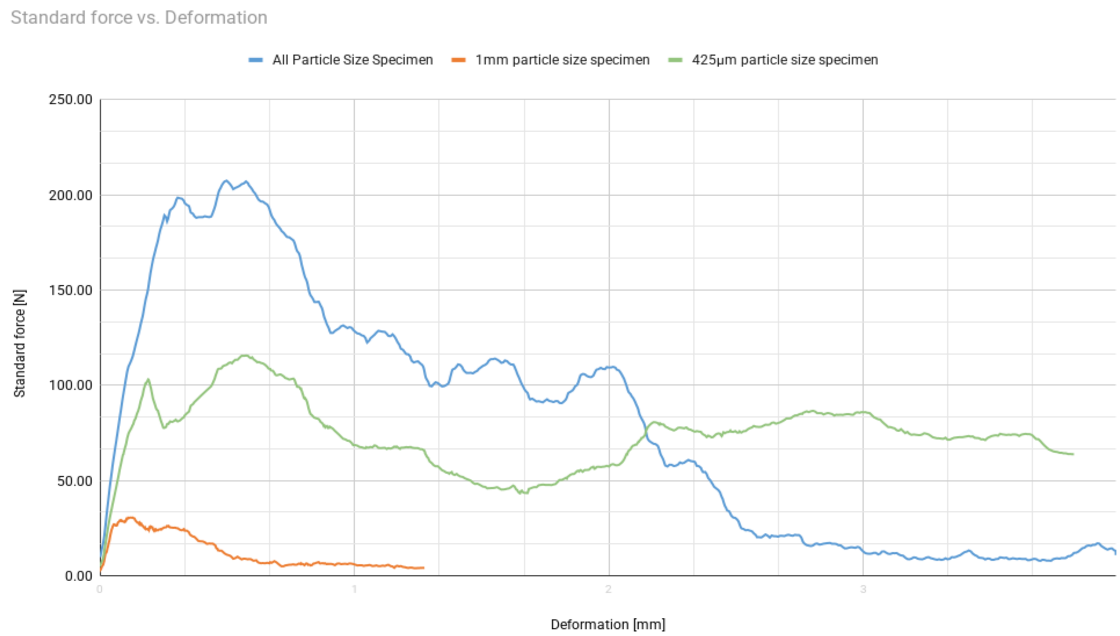

Figure 3_Compression Test Results of 3 Variations of Geopolymer Specimens

Material Test with Martian Regolith Simulant and Phosphoric Acid

The final phase of material experiments aims to refine the previously tested geopolymer synthesis process using Martian regolith simulants – the modified variants Mars Global Hydrated Clay (MGS-1C) and Mars Global Polyhydrated Sulfate (MGS-1S). These two simulants provide a mineralogically accurate representation of basaltic Martian soils (Cannon et al., 2019), while also possessing largely different chemical compositions (Table 4), allowing for an assessment of their suitability in phosphate-based geopolymerization. Compared with alkaline-activated geopolymers, the use of phosphoric acid as the binder has been cited to have a wider affinity for reacting with diverse mineral substrates and compositions (Buchner et al., 2018).

Volcanic Basalt Flour Composition (PRAXIS)	**MGS-1C Clay ISRU Chemical Composition (Exolith Lab)**	**MGS-1S Sulfate ISRU Chemical Composition (Exolith Lab)**
SiO_2 39 wt% **CaO** 16.9wt% **Na_2O** 2.6wt% **Fe_2O_3** 12.3 wt% **Al_2O_3** 10.4 wt% **K_2O** 2.3wt% **P_2O_5** 1.2wt% **MgO** 10wt%	**SiO_2** 56.13 wt% **CaO** 2.02wt% **TiO_2** 0.21 wt% **Na_2O** 1.91wt% **Al_2O_3** 16.89 wt% **K_2O** 0.47wt% **Cr_2O_3** 0.02wt% **P_2O_5** 0.35wt% **SO_3** 1.16wt% **FeO_T** 8.24wt% **MgO** 12.57wt% **MnO** 0.04wt%	**SiO_2** 29.29 wt% **CaO** 14.81wt% **TiO_2** 0.27 wt% **Na_2O** 2.11wt% **Al_2O_3** 6.37 wt% **K_2O** 0.45wt% **Cr_2O_3** 0.13wt% **P_2O_5** 0.32wt% **SO_3** 18.71wt% **FeO_T** 11.25wt% **MgO** 0.07wt% **MnO** 0.07wt%

Table 3_Comparison of the chemical compositions of different Martian regolith simulants

Using different regolith variants allows this study to assess whether phosphate-based geopolymers can be synthesized across a wider range of Martian environments, ensuring that the construction process is adaptable to realistic regolith conditions rather than relying on one idealized simulant to represent the regolith composition across the planet.

RECIPE VARIATIONS	Regolith	Regolith Component (g)	Phosphoric Acid (g)	Water (g)
1	MGS-1 Clay	110	74.8	13.2
2	MGS-1 Sulfate	110	74.8	13.2

Table 4_Martian Regolith Simulant Material Test Recipe Variations

The preliminary results of this final experiment do not show significant variances between the two sample specimens, and a stronger final product compared with the specimens made with the basaltic volcanic flour in the previous round, indicating a successful application of the modified geopolymerization procedure. Through the testing of these two regolith compositions, this study attests to the feasibility of a geopolymerization approach that can be implemented across various Martian sites, reducing the need for site-specific modifications for the formation of the material. The findings will then contribute to the continued development of a scalable, in-situ construction strategy for Martian habitats within the expected lava tube environments of the Rhizome project site, which requires a highly adaptable and consistent building material.

4.0 DISCUSSION

The experimental findings demonstrate both the potential and limitations of geopolymer developments for Martian construction. Through material experiments of the metakaolin-based, volcanic ash-based, and Martian regolith-based geopolymers, the observations revealed that while the materials successfully underwent geopolymerization, the mechanical properties achieved were significantly lower than expected. The measured compressive strength of the material experiment did not reach an acceptable standard and indicates significant changes to the synthesis process.

Several factors may have contributed to the observed discrepancies between the expected and imperial results. One parameter influencing the final strength is the particle size distribution of the solid regolith component. The regolith grain size that is expected on Mars ranges between 1 to 1000µm, but falls primarily within 250–500µm (Zeng et al., 2015). This aligns with the experiment involving the 424 µm particle size, which exhibited a good initial wet-paste consistency of the mixture right after the setting period. During the early phases of geopolymerization, this resulted in optimal workability for 3D printing applications. However, the compression testing results also showed that the mixture which included larger particle sizes exhibited higher compressive strength, indicating a positive significance that aggregates would add to the mixture. The next steps in optimizing the mixture ratios might include variations in the acidic binder concentration, which influences the degree of polymerization and overall mechanical strength (Goryunova et al., 2023), the water content, affecting the workability and porosity (De Kock et al., 2015) and the inclusion of additives, which can work to improve strength, consistency and durability, as per the research findings in Table 2. Additionally, porosity, moisture retention and curing conditions were likely the largest factors that influenced the material properties.

The findings also provide insights into the feasibility of employing these geopolymers in robotic 3D printing applications. A key challenge identified was the trade-off between printability and mechanical performance. The use of robotic fabrication and assembly in-situ in extraterrestrial construction demands a high degree of consistency in material behaviour. The observed variability in performance poses a problem, which needs to be addressed by building upon the approach of the final experiment within this study to ensure predictable results. Modifications to the mixture as mentioned above, such as the inclusion of reinforcing fibres or controlled air evacuation techniques, may improve printability while maintaining structural integrity.

Limitations and Next Steps

Due to the unexpected variability of the material trials, several aspects initially intended as part of the research could not be fully realized within the study's duration – in particular, the material characterization and 1:1 implementation for robotic 3D printing. As such, material characterization will be the next step in validating the mechanical and chemical performance of the developed geopolymer formulations through continued collaboration with experts within TU Delft's Faculty of Mechanical Engineering. Leveraging methods and technologies such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and compressive strength testing will provide further insights into the material properties, phase composition, and mechanical performance under simulated Martian conditions.

The implementation of the geopolymerization process in robotic 3D printing will also require development in the next steps of prototyping. Future work will involve testing extrusion parameters, layer adhesion properties, and printability optimization, which is being currently discussed in collaboration with industry partners specializing in robotic construction, such as Vertico and Concrefy. The objective will be to refine the material's rheology to ensure it can be reliably extruded and built into structurally stable building elements. Simulating Martian environmental conditions during printing will also determine the feasibility of this approach for the intended applications.

5.0 CONCLUSION

A key research question which guided this investigation was the current state of geopolymer development for Lunar and Martian environments and the potential contributions of this study to the field. While there is an abundance of research on alkaline-activated geopolymers for terrestrial applications in recent years, phosphate-activated formulas for Martian construction remain relatively unexplored. The limited studies on phosphoric acid-activated geopolymers for Mars primarily focus on fundamental chemistry, so this study aimed to focus on the key challenges in optimizing geopolymer recipes for conditions such as that associated with the challenges of low-temperature curing. Unlike conventional geopolymer activation methods that rely on high temperatures, construction on Mars will require different curing methods to adapt to the planet's cold climate. Based on the review of literature and the initial experiments, the geopolymer synthesis from phosphoric acid can be determined as a viable option for this purpose.

Another driving aspect of this study is regarding the availability of in-situ materials and climate conditions for in-situ geopolymerization on Mars. To address this, resource mapping and chemical specifications were taken into consideration when choosing both the synthesis pathway and the regolith substitutes used in the experiments. Most tested geopolymer recipes specify one regolith simulant, often JSC MARS-1, or an optimized composition that replicates a single terrestrial deposit, and it is clear that regolith composition has an undeniable role in the success of the geopolymerization process. Within this study, varying compositions were used in the role of the solid component that would react with the binder, which also aimed to develop and refine a procedure for geopolymerization that would be adaptable to a wider range of Martian substrates that can be found at different sites across the planet.

Lastly, the study sought to determine the suitability of geopolymers for the Rhizome 2.0 building project, which would make use of Martian lava tubes as protective habitats. The interaction between the phosphate-based binder and the MGS-1 Martian regolith simulant suggests that in-situ resource utilization (ISRU) is a viable approach for habitat construction. However, the performance inconsistencies indicate that not all regolith compositions might yield an expected response to the process. While geopolymers offer several advantages over other cementitious materials, the low compressive strength observed in this study accepts that further refinement of mixture ratios, curing techniques, and reinforcement strategies is necessary before full-scale implementation. On the other hand, the considerations made for the rheological properties of the material for the purpose of robotic 3D printing yielded positive results in line with the expectations, and can act as a reliable foundation to address extrusion consistency and layering in future 1:1 prototype testing.

This study provides a basis for the continued development of phosphate-based geopolymer materials for Martian construction while acknowledging the need for continued research and consultation with material experts in material composition, in-situ resource adaptation, and controlled environment testing. Despite these challenges, they can be established as a viable potential for scalable construction material in future Mars habitats.

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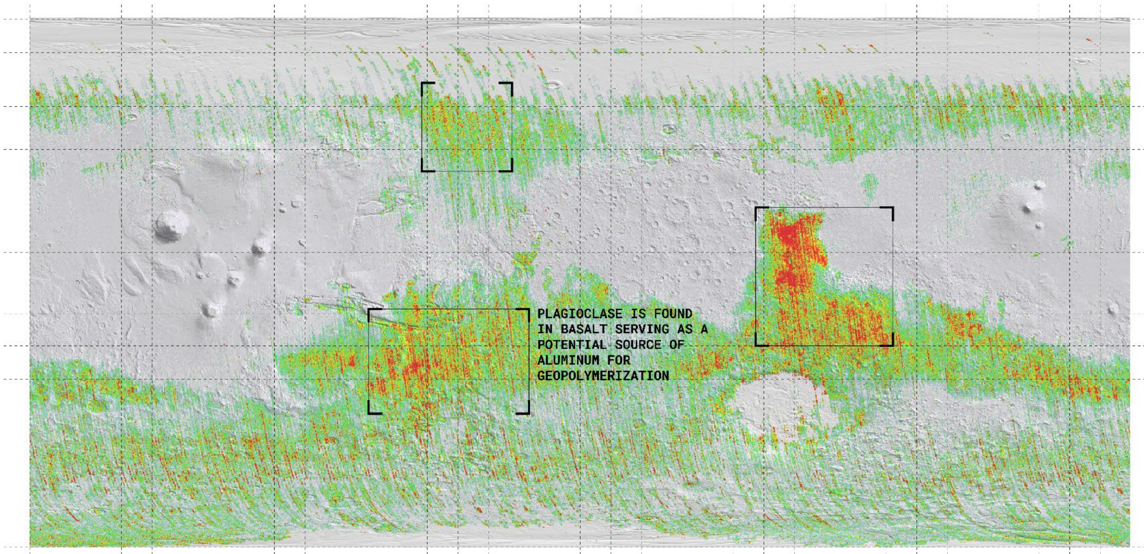
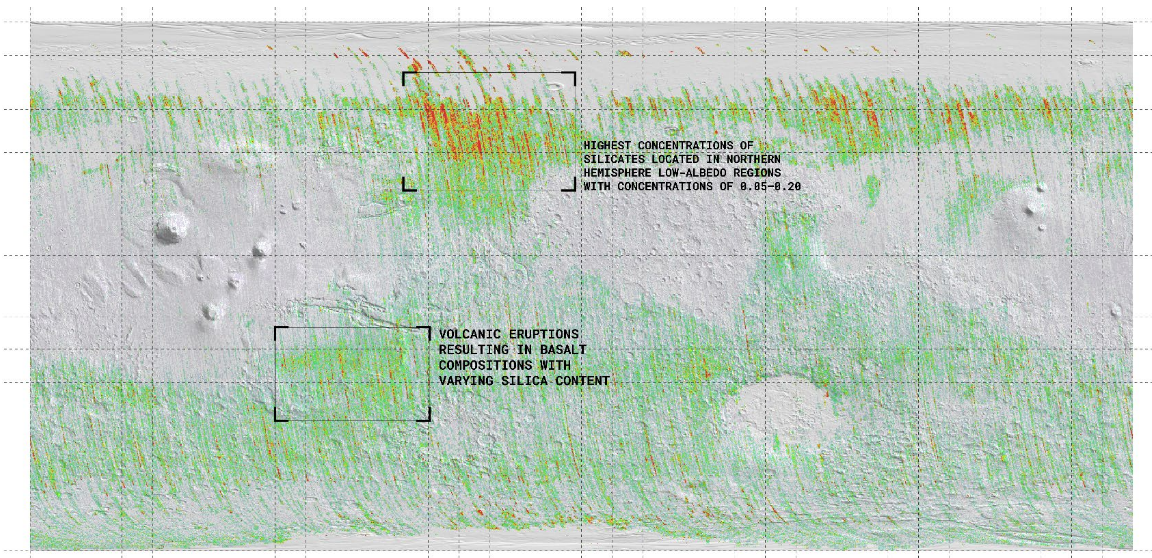
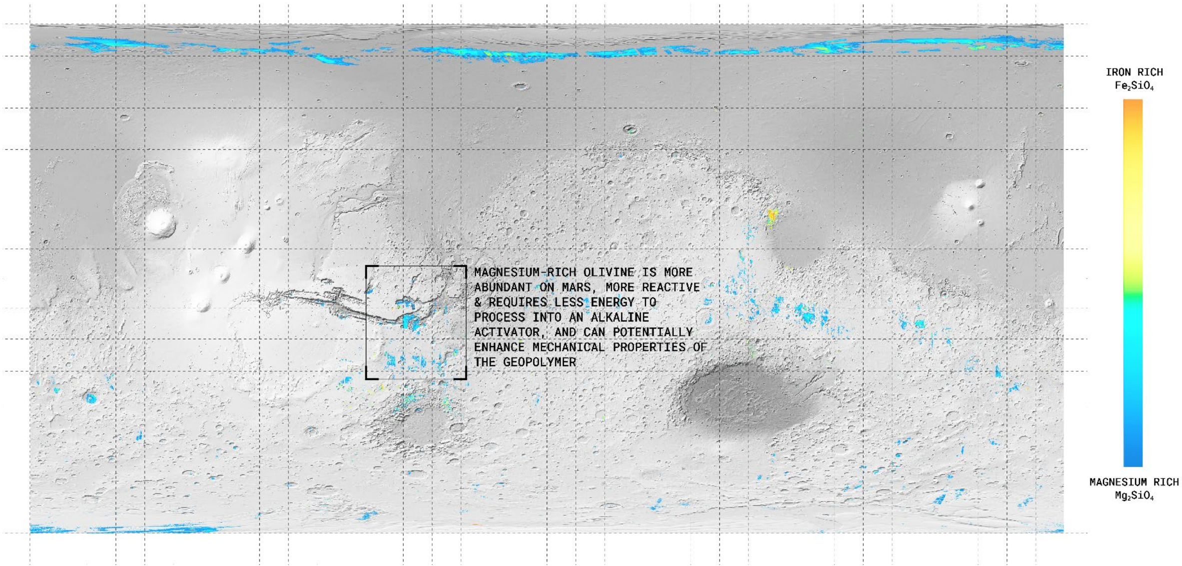
APPENDIX



Appendix A: Mapping aluminum on Mars (Source: author, based on USGS, 2006)



Appendix B_Mapping silicates on Mars (Source: author, based on USGS, 2006)



Appendix C_Mapping olivines on Mars (Source: author, based on USGS, 2006)

MATERIAL RECIPES	Synthesis Route	Material Composition	Weight Percentage (%)	Rheology/ Fibre Additives	Compressive Strength (MPa)
1 (Kozub et al, 2022)	alkaline activation	Volcanic tuff	32.47 wt%	N/A	Unspecified
		Basalt flour	32.47 wt%		
		Olivin (silicates)	0.65 wt%		
		Oxide mixture	34.42 wt%		
2 (Pilehvar et al, 2020)	alkaline activation	Lunar Regolith Simulant	65 wt%	poly-naphthalene sulfonate polymer (FLUBE OS 39)	Unspecified
		Alkaline solution (sodium hydroxide pellets and sodium silicate solution)	35 wt%		
3 (Montes et al, 2015)	alkaline activation	Lunar Regolith Simulant	68 wt%	N/A	16MPa
		Liquid silicate (SiO2/Na2O ratio of 3.22 in water)	32 wt%		
4 (Ma et al, 2021)	alkaline activation	Kaolin clay	unspecified (assumed 65-75%)	Triton x-100 Short basalt fibers (length 600µm and diameter 5µm)	Unspecified
		NaOH (85wt%)	unspecified		
		Sol-silica (40wt%)	unspecified		
5 (Ma et al, 2022)	alkaline activation	Regolith Simulant (created from basalt, hematite, forsterite, potassium feldspar, SiO2, and Al2O3)	unspecified (assumed 65-75%)	Triton x-100 Short basalt fibers (length 600µm and diameter 5µm)	15 MPa
		KOH (96 wt%)	unspecified		
		Sol-silica (40wt%)	unspecified		
6 (Hedayati and Stulova, 2023)	alkaline activation	Mars simulant regolith powder	66-69 wt%	N/A	Unspecified
		Sodium silicate (Na2SiO3)	34-31wt%		
7 (Buchner et al. 2018)	acidic activation	JSC Mars-1A Regolith Simulant	60 wt%	N/A	Unspecified
		Phosphoric acid (85 wt%)	40 wt%		

Appendix D_Geopolymer Synthesis Material Recipes

Material Properties	Hydroxide-based Activators	Silicate-based Activators	Reference
Mechanical Strength	Lower early strength (increases over time)	Higher early + long-term strength	Provis and Bernal (2014)
Workability (for 3D printing)	Better workability, lower viscosity	Lower workability, higher viscosity	Rangan (2008); Zhang et al. (2014).
Setting Time	Slower setting time (180 - 240 min)	Faster setting time (60 - 90 min)	Zhang et al. (2014)
Microstructure + geopolymerization	More porous, lower density (Simpler aluminosilicate network)	Denser, more cohesive (More complex aluminosilicate network)	Davidovits (2008)
Energy Requirement	Lower energy requirement	Higher energy requirement (extracting silicates from mineral compounds found on Mars takes extra energy for processes)	Anderson et al. (2021)

Appendix E_Comparison of Geopolymer Alkaline Activators

Reference	Additive /Variable	Function	Tested Outcomes	Source on Mars
Banerjee et al. 2021; Cesaretti et al. 2014	Basalt Fibers	Tensile strength and crack resistance	Enhanced tensile strength and crack control (~20-30% improvement)	Basalt rocks (volcanic regions)
Montano et al. 2020; Kusumawardhani et al. 2020	Urea ($CO(NH_2)_2$)	Rheology and workability	Increases flowability without reducing strength	Recycled from human waste
De Kock et al. 2015; Malla and Brown 2015	Water (H_2O)	Rheology and workability	The optimal water-to-solids ratio improves printability and reduces cracking	Ice deposits (polar regions and subsurface)
Banerjee et al. 2021; Montano et al. 2020	Silica Fume (SiO_2)	Bonding and strength	Increases compressive strength and reduces porosity	Silica-rich dust
Zhang et al. 2021	Phosphoric Acid (H_3PO_4)	Acidic activator	Accelerates curing and improves compressive strength at lower temperatures	Martian phosphate minerals
Cesaretti et al. 2014; Zhang et al. 2021	Sodium Silicate (Na_2SiO_3)	Alkaline activator	- Enhances compressive and tensile strength - affects setting time, workability, and mechanical properties. - The specific weight ratio of Na2SiO3 to NaOH (sodium hydroxide) affects the foam density and expansion behaviour	Extractable from Martian regolith (silica and sodium available)

Ricciotti et al., 2023	Superplasticizers	Rheology and workability	Used to enhance the fluidity of the geopolymer mixtures, making them more workable for 3D printing.	N/A
Abdelaal and Elkatatny, 2023	Hematite (Fe_2O_3)	Rheology and workability	The thickening time of the hematite-based FFA geopolymer decreased by 81.4 % with increasing hematite from 25 to 75 % BWOB. The proposed additives mixture increased the thickening time from 80 to 580 min.	Basalt rocks

Appendix F_Additives to Geopolymer Synthesis for 3D Printing Optimization