**Synthesizing Geopolymers from Martian Soil Simulants for Potential Use in Water Treatment Membranes on the Red Planet**

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# **Abstract**

This study focuses on characterising geopolymers made from Martian soil simulant as a potential material for water purification membranes. The impact of formulation, curing process and pH is investigated. Three distinct batches of formulations are manufactured and tested. Geopolymers containing fume silica within the range of 1% to 5% exhibit the highest porosity coupled with prolonged mechanical resistance. Sodium silica improves the mechanical resistance and sodium hydroxide (NaOH) dispersion over time. All geopolymeric formulations can effectively remove contaminants from water. The geopolymer characterized by high fume silica content has the highest contaminants reduction due to the higher porosity.

**Keywords:** Mars; Geopolymer; membrane, MSG-1, porosity, pH, contaminants, water.

1. **Introduction**

Exploring distant planets like Mars involves extended missions, including prolonged stay on the planet, due to their great distance from Earth. While we have the technology for space travel, maintaining long-term missions on an alien planet is challenging because of limited resources. This situation calls for creative solutions in using and recycling scarce resources like water on these planets [1], reducing the need to transport materials from Earth.

Recent space missions have revealed that Mars possesses more water resources than previously believed [2], [3]. Water is present on Mars generally in the form of permafrost that covers 14% of the Martian surface [4]. It was also found in underground ice sediments or absorbed into the regolith [5], [6]. And, in 2018, the first stable body of liquid water was identified by the Italian Space Agency [7]. Therefore, by optimizing local water resources, combined with those imported from Earth, through effective pre-treatment and recycling, we could move one step closer to realizing long-term settlements on the Red Planet.

Geopolymers have demonstrated their potential in water treatment [8] thanks to their high specific surface area, active site [9] [10], controllable porosities [11], high structural integrity [12]. Moreover, Geopolymers can be also synthesized from Martian [13] and lunar [14] soil simulants. Consequently, the primary aim of this paper is to evaluate whether geopolymers made from Martian soil simulants can be effectively utilized for water treatment. Considering the lack of information about the composition of the water on the Red plant, the selection of iron (Fe) as a contaminant stem from the abundant presence of iron on the Martian surface. Mars is rich in iron-containing minerals, and the weathering of rocks and minerals releases iron into the environment. This natural abundance makes iron a pertinent choice for assessing potential water contamination scenarios on the Red Planet. Studying iron as a contaminant is essential for understanding its impact on water quality and developing effective strategies for sustainable water management during extended Mars missions.

In this article, we investigate the potential of geopolymers synthesized from Martian simulants for treating contaminants such as Fe2+ in groundwater.

1. **Geopolymers**

Geopolymers are a class of materials characterised by a distinctive structure of a tetrahedral framework connecting aluminium and silicon. This framework demonstrates remarkable resistance to dissolution in water. The aluminium and silica tetrahedra are interconnected alternately, sharing oxygen atoms. This configuration forms an inorganic polymeric structure Si–O–Al, which serves as the fundamental building block for geopolymeric materials.

The mechanism underlying geopolymerisation involves the polycondensation reaction of geopolymeric precursors, specifically alumino-silicate oxides, with alkali polysilicates, resulting in the formation of polymeric Si–O–Al bonds [7] [15]. This polymeric structure is represented as:

where M is the alkaline element, *z* is 1,2, or 3 and *n* is the degree of polycondensation [7] [15].

Geopolymerisation is a chemical reaction that involves aluminosilicate and an alkaline solution, resulting in alkali-activated aluminosilicate binders. Alkali metal salts and hydroxides are essential for dissolving silica and alumina, and sodium hydroxide is commonly used due to its cost-effectiveness. In the geopolymeric structure, the gel phase forms through the co-polymerization of alumina and silica dissolved by the alkali metal. This phase contains both unreacted solid particles and water introduced during mixing with the activating alkaline solution [7] [15]. To maintain structural neutrality in the presence of aluminium’s fourfold charge, cations like sodium (Na), potassium (K), calcium (Ca), and others are required. These cations can be bonded within the matrix through Al-O or Si-O bonds or occupy framework cavities to balance electrical charges. If conditions permit, a physically enclosed cation may be substituted by another cation to aid the diffusion process [15].

The mechanical properties of geopolymers are affected by various factors, including curing temperature, curing time, alkali concentration, pH, and the silicate-to-aluminate ratio and raw material [15], [16], [17].

The curing temperature influences the kinetics of the geopolymerisation. Geopolymerisation is slow at ambient temperatures but accelerates with higher temperatures [16].

Geopolymerisation requires a specific amount of time to occur and maintaining the curing time within 48 hours optimally develops the mechanical properties of geopolymers [18]. Longer curing times can reduce mechanical properties due to shrinkage and dehydration [19].

The concentration of alkali influences the solubility of aluminosilicate, with higher concentrations increasing solubility [15]. However, excessive NaOH can result in undesired morphology, non-uniform hydration, reduced binding strength, and delayed polymer formation. High activator concentrations also hinder the mobility of ionic species, delaying the formation of coagulated structures [18].

The pH influences the settling time, with higher pH decreasing the settling time [20]. High pH decreases the viscosity of the mix increasing the mobility of the ions.

The silicate/aluminate ratio is related to the strength of the geopolymer. For instance, a range of 3,16 to 3,46 had the best strength [15] .

Alexiadis et al. [14] produced geopolymers using JSC LUNAR-1A and JSC MARS-1A simulants as precursors. The JSC MARS-1 simulant, created by NASA in 1998, was the first Martian regolith simulant ever made. MSG-1, developed later, is more mineralogically accurate in representing the basaltic regolith of Mars compared to JSC MARS-1 [21]. **Table 1** compares the JSC MARS-1 and MGS-1 composition with those of the landing points of the Vikings and Pathfinder missions [22].

**Table 1.** Comparison of the chemical composition of the martial simulant MGS-1, JSC MARS-1 and the simulant of the landing point Vikings and Pathfinder. [2]

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | VL-1 | VL-2 | Pathfinder | JSC MARS-1 | | MGS-1 |
|  | Wt%\* | Wt%\* | Wt%\*\* | Wt%\*\*\* | Wt%\*\*\*\* | Wt%\*\*\*\*\* |
| SiO2 | 43.00 | 43.00 | 44.00 | 34.50 | 43.50 | 50.80 |
| Al2O3 | 7.30 | 7.00 | 7.50 | 18.50 | 23.30 | 8.90 |
| TiO2 | 0.66 | 0.56 | 1.10 | 3.00 | 3.80 | 0.30 |
| Fe2O3 | 18.50 | 17.80 | 16.50 | 12.40 | 15.60 | 13.30 |
| MnO | n/a | n/a | n/a | 0.20 | 0.30 | 0.10 |
| CaO | 5.90 | 5.70 | 5.60 | 4.90 | 6.20 | 3.70 |
| MgO | 6.00 | 6.00 | 7.00 | 2.70 | 3.40 | 16.70 |
| K2O | <0.15 | <0.15 | 0.30 | 0.50 | 0.60 | 0.30 |
| Na2O | n/a | n/a | 2.10 | 1.90 | 2.40 | 3.40 |
| P2O | n/a | n/a | n/a | 0.70 | 0.90 | 0.40 |
| SO3 | 6.60 | 8.10 | 4.90 | n/a | n/a | 2.10 |
| Cl | 0.70 | 0.50 | 0.50 | n/a | n/a | n/a |
| LOI | n/a | n/a | n/a | 21.80 | n/a | n/a |
| Total | 89.00 | 89.00 | 89.50 | 101.10 | 100.00 |  |

Note: n/a not analysed; Loss Of Ignition (LOI): mass lost after 2h at 900 C (mostly composed of water and SO2); \* from fluorescence analysis using X-ray (XRF) on Viking 1 (VL-1) and Viking 2 (VL-2) samples;\*\* from spectrometer analysis using X-ray and spectrometer using alpha particles (APXS) of lander Pathway; \*\*\*from XRF; \*\*\*\* from XRF, post LOI; \*\*\*\*\* formulation from [21].

In that study [14] a sodium hydroxide solution was used with varying concentrations. The resulting slurries were dried at 80°C for 3 hours in silicone moulds, followed by 28 days of hardening. These geopolymers exhibited geopolymerisation characteristics through FTIR analysis, compressive strength tests and flexural strength tests. JSC LUNAR-1A geopolymers showed superior strength to Portland cement, while JSC MARS-1A geopolymers had lower resistance.

Beside construction materials, geopolymers have been suggested as materials for water purification membranes. In this case, it is important to have a high porosity to allow water permeation without compromise the durability of the geopolymer.

Prud'homme et al. [23] introduced fume silica into a geopolymeric slurry to study its impact on porosity. The addition of fume silica, thanks to the presence of free silicon (metal) within, leads to the formation of hydrogen gas due to its oxidation in an alkaline aqueous environment. The development of porosity in the geopolymer is attributed to three key factors: the production of gas, an increase in viscosity and material hardening.

Pachana et al. [24] explored the potential of porous geopolymers for treating groundwater and removal of Fe(II) and Mn(II) ions through their precipitation as hydroxides. pH measurements during immersion revealed the release of hydroxide ions from the geopolymers. The concentration of Fe(II) ions was tracked demonstrating the potential to reduce iron and manganese concentrations in water.

1. **Methodology**
   1. **Geopolymer preparation**

Three distinct batches of geopolymers have been manufactured with modifications to the formulations and operational variables. The raw materials used in this study include MGS-1 simulant, an alkali activator (12M NaOH solution), fume silica and sodium silicate (Na2SiO3). The formulations are shown in **Table 2**.

**Table 2.** BATCH 1 formulations

|  |  |  |  |
| --- | --- | --- | --- |
|  | MGS-1 (g) | FS (g) | NaOH 12M (mL) |
| CS | 15 | 0 | 4 |
| FS1 | 15 | 0.15 | 4 |
| FS2 | 15 | 0.3 | 4 |
| FS5 | 15 | 0.75 | 4 |
| FS10 | 15 | 1.50 | 4 |
| FS15 | 15 | 2.25 | 4 |
| FS1a | 15 | 0.15 | 6 |
| FS2a | 15 | 0.30 | 8 |

Note: Control sample (CS); FS1a: sample containing fume silica; FS1a: percentage by mass of fume silica, relative to the mass of precursor; FS1a: sample containing a percentage of fume silica (indicated by the number) and a volume of 12M NaOH greater than 4 mL.

While keeping the quantity of simulant constant, the quantities of fume silica, NaOH, and Na2SiO3 have been varied. The geopolymer mixture was poured into cubical moulds with a volume of 1 cm³. Curing conditions were maintained at a constant temperature of 200°C for either 2 or 3 hours. 10 cubic geopolymers of 1 cm³ per type were manufactured. For each batch of geopolymers, a reference sample containing only the precursor and the 12M sodium hydroxide solution was produced. This sample served as the reference for all analyses conducted in this study and is referred to as the control sample (CS).

The control sample was initially produced to determine the quantity of 12M NaOH necessary for the geopolymerisation of the MGS-1 simulant. Using 15 g of simulant and 4 mL of solid hydroxide solution and subjecting the slurry to curing for 3 hours at 200°C, a solid and rigid geopolymer was obtained. It was found that the ratio of is sufficient to allow an effective process of polycondensation of the simulant.

The first batch of geopolymers aimed to evaluate the effect of the quantity of fume silica and the volumes of NaOH solution on the final geopolymer structure. Fume silica additions ranged from 1% to 15%. calculated relative to the mass of the simulant used:

|  |  |  |
| --- | --- | --- |
|  |  | (1) |

The enhancement of geopolymerisation effectiveness of the slurry has been assessed increasing volumes of 12M sodium hydroxide.

In the second batch of geopolymers, it has been introduced a 50% Na2SiO3 solution to assess its effect on resistance. The geopolymer slurries were cured for 3 hours at 200°C. To explore the potential for reducing energy consumption, it has been prepared a third batch of geopolymers identical in formulation to BATCH 2 (see **Table 3**) but with a reduced curing time of 2 hours at 200°C.

**Table 3.** BATCH 2 and BATCH 3 formulations

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | MGS-1 (g) | FS (g) | NaOH 12M (mL) | Na2SiO3 50% (mL) |
| CS | 15 | 0 | 4 | 0 |
| FS1 | 15 | 0.15 | 4 | 0 |
| FS2 | 15 | 0.3 | 4 | 0 |
| FS5 | 15 | 0.75 | 4 | 0 |
| CSw | 15 | 0 | 2 | 2 |
| FS1w | 15 | 0.15 | 2 | 2 |
| FS2w | 15 | 0.3 | 2 | 2 |
| FS5w | 15 | 0.75 | 2 | 2 |

NOTE: the letter w indicates the Na2SiO3 content at 50% (waterglass)

* 1. **Water absorption capacity**

The overall porosity was investigated by considering the water absorption of the specimens. Water absorption is the amount of water required to fill the porous structure of the specimens during immersion. Water absorption tests were conducted using ASTM standard C642-21 (ASTM. 2022) [25]. The analysis was carried out on BATCH 3 of the geopolymers produced. Each measurement and analysis of adsorption capacity was carried out on a pair of geopolymer for each type of formulation. The test was conducted over a short period of 60 minutes repeating the test 3 times to assess the reproducibility. The wet geopolymers were removed from the support platform and re-weighed to determine any weight change, indicating their water absorption capacity. Following the absorption capacity assessment, wet geopolymers were left to air dry in labelled open containers for 24 hours. The mass of the specimens was measured using the weight scale with a sensitivity of 0.1 g. Specimens were placed in the water again immediately to avoid drying at room temperature. In this context, the absorption capacity is the mass quantity of water that a pair of geopolymers with the same formulation absorbs following immersion under stirring in deionized water, normalized with respect to the mass of the dry samples (pre-wash). The average absorption capacity of each sample is determined by calculating the mean of the values obtained from the three washing cycles,

|  |  |  |
| --- | --- | --- |
|  |  | (2) |

where Ms is the saturated surface dry mass of the specimen after the water absorption and Md is the dry mass of the specimen.

* 1. **pH analysis**

Eight geopolymers (i.e. CS, FS1, FS2, FS5, CSw, FS1w, FS2W, FS5w) were examined for pH modification in pure water. Two samples of each type of geopolymers were weighed using a precision scale. These weighed geopolymers were placed in separate beakers, each containing 150 mL of deionized water. To ensure consistent dispersion, a magnetic stirrer was used at a fixed speed of 250 rpm. To avoid subjecting the geopolymers to undue mechanical stress, they were suspended using a specially designed PVC platform.

pH levels in the immersion water were measured every 5-10 minutes using the XS pH 70 Vio pH meter, previously calibrated with neutral and acidic buffer solutions. After the pH analysis, the entire analysis was repeated three times for each pair of geopolymers to assess their repeatability and the consistency of the results.

* 1. **Treatment of Fe2+ Ions in Aqueous Solution**

This study evaluates the geopolymer's effectiveness in removing contaminants from solutions. Various tests were conducted using different solutions to assess this capability. Four geopolymers (i.e. CS, FS1w, FS2W, FS5) were examined for Fe removal from the aqueous solution with a metal concentration of 200 ppm.

To evaluate the removal efficiency of Fe2+ ions by the geopolymer, a procedure like the pH analysis was employed [24]. A method for measuring the concentration of Fe(II) in aqueous solutions by forming a complex with 1.10-phenanthroline, known as ferroin, which has a distinct red-orange colour [26]. This allows for colorimetric analysis using a UV/vis spectrophotometer. By inputting the absorbance values into a calibration equation, the concentration of remaining Fe(II) ions in the solution can be accurately determined. Two geopolymers of each type were suspended in the beaker using a PVC platform. The system was stirred at 250 rpm with a magnetic stirrer and pH was periodically monitored using a pH meter (XS pH 70 Vio) previously calibrated with acidic and neutral buffers. Each pair of geopolymers underwent analysis for 45 minutes and was subsequently left to air dry for 24 hours. This procedure was repeated three times for each pair of geopolymers. At regular intervals (every 5-10 minutes), a small sample was extracted from the beaker using a Pasteur pipette and placed into a centrifuge tube to assess the precipitation of Fe2+ over time. The test tubes were then centrifuged at 400 rpm for 3 minutes ensuring even weight distribution within the centrifuge.

The residual Fe2+ ions in the solution were determined using the calibration line method. This required the preparation of Fe2+ standards at 1, 2, 3, and 4 ppm. For each standard, variable volumes of the Fe2+ stock solution, a small amount of deionized water, 1 mL of concentrated HCl, and 0.5 mL of 10% hydroxylamine hydrochloride were added to 50 mL volumetric flasks. After a 10-minute wait for the complete reduction of Fe(III) to Fe(II) by hydroxylamine, 5 mL of buffer solution and 2 mL of 0.2% 1.10-phenanthroline solution were added. The volume was adjusted to the mark with deionized water. The reagents were used to form colour complexes according to the 3500-Fe B Phenanthroline Method [27]. After another 20-minute waiting period to allow complexation between Fe2+ and 1.10-phenanthroline to proceed, the absorbance was measured using a UV/vis spectrophotometer (Jasco V-530). A white baseline was initially established for all subsequent measurements. The absorbances of the standards were measured to create the calibration line. With the calibration line prepared, the samples derived from the solution treated by the geopolymers were measured for absorbance and their concentration was determined using the calibration line.

1. Results and discussion
   1. **Sample usability**

From the resulting geopolymers, it was noted that the addition of a quantity of FS influences the usability.



**Figure 1.** BATCH 1 geopolymer after curing. From the left to right: CS, FS1, FS2, FS5, FS10, FS15, FS1a, FS2a.

|  |  |
| --- | --- |
|  |  |
| (a) | (b) |

**Figure 2.** BATCH1 samples: (a) FS5, (b) FS10

In this study, the geopolymers containing 1% and 2% fume silica present a compacted structure, like the control sample, while those containing 5% fume silica are visibly more porous and voluminous, see **Figure 2** (a) and the sample with high FS quantity ( > 10% wt.) are characterised by the formation of hollow chambers at the top of the geopolymer. The hollow chamber is also very fragile, see Figure 2 (b). Furthermore, higher content of FS in the geopolymer decreases the workability of the sample. For instance, the samples with FS content higher than 10% wt are fragile to the point of being unusable for testing.

Regarding volumes of sodium hydroxide solution, a ratio of the volume of liquid to the mass of simulant of is optimal, while higher values (such as those used for the FS1a and FS2a samples) produce geopolymers which collapse on themselves by the end of curing becoming brittle and unusable. This probably occurs because the slurry obtained by mixing the reagents with higher quantities of activating solution is considerably less viscous than those with lower quantities leading to the collapse of the pores in macropores [28]. The most significant issue with this batch of geopolymers occurs within 5 days of air exposure. After this period, the geopolymers, especially those containing less than 2% fume silica, become brittle and unusable. Therefore, this formulation, cannot be used to produce geopolymers that are resistant over time.

Regarding Batch 2, geopolymers formulated with only NaOH as an activating solution are visibly less usable after a week than those with Na2SiO3, which is still rigid and resistant.

However, for the FS5w sample, the effect of the production of a hollow chamber at the top of the geopolymer occurred, like the samples prepared with higher quantities of fume silica, see **Figure 2** (a), making it fragile and impractical.

Regarding Batch 3, the geopolymers obtained show no visible differences compared to those obtained following longer curing times, neither immediately following cooking, after 24 h of cooling, nor following a week of exposure to air. This first qualitative verification seems to prove the hypothesis that curing times of 2 hours are sufficient and effective in producing this type of geopolymers.

* 1. **Absorption capacity**

The absorption capacity is an indication of the permeable pore space (voids) of the material [25] and also of its durability [32]. The test provides valuable insights into the accessible voids within the material. This analysis aids in understanding the quantity of the open pores, critical factors influencing properties such as strength, durability, and thermal conductivity. In addition, the test is indicative of a material's performance and durability in real-world applications. Excessive water absorption can lead to structural changes such as swelling or cracking, impacting the material's efficacy. Water absorption capacity of the geopolymer samples shows significant variations based on the content of FS, NaOH and Na2SiO3. **Table 4** shows the mass before and after the test and absorption capacity of each sample per wash cycle and the average absorption capacity.

**Table 4.** Geopolymers mass and water absorption before and after each cycle and average water absorption of each sample.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Cycle 1 | | Cycle 2 | | Cycle 3 | | Average Waterabs |
|  |  |  |  |  |  |  |  |
| CS | 2.74 | 0.18 | 2.39 | 0.28 | 2.2 | 0.35 | 0.27 |
| FS1 | 2.88 | 0.21 | 2.71 | 0.20 | 2.45 | 0.31 | 0.24 |
| FS2 | 2.67 | 0.28 | 2.54 | 0.23 | 2.27 | 0.34 | 0.28 |
| FS5 | 2.75 | 0.43 | 2.49 | 0.44 | 1.23 | 0.35 | 0.41 |
| CSw | 2.8 | 0.25 | 2.43 | 0.37 | 2.46 | 0.31 | 0.31 |
| FS1w | 2.72 | 0.36 | 2.51 | 0.35 | 2.56 | 0.29 | 0.34 |
| FS2w | 2.9 | 0.31 | 2.87 | 0.31 | 2.51 | 0.44 | 0.35 |
| FS5w | 2.83 | 0.26 | 2.4 | 0.13 | 2.35 | 0.20 | 0.20 |

Table 4 shows a positive correlation between the increasing of the water absorption capacity with FS [23]. The increase in FS reacting with NaOH results in the production of more H2, leading to an increase in voids within the samples and the consequence higher water absorption capacity.

A comparative analysis of average absorption capacity reveals that samples containing NaOH exhibit lower water absorption than those with Na2SiO3 as shown in **Table 5**. Only the sample FS5w shows the lowest value among the samples with similar formulations. The increase in water absorption can be attributed to the following process: at higher NaOH concentrations, a viscous solution produces linked pores in the mortar structure upon drying and the Na2SiO3 stabilises the porous and improves the workability of the geopolymer [16]. Notably, FS5 demonstrates the highest water absorption capacity among the tested samples with a value of 0.41, which is the optimal choice for water absorption and treatment. Contrarily, the sample FS5w demonstrated the lowest water absorption capacity with 0.2. The difference between this sample is attributable to the different mass loses and the consequent variation in void volume. In summary, the void volume allows for deeper water penetration into the sample.

**Table 5.** Geopolymers % Mass Reduction rate/cycle and % Water absorption rate/cycle.

|  |  |  |
| --- | --- | --- |
| Sample | % Mass Reduction rate/cycle | % Water absorption rate/cycle |
| CS | -10% | 39% |
| FS1 | -8% | 26% |
| FS2 | -8% | 14% |
| FS5 | -30% | -9% |
| CSw | -6% | 15% |
| FS1w | -3% | -10% |
| FS2w | -7% | 20% |
| FS5w | -9% | 2% |

These results demonstrate higher water absorption capability of the geopolymer and consequently higher void content. Furthermore, the fast dissolution of NaOH, facilitated by its water solubility, contributes to the overall increase in the water absorption capacity of the geopolymer during the time.

In addition, the mass of dry geopolymers following one or more washes is lower than that of original, untreated dry geopolymers, indicating that the specimens have lost material, see **Table 5**.

This can be caused with two different loss mechanisms: 1) the dissolution in water of the unreacted chemicals [29] and 2) the mechanical losses of geopolymer. The dissolution and mechanical losses remove material from the sample with the consequence of increasing the void volume. The sample with lower FS content has a higher content of NaOH in the geopolymer. For instance, the sample CS and FS5 are the geopolymers that lost the higher amount of mass, respectively 10% and 30% per cycle. The CS lost prevalently unreacted chemicals while FS5 lost mass because is more fragile than others.

The samples without Na2SiO3 show a similar resistance in the water among them, while FS5 is friable and for higher FS contents the sample shows cavities and fragility. For example, FS10 after the first cycle loses the thin geopolymer casing that constituted the cavity at the top of the sample, weighing on its ability to absorb water. Furthermore, the Na2SiO3 increases the resistance in the sample. For instance, the FS5 and FS5w having similar formulation differs in mass losses because the FS5w is more resistant.

The sample with only NaOH shows a higher value of water absorption per cycle while the sample with Na2SiO3 has lower values. Furthermore, the rate of water absorption increases after each cycle as is shown in **Table 4**. The geopolymers with only NaOH increase the water absorbed after each cycle while the sample with Na2SiO3 revealed no discernible trend in the observed patterns if only this variable is observed.

The sample without Na2SiO3 shows a decrease in water absorption rate per cycle with higher FS content. Increasing the FS makes the sample more fragile leading to mass lost, which is less prevalent in samples produced with Na2SiO3 [16]. Finally, the water dissolving the NaOH increases the voids volume within the sample at a high rate. For instance, sample CS has a higher water absorption rate/cycle of 39% because contains more unreacted chemicals within the structure and the samples FS5 show the lowest water absorption rate with a value of -9%. The presence of more voids in FS5 allows water to penetrate deeply into the sample, thereby enhancing the dissolution of NaOH. Despite the higher value of water absorption capacity, high FS content reduces the capacity to absorb water with the cycle because is losing material at a high rate. In addition, the durability of the sample is reduced leading to unusable geopolymer. Contrarily, the FS5w has higher mechanical stability which led to the lowest mass lost among the samples and a constant water absorption per cycle. Therefore, FS5w is most durable sample.

* 1. **pH analysis**

The pH of the aqueous solution plays a crucial role in managing the adsorption process and serves as a pH regulator [30] [31]. Experimental findings demonstrate that for high pH in the solution is associated the ability of the geopolymer to adsorb heavy metals [31]. As the pH of the solution increases, the geopolymer exhibits an augmented capacity for adsorbing heavy metals. Consequently, the adsorption capability of heavy metals diminishes at lower pH levels. To evaluate the effect of the geopolymers and their respective formulation on the pH of the immersion water, the pH trend was evaluated as a function of the retention time of the geopolymers in the system. The analysis was carried out on BATCH 3 of the geopolymers produced. For each type of geopolymer formulation, two groups were used for the analysis, which were subjected to 3 washing cycles with constant water volume and agitation frequency. The first group was the formulation without Na2SiO3 and the second with Na2SiO3.

**Table 6.** Initial and final pH of Geopolymers after each cycle and %Reduction rate/cycle

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Cycle 1 | | | Cycle 2 | | | Cycle 3 | | | %Variation of pH per cycle |
|  | pH initial | pH final | ΔpH | pH initial | pH final | ΔpH | pH initial | pH final | ΔpH |  |
| CS | 5.27 | 11.76 | 6.49 | 5.39 | 10.37 | 4.98 | 4.05 | 9.08 | 5.03 | -12% |
| FS1 | 5.94 | 11.78 | 5.84 | 5.57 | 10.44 | 4.87 | 4.18 | 9.17 | 4.99 | -12% |
| FS2 | 5.79 | 11.86 | 6.07 | 5.51 | 10.28 | 4.77 | 4.8 | 9.34 | 4.54 | -11% |
| FS5 | 5.68 | 11.59 | 5.91 | 5.69 | 9.97 | 4.28 | 5.05 | 8.9 | 3.85 | -12% |
| CSw | 5.27 | 11.29 | 6.02 | 4.87 | 10.02 | 5.15 | 4.9 | 9.13 | 4.23 | -10% |
| FS1w | 4.51 | 11.35 | 6.84 | 4.73 | 10.02 | 5.29 | 4.74 | 9.03 | 4.29 | -11% |
| FS2w | 5.15 | 11.31 | 6.16 | 5.52 | 10.39 | 4.87 | 4.95 | 9.36 | 4.41 | -9% |
| FS5w | 4.87 | 11.01 | 6.14 | 5.04 | 10.38 | 5.34 | 4.15 | 9.66 | 5.51 | -6% |

**Table 6** shows the initial and final pH of geopolymers after each cycle. As regards the first cycle of use, a slight difference can be seen between the final pH reached by the geopolymers of the two groups. In the first group, the pHs reached after one hour of immersion are between 11.86 and 11.59 while in the second group the pHs are slightly lower and between 11.01 and 11.35 as in **Table 6**. The increase in pH is very rapid for all the geopolymers tested, with ΔpH between 5.15 and 6.30 within the first 5 minutes of immersion without an apparent difference between the samples as shown in **Table 6**. The rapid increase in pH against the time confirmed what had been observed with the mass loss in the previous paragraph, where CS has the highest quantity of unreacted chemical compared to the other samples and FS5 with the highest water absorption capacity enables water to penetrate the sample more deeply, facilitating the dissolution of unreacted chemicals from within.

In the second cycle the final pH is lower than that achieved in the first wash: the quantity of NaOH available to be released by the geopolymer to the immersion water is therefore decreased. In the first group, the pHs reached after one hour of immersion are between 9.97 and 10.34 while in the second group, the pHs are slightly higher and between 10.02 and 10.39 as in **Table 6**. The increase in pH is however rapid, with a ΔpH between 4.94 and 4.03 in the first 5 minutes of immersion as shown in **Table 6**. The findings confirm that the second group allows water to access deeply into the geopolymer and release more NaOH compared to the first group.

At the third cycle of use, the geopolymers have significantly less NaOH to offer to the immersion water, as can be seen from the final pH. In the first group, the pHs reached after one hour of immersion are between 8.9 and 9.34 while in the second group, the pHs are slightly higher and between 9.03 and 9.66 as in **Table 6**. The pH increase is also much slower than during the first cycles of use, with a ΔpH of between 2.00 and 1.20 after the first 5 minutes of immersion. The FS5w sample is an exception, which however presents a rapid increase in the early stages, with a pH of 4.81 within the first 5 minutes. **Table 6** shows a higher decrease of pH per cycle in the first group compared to the samples of the second group. The reduction % of pH per cycle in the sample of the first group is between -11% and 12% and for the samples of the second groupis between -6% and -11%. The lower reduction in the sample with Na2SiO3 indicates a slower release of NaOH in the water. This finding indicates that the formulation of the second group allows high pH for a much longer period compared to the first group. This indicates that the NaOH is release gradually but steady influenced by internal structure of void which required a further study.

The authors found a linear correlation between the chemical composition and the initial, final and average pH for the geopolymer studied. The Pearson correlations have been presented in **Table 7**.

**Table 7.** Pearson correlations of the chemical composition and initial, final, ΔpH and %Variation of pH per cycle values

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | 1° cycle | | | 2° cycle | | | 3° cycle | | |  |
|  | pH initial | pH final | ΔpH | pH initial | pH final | ΔpH | pH initial | pH final | ΔpH | %Variation of pH per cycle |
| FS \* | 0.3 | -0.7 | -0.6 | 0.9 | -0.9 | -1.0 | 0.9 | -0.5 | -1.0 | -0.3 |
| FS \*\* | -0.2 | -0.9 | -0.2 | 0.3 | 0.8 | 0.3 | -0.9 | 0.9 | 1.0 | 0.9 |
| NaOH | 0.8 | 0.9 | -0.3 | 0.7 | 0.2 | -0.7 | -0.2 | -0.4 | 0.0 | -0.8 |
| Na2SiO3 | -0.8 | -0.9 | 0.3 | -0.7 | -0.2 | 0.7 | 0.2 | 0.4 | 0.0 | 0.8 |

Note: \* sample with NaOH only; \*\* sample with NaOH and Na2SiO3

In **Table 7**, a strong negative correlation between the increase in FS and the final pH as well as ΔpH has been consistently observed in all geopolymers during the initial cycle. However, this trend reverses in the subsequent two cycles in the second group. Based on this pattern, both geopolymer formulations exhibit a rapid release of NaOH from the surface.

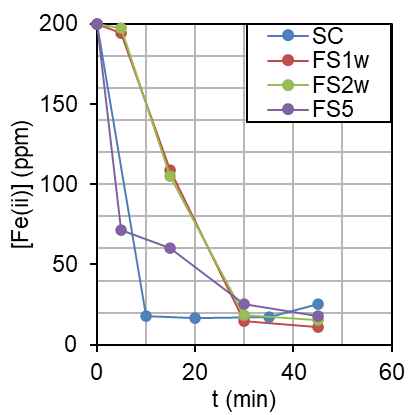
In the second cycle, the first group has negative correlation between the increase in FS and the final pH, while the second group has positive correlation. This trend persists in the third cycle. Additionally, ΔpH demonstrates a strong negative correlation with the first group, contrasting with a positive correlation in the second group, particularly robust in the third cycle. This observation reinforces the notion of distinct geopolymer topologies which for its interconnected pores allows water to penetrate the bulk of the sample. Previous study observed that the formulation with Na2SiO3 has higher porosity and linked porous, while the formulation with NaOH at equal porosity has closed porous [29]. This topology influences the mechanism of NaOH dissolved. For instance, both formulations released NaOH mainly from the surface during the first cycle while the second group allows the dissolution of NaOH from the bulk, keeping the pH at a high value for longer usage. Moreover, the Na2SiO3 has a negative correlation with the final pH with a reversed correlation in the latest, confirming that the above mechanism occurs during the last cycles.

* 1. **Treatment of Fe2+ ions in aqueous solution**

In this section, we primarily focus on the intrinsic capability of the geopolymer in removing Fe2+ ions from water, a common contaminant in groundwater. The geopolymer samples analysed for this purpose are CS, FS5, FS1w, and FS2w, selected based on their optimal absorption capacities. The control sample is the base line, while the other three samples are those presenting the best average absorption capacities. The analysis was conducted for 45 minutes and repeated consecutively three times for each pair of geopolymers. The pH measurement was conducted concurrently with the test to assess the NaOH concentration.

The initial cycle of the experiment serves as a preliminary stage, primarily to remove any excess NaOH from the geopolymer matrix. This step ensures that subsequent cycles accurately reflect the geopolymer’s actual contaminant removal efficacy, rather than the effects of residual NaOH. Thus, while the initial cycles do show a significant removal of Fe2+ ions, it is considered preparatory, and its results are not directly compared with the following cycles.

In the first cycle, an high Fe2+ removal efficiency for all analysed samples was noted, see **Figure 3**, accompanied by the precipitation of Fe(OH)2 in the solution. This suggests that the reduction of the contaminant can be attributed to the reaction with NaOH released from the surface.



**Figure 3.** Concentration of Fe (II) against the retention time for the first cycle using the samples CS, FS1w, FS2w and FS5.

In the second cycle, the geopolymers are less effective in removing Fe2+ precipitation than in the first cycle, as reported in **Figure 4** due to the less NaOH released in the water as observed in the paragraph 4.3. The formation of a precipitate of Fe(OH)3, an orange precipitate that remains suspended together with the ferrous counterpart within the solution under treatment, is visible.

A graph with numbers and lines

Description automatically generated

**Figure 4.** Concentration of Fe (II) against the retention time for the second cycle using the samples CS, FS1w, FS2w and FS5.

In the third cycles, the performance of the geopolymers in Fe2+ removal is the primary focus. These cycles demonstrate the geopolymer's capacity for sustained contaminant removal as reported in **Figure 5**. The results show a notable reduction in Fe2+ concentration, even after the initial excess NaOH is washed out. This is particularly notable in samples FS2w and FS5. The gradual and consistent decrease in Fe2+ removal efficiency observed in these cycles suggests that the geopolymer effectively sustains contaminant removal over time. This pattern underscores the efficacy, lifetime, and durability of the geopolymer in maintaining its contaminant removal capabilities.

A graph with different colored lines and numbers

Description automatically generated

**Figure 5.** Concentration of Fe (II) against the retention time for the third cycle using the samples CS, FS1w, FS2w and FS5.

As shown in **Figure 6**, in the third cycle, the pH is around 6 for all sample indicating low concentration of NaOH in the solution. Thus, it is ruled out that the contaminant removal is attributed to NaOH, emphasizing solely the influence of the active sites within the geopolymer. In fact, it is also observed that the formation of Fe(OH)2 is minimal.

|  |  |
| --- | --- |
| (a) | (b) |
| A chart with numbers and a line graph  Description automatically generated with medium confidence | A graph of ph and cycle  Description automatically generated |
| (c) | (d) |
| A graph of ph and cycle  Description automatically generated | A graph of ph and cycle  Description automatically generated |

**Figure 6.** pH trend against time during the treatment with Fe (II): (a) CS, (b) FS1w, (c) FS2w, (d) FS5.

Additionally, in this case, ferrous hydroxide forms directly on the surface (**Figure 7**) of the geopolymer indicating a distinct mechanism of contaminant removal, wherein Fe2+ is deposited on the geopolymer surface, where active sites facilitate the adsorption of Fe2+



**Figure 7.** CS sample after the third cycle.

This is consistent with [29] that showed that the adsorption of ion occurs in two steps: first the Fe2+ is deposited on the surface and second migrates slowly into the internal pores. Diffusion into the internal pores depends on the internal structure of the voids, which depends on the FS and Na2SiO3 content used to manufacture the sample. In fact, higher FS content results in more pores facilitating the penetration of contaminants. Moreover, higher porosity also means higher superficial area and more active sites, enhancing the effectiveness of contaminant removal.

This is particularly effective for the CS which even at lower retention times, is much less effective in precipitating Fe(II) compared to the other geopolymers analysed. The geopolymers containing sodium metasilicate as an activating co-solution (samples FS1w and FS2w) present a Fe2+ precipitation efficacies that are very similar to each other, while the FS5 sample proves to be the most effective in this last cycle of use.

**Conclusions**

This study demonstrates that geopolymers can effectively remove contaminants like Fe2+ ions from water. This capability is attributed to the high porosity and specific composition of the geopolymers, which facilitate adsorption and precipitation of contaminants on the active sites of the geopolymeric structure. The influence of various parameters such as fume silica content, sodium hydroxide, and sodium silicate concentrations, along with curing process and pH, has been thoroughly investigated. While high porosity is advantageous for water treatment as it implies more pores accessible to water, enhancing the filtration and adsorption processes, it also presents a trade-off by making the samples more fragile. This increased fragility due to higher porosity necessitates a careful balance between achieving sufficient porosity for effective water treatment and maintaining the structural integrity of the geopolymer. Our findings reveal that geopolymers with an optimal range of fume silica (1% to 5%) exhibit the best combination of porosity and usability.

The curing process and the pH of the environment are also important in determining the final properties of the geopolymers. Shorter curing times and higher pH levels are favourable for achieving desirable characteristics in the final product. However, it is also noted that excessive water absorption can lead to structural changes in the geopolymers, which may impact their long-term performance in water treatment applications.

The synthesis of geopolymers from Martian soil simulants opens new avenues for sustainable resource utilization in space missions, particularly for Mars exploration. The ability to create effective water treatment membranes from locally available materials can significantly reduce the dependency on Earth-supplied resources, paving the way for longer and more sustainable manned missions to Mars. In particular, this study marks a significant step towards developing efficient and sustainable water purification systems. However, further investigation is required to optimize the production process and to explore the long-term stability of these geopolymers in real-world water treatment scenarios.

1. **References**

[1] Karl, D., Cannon, K.M., Gurlo, A., 2022. Review of space resources processing for Mars missions: Martian simulants, regolith bonding concepts and additive manufacturing. Open Ceram. 9, 100216. https://doi.org/10.1016/j.oceram.2021.100216

[2] Mattei, E., Pettinelli, E., Lauro, S.E., Stillman, D.E., Cosciotti, B., Marinangeli, L., Tangari, A.C., Soldovieri, F., Orosei, R., Caprarelli, G., 2022. Assessing the role of clay and salts on the origin of MARSIS basal bright reflections. Earth Planet. Sci. Lett. 579, 117370. https://doi.org/10.1016/j.epsl.2022.117370

[3] Lauro, S.E., Pettinelli, E., Caprarelli, G., Baniamerian, J., Mattei, E., Cosciotti, B., Stillman, D.E., Primm, K.M., Soldovieri, F., Orosei, R., 2022. Using MARSIS signal attenuation to assess the presence of South Polar Layered Deposit subglacial brines. Nat. Commun. 13, 1–10. https://doi.org/10.1038/s41467-022-33389-4

[4] Feldman, W.C., Prettyman, T.H., Maurice, S., Plaut, J.J., Bish, D.L., Vaniman, D.T., Mellon, M.T., Metzger, A.E., Squyres, S.W., Karunatillake, S., Boynton, W. V., Elphic, R.C., Funsten, H.O., Lawrence, D.J., Tokar, R.L., 2004. Global distribution of near-surface hydrogen on Mars. J. Geophys. Res. Planets 109, 1–13. https://doi.org/10.1029/2003JE002160

[5] Dundas, C.M., Bramson, A.M., Ojha, L., Wray, J.J., Mellon, M.T., Byrne, S., McEwen, A.S., Putzig, N.E., Viola, D., Sutton, S., Clark, E., Holt, J.W., 2018. Exposed subsurface ice sheets in the Martian mid-latitudes. Science (80-. ). 359, 199–201. https://doi.org/10.1126/science.aao1619

[6] O’Neill, K.T., Fridjonsson, E.O., Smeed, D., Hopper, T.A.J., Johns, M.L., 2023. Characterising water in Lunar and Martian regolith materials using nuclear magnetic resonance. Icarus 399, 115544. https://doi.org/10.1016/j.icarus.2023.115544

[7] Diez, A., 2018. Liquid water on Mars. Science (80-. ). 361, 448–449. https://doi.org/10.1126/science.aau1829

[8] Bai, C., Colombo, P., 2018. Processing, properties and applications of highly porous geopolymers: A review. Ceram. Int. 44, 16103–16118. https://doi.org/10.1016/j.ceramint.2018.05.219

[9] Liang, K., Wang, X.Q., Chow, C.L., Lau, D., 2022. A review of geopolymer and its adsorption capacity with molecular insights: A promising adsorbent of heavy metal ions. J. Environ. Manage. 322, 116066. https://doi.org/10.1016/j.jenvman.2022.116066

[10] Ettahiri, Y., Bouargane, B., Fritah, K., Akhsassi, B., Pérez-Villarejo, L., Aziz, A., Bouna, L., Benlhachemi, A., Novais, R.M., 2023. A state-of-the-art review of recent advances in porous geopolymer: Applications in adsorption of inorganic and organic contaminants in water. Constr. Build. Mater. 395. https://doi.org/10.1016/j.conbuildmat.2023.132269

[11] Raza, M.H., Khan, M., Zhong, R.Y., 2024. Strength, porosity and life cycle analysis of geopolymer and hybrid cement mortars for sustainable construction. Sci. Total Environ. 907, 167839. https://doi.org/10.1016/j.scitotenv.2023.167839

[12] Zhang, Z., Li, L., He, D., Ma, X., Yan, C., Wang, H., 2016. Novel self-supporting zeolitic block with tunable porosity and crystallinity for water treatment. Mater. Lett. 178, 151–154. https://doi.org/10.1016/j.matlet.2016.04.214

[13] Taylor, L., Alberini, F., Sullo, A., Meyer, M.E., Alexiadis, A., 2018. Study of the rheological properties of water and Martian soil simulant mixtures for engineering applications on the red planet. Adv. Sp. Res. 61, 1490–1500. https://doi.org/10.1016/j.asr.2017.12.037

[14] Alexiadis, A., Alberini, F., Meyer, M.E., 2017. Geopolymers from lunar and Martian soil simulants. Adv. Sp. Res. 59, 490–495. https://doi.org/10.1016/j.asr.2016.10.003

[15] Khale, D., Chaudhary, R., 2007. Mechanism of geopolymerization and factors influencing its development: A review. J. Mater. Sci. 42, 729–746. https://doi.org/10.1007/s10853-006-0401-4

[16] Saha, S., Rajasekaran, C., 2017. Enhancement of the properties of fly ash based geopolymer paste by incorporating ground granulated blast furnace slag. Constr. Build. Mater. 146, 615–620. https://doi.org/10.1016/j.conbuildmat.2017.04.139

[17] He, P., Wang, M., Fu, S., Jia, D., Yan, S., Yuan, J., Xu, J., Wang, P., Zhou, Y., 2016. Effects of Si/Al ratio on the structure and properties of metakaolin based geopolymer. Ceram. Int. 42, 14416–14422. https://doi.org/10.1016/j.ceramint.2016.06.033

[18] Palomo, A., Grutzeck, M.W., Blanco, M.T., 1999. Alkali-activated fly ashes: A cement for the future. Cem. Concr. Res. 29, 1323–1329. https://doi.org/10.1016/S0008-8846(98)00243-9

[19] Mustafa Al Bakria, A.M., Kamarudin, H., Bin Hussain, M., Khairul Nizar, I., Zarina, Y., Rafiza, A.R., 2011. The effect of curing temperature on physical and chemical properties of geopolymers. Phys. Procedia 22, 286–291. https://doi.org/10.1016/j.phpro.2011.11.045

[20] Phair, J.W., Van Deventer, J.S.J., 2002. Effect of the silicate activator pH on the microstructural characteristics of waste-based geopolymers. Int. J. Miner. Process. 66, 121–143. https://doi.org/10.1016/S0301-7516(02)00013-3

[21] Cannon, K.M., Britt, D.T., Smith, T.M., Fritsche, R.F., Batcheldor, D., 2019. Mars global simulant MGS-1: A Rocknest-based open standard for basaltic martian regolith simulants. Icarus 317, 470–478. https://doi.org/10.1016/j.icarus.2018.08.019

[22] Allen, C.C., Jager, K.M., Morris, R. V., Lindstrom, D.J., Lindtsrom, M.M., Lockwood, J.P., 1998. Martian soil simulant available for scientific, educational study. Eos, Trans. Am. Geophys. Union 79, 405–409. https://doi.org/10.1029/98eo00309

[23] Prud’homme, E., Michaud, P., Joussein, E., Peyratout, C., Smith, A., Arrii-Clacens, S., Clacens, J.M., Rossignol, S., 2010. Silica fume as porogent agent in geo-materials at low temperature. J. Eur. Ceram. Soc. 30, 1641–1648. https://doi.org/10.1016/j.jeurceramsoc.2010.01.014

[24] Pachana, P.K., Rattanasak, U., Nuithitikul, K., Jitsangiam, P., Chindaprasirt, P., 2022. Sustainable utilization of water treatment residue as a porous geopolymer for iron and manganese removals from groundwater. J. Environ. Manage. 302, 1–18. https://doi.org/10.1016/j.jenvman.2021.114036

[25] Method, S.T., 2000. iTeh Standards iTeh Standards Document Preview 08, 3–4. https://doi.org/10.1520/C0642-13.10.1520/C0642-21.2

[26] Rakestraw, N.W., Mahncke, H.E., Reach, E.F., 1936. Determination of Iron in Sea Water. Ind. Eng. Chem. - Anal. Ed. 8, 136–138. https://doi.org/10.1021/ac50100a027

[27] 3500-Fe B. Phenanthroline Method. 2018. Standard Methods Online - Standard Methods for the Examination of Water and Wastewater.

[28] Masi, G., Rickard, W.D.A., Bignozzi, M.C., van Riessen, A., 2014. The Influence of Short Fibres and Foaming Agents on the Physical and Thermal Behaviour of Geopolymer Composites. 13th Int. Ceram. Congr. - Part F 92, 56–61. https://doi.org/10.4028/www.scientific.net/ast.92.56

[29] Zhang, Xuhao, Zhang, Xiao, Li, X., Liu, Y., Yu, H., Ma, M., 2022. Porous geopolymer with controllable interconnected pores—a viable permeable reactive barrier filler for lead pollutant removal. Chemosphere 307, 136128. https://doi.org/10.1016/j.chemosphere.2022.136128

[30] Chindaprasirt, P., Rattanasak, U., 2020. Synthesis of porous alkali-activated materials for high-acidic wastewater treatment. J. Water Process Eng. 33, 101118. https://doi.org/10.1016/j.jwpe.2019.101118

[31] Cheng, T.W., Lee, M.L., Ko, M.S., Ueng, T.H., Yang, S.F., 2012. The heavy metal adsorption characteristics on metakaolin-based geopolymer. Appl. Clay Sci. 56, 90–96. <https://doi.org/10.1016/j.clay.2011.11.027>

[32] Danish, A., Oz, A., Ozbakkaloglu, T., 2023. Resources , Conservation & Recycling Performance evaluation and cost analysis of prepacked geopolymers containing waste marble powder under different curing temperatures for sustainable built environment 192. https://doi.org/10.1016/j.resconrec.2023.106910

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