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# **A Review of Sulfur Concrete Properties and Applications**

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**ABSTRACT:** This paper is a thorough review of Sulfur Concrete, with emphasis on its mixing, mechanical properties and durability characteristics. Concrete with molten Sulfur as a binder is now the main choice of material considered for extra-terrestrial construction, hence, this paper also addresses its possible utilization in the construction of structures on Mars. On earth, due to its high resistivity against acid and salt, it has been used for many years as a substitute for Cement Concrete in many applications. Nevertheless, further advantages of using Sulfur Concrete can be made apparent through conventional compression, tensile, flexural and durability tests. The objective of such testing is to investigate the optimal Sulfur contents at which high strengths and durability results are obtained. Despite the fact that Sulfur generally results in weaker and less homogeneous materials, conclusions of various testing methods were in agreement that Sulfur Concrete with optimal Sulfur contents delivers compressive, tensile and flexural strengths higher than cement-based concrete.

## **I. INTRODUCTION**

In recent years, human beings' settlement on Mars have been the major focus of space exploration [1]. The most significant step toward that goal is to build structures on the planet. Such ambitious futuristic plans are widening the horizon of building technology, and opening doors of new possibilities. However, scientists and engineers are faced with a plethora of problems concerning extra-terrestrial construction. The challenge is finding the materials to build an environment and a human friendly habitat [2], other obstacles would be the time and extremely high cost of transportation of those materials from earth. Wilcox [3], suggests that the most intuitive solution is to utilize Mars' raw materials. Several researchers believe that concrete appears to be the most suitable material for construction on the moon or other planets. In his research, Brinegar [2], considers concrete as the main material for building on Mars. Hence, it seems that initial structures on Mars would be made of concrete. The issue is that water – one of concrete's major components – is not found in its liquid state, due to the extreme low atmospheric pressure on the planet. Mars' soil is rich in Sulfur; thus, researchers have examined the mixing of aggregate with molten Sulfur and developed a type of concrete known as "Sulfur Concrete". For many years, concrete with Sulfur as a binder has been a substitute for conventional cement concrete in diverse applications on earth [4]. Utilization of Martian Soil as aggregate is also investigated and tested for in-situ construction on Mars. This is a literature review of the viability of Sulfur Concrete as a material for extra-terrestrial construction, and focuses on its compressive, tensile and flexural strength through conventional concrete material testing.

## **II. SULFUR CONCRETE AS A CONSTRUCTION MATERIAL**

Sulfur Concrete has been utilized as a construction material in the 1920s, so it is not a newly introduced concept in the industry. The global company, Shell-Oil, is known for using Sulfur in manufacturing some of their products in similar manner to mixing and manufacturing concrete, where Sulfur is melt, mixed with aggregates and then cooled down forming a substantial material [1]. Over the years, Sulfur Concrete was developed in the industry and was a material used in infrastructure projects. Its primary initial applications were in the construction of sewer lines and drainage facilities [5]. In 2009, the UAE replaced 80 meters of sewer lines made of conventional concrete with Sulfur Concrete [4]. Due to its high acid and salt-water resistivity, it is also utilized in hazardous waste disposals, where conventional concrete is expected to rapidly deteriorate [6]. Vlahovic et al. [4], stated that a well-mixed Sulfur Concrete would have a promising mechanical performance, and economic and environmental advantages, making it an ideal choice of a construction material to build a small-scale space sanctuary for humans on Mars.

In addition, it is believed that the atmospheric pressure and weather on the planet could be quite suitable for using Sulfur as a binder for initial construction [4]. Figure 1, illustrates the different phases of matter for Sulfur exposed to certain temperatures and atmospheric pressures on Mars and on the Moon. It can be noted that the Rhombic (stable) state of Sulfur is found in pressure conditions three orders of magnitude above the vapor state, the authors mentioned that because the atmospheric pressure on Mars is 0.636 kPa and temperatures are less than or equal to 35 degrees Celsius, sublimation, a major concern for Sulfur Concrete utilization on the moon, and melting of Sulfur would not be a concern for building initial structures and roadways on Mars. However, reassessment of Sulfur Concrete's fire resistance will be necessary for long term human settlements.

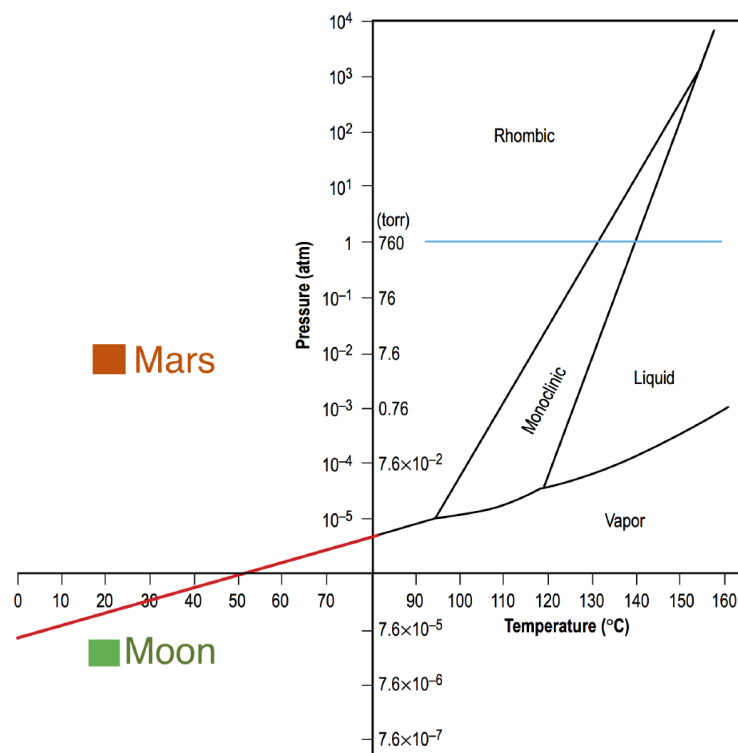


Figure 1. Phases of matter for Sulfur in different environmental conditions [7].

### III. MIXING OF SULFUR CONCRETE

Sulfur Concrete is manufactured by mixing molten Sulfur with aggregate. During the process, a non-stable form of Sulfur transforms into a stable polymorph [1]. Khademi and Kalasar [5], discuss another way to produce Sulfur Concrete, in which the Sulfur binder is in powder form, mixed with the aggregate until it is molten and cooled down forming the concrete. As a binder, Sulfur delivers a cohesive construction material. However, without chemical modification to the mixture, the cool down of the molten Sulfur during the manufacturing process causes it to shrink, resulting in stresses and voids in the mixture [8]. Moreover, testing samples resulted in low stability, and degradation after cycles of freezing and defrosting with humidity and immersion in water [4]. Therefore, durability is a big concern for normal, unmodified Sulfur Concrete.

To improve its durability, researchers investigated modifying the Sulfur binder by adding chemical additives [1]. Dugarte et al. [9], prepared Modified Sulfur Concrete samples. First, the Sulfur was enhanced by reacting it with an olefinic hydrocarbon polymer, which stabilizes the Sulfur during the mixing process. Furfural could also be added to liquidized Sulfur to further improve its stabilization [10]. Moreover, Anyaszka et al. [11], added dicyclopentadiene to



molten Sulfur to enhance the mechanical performance of the binder, and styrene to control its viscosity. Khademi and Kalasar [5], used Sulfamethoxazole (SMZ) as an additive, it was found that having SMZ being only 3.3% of a mixture with 18% Sulfur binder, increases the compressive strength from 25 MPa to 27.5 MPa and have 28-days strength of 33 MPa.

Aggregate is selected upon acceptable mechanical testing results and economic aspects. Intuitively, the primary choice would be aggregate found on Mars. In their research, Wan et al. [1], mixed a 1 mm Martian aggregate simulant with Sulfur binder to produce testing samples. The simulant is mostly composed of oxide and dioxide compounds such as: Iron Oxide (FeO), Manganese Oxide (MnO) and Silicon Dioxide (SiO<sub>2</sub>) with varying percentages. Martian aggregate simulant is recreated by gathering and mixing the compounds [2].

In an assessment study of Sulfur Concrete, Lewandowski and Kotynia [10], used 4 types of aggregate to prepare samples, Gravel, Sand, Granite and Dolomite. In the experimental program, 15 cuboid samples were prepared by mixing heated aggregate with fly ash and phosphogypsum additives, and molten Sulfur modified by either dicyclopentadiene (dcpd), turpentine, styrene or furfural. The samples were set up with different compositions of varying Sulfur, aggregate, modifiers and additives percentages. Coarse aggregate percentages were no less than 52%, while fine aggregate content in the samples varied from 6.4% to 62.5%. Pure molten Sulfur percentages ranged from 19% to 24.5%. Optimal results were later achieved with modifying the Sulfur binder with 1% to 1.3% of dicyclopentadiene and the chemical was added to 11 samples. Usage of styrene and turpentine was minimal. Additives are used to attain a grain curve as per the ACI 5482 code. Fly ash and phosphogypsum percentages were from 7.8% to 14% and used on 10 samples.

The Samples were used to investigate the strength parameters and optimal mix ratios through compression, bending and freeze-thaw testing. Lewandowski and Kotynia [10], concluded that high coarse aggregate content increases the compressive strength of the mix and additives did not affect the Sulfur binder and samples with styrene modifier achieved drastically low compressive strengths. The curing time of the samples did not influence both the compressive and flexural strengths.

Furthermore, the use of fillers such as talc and micro-silica in the production of modified Sulfur Concrete is recommended. Fillers blend with the Sulfur binder forming a paste that coats the aggregate, the function of the paste is to reduce the shrinkage of Sulfur and fill the voids during the mixing process, consequently, reducing the amount the Sulfur required and strengthening the mixture by increasing its density [4]. In their experimental program, Vlahovic et al. [4], added 7% of four types of fillers in particle sizes less than 75 $\mu$ m to the mixture of testing samples: Talc, Alumina, Micro-silica and Fly ash.

#### **IV. MECHANICAL PROPERTIES OF SULFUR CONCRETE**

##### **A. COMPRESSIVE STRENGTH**

In a Sustainability Evaluation study, Dugarte et al. [9], investigated one-day compressive strength of Sulfur Concrete, by performing an ASTM C93 Standard compression test on two cylindrical specimens with diameter and height dimensions of 15 cm and 30 cm, respectively, with varying Sulfur Cement binder and aggregate percentages. Results show that a concrete mix of 30% (by volume) of Sulfur Cement has a compressive strength of 27.07 MPa. Separate compression tests were carried out on samples with unmodified and modified Sulfur [5]. It was highlighted that after 14 days, samples containing 18% of unmodified Sulfur had a growth rate of 25% in compressive strength, reaching 25 MPa. Samples with Sulfur modified by the addition of SMZ and dicyclopentadiene had a total of 68% growth in compressive strength in 28 days, where the results increased from 25 MPa to 42 MPa.

In their study, Wan et al. [1], conducted an unconfined compression test to 1-in, Martian Concrete cube specimens having 1 mm aggregate of Martian Soil and molten Sulfur as a binder (Mars 1A 1mm), as well as recast Martian Concrete Specimens (Mars 1A 1mm R.) with Sulfur mix ratio ranging from 35% to 60% (by weight). A servo-hydraulic frame was utilized to apply a maximum load of 110 kips at a rate of 0.003 mm/s. Results showed that the compressive strength increases when the Sulfur ratio percentage increases from 35% to 50% (by weight), the

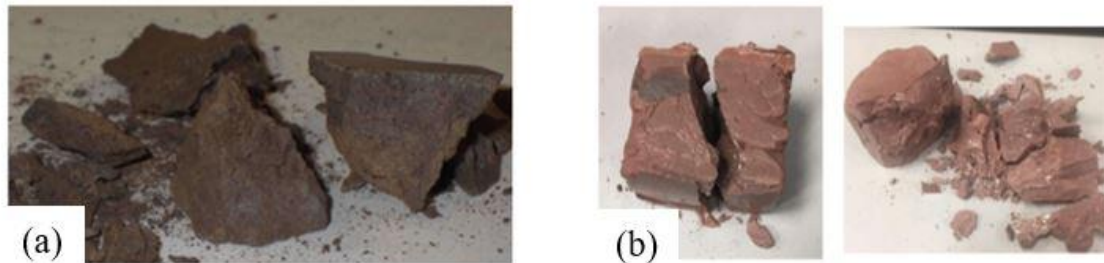


Figure 2. (a) Unconfined Compression Test cone type failure [1], (b) Compression Test breaking patterns [2].

compressive strength was found optimal (48 MPa) in (Mars 1A). However, increasing the amount of Sulfur in the concrete mix will result in lower compressive strengths [5], since large thicknesses of Sulfur layers around the aggregate particles will result in brittleness to the material [12]. This was indicated by the unconfined compression test results, as the percentage of Sulfur increased from 50% to 60% by weight, the compressive strength of the concrete mix decreased to 42 MPa, and cone type failure of the cube specimens was observed (Figure 2.a). The compression test results obtained in [2] are in agreement with this conclusion. A compression test was carried on two 1-in cube specimens. The test was conducted using InstronSatec Compression machine, in which the specimens are compressed until a sudden fall of resistance is measured [2]. The compressive strengths obtained were drastically low, specimens achieved only 18% of the unconfined compressive strength obtained by Wan et al. [1], with different break patterns as shown in Figure 2.b. Recast can further increase the compressive strength of Sulfur Concrete. Experimental testing showed that recast of samples with optimal Sulfur content, increased the compressive strength from 48 MPa to 63 MPa [1]. Moreover, it is suggested that better mixing could also factor in increasing the compressive strengths, and that an ideal mixture of Sulfur Concrete would typically have compressive strength well above 50 MPa.

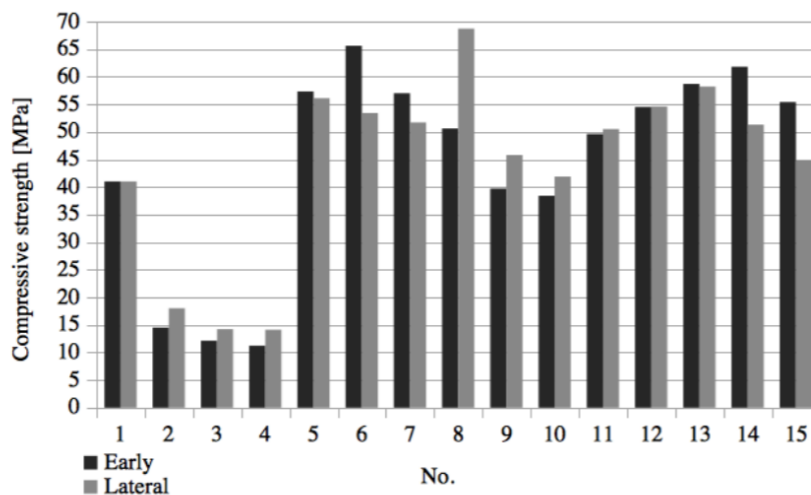


Figure 3. Early and Late compressive strength of samples of different mix ratios [10].

Compression testing is conducted on 15 cuboid samples with dimensions (40 x 40 x 160 mm) to examine the early (1-4 days) and late (28 days) compressive strengths [10]. Each sample is uniquely mixed with different Sulfur binder, aggregate, modifiers and additives percentages. Testing was carried out as per European or National Polish standards. Figure 3, shows the early and late compression test results obtained for each sample. High compressive strengths were

obtained, and it can be observed that there is a clear dispersion in the results. The fluctuation of the results is due to changes in temperature as samples were casted in a limited time [10]. However, it can be noted that almost all samples achieved late compressive strengths above 40 MPa. Sample (1) had 30% of unmodified Sulfur and achieved early and late compressive strengths of 41 MPa. Sample (6) had the highest early strength of 65.5 MPa and had a mixture composed of 19% Sulfur, 1% dicyclopentadiene modifier, 60% Granite (coarse aggregate), 20% Sand (fine aggregate) and no additives. Sample (8) had the highest late compressive strength of 68.7 MPa and had a mixture composed of 21.1% Sulfur, 1.1% dicyclopentadiene modifier, 54.4% Gravel (coarse aggregate), 15.8% Sand (fine aggregate) and 7.8% fly ash additive.

### **B. TENSILE STRENGTH**

The tensile strength of Sulfur Concrete was examined by the Modulus of Rupture and Splitting tests [1]. The tests were conducted only on recast 1-in cubes Martian Concrete samples; the load was applied at a rate of 0.003 mm/s until failure. The splitting tensile strengths results were 3.6 MPa, 3.9 MPa and 2.72 MPa for corresponding Sulfur contents of 47.5%, 50% and 52.5% (by weight), respectively. According to the ACI, the tensile strength of conventional concrete is 1/10 of its compressive strength and typically ranges from 2.2 MPa – 4.2 MPa. Comparing these values with the results of the tensile strength obtained by Wan et al. [1], it can be concluded that if the optimal Sulfur content in the mixture is used, and thus, high tensile strengths could be achieved.

### **C. FLEXURAL STRENGTH**

Fracture tests are to be conducted to study the flexural behaviour of Sulfur Concrete. Nine Sulfur Concrete prism shaped specimens with dimensions of (4 x 4 x 16 cm) were examined for flexural strength [12]. A maximum load of 100 kN was applied using the Amsler Press as per standardized method (SPRS EN 196-1: 2008). Portland Cement Concrete specimens were also tested for comparison. The maximum flexural strength of Sulfur Concrete was 9.47 MPa, with 45% of Sulfur as binder, while the maximum strength for Portland Cement Concrete was 6.25 MPa.

In their mechanical characterization of Sulfur Martian Concrete, a Three-Point Bending (TPB) Fracture Test was conducted on 1 x 1 x 5 in beam specimens [1]. Employing the servo-hydraulic frame, a maximum load of 5 kips or 22.2 kN was applied at a rate of 0.0001 mm/s. Testing was conducted on 4 cast and 6 recast samples. The flexural strength of cast samples increased when the Sulfur binder weight percentage increased from 40% to 50%, with increasing the Sulfur percentage to 60%, a sharp decrease in strength was observed. Recast samples achieved higher flexural strengths. The highest nominal flexural strength for cast samples was 1.65 MPa, which corresponds to Sulfur content of 45% (by weight). As for the recast, the highest strength recorded was 2.3 MPa at Sulfur content of 50% (by weight). Both cast and recast samples shared a flexural strength of 1.75 MPa at Sulfur percentage of 52.5% by weight. Nonetheless, increasing the Sulfur content lowers the flexural strength [5]. This was addressed by Wan et al. [1], in their discussion of the fracture energy of the Martian Concrete obtained from the TPB test. Concrete mixtures with Sulfur content more than 50% (by weight) have lower strengths and exert lower fracture energies than with optimal content. Hence, it is implied that adequate contents of Sulfur coupled with recast and applying pressure while pouring in formwork can further boost the flexural strength of the mixture.

In addition, extensive usage of coarse aggregate can influence the bending strengths of samples to vary during the different stages of incubation. Lewandowski and Kotynia [10], obtained high bending strength of 10 MPa and 10.4 MPa for sample mixtures having coarse aggregate of 52% and 54.4%, respectively. Results showed that increasing the coarse aggregate percentages to 60% and 62.5% decreased the flexural strengths to 4.3 MPa and 3.8 MPa, respectively.

## **V. DURABILITY OF SULFUR CONCRETE**

### **A. FREEZE-THAW RESISTANCE**

To study the freeze-thaw durability of Sulfur Concrete made of lunar aggregate, twenty-four (1 and 2-in) cube samples were tested in compression, after they were exposed to light and severe temperature change cycles [13]. The compression test was carried out by a Universal Hydraulic Machine that applied the load at a constant velocity of 0.127 cm/minute. The samples were prepared with two different mixture compositions, the first composition (mixture “a”)



was composed of 35% Sulfur and 65% lunar aggregate (JSC-1), the second composition (mixture “b”) contained 25% Sulfur, 55% lunar aggregate, and 20% Silica. The 2-in samples were subjected to 50 cycles of light freeze-thaw exposure of  $-2\text{ }^{\circ}\text{C}$ , while the 1-in samples to 80 cycles of severe exposure of  $-101$  and  $-191\text{ }^{\circ}\text{C}$ . Samples had an average compressive strength of 7 MPa. The highest compressive strength recorded was approximately 9 MPa for a 1-in sample of mixture “b”. The lowest recorded strength was approximately 3 MPa for a 2-in sample of mixture “a”. Compression testing was also performed on samples that had non-cycling temperature changes. It was found that cycled samples achieved compressive strengths five times less than non-cycled samples. It is believed that freeze-thaw cycles affect the homogeneity of the material, causing the Sulfur binder to de-bond with the aggregate particles [13]. They concluded that de-bonding occurs at different temperatures due to two reasons: the different expansion coefficients of aggregate and Sulfur, and Sulfur transition from elastic to plastic behaviour.

To measure the freeze-thaw resistance of Sulfur Concrete, volumetric surface method was used [10]. Testing was performed on 15 cuboid specimens of varying mixture compositions to examine the required resistance for road infrastructure, as per Polish Standards. When compared, the required standard strengths for two specimens experienced 85% strength loss after 150 cycles. After 200 cycles, only three specimens exceeded 30% strength loss, the specimen with the least strength loss of 11% had a mixture composed of 22.5% modified Sulfur, 61% sand and no coarse aggregate. Additionally, the minimum freeze-thaw exposure cycles are 150 as per standards for infrastructure applications [10]. Overall, specimens did not meet the required strengths. Nonetheless, the numbers are drastically higher than those reported by Toutanji and Grugel [13].

## **B. ABRASION RESISTANCE**

Further freeze-thaw resistance investigations were made by several researchers. Eight Samples were subjected to 28 and 56 immersion cycles in 3% de-icing salt solution. Satisfactory mass and density loss results were measured, and samples demonstrated great resistance. After 56 cycles, all samples had an increase in mass and density. The most mass and density increase measured was 1.12 g and  $0.11\text{ kg/m}^2$ . Such results qualify the samples for the 4<sup>th</sup> highest abrasion resistance according to Polish Standards of Testing methods (PN-EN 1338:2005) [10].

The abrasion resistance of Sulfur Concrete in harsh environments was examined by immersing prism shaped specimens in three solutions: 3% NaCl, 20%  $\text{H}_2\text{SO}_4$  and 10% HCL [4]. The mass change was then measured by a digital laboratory scale. Conventional Portland Cement Concrete specimens were also experimented for comparison. In the NaCl solution, Portland Cement Concrete lost 5.91% of its mass after a week of immersion and 18.9% after two months of immersion. The 20% of  $\text{H}_2\text{SO}_4$  and 10% of HCL PCC samples had 19.6% and 21.2% loss of mass, respectively, after two months of immersion. It was stated that further examination was stopped due to the severe degradation of the samples. As for Sulfur Concrete, samples with added talc filler were shown to have minimal mass loss after being immersed for longer time periods. After being immersed in the NaCl,  $\text{H}_2\text{SO}_4$  and HCL solutions for 300 days, samples had a mass loss of -0.5%, 0% and 1.2%.

## **VI. CONCLUSIONS**

Initial structures on Mars are more likely to be constructed by Sulfur Concrete due to the abundance of Sulfur on the planet, and lack of water [3]. The suitable environmental conditions on Mars and promising economic advantages and mechanical performance of Sulfur Concrete further support its utilization [1].

Usage of pure molten Sulfur as binder delivers a cohesive material that performs well in acid and salt-rich environments [6]. Chemical modifiers are to be added to the mix to react with Sulfur to improve the durability of the material [1]. Dicyclopentadiene is added to further improve the performance of the binder, styrene reacts with Sulfur and control its viscosity [11]. As for the aggregate, Martian Soil is the primary choice, where it was used as aggregate to prepare cast and recast samples [1], strength results obtained from mechanical testing were acceptable. Coarse aggregate of size (2-8 mm) is expected to further increase the strength of the mix, however, the type of the coarse aggregate does not affect it. While the mixture composition ratios directly affect its performance, it is not influenced by the curing time [10].



If perfectly mixed, Sulfur Concrete could yield compressive strengths above 50 MPa. Unmodified Sulfur Concrete reaches maximum compressive strengths of 48 MPa with 50% of Sulfur (by weight) [1]. The modified samples containing (19-21%) of Sulfur reach early and late compressive strengths of 65.5 MPa and 68.7 MPa, respectively, [10]. The maximum tensile and compressive strengths were both observed at the same optimal Sulfur content [1].

Three-Point bending fracture tests were conducted to samples with Martian aggregate [1], the maximum strength was found at 50% of Sulfur (by weight) and values were 1.65 MPa and 2.3 MPa for cast and recast samples, respectively. The maximum flexural strength was found to be 9.47 MPa at an optimal Sulfur Content of 45%, similar Portland Cement samples achieved only 6.25 MPa [12].

Lower compressive and flexural strengths are anticipated when Sulfur content is increased [5]. Samples having 60% of Sulfur (by weight) experienced cone type failure in compression testing at 41 MPa, and bending rupture was observed at 0.5 MPa [1]. Furthermore, samples of recreated Martian Soil obtained by, Brinegar [2], achieved only 18% of the compressive strength obtained by Wan et al. [1]. As the modified Sulfur percentage increased from 19% to 24.5%, the late compressive strength decreased from 68.7 to 45.8 MPa [10]. This is due to the large layers of Sulfur surrounding the aggregate causing the material to become more brittle [12].

The freeze-thaw resistance of modified Sulfur Concrete was examined for infrastructure utilization [10]. Maximum strength obtained was 46.8 MPa for mixture composition of 21.1% Sulfur, 54.4% coarse aggregate and 15.8% fine aggregate. Sulfur Concrete was also proven to have high freeze-thaw resistance in de-icing salt solution and samples gained density and mass after 56 cycles.

Abrasion resistance of Sulfur Concrete in highly deteriorating environments was investigated comprehensively by Vlahovic et al. [4]. Samples were immersed in concentrated salt and acid solutions for more than 300 days and were shown to have minimal loss of mass.

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