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Development of Waterless Extra-Terrestrial Concrete Using Martian Regolith

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Abstract

Human colonization on Martian land is gaining significant attention in universal planetary exploration activities that demand in-situ resource utilization in the development of construction and building materials for human habitation. This research emphasizes the utilization of Martian regolith simulant to create extra-terrestrial concrete (ETC) with a property suitable for constructing human habitat on Mars. Mechanical, phase transition, and microstructure properties of Martian regolith based-ETC under varied temperature conditions (high: 40 ºC and 50 ºC; low: 0 ºC) on Mars were investigated. The optimal mixture proportion of ETC had 70% of Martian regolith and exhibited a compressive strength of 27 MPa. The formulated ETC could retain up to 25 MPa of compressive strength under high (40 ℃ and 50 ℃) and could reach up to 35 MPa under low (0 ℃) temperature conditions. The change in compressive strength was attributed to the sulfur sublimation and pore closure brought on by freezing at high and low 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 [Jennifer et al., 2022]. The 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 [Werkheiser, et al., 2015; Khoshnevis et al., 2016; Naser, 2019].

A research team from Northwestern University [Troemer et al., 2021] developed a novel way for making Martian concrete using naturally available materials on Mars. Rovers' data from NASA provides information that the red planet lacks liquid water but is found in a frozen state [NASA report 2022]. However, developed Martian concrete was designed without water, unlike the conventional concrete prepared on Earth [Troemer et al., 2021]. It is reported that planet Mars contains high levels of sulfur (SO_3) concentration on its surface (approximately 37 wt%) [Scheerbaum, 2000]. The records also suggested a raised concentration of sulfur in the core [Rapp et al., 2006]. For that reason, the chief constituent considered in the development of Martian concrete is "sulfur", which acts as a binding material when heated to about 140 °C [Toutanji et al., 2005; Troemer et al., 2021]. 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 can be prepared by hot-mixing (using alternative sources of heating including solar energy) Martian regolith with molten sulfur, followed by casting and cooling [Toutanji et al., 2005; Troemer et al., 2021]. The phenomenon here is that once the mixture starts cooling, liquid sulfur initially crystallizes to monoclinic sulfur (S_β) at 115 ºC, and further cooling below 96 ºC transforms to orthorhombic sulfur (S_α) [Wan et al., 2016]. S_α is a stable form of sulfur at room temperature. This solidification process of liquid sulfur takes place quickly, i.e., within 24 hours, binding the regolith strongly to produce a rapid-hardening construction material. In the case of waterless Martian concrete, sulfur functions as a thermo-plastic material with the ability to hold the non-reactive Martian regolith together [Toutanji et al., 2008]. 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. Apart from this fact, it is also a carbon-neutral construction material, unlike cement concrete on Earth. Researchers have used 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 [Toutanji et al., 2005; Toutanji et al., 2008; Troemer et al., 2021]. 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% martial soil simulant and 50% molten sulfur [Troemer et al., 2021].

Several other approaches considered for extraterrestrial construction are conventional OPC concrete formulated with regolith as aggregate [Neves et al., 2020], epoxy/polymer-based binder cement [Naser, 2019; Naser and Chehab, 2020] and alkali activate/geopolymer binder system [Montes et al., 2015; Davis et al., 2017; Pilehvar et al., 2020; Zhou et al., 2020]. The epoxy/polymer-based binder system requires supplementary earthly resources for the bulk of the binder [Naser, 2019; Naser and Chehab, 2020]. While researchers have demonstrated the possibility of producing geopolymer binders using extraterrestrial regolith simulant itself. However, to produce a geopolymer binder it is required to dissolve and activate regolith rich in aluminosilicate minerals and that necessitates some solution/activator [Montes et al., 2015; Pilehvar et al., 2020]. Even though sulfur is not an abundantly available material on the Lunar surface, the sulfur-based binder may serve as an appropriate binder material for Martian constructions owing to its abundancy on the Martian surface [King and McLennan, 2010; Khoshnevis et al., 2016].

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 ºC during winter, and near the equator, temperature may reach up to 20 ºC during summer. Nevertheless, night temperature can fall to about -73 ºC [Scheerbaum, 2000]. Therefore, building infrastructure on Mars is an engineering challenge [Jennifer et al., 2022]. Following this fact, it is important to understand the behavior of Martian concrete formulated using Martian regolith and sulfur ingredient at extreme temperature cycles of Mars. However, a very few studies focused on the performance of Martian concrete under extreme temperature conditions of Mars. In this study, at first, Martian regolith concrete was prepared using the varied proportion of Martian regolith simulant and sulfur to determine the optimum mix in correspondence to compressive strength. 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 temperature of Mars at the laboratory were evaluated using characterization techniques such as quantitative Xray diffraction (QXRD), thermogravimetric analysis (TGA), Fourier-transform Infrared spectroscopy, and Scanning Electron Microscope (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 were 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.

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

Oxide composition (wt%)	
SiO_2	44.2414
Al_2O_3	13.4357
Fe_2O_3	20.9348
SO_3	5.9177
CaO	7.3779
Na_2O	0.5706
MgO	6.3571
K_2O	0.5256
Cl	0.0229
Cr_2O_3	0.2381
MnO	0.1384
NiO	0.1772
SrO	0.0628
Specific gravity	2.83

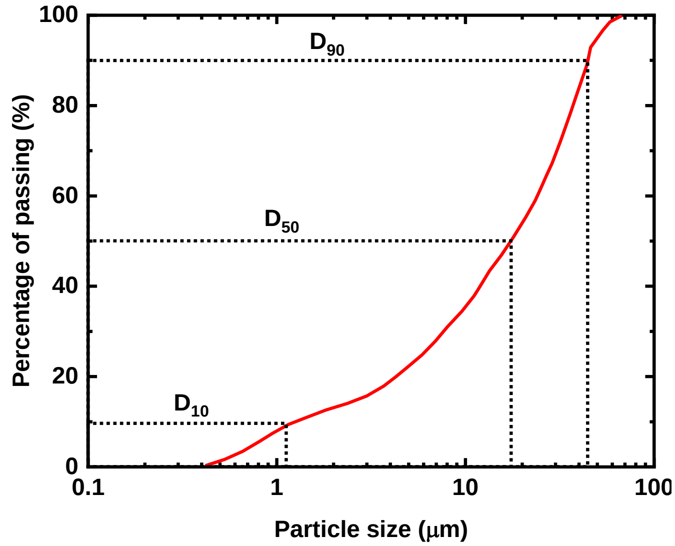

Fig. 1. Particle size distribution of Martian regolith simulant (MGS-1).

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, respectively.

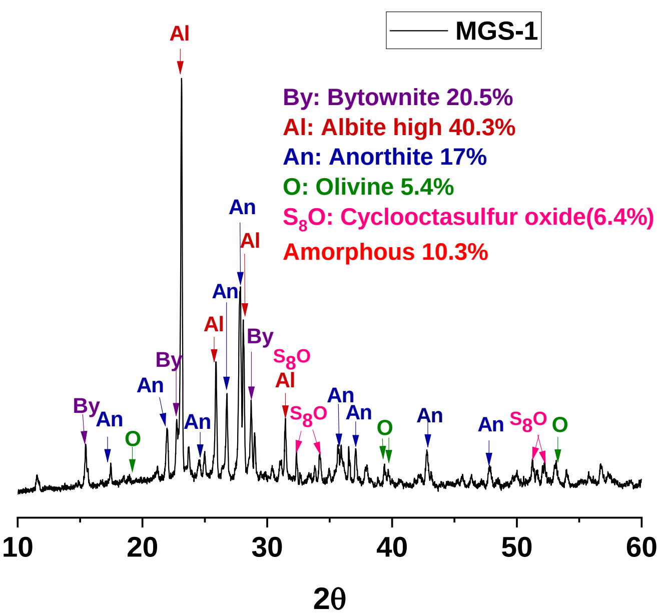

Fig. 2. XRD pattern of Martian regolith simulant (MGS-1).

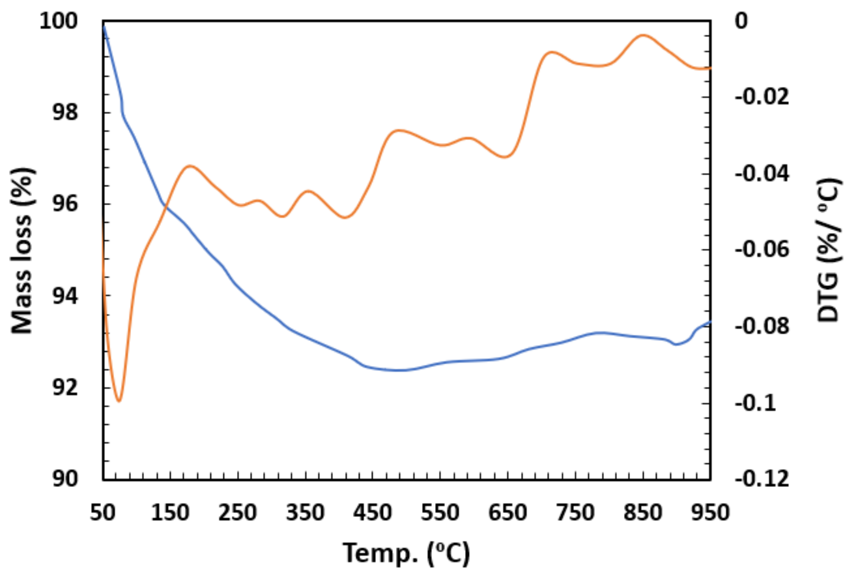

Fig. 3. TG-DTG curve of Martian regolith simulant (MGS-1).

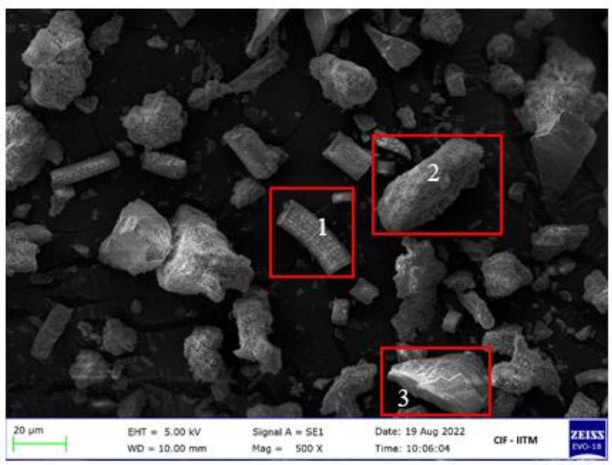

Fig. 4. Morphology of Martian regolith simulant (MGS-1).

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: $(Ca,Na)[Al(Al,Si)SiO_8]$

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). The thermogravimetric analysis (TGA) of MGS-1 (Fig. 3) revealed multiple endothermic and exothermic peaks associated with the decomposition of glass 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, i.e., 1) perforated tubular structure (Olivine: $MgFe_2SiO_4$) 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 presents 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 shows various mix proportions of waterless Martian concrete used in the study.

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

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 the sulfur particle 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 hours, the specimens were de-moulded and tested for compressive strength. Fig. 5 shows the process of producing Martian concrete.

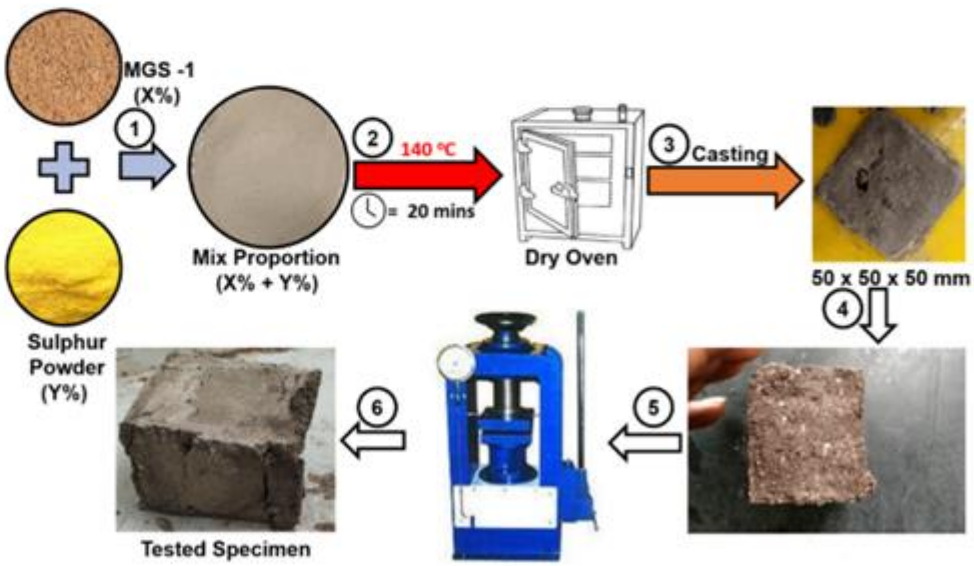

Fig. 5. Process of producing Martian concrete.

After that laboratory-scale tests were conducted on the Martian concrete specimens on exposing 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 ºC at noon and drops to -73 ºC at night during summer near the equator. However, the temperature may reach up to -125 ºC during winter near the poles [Scheerbaum, 2000]. A typical variation of temperature on the Martian surface is shown in Fig. 6.

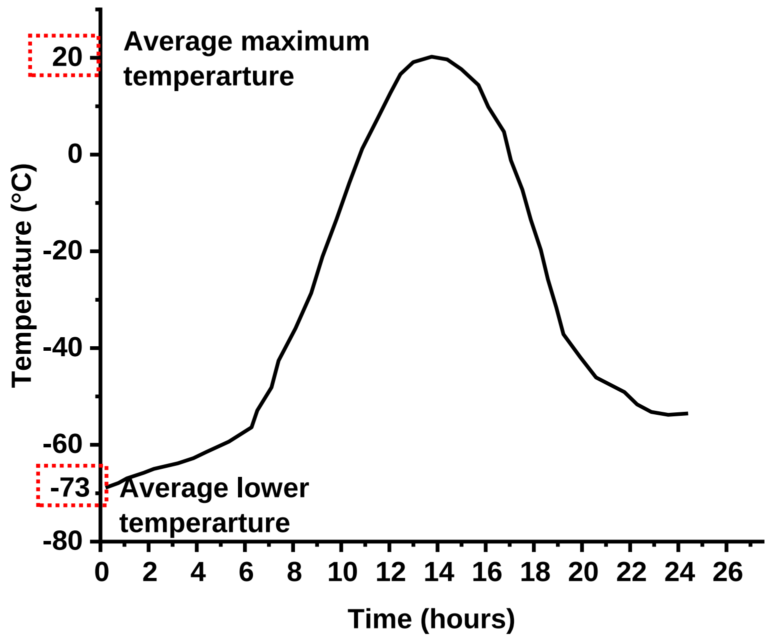

Fig. 6. Typical temperature variation curve on the Martian surface as per Mars exploration Rover data of NASA [www.nasa.gov].

To assess the behavior of Martian regolith simulant-based ETC under extreme temperatures, experiments were conducted considering the high and low-temperature tests at the laboratory scale. Temperature resistance tests of Martian regolith simulant-based ETC were carried out under different temperatures such as 50 ºC, 40 ºC, and 0 ºC. Specimens exposed to different temperatures for the duration of 7 and 28 days were tested for compressive strength.

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. 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 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 high and low-temperature environment. XRD pattern of fine powdered samples (passing through 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 75 µm sieve using FEI-Quanta FEG 200F. Samples were heated to a temperature of 35-950 ºC (heating rate: 10 ºC/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 s. The FTIR spectroscopy was performed on powdered samples that had passed through a 75 µm 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 hours. 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 hours. Further increase in sulfur content to 35% showed a reduction in compressive strength i.e., 21 MPa. 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.

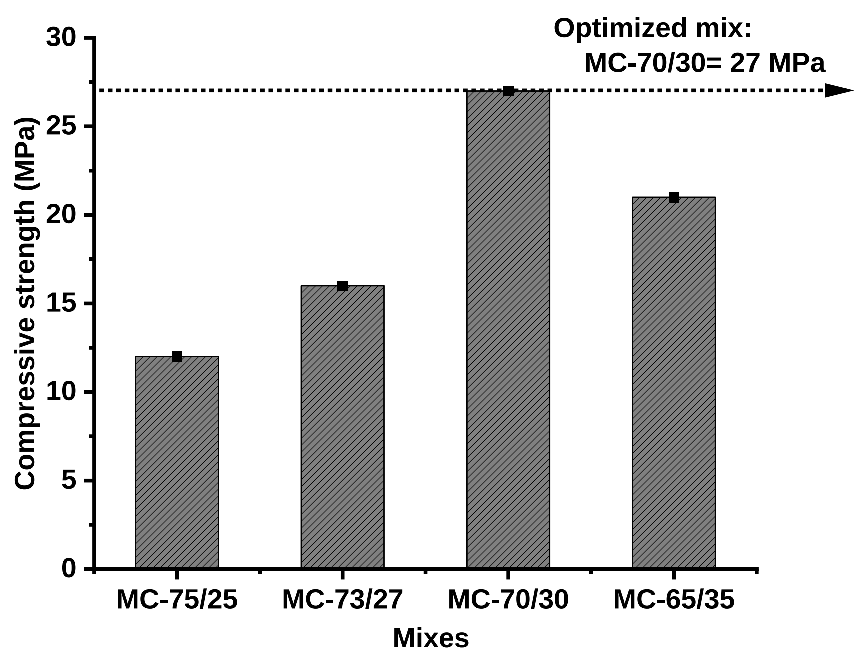

Fig. 7. Compressive strength of ETC containing Martian regolith simulant after 24 hours.

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 high and low-temperature conditions

Compressive strength of ETC containing Martian regolith simulant exposed to high (40 ℃ and 50 ℃) and low (0 ℃) for the period of 7 and 28 days is presented in Fig. 8.

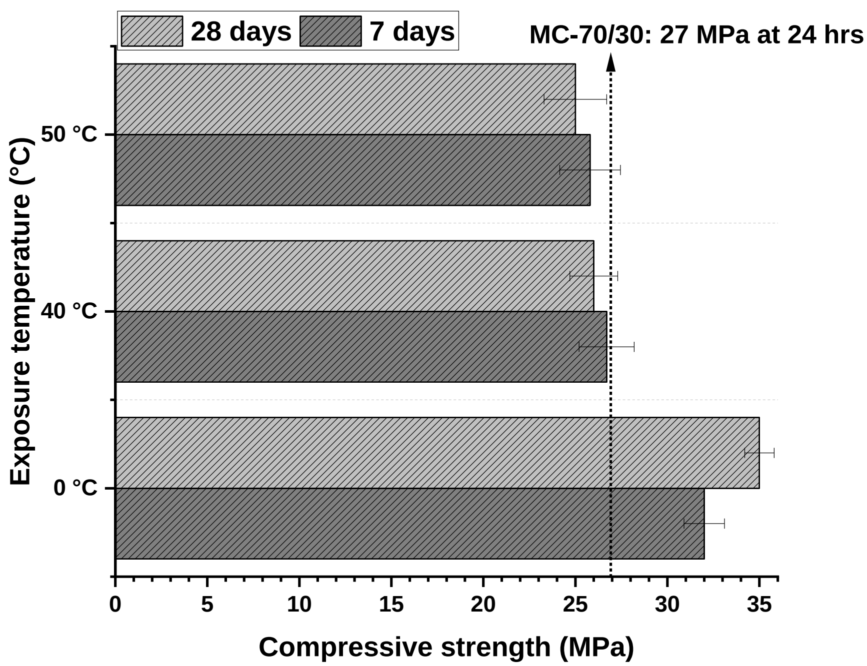

Fig. 8. Compressive strength of ETC containing Martian regolith simulant at varied temperature condition.

From Fig 8, it can be seen that at high temperature of 40 ℃ and 50 ℃, compressive strength of Martian concrete had little effect, and values were found to be reduced by 1% to 4% at 7 days of exposure and 3% to 7% at 28 days of exposure, respectively. However, the compressive strength of designed Martian regolith simulant-based ETC could able to maintain the nominal concrete 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 et al. (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 the impact of lower lunar pressure [Grugel et al. 2008; Grugel et al., 2016]. In this concern, 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, can reach up to 35 MPa after 28 days, surpassing that of the reference specimen (MC70/30). This is 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. Therefore, it is understood that Martian regolith simulant-based ETC performs better in terms of compressive strength at low-temperature conditions.

3.3 Mineralogical and phase transformation properties of Martian regolith simulant-based ETC exposed to high and low-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 40°C, 50°C, and 0°C for 7 and 28 days.

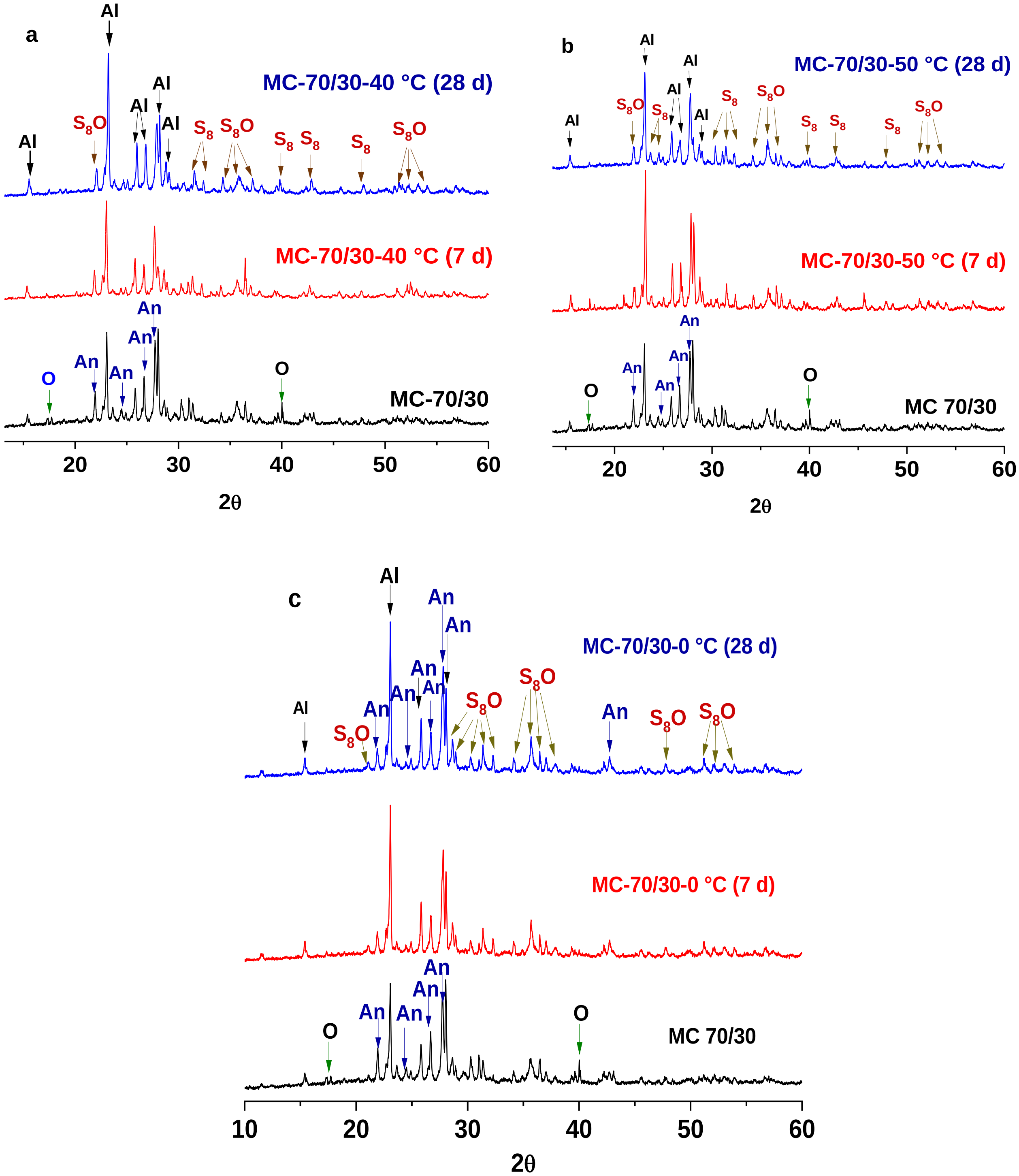

Fig. 9. XRD patterns of Martian concrete exposed to a) 40 ºC, b) 50 ºC, and c) 0 ºC for 28 days.

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 are 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 ºC and 50 ºC 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., 40 °C, 50 °C, and 0 °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.

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

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

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

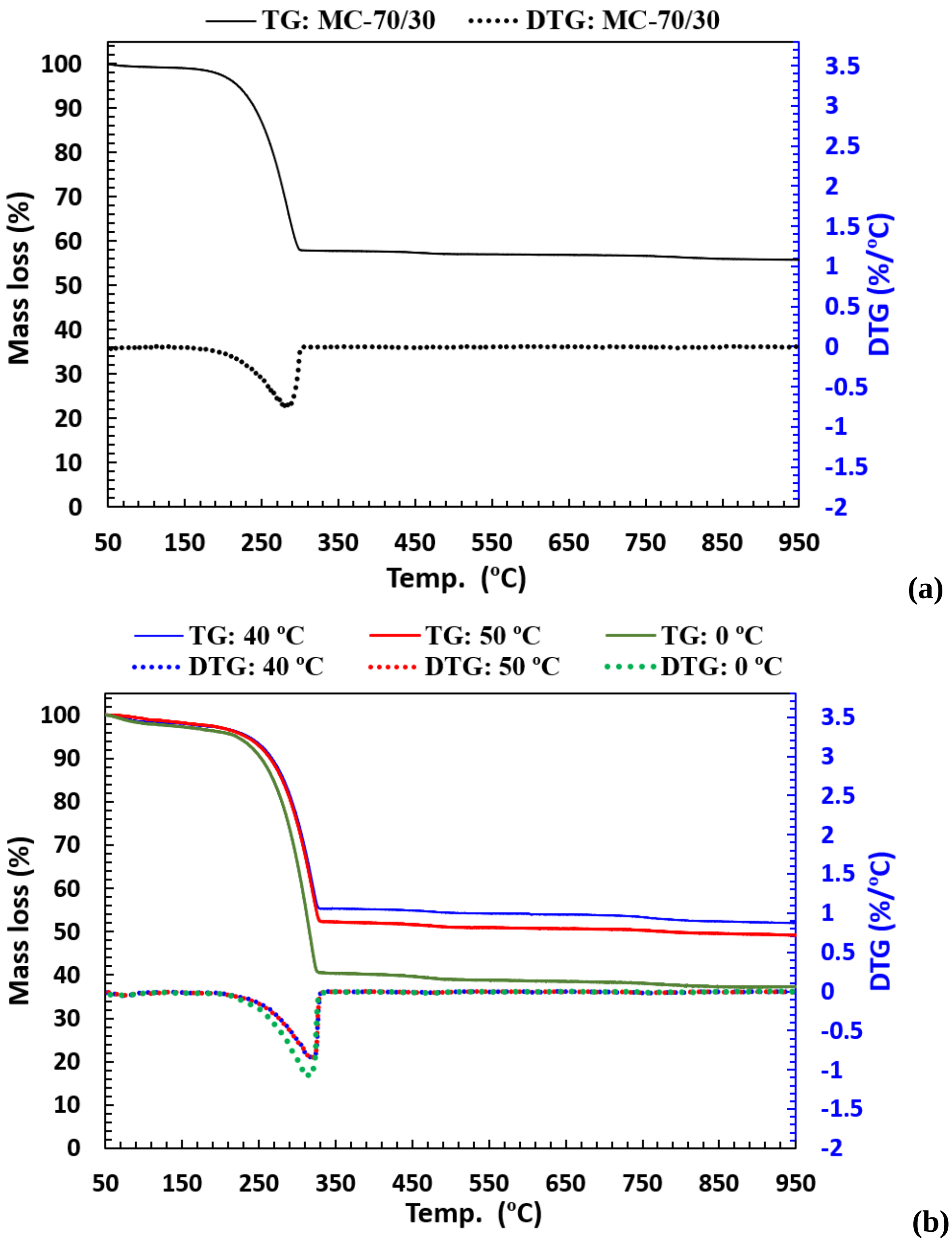

Fig. 10. TG-DTG curve of Martian regolith simulant-based ETC to a) MC-70/30 b) MC-70/30 after exposure to 40 °C, 50 °C, and 0 °C for 28 days.

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 ºC	40.65
MC-70/30-40 ºC	7 days	166-350 °C	41.27
	28 days	166-350 °C	42.05
MC-70/30-50 ºC	7 days	166-350 °C	43.77
	28 days	166-350 °C	45.57
MC-70/30-0 ºC	7 days	193-322 °C	41.06
	28 days	193-322 °C	55.48

The major endothermic peak was noticed at the temperature boundary of 193-312 ºC 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 high (40 °C and 50 °C) and low (0 °C) temperatures were measured to be 166-350 °C and 193-322 °C, respectively. 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 200-300 °C, and then ends at around 330-350 °C. TG-DTG plot of pure sulfur used in the study is illustrated in Fig. 11.

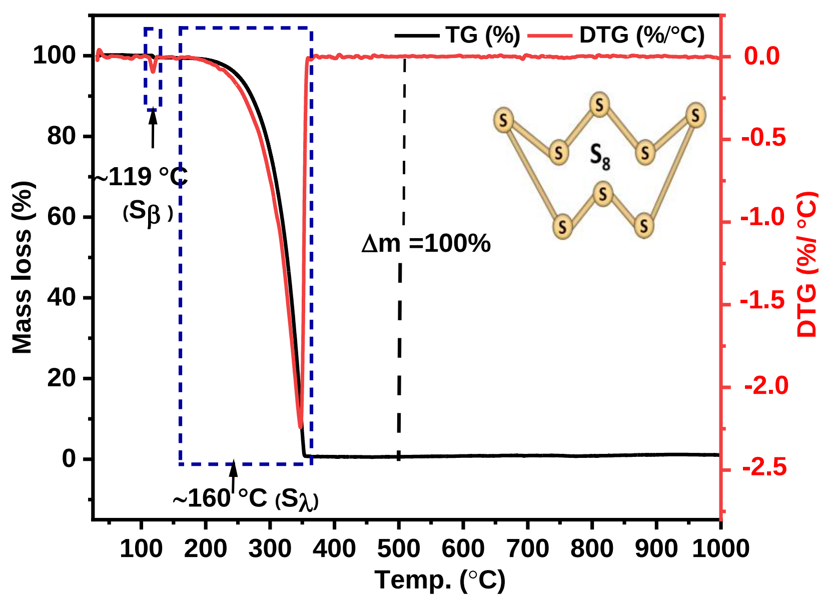

Fig. 11. TG-DTG curve of pure sulfur.

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 γ-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 of sulfur at ambient conditions (<96 ºC) and a temperature above 96 ºC 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 ºC 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 ºC [Wan et al., 2016]. S_{γ} sulfur is the densest allotrope of S_8 sulfur, which is formed when molten sulfur (heated above 150 ºC) 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 ºC 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 resulted from the vaporization of sulfur stored in the pores of the matrix is 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 40 ºC, 50 ºC, and 0 ºC for 28 days was found to be increased to 42%, 45%, and 55%, respectively (Table 5). The mass loss of ETC associated to the λ-transition temperature of sulfur was recorded at the temperature boundaries of 166-350 °C (for 40 ºC and 50 ºC exposed samples) and 193-322 °C (for 0 ºC 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 40 ºC, 50 ºC, and 0 ºC for 28 days are shown in Fig. 11

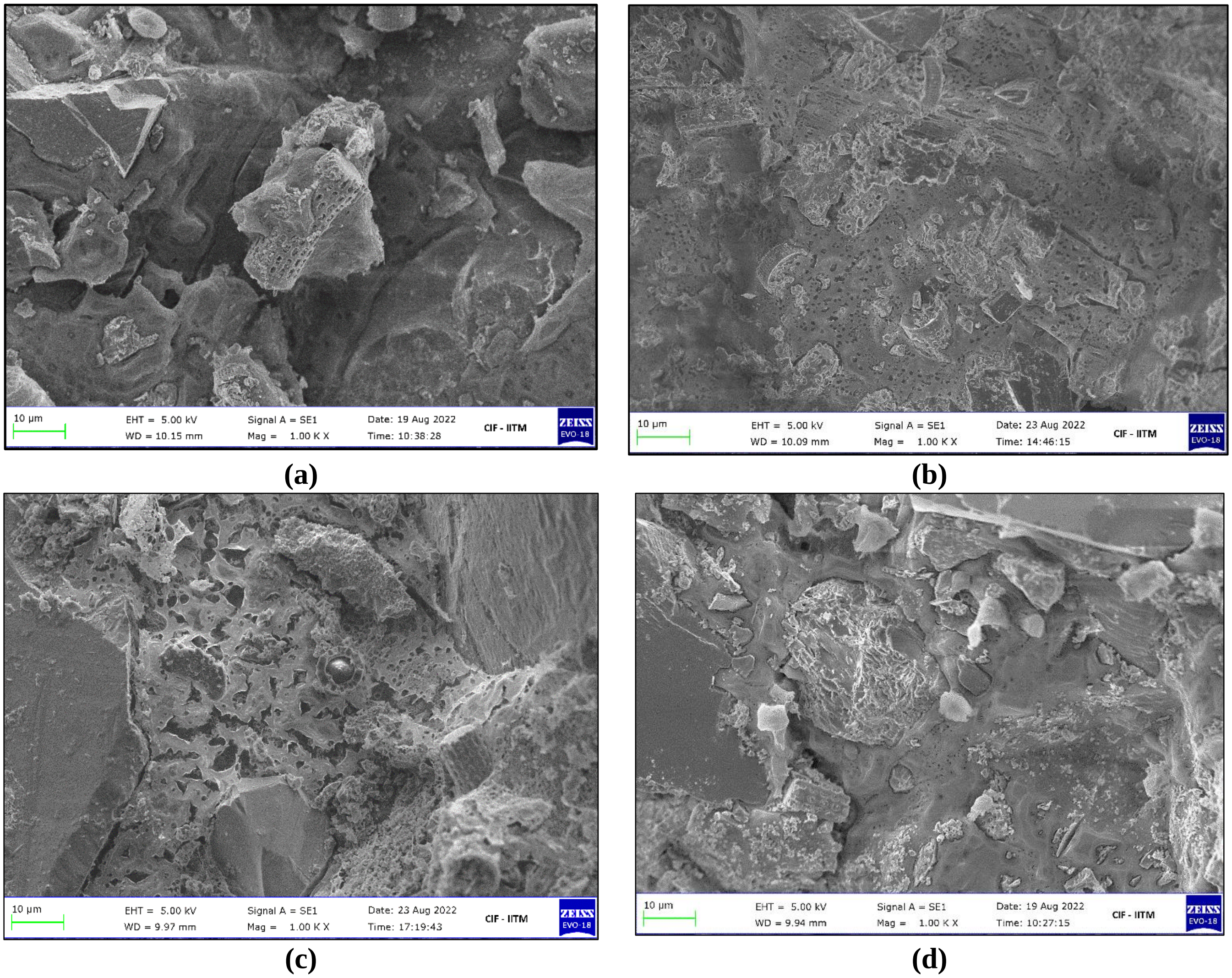

Fig. 11. Morphology of ETC exposed to a) before exposure b) 40 ºC to 28 days c) 50 ºC to 28 days and d) 0 ºC to 28 days flocculates.

There are no obvious large defects in the internal structure observed in ETC after exposure to 40 ºC and 50 ºC, as evident in Figure 11. Morphology of ETC tends to get porous when exposed 40 ºC and 50 ºC. This can be ascribed to the sublimation and disintegration of the sulfur phase in the matrix of ETC (Fig. 11b and Fig.11c). This could be one of the probable reasons for the reduction in compressive strength of ETC under 40 ºC and 50 ºC. While Fig. 11d shows a more dense and homogenous morphology with filled pores in the matrix. This may be attributed to the pores filled due to the freezing activity at a low temperature of 0 ºC and thereby contributes to the enhancement in the strength performance of ETC.

The temperature and pressure condition are the important features that affects 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 ºC due to the sublimation of sulfur (S_β: monoclinic sulfur) at high temperature (>115 ºC). However, maximum temepratures on the Mars near equator would be 30 ºC, where sublimation of sulfur is inconsequential and takes place at a slow pace (NASA.gov). 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 ºC and S_β to S_α at 96 ºC may lead to the 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 Martian concrete was produced using Martian regolith simulant as aggregate and sulfur as a binding ingredient. Emphasis has been given to understanding the disparity in mechanical, mineralogical, phase transition, and morphological properties of Martian concrete under the varied temperature conditions (40 ºC, 50 ºC, and 0 ºC). 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 hours as a result of the molten sulfur crystallization phenomenon at ambient temperature.
- Phases belonging to feldspar families such as anorthite ($CaAl_2Si_2O_8$), albite ($NaAlSi_3O_8$), and olivine ($MgFe_2SiO_4$) are 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 ºC and 50 ºC 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 ºC. This was evidenced by homogenous morphology with filled pores in the matrix of ETC and mineral phases remained unaltered under 0 ºC.
- The significant phase transition peak associated with the transition of λ-sulfur (S_λ) at the

temperature range of 160-350℃ for pure sulfur (S_8) shifts to 193-312 ºC in case of ETC produced using sulfur. Further, for ETC subjected to high (40°C and 50°C) and low (0°C) temperatures, changes in the onset and end temperatures were identified to be 166-350°C and 193-322°C, respectively.

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Conflict of Interest

The authors have no conflicts of interest to disclose.