ARTICLE IN PRESS

Available online at www.sciencedirect.com

ScienceDirect

Advances in Space Research xxx (xxxx) xxx

ADVANCES IN SPACE RESEARCH (a COSPAR publication)

www.elsevier.com/locate/asr

Development of waterless extra-terrestrial concrete using Martian regolith

Snehal K. [a], Priyanshu Sinha [b], Piyush Chaunsali [c,*]

[a] Department of Civil Engineering, MNNIT Allahabad, Prayagraj, India
[b] University of West England, BS16 1QY, United Kingdom
[c] Department of Civil Engineering, IIT Madras, Chennai, India

Received 20 April 2023; received in revised form 13 July 2023; accepted 18 July 2023

Abstract

Human colonization on Martian land is gaining significant attention in space exploration activities that demand in-situ resource utilization in the development of construction and building materials for human habitation. This research explores the utilization of Martian regolith simulant and sulfur to create extra-terrestrial concrete (ETC) with a property suitable for constructing human habitat on Mars. The primary objective of the study is to maximize the utilization of Martian regolith simulant to achieve the desired compressive strength of 25 MPa (average compressive strength specified for concrete used in residential buildings on Earth). Mechanical properties, phase transition, and microstructural characteristics of Martian regolith based-ETC under varied temperature conditions (0 °C, 40 °C, and 50 °C) on Mars were investigated. The optimal mixture proportion of ETC had 70% (by wt.) of Martian regolith and exhibited an average compressive strength of 27 MPa. The formulated ETC could retain up to 25 MPa of compressive strength at 40 ℃ and 50 ℃, and could reach up to 35 MPa at 0 ℃ temperature conditions. The change in compressive strength was attributed to the sulfur sublimation and pore closure brought about by freezing at extreme temperatures, respectively.

Keywords: Martian regolith simulant; Sulfur; Microstructure; Mineralogy; Extreme temperature

1. Introduction

Colonization of Mars has become an active target of space exploration since 20th century. Global public and private space organizations have set a goal for the settlement of human race on the red planet (Mars) by 2050 (Murgatroyd and Hodges, 2001; Scott et al., 2017). One of the prime goals of the colonization effort is to maintain human life on the surface of Mars. Therefore, building a permanent and durable infrastructure for human inhabitation on Martian land has turned out to be the focus of research in universal planetary exploration activities (Mills et al., 2022). In this regard, several approaches have been considered for extra-terrestrial construction which include conventional ordinary Portland cement (OPC) concrete formulated with regolith as aggregate (Neves et al., 2020), epoxy/polymer-based binder cement (Naser, 2019; Naser and Chehab, 2020), and alkali-activated/geopolymeric binder system (Montes et al., 2015; Davis et al., 2017; Pilehvar et al., 2020; Zhou et al., 2020). However, these approaches require supplementary earthly resources and conveyance of building and construction materials from Earth to Mars is highly expensive and is going to be a challenging task. Instead, the most feasible approach is to use the indigenous resources as construction materials for building any permanent structures on Mars

* Corresponding author.
E-mail address: pchaunsali@iitm.ac.in (P. Chaunsali).

https://doi.org/10.1016/j.asr.2023.07.036
0273-1177/© 2023 COSPAR. Published by Elsevier B.V. All rights reserved.

Please cite this article as: S. K., P. Sinha and P. Chaunsali, Development of waterless extra-terrestrial concrete using Martian regolith, Advances in Space Research, https://doi.org/10.1016/j.asr.2023.07.036

(King and McLennan, 2010; Werkheiser, et al., 2015; Khoshnevis et al., 2016; Naser, 2019).

To that end, a team of researchers (Troemer et al., 2021) developed a novel way for making Martian concrete using locally available resources on Mars. Rovers' data from NASA provide information that the Red planet lacks liquid water but is found in a frozen state (NASA report 2022). However, unlike conventional concrete prepared on Earth, Martian concrete needs to be designed without water (Troemer et al., 2021). It is reported that the planet Mars contains high levels of sulfur concentration on its surface (Scheerbaum, 2000). The records also indicate a higher concentration of sulfur in the Martian core (Rapp et al., 2006). For that reason, the chief constituent considered in the development of Martian concrete has been "sulfur", which acts as a binding material when heated to about 140 °C (Toutanji et al., 2005; Troemer et al., 2021;Hu et al., 2022). Another possible constituent that is abundantly found on the Red planet is "Martian soil" or "Martian regolith", which can be used as a source of aggregate. Martian concrete was prepared by hot-mixing (using alternative sources of heating including solar energy) Martian regolith with molten sulfur, followed by casting and cooling (Brinegar, 2019; Troemer et al., 2021; Li et al., 2021). The phenomenon here is that as the mixture cools, liquid sulfur endures crystallization. Firstly, transforming into monoclinic sulfur (S_β) at 115 °C, and further at the temperature underneath 96 °C monoclinic sulfur (S_β) transforms into orthorhombic sulfur (S_α), which is a stable polymorph of sulfur at room temperature. Solidification process of liquid sulfur happens quickly, generally within 24 h, resulting in a Martian regolith based strongly bonded rapid-hardening construction material (Wan et al., 2016). Toutanji and Grugel (2008) report that, in case of waterless Martian concrete, sulfur functions as a thermo-plastic material with the ability to hold the non-reactive Martian regolith together. The major advantage of Martian concrete over Earth's concrete is that this concrete can be reused by reheating until sulfur melts and gets back to a malleable state (Reches, 2019). Apart from this fact, it is also a carbon–neutral construction material, unlike Portland cement concrete on Earth (Li et al., 2021). Landers and rovers from NASA successfully discovered that partial Martian conditions such as day length, seasons, and surface conditions match with Earth (NASA report 2022). However, Mars has a much thinner, colder, and low gravity atmosphere versus Earth. Near the poles, the temperature can drop up to −125 °C during winter, and near the equator, temperature may reach up to 20 °C during summer. Nevertheless, night temperature can fall to about −73 °C (Scheerbaum, 2000). Therefore, building infrastructure on Mars is an engineering challenge . Following this fact, it is important to understand the behavior of waterless Martian concrete formulated using Martian regolith and sulfur at extreme temperature cycles of Mars. However, very few studies focused on the performance of Martian concrete under extreme temperature conditions of Mars.

In recent years, several research endeavors have explored the potency of using Martian regolith and sulfur as principal constituents in concrete production for future space exploration and colonization initiatives. Martian regolith simulants (mixture of TiO_2, Fe_2O_3, SiO_2, Al_2O_3, and other constituents) with a proportion nearly similar to actual Martian regolith have been utilized by researchers to uncover the feasibility of using these materials in extraterrestrial concrete (Toutanji et al., 2005; Toutanji and Grugel, 2008; Brinegar, 2019; Troemer et al., 2021; Abdeen et al., 2023). According to the findings of Wan et al. (2016), concrete made with sulfur and Martian regolith showed higher compressive strength compared to concrete produced using sulfur and ordinary sand. Smaller particle size of Martian regolith and the presence of additional sulfates and poly sulfates in Martian regolith are the associated factors that contributed to the strength of Martian concrete. They were able to fabricate the Martian concrete blocks (with a compressive strength of 50 MPa), which are two and a half times stronger than the Earth's conventional concrete, using 50% Martian soil simulant and 50% molten sulfur. In subsequent years Brinegar (2019) identified that Martian concrete composed of commercially available Martian regolith simulants failed to achieve the actual compressive strength noticed in original Martian regolith. This was attributed to the fact that all the oxide composition present in original Martian soil simulant was not fully replicated in simulated Martian regolith in laboratory. Li et al. (2021) proposed further improvement in the field by presenting a new-fangled way to produce energy-efficient Martian concrete. Their approach specified the use of sulfur and magnetite as constituents and microwave heat energy to facilitate concrete casting. Developed concrete achieved a compressive strength of 17 MPa on Earth and it was estimated to have higher strength in Martian conditions (∼45 MPa). Some studies also proposed the use of a convex lens to concentrate the solar light for melting sulfur (Wan et al., 2016). Another study by Shahsavari et al., (2022) concluded that Martian concrete, produced with 30 % sulfur and compacted under 2 MPa pressure, exhibited the highest values of unconfined compressive strength (UCS), and tensile strength. Recently, Akono (2023) reported a microporous structure of Martian concrete exhibiting a distinct matrix-inclusion morphology with nonlinear fracture behavior, having a fracture toughness value of 0.48–0.7 MPa $\sqrt{m}$ for same formulation proposed by Wan et al (2016) earlier. Literature also reported that addition of additives such as fibers is likely to improve the ductile property of sulfur concrete (Omar and Issa, 1994; Meyers and Toutanji et al., 2007). Even though waterless Martian concrete satisfies the adequate mechanical performance for construction applications on celestial bodies like Mars, uncertainties regarding its behavior under varied temperatures, vacuum, gravity difference, and radiation conditions are still unclear.

In this study, at first, Martian regolith concrete was prepared using a varied proportion of Martian regolith simulant and sulfur to determine the optimum mix in correspondence to compressive strength. The study emphasizes the maximum utilization of Martian regolith simulant with a capacity to achieve the desired compressive strength of 25 MPa (average compressive strength specified for concrete used in residential buildings on Earth). Then, the performance and transformation in the microstructure of produced Martian regolith simulant-based ETC under extreme temperature conditions were investigated. The microstructure of Martian concrete before and after exposure to varied climatic temperatures of Mars at the laboratory was evaluated using characterization techniques such as X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Fourier-Transform Infrared Spectroscopy, and Scanning Electron Microscopy (SEM).

2. Experimental investigation

2.1. Materials

A Martian regolith simulant (MGS-1) procured from the Exolith Lab (Florida, USA) and commercially available 99.8% pure sulfur powder was used in this work. The oxide composition and specific gravity value of the MGS-1 are given in the Table 1. The major components of Martian soil are SiO_2, Al_2O_3, and Fe_2O_3, which account for more than 75% of the overall oxide composition. The particle size distribution curve of MGS-1 is shown in Fig. 1. The D_{10}, D_{50}, and D_{90} values of the Martian regolith simulants are found to be 1.07 μm, 17.5 μm, and 43.8 μm, respectively.

X-ray diffraction (XRD) pattern, thermogravimetric (TG-DTG) curve, and scanning electron micrograph (SEM) with energy dispersive spectroscopic (EDS) information of MGS-1are shown in Figs. 2-4 and Table 2.

According to XRD pattern (Fig. 2), albite ($NaAlSi_3O_8$), anorthite ($CaAl_2Si_2O_8$), bytownite ($(Ca,Na)[Al(Al,Si)SiO_8]$) and olivine ($MgFe_2SiO_4$) are the most common minerals observed in Martian regolith simulant (MGS-1). Thermogravimetric analysis (TGA) of MGS-1 (Fig. 3)

Table 1
Oxide composition and specific gravity value of the MGS-1.

Oxide composition (wt%)	
SiO_2	44.24
Al_2O_3	13.44
Fe_2O_3	20.94
SO_3	5.92
CaO	7.38
Na_2O	0.57
MgO	6.36
K_2O	0.53
Cl	0.02
Cr_2O_3	0.24
MnO	0.14
NiO	0.18
SrO	0.06
Specific gravity	2.83

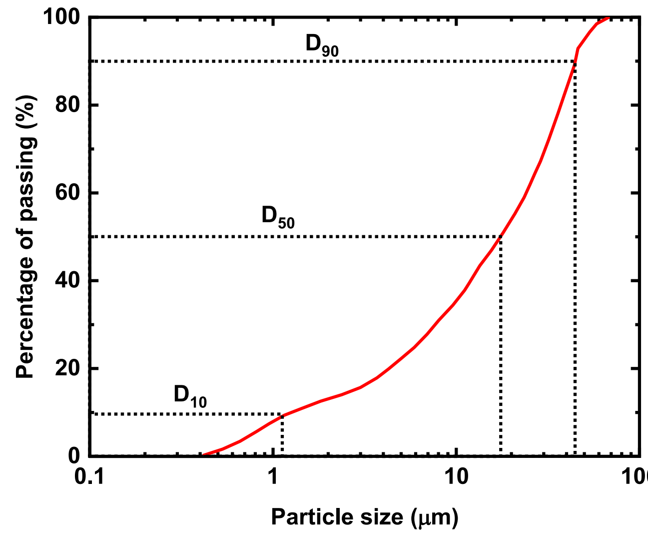

Fig. 1. Particle size distribution of Martian regolith simulant (MGS-1).

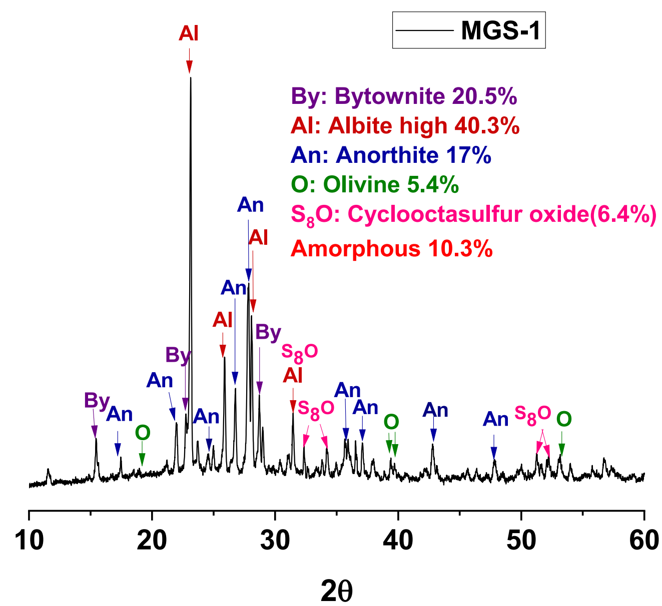

Fig. 2. XRD pattern of Martian regolith simulant (MGS-1).

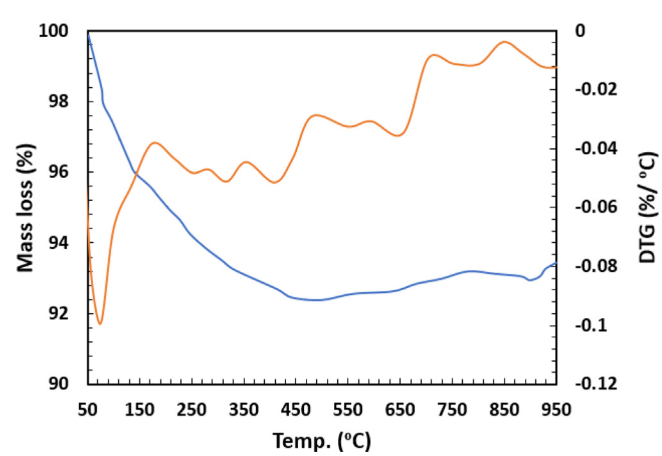

Fig. 3. TG-DTG curve of Martian regolith simulant (MGS-1).

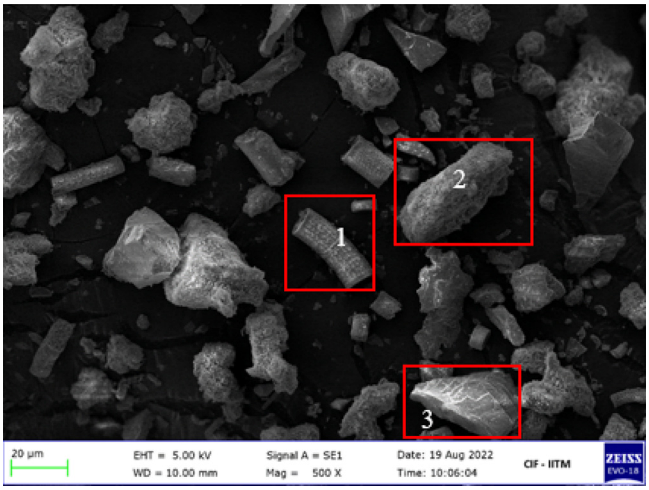

Fig. 4. Morphology of Martian regolith simulant (MGS-1).

revealed multiple endothermic and exothermic peaks associated with the decomposition of glassy phases. It is reported that endothermic peaks corresponding to the decomposition of major mineral phases such as albite, olivine, etc., are noticed at the temperature range of 1000–1600 °C. The complete decomposition of mineral phases of MGS-1 was not recorded in the TG analysis, since the MGS-1 possesses its characteristic decomposition temperature above 1000 °C. However, MGS-1 exhibited a mass loss of about 9% till the maximum recorded temperature of 950 °C. SEM micrographs of MGS-1 (Fig. 4) illustrated a complex structure with three major morphologies: 1) perforated tubular structure (Olivine: $MgFe_2SiO_4$), 2) smooth irregular structure (Albite: $NaAlSi_3O_8$; Olivine: $MgFe_2SiO_4$), and 3) angular structure (Anorthite: $CaAl_2Si_2O_8$; Albite: $NaAlSi_3O_8$; Bytownite: (Ca,Na)[Al(Al,Si)SiO_8]). Table 2 shows the elemental composition of various morphologies observed in the Martian regolith simulant (MGS-1).

2.2. Preparation of Martian regolith simulant-based ETC

Martian regolith simulant-based ETC specimens were cast in varying proportions of Martian simulant and sulfur.

Table 3
Mix proportion of Martian concrete.

Mix designations	MGS-1(%)	Sulfur (%)
MC-75/25	75	25
MC-73/27	73	27
MC-70/30	70	30
MC-65/35	65	35

Table 3 shows various mix proportions of waterless Martian concrete used in the study.

Martian concrete was synthesized by blending both Martian simulant and sulfur powder at various proportions as mentioned in Table 3. It is important to note that the agglomeration of sulfur particles was removed during the process of mixing. Next, the uniformly spread blended samples placed on the metal tray were kept in the oven and maintained at 140 °C for about 20 mins. Interval mixing (every 5 min) was performed to ensure the consistency of paste. Then, the tray was taken out of the oven and the paste was placed in the acrylic mould of size 50 × 50 × 50 mm and was compacted using a wooden block. After 24 h, the specimens were de-moulded and tested for compressive strength. Fig. 5 shows the process of producing Martian concrete. Subsequently, laboratory-scale tests were conducted on the Martian concrete specimens exposed to extreme temperature conditions.

2.3. Laboratory scale test on extreme temperature conditions

Due to the thinner, colder, and low gravity atmosphere of Mars, buildings on the Martian surface would suffer extreme temperature cycles and thermal shocks. The temperature on the Martian surface may reach up to 20 °C at noon and drops to −73 °C at night during summer near the equator. However, the temperature may reach up to −125 °C during winter near the poles (Scheerbaum, 2000). A typical variation of temperature on the Martian surface is shown in Fig. 6.

To assess the behavior of Martian regolith simulant-based ETC under extreme temperatures, temperature susceptibility of Martian regolith simulant-based ETC was examined under three temperatures (0 °C, 40 °C and 50 °C) . As per Rover's data, maximum temperature reached

Table 2
Elemental composition of Martian regolith simulant (MGS-1).

Point (morphology)	Si	Al	O	C	Na	Mg	S	Ca	Fe	K	Mineral phases
	Atomic weight %										
1(Perforated tube)	23.89	1.37	70.82	–	–	1.23	1.68	0.25	0.69	0.07	Olivine: $MgFe_2SiO_4$ Anorthite: $CaAl_2Si_2O_8$
2(Smooth irregular)	16.75	6.98	64.57	–	4.58	2.48	0.58	2.52	–	0.33	Anorthite: $CaAl_2Si_2O_8$ Albite: $NaAlSi_3O_8$
3(angular)	16.37	14.62	57.26	2.37	2.15	–	–	6.94	–	–	Anorthite: $CaAl_2Si_2O_8$ Albite: $NaAlSi_3O_8$ Bytownite: (Ca,Na)[Al(Al,Si)SiO_8]

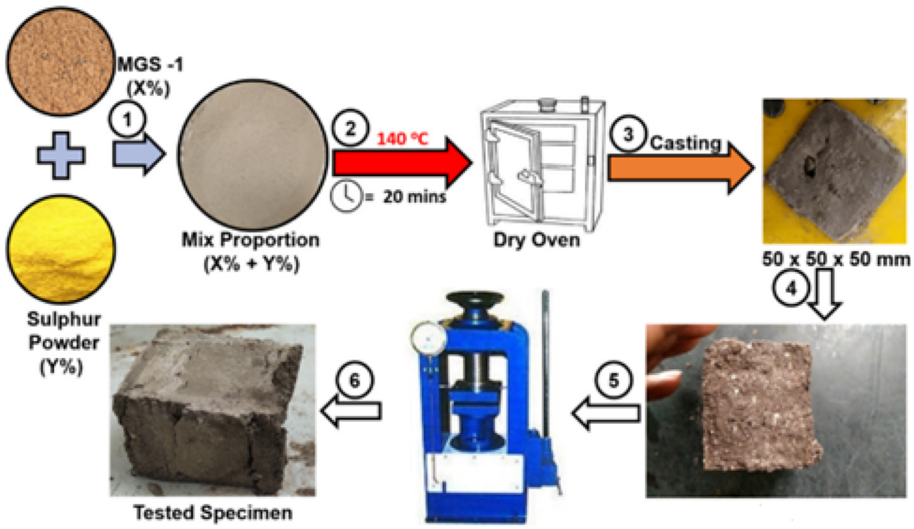

Fig. 5. Process of producing Martian concrete.

at the Martian surface to date is 30 °C (average of 20 °C). Considering this fact temperature resistance test was conducted by exposing the Martian concrete to an oven set at two temperatures setting of 40 °C and 50 °C for the duration of 7 and 28 days. The study's choice of 40 °C and 50 °C was made after taking into account the higher side of the experienced maximum temperature on Mars and high temperature-sensitivity of sulfur used in making ETC. Further, a freezer set for a maximum of 0 °C was used to carry out the freezing temperature resistance. It is to be noted that testing at temperatures below 0 °C requires a cryogenic environment which requires a constant supply of liquid nitrogen. Hence, the test was carried out in a laboratory freezer and the lowest temperature considered in the current study is 0 °C. Specimens exposed to different temperatures for the duration of 7 and 28 days were tested for compressive strength.

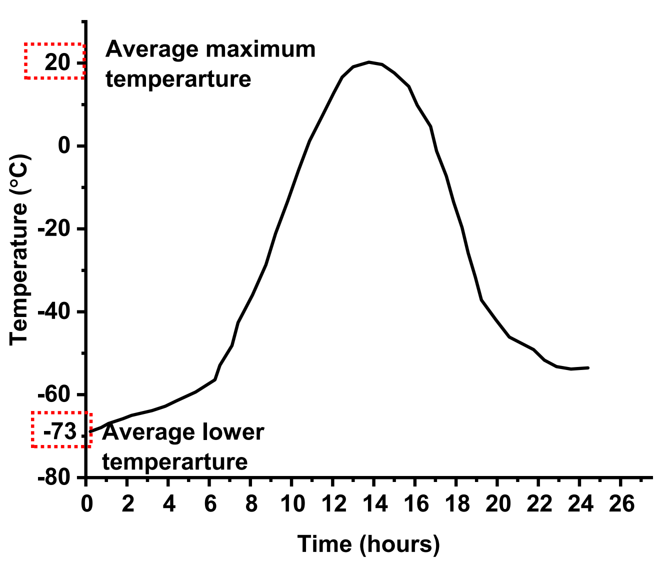

Fig. 6. Typical temperature variation curve on the Martian surface as per Mars exploration Rover data of NASA [www.nasa.gov].

2.4. Test methods

2.4.1. Compressive strength

The compressive strength test of Martian concrete specimens was conducted as per IS 4031 (Part 6), 1988. Specimens were tested using a hydraulic compression testing machine of capacity 250 kN at the loading rate of 35 N/mm^2/min. The average of three specimens was recorded as the compressive strength of concrete.

2.4.2. X-ray diffraction (XRD)

X-ray diffraction was used to characterize the mineralogical composition of Martian concrete exposed to extreme temperature environments. XRD pattern of finely powdered samples (passing through a 75 μm sieve) was obtained through MiniFlex Rigaku powder X-ray diffraction instrument operated with Cu Kα radiation (40 kV/40 mA). The scanning speed, step size, and deflection angle (2θ) were all kept constant at 2°/min, 0.01° and 10° to 70°, respectively. Quantitative analysis of XRD data was performed using X'Pert High Score Plus software allied with Rietveld analysis.

2.4.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out for powdered samples passing through a 75 μm sieve using FEI-Quanta FEG 200F. Samples were heated to a temperature of 35–950 °C (heating rate: 10 °C/min) in a nitrogen purge environment (flow rate: 20 ml/min). TGA was done on samples that were exposed to various temperatures for the period of 7 and 28 days.

2.4.4. Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) was used to identify the change in the functional group of Martian concrete. The FTIR spectroscopy was performed on powdered samples that had passed through a 75 µm size sieve. FTIR spectra were obtained from Bruker (Alpha II) FTIR equipment at the wavenumber range of 1650 to 600 cm^{-1} with a resolution of 2 cm^{-1} and at 32 scans. Attenuated total reflection (ATR) sampling mode was used to run the samples.

2.4.5. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS)

Chunks of the crushed sample were vacuum dried and gold-sputtered to analyze the microstructure. A JEOL, JSM-638OLA, scanning electron microscope (SEM) was used for characterizing the morphological characteristics of Martian concrete samples.

3. Results and discussion

3.1. Compressive strength of Martian regolith simulant-based ETC

Extra-terrestrial concrete (ETC) was developed on Earth using Martian regolith. Fig. 7 shows the compressive strength of ETC after 24 h. It can be seen that the compressive strength of Martian concrete gradually increased with the increase in the binder content, i.e., sulfur up to a certain limit. Specimens with 70% Martian regolith simulant and 30% sulfur content attained the compressive strength of 27 MPa in 24 h (close to the desired compressive strength of 25 MPa). Further increase in sulfur content to 35% showed a reduction in compressive strength. This could be attributed to the increased level of crystallinity brought about by the cooling-induced crystallization of sulfur. It is reported that the compressive strength of Martian simulant-based composite depends on the particle size of the regolith and the crystallization of sulfur (Wan 2016). Finer particle size and well-graded Martian regolith contribute to the more compacted Martian concrete. The sulfur, as well as sulfate/poly-sulfate phases engendered from the ample metals existing in the Martian regolith, also add to the strength of Martian concrete.

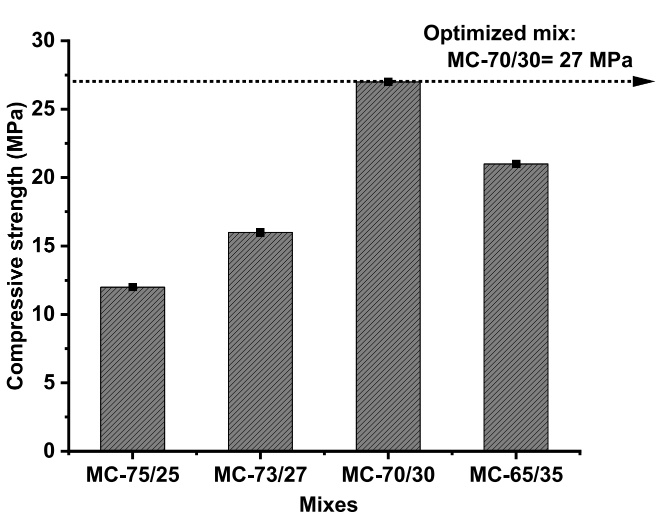

Fig. 7. Compressive strength of ETC containing Martian regolith simulant after 24 h.

Even though mechanical characteristics are sufficient to satisfy the building requirements on the Martian surface, the mechanical properties of ETC under Martian environment are not well-explored. The optimal proportion (based on compressive strength) of Martian regolith simulant and sulfur content for producing a waterless Martian concrete was found to be 70% and 30%, respectively (Fig. 7). In the next stage, the optimized ETC was studied for its mechanical and microstructural characteristics at Martian surface temperature condition.

3.2. Compressive strength of Martian regolith simulant-based ETC under extreme temperature conditions

The compressive strength of ETC containing Martian regolith simulant exposed to three temperatures (0 ℃, 40 ℃, and 50 ℃) for the period of 7 and 28 days is presented in Fig. 8.

From Fig. 8, it can be seen that the temperature of 40 ℃ and 50 ℃ had little effect on compressive strength of Martian concrete , and values were found to be reduced by 1% to 4% at 7 days of exposure and 3% to 7% after 28 days of exposure, respectively. However, the designed Martian regolith simulant-based ETC could be able to maintain the average strength of 25 MPa under the temperature of 40 ℃ to 50 ℃. It is important to note that melting of sulfur takes place at the temperature of 120 ℃, while the temperature on the Martian surface near equator can reach up to 20–30 ℃. Therefore, sulfur-based Martian concrete is less susceptible to Martian surface temperature. According to Grugel and Toutanji (2016), sulfur sublimation occurs at a high temperature of 120 °C over two hours, and the rate of sublimation increases significantly as the temperature rises. At the same time, it was also estimated to take 3.7 years to submilate 1 cm layer of sulfur at 15 °C due to the impact of lower lunar pressure (Grugel and Toutanji, 2008; Grugel and Toutanji, 2016). Hence, sulfur-based lunar regolith composite is not an ideal approach for lunar constructions as the temperature on Moon reaches 120 ℃ near the equator. However, this might be one of the most ideal solutions for developing infrastructure on Mars.

As seen in Fig. 8, the compressive strength of Martian concrete, when exposed to low temperatures of 0 °C, could reach up to 35 MPa after 28 days, surpassing that of the reference specimen (MC70/30). This was due to closing of pores in the Martian concrete as a result of freezing activity (Montejo et al., 2008). The strength increases as the ice strength increases with the drop in temperature.

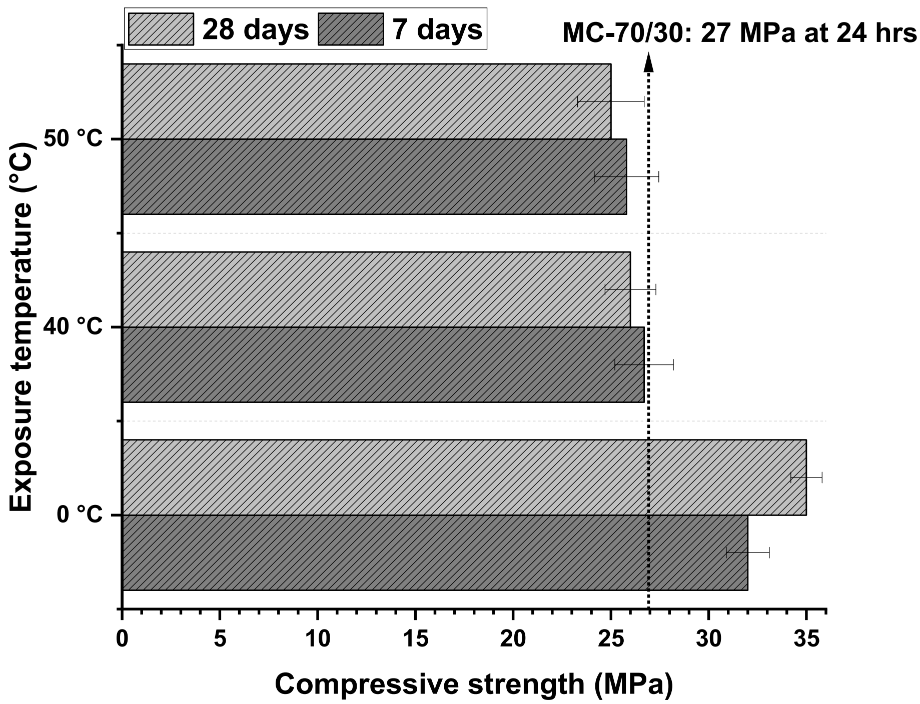

Fig. 8. Compressive strength of ETC containing Martian regolith simulant at varied temperature conditions.

Therefore, it is understood that Martian regolith simulant-based ETC performs better in terms of compressive strength at low-temperature conditions.

Apart from temperature conditions, radiation shielding is certainly imperative to be considered for buildings and habitats on extraterrestrial bodies like Mars, which are susceptible to higher levels of cosmic and solar radiation. Even though, current study identifies the optimum formulation of Martian concrete composed of simulated Martian regolith and sulfur to offer desirable compressive strength with the potential to endure simulated temperature conditions on Mars. Its stability against radiation in extraterrestrial environment is still unidentified. Therefore, further studies on Martian concrete in simulated Martian environments and authentic extraterrestrial conditions will be instrumental in refining the formulation by introducing different additives and reinforcement possessing the capacity to attenuate radiation-prone effects and understanding the practical viability of using Martian concrete for radiation shielding.

3.3. Mineralogical and phase transformation properties of Martian regolith simulant-based ETC exposed to extreme temperature conditions

Variation in the mineralogical composition of Martian concrete exposed to different temperature conditions was monitored using XRD. Fig. 9 displays the XRD patterns of Martian concrete exposed to 0 °C, 40 °C, and 50 °C for 7 and 28 days.

Anorthite (An), albite (Al), and olivine (O) are the three main mineral phases seen in the Martian concrete, these phases were also evident in the Martian regolith simulant. In addition to that, cyclooctasulfur oxide (S_8O) and octasulfur (S_8) phases were noticed in Martian concrete at higher percentage than Martian regolith simulant. Bytownite, a plagioclase mineral observed in Martian regolith simulant, was found to be changed to anorthite (An) phase when heated with sulfur to create Martian concrete. Bytownite is composed of 80–90% anorthite and 10–20% albite. After exposure to 40 °C and 50 °C anorthite phases were seen to be replaced by albite phase at both 7 and 28 days of exposure (Fig. 9 a-b). It is reported that sulfur sublimates (i.e., phase change of sulfur from solid to gas without transitioning through a liquid state) in the temperature range of 25 °C to 50 °C and this phase transition leaves the structure of the S_8 ring unaltered (Nash, 1987).

At 0 °C, all mineral phases remained the same as they were at MC-70/30 (without exposure to temperature), in contrast to the Martian concrete specimens exposed to 40 °C and 50 °C (Fig. 9c). However, in all exposed temperature conditions, i.e., 0 °C, 40 °C, and 50 °C the olivine (O) phase was observed to have disappeared. Quantitative X-ray diffraction (QXRD) analysis was used to determine the fraction of mineral phases formed in Martian concrete when exposed to varied temperature conditions and the same has been listed in Table 4.

To evaluate the phase transformation of Martian regolith simulant-based ETC before and after exposure to 0 °C, 40 °C, and 50 °C, thermogravimetric analysis was performed at 7 and 28 days of exposure time. For brevity, TG-DTG plots of Martian regolith simulant-based ETC (MC-70/30) before and after 28 days of temperature exposure are illustrated in Fig. 10.

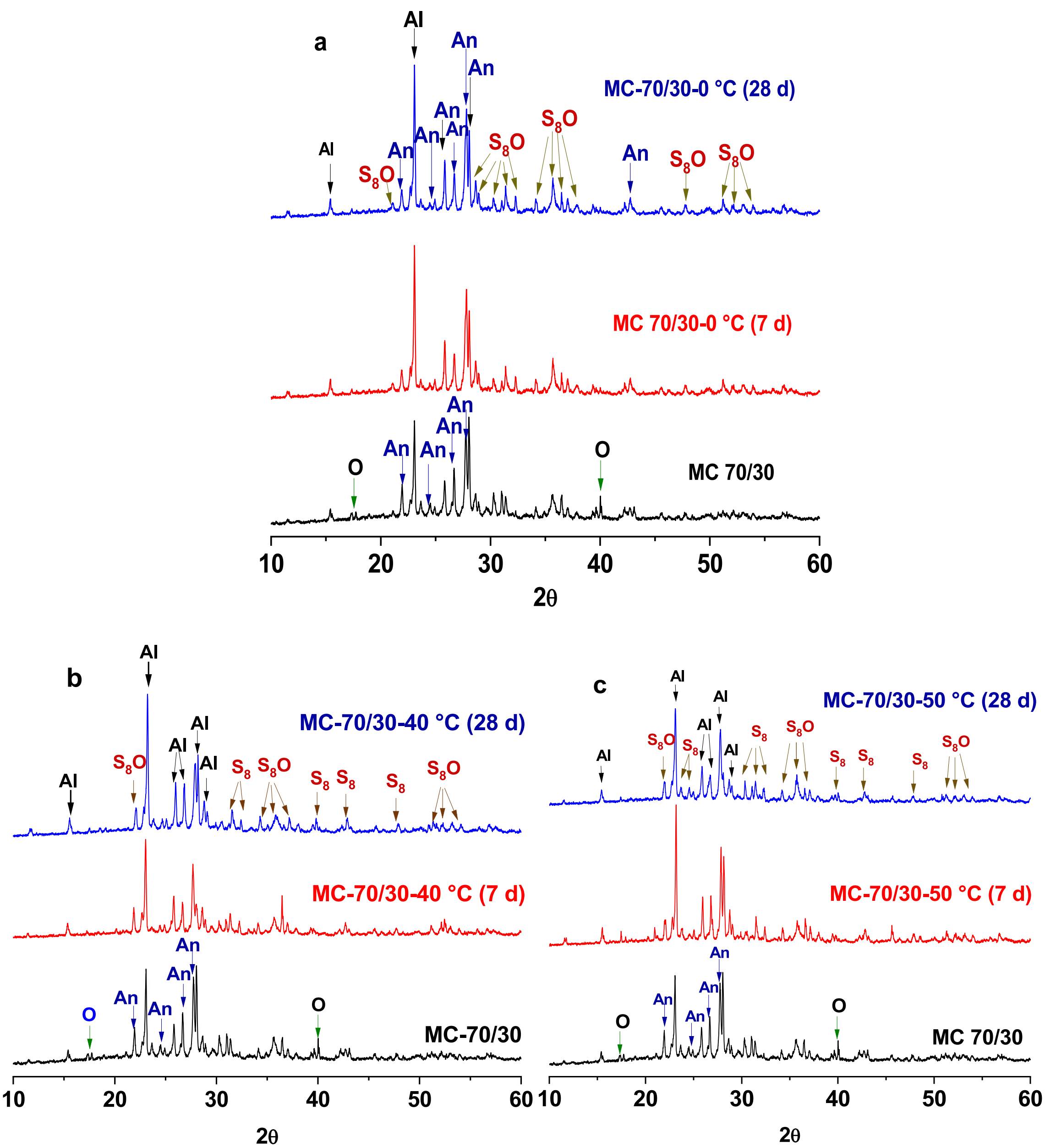

Fig. 9. XRD patterns of Martian concrete exposed to a) 0 °C, b) 40 °C, and c) 50 °C for 28 days.

Table 4
Phase composition of Martian regolith simulant-based ETC exposed to 0 °C, 40 °C, and 50 °C for the duration of 7 and 28 days.

Phase composition	MC-70/30						
	Before exposure	0 °C		40 °C		50 °C	
		7 days	28 days	7 days	28 days	7 days	28 days
Cyclooctasulfur oxide (S_8O)	16.7%	26.2%	29.2%	17.7%	19.5%	12.65%	18.9%
Albite (Al)	26.7%	16.1%	8.8%	29.3%	27.2%	37.4%	32.9%
Octa sulfur (S_8)	–	–	–	13.3%	14.9%	20.0%	22.2%
Anorthite (An)	4.2%	21.7%	17.2%	–	–	–	–
Olivine (O)	3.8%	–	–	–	–	–	–

The major endothermic peak was noticed at the temperature boundary of 193–312 °C for MC-70/30 (Fig. 10). When Martian concrete was exposed to temperatures of 40 °C and 50 °C (Fig. 10a-b), the same endothermic peak was found to be broadened. The onset and end temperatures for the Martian concrete exposed to 0 °C were

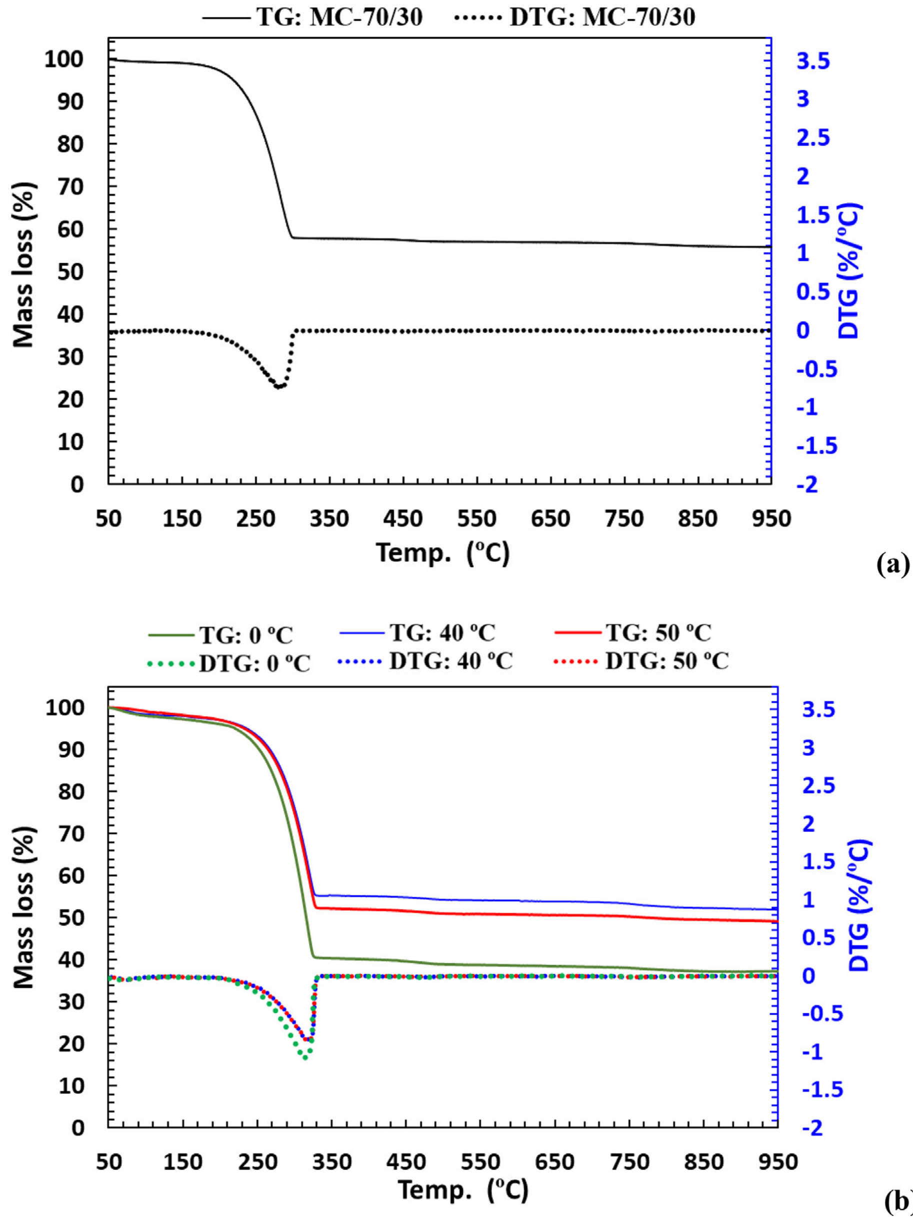

Fig. 10. TG-DTG curve of Martian regolith simulant-based ETC of MC-70/30 a) before , and b) after exposure to 0 °C, 40 °C, and 50 °C for 28 days.

measured to be 193 and 322 °C, and these were 166 and 350 °C for 40 °C and 50 °C. This endothermic peak corresponds to the decomposition of sulfur components in the Martian concrete. Generally, pure sulfur (S_8) begins to evaporate at roughly 160 °C, grows gradually to reach its maximum between 200 and 300 °C, and then ends at around 330–350 °C. TG-DTG plot of pure sulfur used in the study is illustrated in Fig. 11.

Understanding the phase transformation of sulfur requires knowledge of the allotropic forms of the element. Orthorhombic α-sulfur (S_α), monoclinic β-sulfur (S_β), and monoclinic ϒ-sulfur (S_γ) are the three most prevalent allotropes found in *cyclo*-octa sulfur (S_8) (Steudel, 2003). All the *cyclo*-octa sulfur allotropes have puckered rings of S_8 with different spatial arrangements (Norman and Alan 1997). α-sulfur (S_α) is the thermodynamically stable form

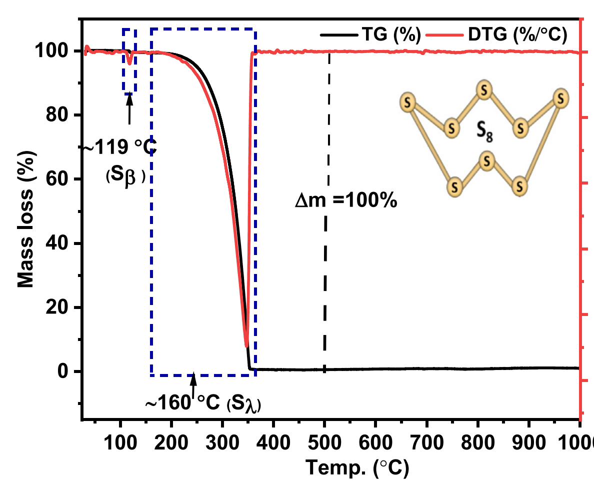

Fig. 11. TG-DTG curve of pure sulfur.

Table 5
Thermogravimetric mass loss percentage at λ-transition temperature of sulfur.

Mix designation		Temperature boundary (λ-transition)	Mass loss (%)
MC-70/30		193–312 °C	40.65
MC-70/30–0 °C	7 days	193–322 °C	41.06
	28 days	193–322 °C	55.48
MC-70/30–40 °C	7 days	166–350 °C	41.27
	28 days	166–350 °C	42.05
MC-70/30–50 °C	7 days	166–350 °C	43.77
	28 days	166–350 °C	45.57

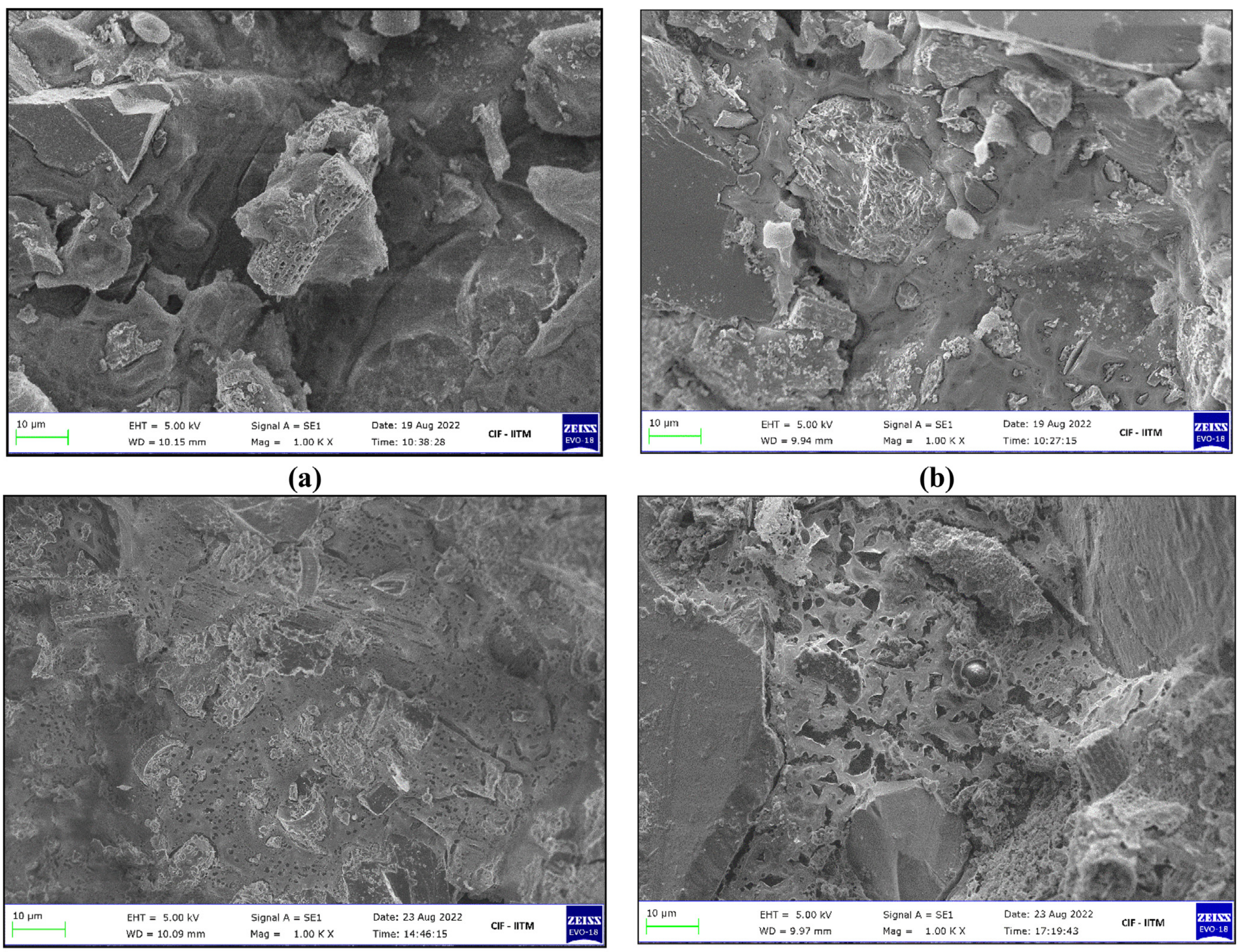

Fig. 12. Morphology of ETC: a) before exposure, b) after exposure to 40 °C for28 days, c) after exposure to 50 °C for 28 days, and d) after exposure to 0 °C for 28 days.

of sulfur at ambient conditions (<96 °C) and a temperature above 96 °C the S_α sulfur changes to the monoclinic β-sulfur (S_β) (Norman and Alan 1997). Melting of S_β sulfur takes place at approximately 115 °C that is revealed by a small endothermic peak in DTG curve (Fig. 11). However, S_β is metastable and can transform back into S_α when the temperature drops below 96 °C (Wan et al., 2016). S_γ sulfur is the densest allotrope of S_8 sulfur, which is formed when molten sulfur (heated above 150 °C) is quenched by chilling solutions (Steudel, 2003), this transformation is not observed in Fig. 11. A significant endothermic peak noticed at the temperature of ∼ 160 °C is associated to the transition of λ- sulfur (S_λ) (Fig. 11) (Eilene, 1982). After melting of S_β sulfur, rings of S_8 get converted to linear polymeric bi-radical molecules (-S-S_6-S-) in the temperature range of about 160–350 °C, which is indicated by an endothermic reaction called λ-transition (Carotenuto et al., 2013). In the case of pure sulfur, 100% mass loss has been recorded at the temperature range of 160–350 °C indicating the complete decomposition of sulfur.

It can be seen from Fig. 10 and Table 5 that the total mass loss of ETC, resulting from the vaporization of sulfur stored in the pores of the matrix, was measured to be 40.65% (at the temperature range of 193–312 °C). Further, it is important to note that the mass loss of ETC subjected to 0 °C, 40 °C, and 50 °C for 28 days was found to be increased to 55% (193–322 °C), 42% (166–350 °C), and 45% (166–350 °C, respectively (Table 5). The mass loss of ETC associated with the λ-transition temperature of sulfur was recorded at the temperature boundaries of 166–350 °C (for 40 °C and 50 °C exposed samples) and 193–322 °C (for 0 °C exposed samples). Even though proportioned ETC comprised only 30% of sulfur content, the increased percentage of sulfur in ETC recorded from TGA quantification could be attributed to the additional sulfur composition present in Martian regolith simulant (Fig. 2).

3.4. Morphological characteristics

The morphology of Martian concrete before and after exposing to 0 °C, 40 °C, and 50 °C for 28 days are shown in Fig. 12.

There are no obvious large defects in the internal structure observed in ETC after exposure to 40 °C and 50 °C, as evident in Fig. 12. Morphology of ETC tends to become porous when exposed to 40 °C and 50 °C. This can be ascribed to the sublimation and disintegration of the sulfur phase in the matrix of ETC (Fig. 12b and Fig. 12c). This could be one of the probable reasons for the reduction in compressive strength of ETC under 40 °C and 50 °C. While Fig. 12d shows a more dense and homogenous morphology with filled pores in the matrix. This may be attributed to the pores filling due to the freezing activity at a low temperature of 0 °C, thereby contributing to the strength enhancement of ETC.

The temperature and pressure condition are the important features that affect the robustness of ETC made up of sulfur. Grugel and Toutanji (2008) observed significant formation of pores and flaws in sulfur based lunar concrete at 120 °C due to the sublimation of sulfur (S_β: monoclinic sulfur) at high temperature (>115 °C). However, the maximum temperature on Mars near equator would be 30 °C, where sublimation of sulfur is inconsequential and takes place at a slow pace (NASA.gov). The durability of ETC made up of sulfur is significantly influenced by the temperature cycle on Mars as well. Solidification of ETC takes place by the process of cooling crystallization of sulfur. It is reported that transformation of S_λ to S_β sulfur when temperature drops to 115 °C and S_β to S_α at 96 °C may lead to volumetric changes in sulfur causing variation in the microstructure of ETC (Wan et al., 2016). In our current work, controlling hardening of Martian regolith simulant-based ETC was challenging. Future research should be directed to explore additives to control the hardening rate of this type of ETC.

4. Conclusions

In this study, ETC (Martian concrete) was developed using Martian regolith simulant as aggregate and sulfur as a binding ingredient. Based on the study, following conclusions were drawn:

- The Martian concrete proportioned with 70% Martian regolith simulant and 30% sulfur achieved the optimal compressive strength of 27 MPa at 24 h as a result of molten sulfur's crystallization at ambient temperature.
- Phases belonging to feldspar families such as anorthite ($CaAl_2Si_2O_8$), albite ($NaAlSi_3O_8$), and olivine ($MgFe_2SiO_4$) were the three main mineral phases seen in the ETC, similar to Martian regolith simulant. In addition to that, cyclooctasulfur oxide (S_8O) and octasulfur (S_8) phases were also noticed at higher percentage in ETC.
- The slow and low sublimation of sulfur at the temperature of 40 °C and 50 °C showed less significant influence on compressive strength reduction (<10%) for ETC. At the same time, approximately 30% increase in compressive strength was recorded for ETC low temperature of 0 °C. This was evidenced by homogenous morphology with filled pores in the matrix of ETC and mineral phases remained unaltered under 0 °C.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge the financial support from the Ministry of Education, Govt. of India, via Institute of Eminence Research Initiative Project (Project No. SB20210837MEMHRD008655) on Extra Terrestrial Manufacturing (ExTeM) at the Indian Institute of Technology Madras.

References

Abdeen, Z., ElDaba, K., Gamal, R., Helmy, Z., Ibrahim, G., Sawan, O., AbouZeid, M.N., 2023. In: Exploring Potential Building Materials for Planet Mars. Springer, Singapore, p. 247.

Akono, A.T., 2023. Influence of martian soil simulant on microstructural heterogeneity and mechanical response of martian concretes. Mech. Res. Commun. 127 104013.

Brinegar, J, 2019. Investigation of Sulfur Concrete Mixes for Mars Infrastructure, University Honors College Middle Tennessee State, Thesis.

Carotenuto, G., Romeo, V., Nicola, S.D., Nicolais, L., 2013. Graphite nanoplatelet chemical cross-linking by elemental sulfur. Nanoscale Res. Lett. 8, 94.

Davis, G., Montes, C., Eklund, S., 2017. Preparation of lunar regolith based geopolymer cement under heat and vacuum. Adv. Space Res. 59, 1872–1885.

Eilene, T., 1982. A primer on sulfur for the planetary geologist. NASA Contractor Report 3594, Grant NAGW-132, Office of Space Science and Applications, Washington, DC, USA: National Aeronautics and Space Administration, Scientific and Technical Information Branch. p. 4.

Grugel, R.N., Toutanji, H., 2016. Viability of sulfur ‘‘concrete” on the moon: Environmental considerations. In: 44th AIAA Aerospace Sciences Meeting 2006, Reno, NV, pp. 6321-6326.

Grugel, R.N., Toutanji, H., 2008. Sulfur ‘‘concrete” for lunar applications – Sublimation concerns. Adv. Space Res. 41 (1), 103–112.

Hu, Z., Shi, T., Cen, M., Wang, J., Zhao, X., Zeng, C., Zhou, Y., Fan, Y., Liu, Y., Zhao, Z., 2022. Research progress on lunar and Martian concrete. Const. Build. Mater. 343, 128117 (ISSN 0950–0618).

IS 4031 (Part 6)-1988, Method of Physical Test for Hydraulic Cement, Part 6 Determination of Compressive Strength of Hydraulic Cement other than Masonry Cement, Bureau of Indian Standards, New Delhi.

Khoshnevis, B., Yuan, X., Zahiri, B., Zhang, J., Xia, B., 2016. Construction by Contour Crafting using sulfur concrete with planetary applications. Rapid Prototyp. J. 22, 848–856.

King, P.L., McLennan, S.M., 2010. Sulfur on mars. Elements 6, 107–112.

Li, H., Meng, H., Lan, M., Zhou, J., Xu, M., Zhao, X., Xiang, B., 2021. Development of a novel material and casting method for in situ construction on Mars. Powder Technol. 390, 219–229.

Meyers, C., Toutanji, H., 2007. Analysis of lunar-habitat structure using waterless concrete and tension glass fibers. J. Aerosp. Eng. 20 (4), 220–226.

Mills, J.N., Katzarova, M., Wagner, N.J., 2022. Comparison of lunar and Martian regolith simulant-based geopolymer cements formed by alkali-activation for in-situ resource utilization. Adv. Space Res. 69, 761–777.

Montejo, L.A., Sloan, J.E., Kowalsky, M.J., Hassan, T., 2008. Cyclic response of reinforced concrete members at low temperatures. J. Cold Reg. Eng. 22 (3), 79–102.

Montes, C., Broussard, K., Gongre, M., Simicevic, N., Mejia, J., Tham, J., Allouche, E., Davis, G., 2015. Evaluation of lunar regolith geopolymer binder as a radioactive shielding material for space exploration applications. Adv. Space Res. 56, 1212–1221.

Murgatroyd, C., Hodges, P., 2001. Building on MARS. Hydrocarbon Eng. 6.

Mars. Nasa.gov, NASA Science Mars Exploration 2022: all.

Mars exploration rover, Jet propulsion Laboratory, California Institute of Technology, mars.nasa.gov.

Naser, M.Z., 2019. Extraterrestrial construction materials. Prog. Mater. Sci., 105

Naser, M.Z., Chehab, A.I., 2020. Polymers in space exploration and commercialization. Polymer Sci. Innovative Appl.

Nash, D.B., 1987. Sulfur in vacuum: Sublimation effects on frozen melts, and applications to Io’s surface and torus. Icarus 72 (1), 1–34.

Neves, J.M., Ramanathan, S., Suraneni, P., Grugel, R., Radlińska, A., 2020. Characterization, mechanical properties, and microstructural development of lunar regolith simulant-portland cement blended mixtures. Construction and Building Materials 258, 120315.

Norman, G.N., Alan, E., 1997. Chemistry of the Elements, second ed. Butterworth-Heinemann.

Omar, H. A., Issa, M., 1994. Production of lunar concrete using molten sulfur. In: Proceedings: 4th Conf. on Space, Citeseer (1994) 952–959.

Pilehvar, S., Arnhof, M., Pamies, R., Valentini, L., Kjøniksen, A.L., 2020. Utilization of urea as an accessible superplasticizer on the moon for lunar geopolymer mixtures. J. Clean. Prod. 247.

Rapp, D., Mungas, G.S., Easter, R.W., Johnson, K.R., 2006. Accessible water on mars and the moon. In: Earth and Space 2006 – 10th Biennial International Conference on Engineering, Construction, and Operations in Challenging Environments, League City/Houston, TX, 74.

Reches, Y., 2019. Concrete on Mars: options, challenges, and solutions for binder-based construction on the Red Planet. Cem. Concr. Compos. 104 103349.

Scheerbaum, G., 2000. In-Situ manufacture of Martian construction materials. Space 2000, 934–940.

Scott, A.N., Oze, C., Tang, Y., O’Loughlin, A., 2017. Development of a Martian regolith simulant for in-situ resource utilization testing. Acta Astronaut. 131, 45–49.

Shahsavari, M.H., Karbala, M.M., Iranfar, S., Vandeginste, V., 2022. Martian and lunar sulfur concrete mechanical and chemical properties considering regolith ingredients and sublimation. Constr. Build. Mater. 350 128914.

Steudel, R., 2003. Elemental Sulfur and Sulfur-Rich Compounds II. Topics Curr. Chem. 231, 1–228.

Toutanji, H., Glenn-Loper, B., Schrayshuen, B., 2005. Strength and durability performance of waterless lunar concrete. In: 43rd AIAA Aerospace Sciences Meeting and Exhibit, 2005, p. 1436.

Toutanji, H., Grugel, R.N., 2008. Mechanical properties and durability performance of waterless concrete. Earth & space 2008. Eng. Sci. Construct. Operat. Challenging Environ., 1–8

Troemner, M., Ramyar, E., Marrero, R., Mendu, K., Cusatis, G., 2021. A Martian concrete for additive construction Application utilizing in situ resources. ASCE Earth and space.

Wan, L., Wendner, R., Cusatis, G., 2016. A novel material for in situ construction on Mars: experiments and numerical simulations. Constr. Build. Mater. 120, 222–231.

Werkheiser, N.J., Fiske, M.R., Edmunson, J.E., Khoshnevis, B., 2015. Development of additive construction technologies for application to development of lunar/martian surface structures using in-situ materials. In: CAMX 2015 - Compos. Adv. Mater. Expo, pp. 2395–2402.

Zhou, S., Lu, C., Zhu, X., Li, F., 2020. Preparation and characterization of high-strength geopolymer based on BH-1 lunar soil simulant with low alkali content. Engineering.