Development of Geopolymers for 3D Printing Applications on Mars

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INTRODUCTION AND BACKGROUND

Geopolymers have emerged in the last few decades as a cementitious material seen as an alternative to concrete with significantly reduced greenhouse emissions. On Earth, the material can be composed of recycled industrial waste and fly ash, but they have also become 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 basaltic composition of Martian regolith. Using these materials can help address the challenges and expenses associated with transporting construction materials from Earth to extraterrestrial environments (Ma et al., 2022).

The research will be a part of the project *Rhizome 2.0: Scaling-up Capability of Human-Robot Interaction Supported Approaches for Robotically 3D-printing Extraterrestrial Habitats*[1], led by Dr. Henriette Bier, and funded by the European Space Agency and Vertico. It will be implemented under the supervision of Dr. Bier and PhD cand. Arwin Hidding at the Robotic Building (RB) lab at TU Delft's Faculty of Architecture and the Built Environment. As the aim of the project is to demonstrate the scalability of designed habitats on Mars, the cementitious nature of geopolymers allows for additive manufacturing on the site of construction with the aid of robotics.

The subsequent research aims to extend current understanding by conducting experiments and testing real-scale prototypes in controlled environments, including the collection of volcanic ash from Sicily to simulate Martian basalt soil. Further testing with 1:1 scale aggregates and fibers 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. This approach aims to contribute to the development of resource-efficient construction practices through working prototypes and material characterization for future Martian exploration and habitation.

The project builds on the paper by Calabrese et al. (2024) in *Review of Cementless Materials for 3D Printing of off- and on-Earth Habitats*, and argues for geopolymers as a viable material option. 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.

[1]http://www.roboticbuilding.eu/project/rhizome-2-0/

Literature Review.

The project starts with an overview of the current state-of-the-art geopolymer research, which 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 binders, water availability, energy sources, aggregate options, properties of fresh materials, structural requirements, and durability concerns (Reches, 2019), which encompass both compression and flexural strength assessments, pivotal for evaluating the efficacy of geopolymer materials in Martian conditions.

Geopolymer Composition
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 confirmed to have reliable sources of aluminum and silicon necessary for the formation of amorphous aluminosilicate networks (Ma et al, 2022). To achieve geopolymerization while using different Martian and Lunar simulants, different 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.

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◦ near the equator, and the average surface pressure on Mars is also about 0.6% that of Earth's (Reches, 2019). The atmospheric pressure and temperature inside lava tubes might be slightly different from the surface pressure, but 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, while a day on Mars is 24h37m, it will also be important to look at the effect of temperature on the curing process.

The curing time is crucial in our experiments for understanding the curing times to avoid clogging the extruder. Curing also is dependent on the size/thickness and material composition. A mould may be used to check the curing time before 3D printing. Differential scanning calorimetry (DSC) analysis is used for evaluation. Although pressure does not seem to affect the curing time, the porosity of the specimens was directly related to the curing pressure of the specimens. 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 alkali 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 80 µm, with the average being 10.68 µm, while other studies show particle sizes closer to 125 µm. 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 shapes 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 printed concrete, moulds were often used, which may affect the 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. These additions to manipulate the strength and rheology of the geopolymer during and after 3-D printing will be a main area of investigation in this subsequent research.

APPROACH

To explore the current advancements in geopolymer material printability using Martian in-situ resources, the research will be guided by the following questions and objectives.

1. What is the state-of-the-art of geopolymer material on Earth?

- ➔ Review current and ongoing research in geopolymer composition and applications for small-scale and large-scale in-situ building.
- ➔ Investigate 3D printing methods and influencing factors.

2. What are the available in-situ materials to be used for geopolymerization on Mars?

- ➔ Analyze Martian regolith's basaltic composition for its suitability in geopolymerization
- ➔ What is the feasibility of retrieving Martian resources, such as water and alkaline activators, necessary for geopolymerization?

3. What factors contribute to the geopolymerization for maximum strength (compression and

tension) for building applications?

- ➔ Further research and testing of fibres and reinforcing agents to enhance the compressive and tensile properties, as well as the rheology for 3D printing purposes could be a substantial contribution to the existing research.

4. Are geopolymers suitable for the Rhizome 2.0 building project in Mars' empty lava tubes?

- ➔ Evaluate the mechanical properties and durability of optimized geopolymers under simulated Martian conditions.
- ➔ Assess compatibility with robotic 3D printing technologies.

METHODOLOGY

The research methodology will follow four main steps to develop and assess geopolymer materials for potential use in Martian construction. These include the initial research and experiments to become familiar with the material, as well as the material testing with a Mars simulant, followed by material characterization. The final step involves using the refined material recipe for robotic 3D printing trials in collaboration with industry specialists.

1. Initial Material Experiments

The first steps of the research process are a series of initial material experiments to develop metakaolin geopolymer recipes, referencing existing recipes and "geopolymer toolkits". These experiments will involve testing the ratios and combinations of metakaolin with alkaline activators to achieve desirable properties such as workability in terms of 3D printing, setting time, and compressive strength.

2. Testing Mars Regolith Simulant

To simulate conditions that may be encountered on Mars, volcanic ash collected from Sicily's empty lava tubes will be used as a Mars simulant regolith in our experiments. This material closely mimics the basaltic composition that would be found within similar empty lava tubes on Mars. The simulant regolith will be tested with the developed recipes to determine their suitability for 3D-printed construction.

3. Material Characterization

Material characterization will be conducted in collaboration with material experts at TU Delft. This will involve a comprehensive analysis of the geopolymer samples, including mechanical testing, microstructural analysis, and durability assessments, with aid from experts and technology from the Faculty of Mechanical Engineering. Techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and compressive strength testing can be used to understand the material properties and performance under simulated Martian conditions.

4. Robotic 3D Printing

The final output of the research will involve robotic 3D printing of the optimized geopolymer formulations. This will be completed in partnership with industry experts specializing in robotic construction, such as Vertico and Concrefy. The focus will be on developing scalable robotic 3D printing techniques that can be used to build structural components using the geopolymer material. The printing process will be tested and refined to ensure precision, consistency, and structural integrity of the printed elements, simulating the conditions that are expected to be encountered on Mars.

RESEARCH OUTLINE + TIMELINE

The following is the outline and timeline estimate for which the project process and research paper will follow:

1.0 INTRODUCTION

2.0 LITERATURE REVIEW -- (*Jan-April 2024)*

> State-of-the-art geopolymer research

> On-site material resources

> mechanical properties + curing conditions

3.0 EXPERIMENTAL PROTOTYPES ----------------------------- (*May-Nov 2024)*

> Initial recipe testing (syringe + robotic arm) *June 2024*

> Sicily lava tube trip for material collection *June 2024*

> Testing with simulant and material characterization *Sept-Nov 2024*

4.0 PRINTING COMPONENTS FOR RHIZOME 2.0 ---------- (*Jan-Feb 2025)*

> 1:1 prototype testing with industry concrete 3D printers *Jan 2025*

5.0 CONCLUSION -- (*Mar 2025)*

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