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ABSTRACT

This report summarizes the state of the art of sulfur concrete. Sulfur concrete is created by mixing molten sulfur with aggregate and allowing the mixture to solidify. Ultimate strength is reached in a short time. It exhibits favorable fatigue properties and has excellent resistance to acids, salts, and many organic compounds. Works well as a rapid runway repair material. Sulfur concrete also has unfavorable properties. It has poor durability when exposed to large temperature change and to wet curing conditions. The material is also brittle. All of these properties and examined in some detail and modifications (dicyclopentadiene and sulfurcrete) are proposed to overcome the unfavorable properties.

CE-685

PROPERTIES OF SULFUR CONCRETE

Submitted
in
Partial Fulfillment
of the
Requirements
for the
Master of Engineering Degree

to

Dr. Charles M. Hix
Dr. Donald McDonald
Dr. C.C. Mathewson

by

Thomas E. Bretz, Jr.

6 July 1979

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SI - English Unit Conversions

Area
1 square meter (m^2) = 10.76 ft^2

Density
1 kilogram per cubic meter (kg/m^3) = 0.0624 pcf

Length
1 millimeter (mm) = 0.1 centimeter (cm) = 0.03937 in

Mass
1 kilogram (kg) = 2.205 lb

Pressure
1 megaPascal (MPa) = 10^{-3} GPa = 145.04 psi

Temperature
1 degree Celsius (^{o}C) = (^{o}F - 32)/1.8

Thermal Conductivity

1 watt per meter degree Celsius ($W/(m^{o}C)$ = 6.933 Btu in/($ft^2 h^{o}F$)

Viscosity
1 Pascal second (Pa s) = 10 poise

Volume
1 cubic meter (m^3) = 35.315 cy

PROPERTIES OF SULFUR CONCRETE

INTRODUCTION

Sulfur concrete is a thermoplastic mixture of elemental sulfur with fine and coarse aggregate. To prepare this concrete, sulfur is heated beyond its melting point and then mixed with aggregate. Upon cooling, the sulfur solidifies and binds the aggregate into a hard, concrete material. Sulfur concrete attains excellent structural strength, low permiability, exposure resistance, and chemical resistance. Sulfur concretes can be as strong or stronger than conventional concretes. Full strength can be reached in hours, not days, as with portland cement concretes.[1]

Sulfur has been used as an aggregate cementing binder for centuries. Prior to the American Revolution, sulfur mortars were used in North America to seal cast iron water pipes. However, sulfur, as a binder, was not formally recognized until after the advent of the patent system. One of the earliest patents was in 1844 when sulfur was used in an improved waterproof cement.[2] By 1900, sulfur compostions for pavements, conduits, and roofing were patented. Sulfur-sand mortar was successfully used in pouring joints for a sewer conveying acid waste from a pulp mill in 1920.[3]

Duecker, in the 1930's, reported on the potential for sulfur-aggregate compositions in construction and repair of acid tanks, flooring, and corrosion-resistant pipes. Duecker also reported that for some purposes sulfur compositions were very brittle and deteriorated under severe temperature fluctuations. However, by adding a plasticizer to the sulfur, Duecker was able to obtain a product of extraordinary resistance to impact and abrasion having admirable strength even under severe temperature fluctuation.[4]

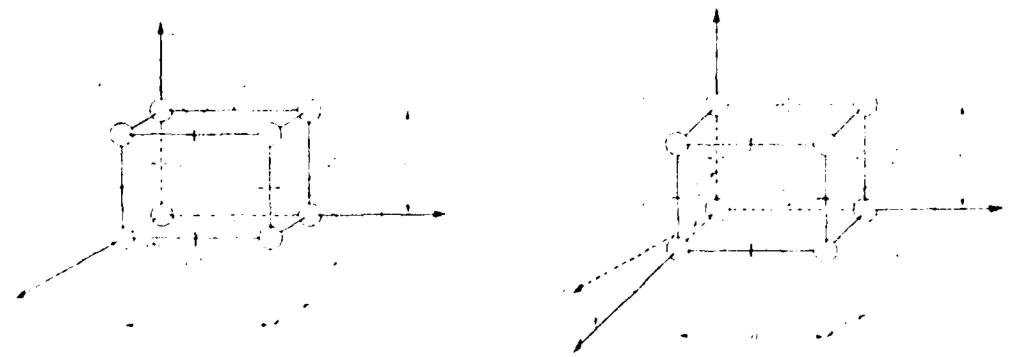
By the late 1930's, sulfur cements were being used in numerous industries. Then, with rapid development of petroleum based materials in the 1940's, coupled with the expense of sulfur cements (five times that of portland cement), there was a decline in the use of and in research on sulfur cements. It was not until the 1960's that sulfur composite development began reviving.[2] This revival was, in part, due to the increasing surplus of sulfur.

In 1975, world production of elemental sulfur exceeded 32.5 million tons. The U.S., the world's leading producer, has the potential to produce 40 million tons of sulfur by the year 2000. The predicted consumer demand by 2000 is 30 million tons. In Canada the stockpile of sulfur was about 19 million tons in 1977 with supply exceeding demand by 2-3 million tons per year.[5] One reason for this surplus of sulfur, especially in Canada, is the large number of sour gas processing plants which remove hydrogen sulfide from gas and convert it to sulfur before the gas is distributed to customers. Another source of sulfur is through its recovery during oil refining to comply with pollution control regulations.[6] A third major source of sulfur is exploitation by the Frasch process of large deposits of sulfur in association with the salt domes of the

Gulf Coast.[5] Thus, the impetus has been provided to develop a use for this surplus of sulfur. One such use which has received a great deal of attention in the 1970's is sulfur concrete.

SULFUR

In order to understand the mechanical properties of sulfur concrete, it is first necessary to investigate the nature of sulfur. Sulfur is a chemical element with atomic number of 16 and atomic weight of 32.06. It exists as orthorhombic and monoclinic crystals (figure 1). Ordinary commercial sulfur has a bulk density of between 24 and 90 pounds per cubic foot and melts at 234°F. (melting temperature is reported as being as high as 246° in some articles).[8]



Simple orthorhombic structure. $a \neq b \neq c$. Axes are at right angles.

Simple monoclinic structure. $a \neq b \neq c$. $\beta \neq 90°$.

Figure 1. Orthorhombic and Monoclinic Structures (Ref. 7).

Above the melting point, liquid sulfur is straw colored with a viscosity similar to water. Above 320°F., the color changes to amber and there is a sharp increase in viscosity, making the material difficult to handle.[9] Figure 2 shows the viscosity of sulfur in its molten state as a function of temperature.

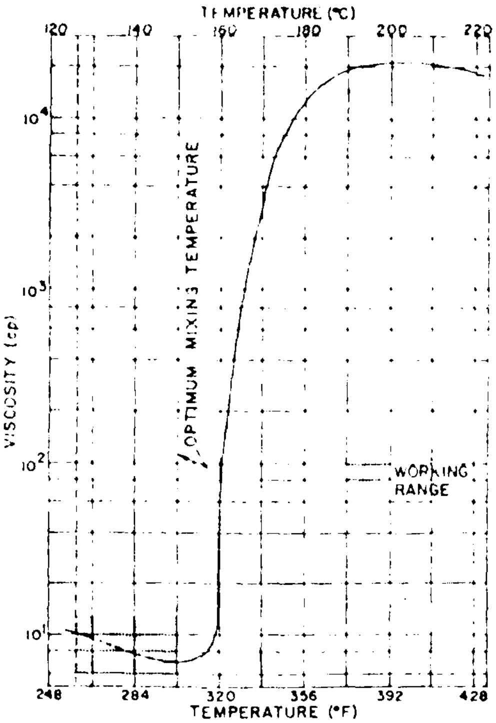


Figure 2. Viscosity-temperature curve
for liquid sulfur (Ref. 10).

As sulfur is cooled from the molten state to below 95.5°C. (203°F.), allotropic transformation from an unstable monoclinic form to the stable orthorhombic crystalline structure occurs.[11] This reversion rate is shown in figure 3. Figure 4 is phase equilibrium diagram for sulfur.

The change from molten sulfur to its orthorhombic form is accompanied by a 13 percent increase in density,[5] which corresponds to a 7.9 percent decrease in volume.[3] Consequently, the resulting product is highly stressed, and any process that will relieve the stresses, such as thermal

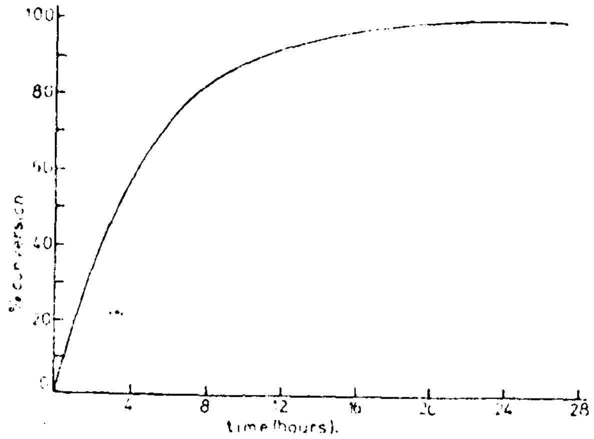


Figure 3. Reversion rate of monoclinic sulfur to orthorhombic sulfur at ambient temperature (Ref. 12).

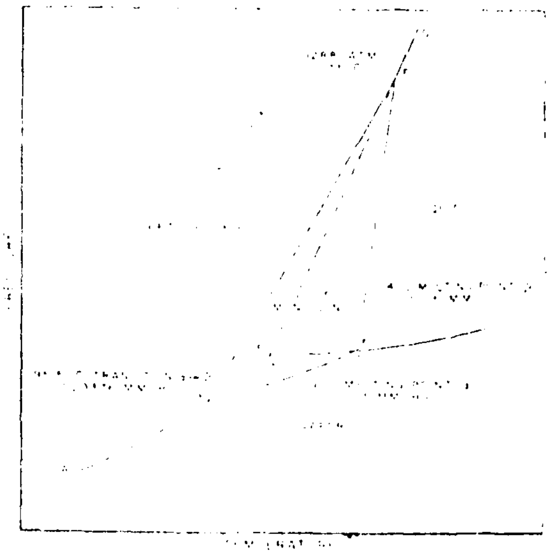


Figure 4. Phase equilibrium diagram of sulfur, schematic (Ref. 15).

cycling, will cause a strength reduction or even disintegration of the hardened sulfur.[11] It has also been reported that strength will decrease as orthorhombic crystals increase in size.[13] Gillot, et. al.,[5] have conducted scanning electron microscopy studies of sulfur as it cools, and the resulting micrographs have actually shown the change in grain boundaries and crystal morphology, and the development of cracks within a few hours after hardening was observed. Currell[14] describes orthorhombic sulfur as a "powdery crystalline material."

Dale and Ludwig[12] reported on the mechanical properties of the sulfur allotropes. They describe the monoclinic form of sulfur as being translucent with a yellow to orange color. It is also described as having a "waxy hand" and a cutting characteristic like parafin wax. The Shore hardness was given as 95. Orthorhombic sulfur is described as being opaque and light yellow in color. It is friable and has a Shore hardness of 90. During tests of sulfur samples, it was discovered that the transition from the monoclinic to the orthorhombic form occurs from the faster cooling surface of the material towards the warmer center. Thus, a sample may have characteristics of both allotropic forms.

Raymont[2] summarized much of the work done in developing additives to improve the physical properties of sulfur. He quoted Bleecker (from a 1928 patent) on the formulation of additives: "(it is important) to provide . . . certain treatments which prevent the growth of large sulfur crystals and promote the formation of small crystals desirably to or near the point of being amorphous." He also quoted Duecker (1934): "The failure of commercial sulphur cements may be attributed to the changes in the crystalline structure of sulphur . . . accelerated by fluctuating temperatures." Several plastic sulfur compositions were developed in the 1930's, 40's, and 50's, but due to high sulfur cement costs compared to portland cement, there was a decline in their use, and research and development was limited. During the 1960's, major efforts were again made to devise optimized placticizers for sulfur.

Almost all the chemicals used to modify sulfur are either polymeric polysulfides or substances that react with sulfur to form polymeric sulfides. All plasticization reactions are completed when a placticizer is mixed with molten sulfur. A theory presented by Raymont is that the roll of the placticizer is to bind the excess crystals in the hardened sulfur; ie., the placticizer is a cement in itself, using sulfur as a filler.[2]

Currell[14] discusses the importance of additives in improving sulfur's properties. As previously mentioned, when sulfur cools from the molten state, it crystallizes. Currell states that "the crystallization of sulphur may . . . be controlled by the use of suitable additives . . . reversion to the orthorhombic form can be stopped . . ." Thus, the purpose of placticizing sulfur is to retard or prevent the growth of the orthorhombic crystals. Placticizing should produce a durable sulfur which is more able to withstand the aforementioned stress relieving processes (eg., freeze-thaw). It follows, then, that placticized or modified sulfur concrete should have improved characteristics over unmodified sulfur concrete. Both types of concretes will be discussed in the following sections of this report.

SULFUR CONCRETE (unmodified)

Comparison to Portland Cement Concrete

The formation of sulfur concrete is based on completely different principles than is the formation of portland cement concrete. Sulfur concrete results from the binding action caused by solidification of molten sulfur around aggregate. Portland cement concrete, however, results from the binding action caused by chemical reactions between cement and water.[2] Despite the differences in formation of the two products, there are many similarities in their properties. Table 1 compares some typical properties of sulfur concrete and portland cement concrete.

Table 1

Comparison of Sulfur Concrete to

Portland Cement Concrete (Ref. 2)

Property	Sulfur Concrete	Portland Cement Concrete
Density	1700-2700 Kg/m^3 (106-168 pcf)	2400 Kg/m^3 (150 pcf)
Air Voids	<1-10%	10%
Compressive Strength	28-70 MPa (4060-10,150 psi)	34.5 MPa (5000 psi)
Modulus of Rupture	3.4-10.4 MPa (490-1500 psi)	3.7 MPa (540 psi)
Tensile Strength	2.8-8.3 MPa (400-1200 psi)	3.5 MPa (500 psi)

(Continued)

Table 1 (continued)

(Property)	(SC)	(PCC)
Modulus of Elasticity	20-45 GPa (2.9-6.5 x 10^6 psi)	28 GPa (4.0 x 10^6 psi)
Coefficient of Thermal Expansion	8-35 x 10^{-6} per °C. (14-63 x 10^{-6} per °F.)	11 x 10^{-6} per °C. (20 x 10^{-6} per °F.)
Thermal Conductivity	0.4-2.0 W/m°C. (2.8-13.9 Btu in. per $ft^2h°F$.)	1.6 W/m°C. (10.9 Btu in. per $ft^2h°F$.)
Water Absorption	0-1.5%	3%

The sulfur concrete values above represent a range of values that are typical of different mixes. The portland cement concrete values represent one typical mix.

Strength of Sulfur Concrete

A significant advantage of sulfur concrete over portland cement concrete is its strength development. Whereas portland cement concrete requires about 28 days for hydration to achieve 90 percent of its ultimate strength,[16] sulfur concrete can reach 90 percent of its ultimate strength in only 6 hours (figure 5).[17]

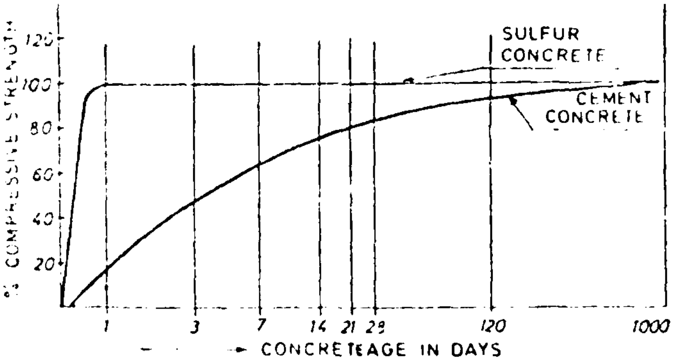


Figure 5. Strength gain of sulfur concrete (Ref. 16).

Flexural strength of sulfur concrete compares to the compressive strength as would be expected with portland cement concretes.[1] Modulus of rupture values reported by Lee and Klaiber were 9.7 to 17.1 percent of compressive strengths.[18] Sullivan and McBee obtained values of 6.3 to 13.5 percent of compressive strength.[1] These values are compared to typical portland cement concrete modulus of rupture values of about 10 percent.[2] Figure 6 gives a comparison of the flexural strength-compressive strength relationships of sulfur concrete and portland cement concrete.

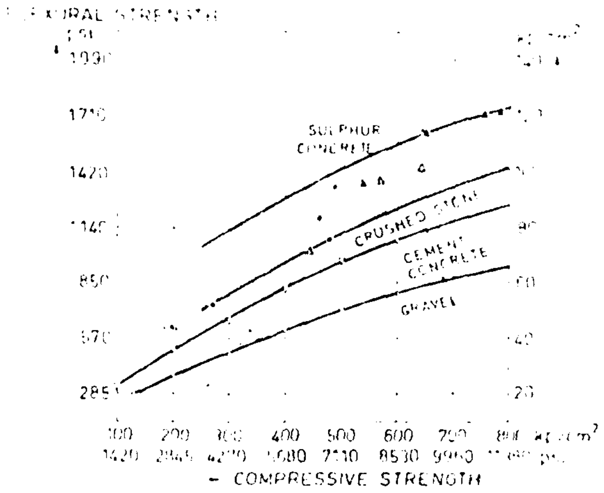


Figure 6. Comparison of the ratio between the flexural and compressive strengths of portland cement concrete and sulfur concrete (Ref. 16).

The strength of sulfur concrete is dependent on several factors. These factors include mix design, type of aggregate,[13] age of concrete when tested, size of specimen, specimen mold material, hydrogen sulfide content of sulfur, and temperature of testing.[5] Each of these factors is discussed below.

Mix design.

Raymont states that the optimum amount of binder required to achieve maximum strength is determined by the voids in the aggregate. "Ideally of course, for strength, the binder (sulfur) would fill all voids; therefore, careful grading of the aggregate to minimize the voids content can permit use of minimum binder levels while still maintaining good strength properties."[2] The best proportions of sulfur, fines, and coarse aggregate will depend primarily on the aggregate's surface texture, size, and gradation.[13] It is generally desirable to use the least amount of sulfur possible to allow for adequate workability and acceptible strength. Furthermore, problems of shrinkage, thermal expansion, flammability, etc., will be minimized with lower sulfur quantities. A high proportion of fines in sulfur concrete is also beneficial in that they act as nucleation sites for the growth of small, random crystals, they prevent or minimize segregation and separation of mix, and they tend to improve workability.[2] Figure 7 compares a typical design for a sulfur concrete mix to that of a portland cement concrete mix. Figure 8 gives an aggregate gradation range for the two concretes.

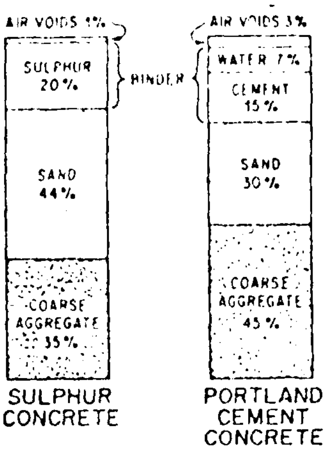


Figure 7. Comparative mix designs for sulfur and portland cement concretes (Ref. 2).

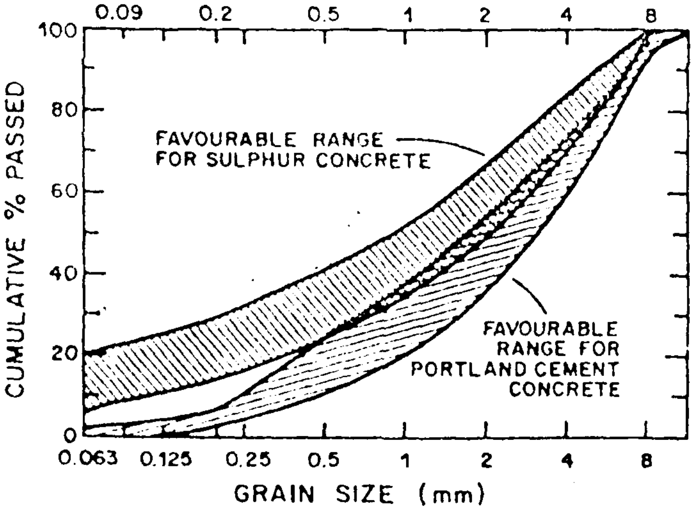


Figure 8. Typical aggregate gradation for sulfur and portland cement concretes (Ref. 2).

Type of aggregate.

There is some evidence that crushed coarse aggregates produce higher strength mixes. One reason for this was given by Gregor and Hackl.[16] When crushed stones are compacted, the sharp grains form a close, matted structure; thus, they have good inner binding and adhere better in the concrete. In testing aggregate effect on strength, Gregor and Hackl found that spherical river gravel resulted in a 4 day compressive strength of 487 kp/cm^2 (6915 psi) and flexural strength of 95 kp/cm^2 (1350 psi). With acidic granulit aggregate (crushed), they obtained 645 kp/cm^2 and 114 kp/cm^2 (9160 and 1619 psi) for compression and flexure; and with basic basalt (crushed), they obtained the highest values: 787 kp/cm^2 and 112 kp/cm^2 (11,175 and 1590 psi).

Sullivan and McBee[1] tested various aggregates also. With volcanic rock and desert sand, they obtained a 1 day compressive strength of 7275 psi with flexural strength of 750 psi. With limestone and desert sand, values were 5335 psi and 580 psi.

It is difficult to compare the two above tests (different test procedures, times of tests, mixes, etc.); however, by looking at each by itself, it is evident that aggregate type does have an effect on strength of sulfur concrete. It is also evident that even with those aggregates that give lower strengths (eg., spherical river gravel used by Gregor and Hackl or limestone used by Sullivan and McBee), the strengths are still high enough to be comparable to portland cement concrete.

Age of specimen.

As previously mentioned, sulfur concretes gain strength very rapidly. Loov[13] provides test results on strength gain of sulfur concrete (table 2).

Table 2

Rate of Strength Gain of Sulfur Concrete (Ref. 13).

Age	Strength (psi)	Percent of 28-day compressive strength
45 minutes	3400	59
1½ hours	3650	63
3 hours	4700	81
6 hours	5000	86
28 days	5800	100

Loov stated that sulfur concrete rapidly gains strength as the sulfur is crystallizing in the monoclinic form. As the temperature drops below 95.4°C. (203°F.), the monoclinic sulfur begins converting to orthorhombic. From figure 3 on page 6, it appears that the conversion to orthorhombic sulfur is complete in about 20 hours. Dale and Ludwig[12] have shown that the transition points (ie., liquid to solid monoclinic, solid monoclinic to orthorhombic) are dependent on temperature/pressure (figure 4, page 6). Thus, it appears that the strength of sulfur concrete is, indeed, dependent on cooling time. Also, it appears that once the orthorhombic transition is complete, the strength should be at its ultimate. The results of strength versus time tests by Dale and Ludwig tend to support this theory (figure 9).

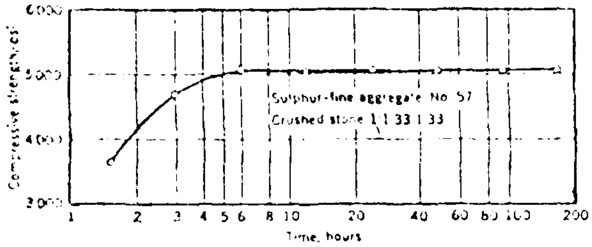


Figure 9. Strength vs time for sulfur concrete (Ref. 9).

Data from Sullivan and McBee[1] also show the effects of time on compressive strength. Out of 14 samples tested, they obtained an average 28 day compressive strength of only 6.1 percent greater than initial compressive strengths (note: Sullivan and McBee did not specifically test for the ultimate strength theory; therefore, their paper did not say how many hours of cooling corresponds to "initial" compressive strength; rather, they said that "initial" represented 1 day). The slight increase of 28 day over initial compressive strength may be due to the initial strengths not being at ultimate, ie., conversion to orthorhombic may not have been complete. Another theory on residual strength gain presented by Loov[13] is that strength continues to increase slightly as the orthorhombic sulfur is slowly converting to an amorphous form.

Since strength is dependent on cooling time, there have been attempts to decrease this time by quenching samples to very low temperatures (-79°C.) followed by normal air cooling.

Shrive stated that this quenching, which "probably causes a highly distorted intra- and inter-crystalline structure . ." results in weaker samples.[19] It has also been shown that if sulfur cooling is prolonged, crystals become larger and the sulfur weaker.[13] Thus, it is desirable to cool the sulfur concrete as quickly as possible, but not too drastically, to achieve higher strengths.

Size of specimen.

The size of a sample has been shown to have an effect on the strength. Malhotra[6] found that compressive strengths of 4-inch by 8-inch cylinders ranged from 4785 to 6730 psi. Corresponding strengths of 6- by 12-inch cylinders were between 3790 and 5005 psi. Malhotra theorizes that the lower strength of the larger samples is due, at least partially, to the slower rate of cooling caused by the larger mass of hot concrete and the subsequent formation of larger crystals in the sulfur. Shrive[19] supports this theory. He states that "as the mold size increases, the total heat content of the cast material will increase, so overall cooling will be slower and the crystals larger. In a large specimen, the center will cool sufficiently to allow the growth of large crystals." Microscopic studies of the center and edges of samples showed that the large samples had increased crystal sizes over the small samples.

Mold material.

The above effects of slow cooling are also seen when considering mold material. Fiber mold specimens take longer to cool than steel molds due to lower thermal conductivity of the fiber material. Consequently, specimens cast into fiber molds have larger crystals and lower strengths.[19] Shrive reported that specimens cast into fiber molds had about half the strength of those cast in the same size steel molds.[20]

Hydrogen sulfide content of sulfur.

In a 1976 paper on the effects of hydrogen sulfide on the strength of sulfur, Jordaan, et. al.[21] describe tests they conducted on raw sulfur and sulfur concrete. In Canada sulfur is generally obtained from commercial sour gas recovery plants which convert hydrogen sulfide in gas to sulfur; therefore, the effects of any unconverted hydrogen sulfide that may be present in the sulfur must be known. Figure 10 gives the results of tests with varying amounts of hydrogen sulfide in sulfur.

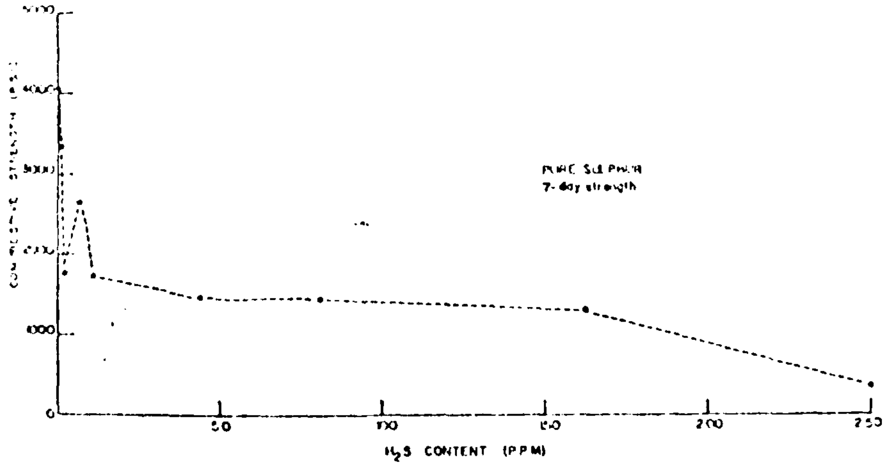


Figure 10. Effect of H_2S on compressive strength of raw sulfur (Ref. 21).

From figure 10, it is seen that there is a significant decrease in strength of raw sulfur with just a small amount of hydrogen sulfide. At 162 ppm, the compressive strength was reduced by 67 percent, and at 251 ppm, 90 percent. Jordaan explains that the strength decrease associated with hydrogen sulfide is possibly due to the chemical equilibrium between the hydrogen sulfide disolved in sulfur and the product of their interaction, hydrogen polysulfides. It is likely that these polysulfides alter the crystalline structure of sulfur. Thus, the greater the hydrogen sulfide content, the lower the strength.

Jordaan made another interesting discovery when some batches were tested at 7 days, then again at 40 days. Table 3 shows the results of these tests.

Table 3

Effect of H_2S on strength of sulfur

at 7 and 40 days (Ref. 21)

H_2S level	Compressive Strength		Modulus of Rupture	
	7 days	40 days	7 days	40 days
2 ppm	1787 psi	2299 psi	888 psi	975 psi
251 ppm	395 psi	1216 psi	169 psi	253 psi

Both the compressive strength and modulus of rupture increased significantly between 7 and 40 days. Jordaan theorized that hydrogen sulfide acts as a strength retarder, and strength recovery occurs due to instability of the hydrogen polysulfides which decompose slowly with time. Thus, sulfur slowly gains strength as the deleterious hydrogen polysulfides decompose allowing the sulfur to convert to its natural crystalline structure.

In addition to testing raw sulfur, Jordaan investigated the effects of hydrogen sulfide on sulfur concrete. Concretes were made with different mixtures of pyrrhotite and flyash fillers and at different hydrogen sulfide contents. Results of these strength tests are shown in figure 11.

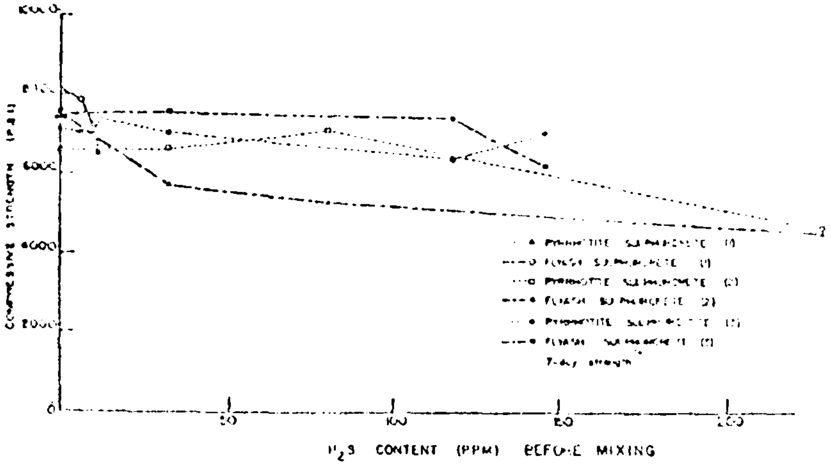


Figure 11. Effect of H_2S on compressive strength of sulfur concretes (Ref. 21).

Several possible reasons for the lesser effect of hydrogen sulfide on sulfur concrete than on raw sulfur were provided. Because of the longer cooling time caused by higher aggregate temperatures (450°F. vs. 250°F. for raw sulfur), it is possible that little hydrogen sulfide remained in the sulfur concrete at test time. Another possibility was that since concrete strength is dependent several other factors, such as aggregates, the effect of the hydrogen sulfide may have been outweighed.[21]

Temperature.

Shrive[19] investigated the effects of temperature on the strength of sulfur composites. He found that strength is dependent on the temperature. Figure 12 shows the relationship between strength and temperature that Shrive obtained.

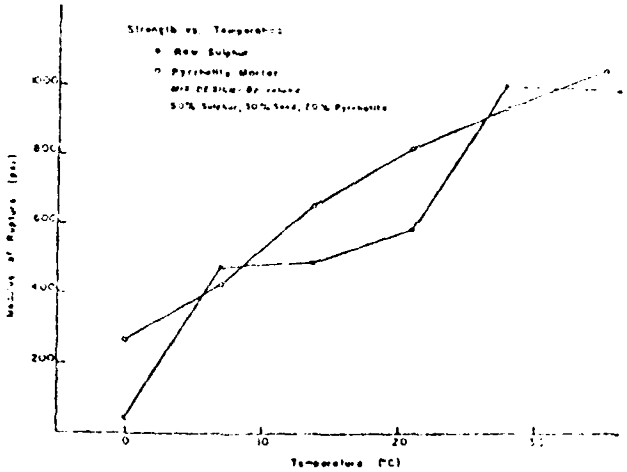


Figure 12. Modulus of rupture vs. temperature for raw sulfur and a sulfur mortar (Ref. 19).

The above results were obtained with a sulfur mortar and raw sulfur; however, sulfur concrete could be expected to behave similarily. No additional data on this temperature effect were found.

It has been shown that sulfur concrete gains strength very rapidly, obtaining 90 percent of its ultimate strength in only hours. Furthermore, ultimate compressive strength ranges from about 4000 psi to over 10,000 psi. The strength properties of sulfur concrete are, however, dependent on several factors, including mix design, aggregate, age, size of test sample, sample mold material, hydrogen sulfide, and temperature.

Stress-strain Relationship.

Sulfur concrete exhibits a very linear stress-strain relationship until the point of failure. No reduction in stiffness occurs indicating a brittle material. Figure 13 shows a typical sulfur concrete stress-strain curve plus, for comparison, a portland cement concrete stress-strain curve.

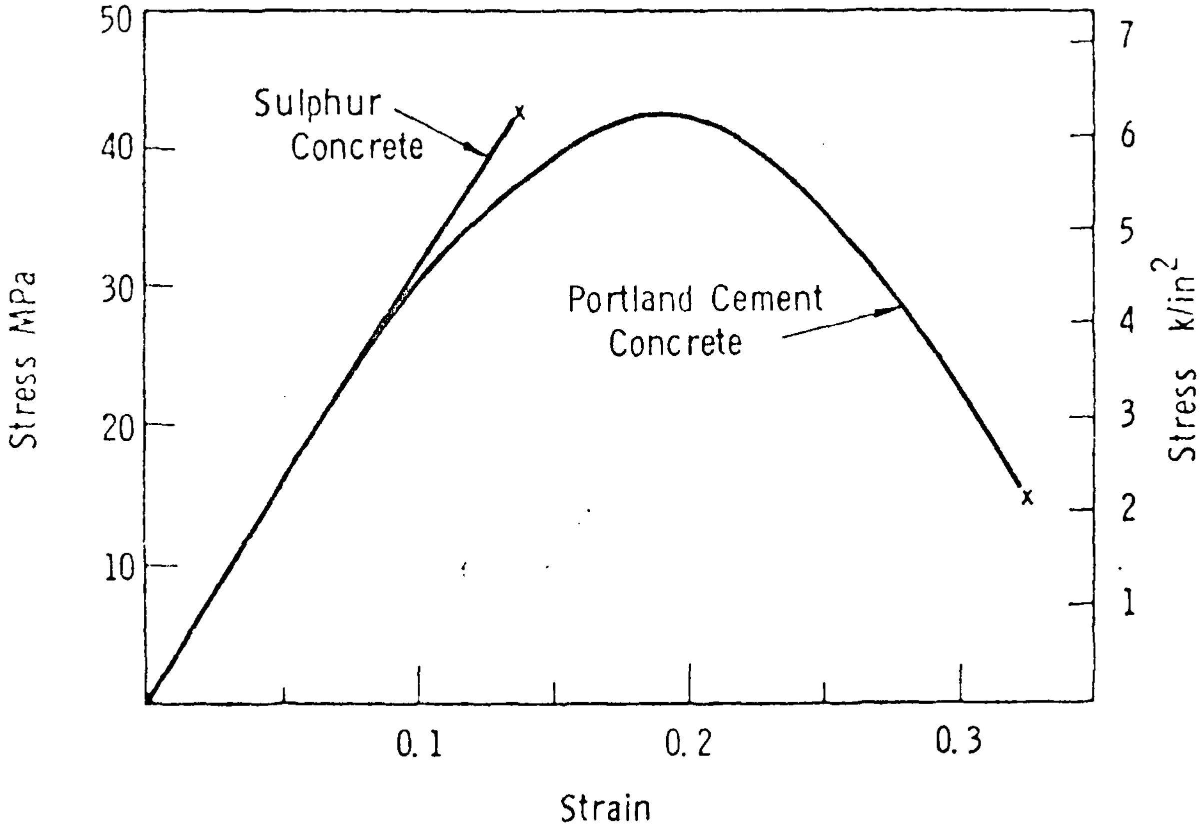


Figure 13. Stress-strain curves for sulfur and portland cement concretes (Ref. 13).

The brittle behavior of sulfur concrete means that the normal ultimate strength design methods used for conventional concretes would require modification for use with sulfur concrete design.[2]

Loov[13] stated that sulfur concrete's modulus of elasticity should be approximately the same as an equal strength portland cement concrete, 4.4 x 10^6 psi. Sullivan and McBee obtained values from 3.9 to 4.7 x 10^6 psi.[1]

Creep.

Raymont[2] reported that creep behavior of sulfur concrete differs significantly from portland cement concrete. Creep of sulfur concrete should be greater than regular concrete, and at higher temperatures and high binder (sulfur) contents, the creep will even be greater. Figure 14 shows the creep of sulfur concrete compared to portland cement concrete.

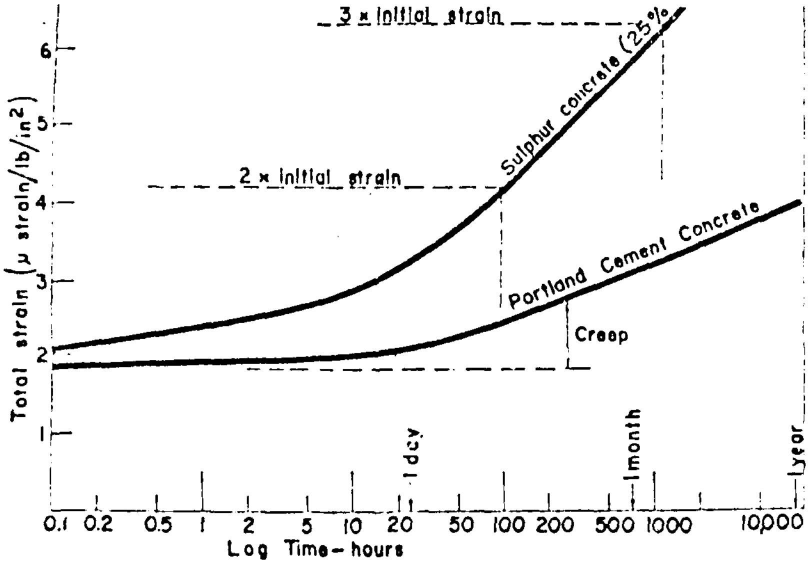


Figure 14. Creep behavior of sulfur and portland cement concretes (Ref.17).

Fatigue.

Lee and Klaiber[18] compared sulfur concrete fatigue characteristics to those of portland cement concrete. They showed that sulfur concrete has "drastically" different fatigue behavior. Surprisingly, considering the brittle nature of sulfur, sulfur concrete withstands repeated loadings at a much higher percent modulus of rupture than conventional concrete. They also showed that sulfur concrete has an endurance limit of about 85 to 90 percent modulus of rupture compared to about 50 to 55 percent for portland cement concrete. Figure 15 shows fatigue curves for both materials.

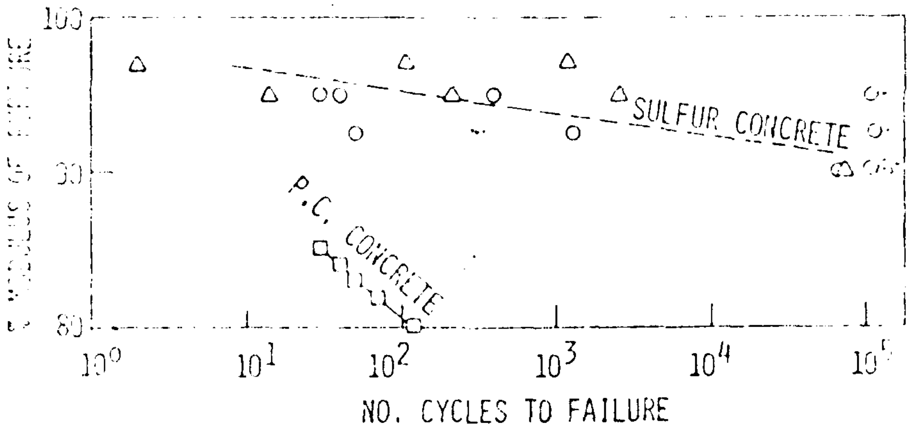


Figure 15. Fatigue curves for sulfur and portland cement concretes (Ref. 18).

This fatigue relationship means that for pavements of equal thickness, sulfur concrete should be able to withstand a greater traffic load application than portland cement concrete pavements.[18]

Durability.

Durability of sulfur concrete has been questionable for many years. Raymont[2] explains: "The combination of a low thermal conductivity with a high coefficient of expansion can lead to severe internal stresses when products are subjected to rapid temperature fluctuations." There have been numerous explanations of the durability problem, including allotropic transformation, crystal modification and recrystalization, intercrystal movement, thermal expansion stressing, and aggregate problems. Much research has been accomplished to better understand sulfur concrete's durability. Malhotra[8] tested durability by exposing sulfur concrete specimens to freeze-thaw cycles (+40°F. to 0°F., 8 cycles per day). He found that the residual flexural strength of the specimen was between 5.9 and 14.7 percent of the original flexural strength; ie., the concrete had essentially lost all its flexural strength. Furthermore, his specimens had all received extensive damage after exposure to less than 75 cycles of freeze-thaw.

Shrive, et. al.,[19] also investigated the durability of sulfur concrete under temperature fluctuations (+52°F. to +20°F., 6 cycles per day). Using a pyrrhotite aggregate for the concrete, they did not find a marked decrease in strength with temperature cycles. They did, however, see a decrease in strength with pyrrhotite sulfur mortar and raw sulfur. Figure 16 has the results of Shrive's work.

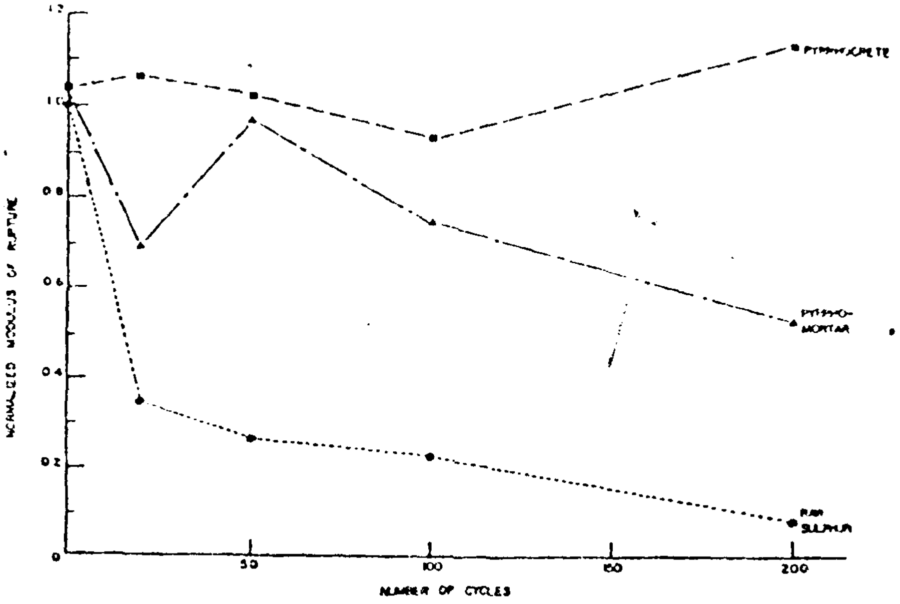


Figure 16. Normalized modulus of rupture vs. temperature cycles (Ref. 19). Note: normalized modulus of rupture is the ratio of strength of specimens subjected to freeze-thaw to strength of specimens kept at constant temperature.

It is interesting that Malhotra's results and Shrive's appear inconsistent in that Malhotra observed strength loss under freeze-thaw while Shrive did not. One factor may be that Shrive's temperature range was less than Malhotra's. Also, Shrive's aggregate, containing pyrrhotite, differred from Malhotra's, which consisted of crushed river gravel and local sand with silica flour added to increase workability. Thus, it appears that aggregate choice may have an effect on the freeze-thaw resistance of sulfur concrete.[2]

Sullivan and McBee[1] tested the durability of sulfur concrete exposed to water. They cast sulfur concrete in the form of boxes intended to hold water. In all cases when the boxes were filled with water, cracks developed, and the water leaked out. It was suggested that the boxes failed because of stresses from the allotropic transformation while sulfur was cooling along with the shrinkage from liquid sulfur to the solid state. An aging test was also conducted in which specimens were aged under moist and dry conditions. Those aged in the moist conditions (95 percent relative humidity, continuous fine mist of water, and 80°F.) all deteriorated in compressive strength, and some even disintegrated. The dry-aged samples did not show a decrease in strength.

Shrive also investigated durability of sulfur concrete exposed to water.[19] He discovered that the effects of water depend on the mineral content of the aggregates in the concrete. If swelling clays are present, specimens of sulfur concrete are susceptible to disintegration when immersed in water. An immediate solution to the water problem, therefore, is to avoid aggregates containing swelling clays. Alternate solutions provided are to paint, coat, or impregnate the surface of the concrete; however, a single crack in this treated surface would allow water to penetrate and cause deterioration.

Raymont[2] commented on the damaging effect of water. He states that this effect is a function of the aggregate, not the binder. If aggregates are contaminated with any swelling clay, which many North American aggregates contain, then resulting sulfur concretes will be susceptible to water-caused deterioration. Gamble, et. al., in a preliminary test on durability stated that as little as three percent by weight of a swelling clay will result in cracks when sulfur concrete is immersed in water for one day.[22]

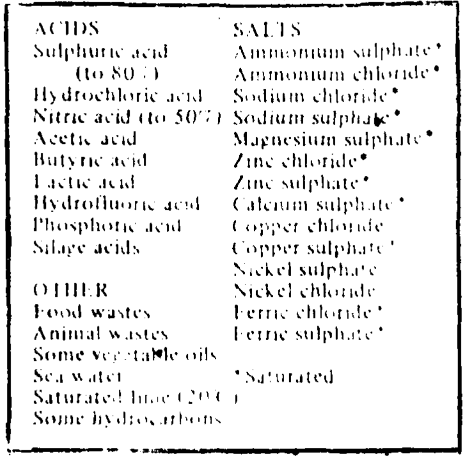
From the above discussion, it appears that sulfur concrete's durability is of question. Given the proper conditions, durability to freeze-thaw and to water may not be a problem. However, obtaining the proper conditions may be impractical or even impossible. Thus, sulfur concrete's durability must be considered a limiting factor.

Chemical Properties.

Sulfur concretes can be made with excellent resistance to most acids and salts and to many organic materials and solvents. Table 4 provides a list of some of the substances to which sulfur concretes are resistant.

Table 4

Substances to which sulfur composites are resistant (Ref. 2)



ACIDS	SALTS
Sulphuric acid	Ammonium sulphate*
(to 80%)	Ammonium chloride*
Hydrochloric acid	Sodium chloride*
Nitric acid (to 50%)	Sodium sulphate*
Acetic acid	Magnesium sulphate*
Butyric acid	Zinc chloride*
Lactic acid	Zinc sulphate*
Hydrofluoric acid	Calcium sulphate*
Phosphoric acid	Copper chloride
Silage acids	Copper sulphate*
	Nickel sulphate
OTHER	Nickel chloride
Food wastes	Ferric chloride*
Animal wastes	Ferric sulphate*
Some vegetable oils	
Sea water	*Saturated
Saturated lime (20°C)	
Some hydrocarbons	

To produce specific acid resistant concretes, the correct aggregates must be used. For example, acid resistant concretes should have siliceous aggregates as opposed to limestone.[2]

There are also chemicals that cause deterioration of sulfur concretes. These chemicals include strong oxidizing agents (such as chromic acid), strong alkalies (such as calcium hydroxide), some hydrocarbons, and some organic solvents.[2]

It is significant to mention that sulfur, in the presence of sunlight and water, may react to form an acid.[17] This combination of sulfur, water, and the sun's ultraviolet radiation can result in sulfurous and sulfuric acids.[2] Thus, if sulfur concrete has been reinforced, rapid corrosion of the steel may occur if the acids contact it.[13] Sulfur has been shown to oxidize slowly in the presence of moisture alone (the ultraviolet light accelerates the reaction). It is, however, unlikely that large volumes of sulfur concrete would be affected by oxidation from moisture. Smaller products, like park benches or street curbs may be marked by the oxidation, and structures with exposed steel may be affected.[13]

Sulfur concrete exposed to soils can also be oxidized by bacteria. Raymont[2] states that "under the appropriate conditions, microbiological degradation could be a serious problem." The damaging bacterial strains, primarily Thiobacillus thiooxidans, require warmth, moisture, and nutrients to reproduce and cause damage.[2] The optimum growth temperature for this bacterial strain is 28 to 30°C. (82 to 86°F.); thus, it would be expected that attack would be more severe in sulfur exposed to hot climates.[13] Cold soils in dry climates do not appear to support the bacteria. Various bacteriacides have been investigated; however, due to undesirable side effects, leaching of the chemicals, and cost, results have not been encouraging. Further work is required to determine the extent of the problem. Rate of attack on massive sulfur composites may, in fact, be so slow as to be negligible.[2]

Flammability and Heat Susceptibility.

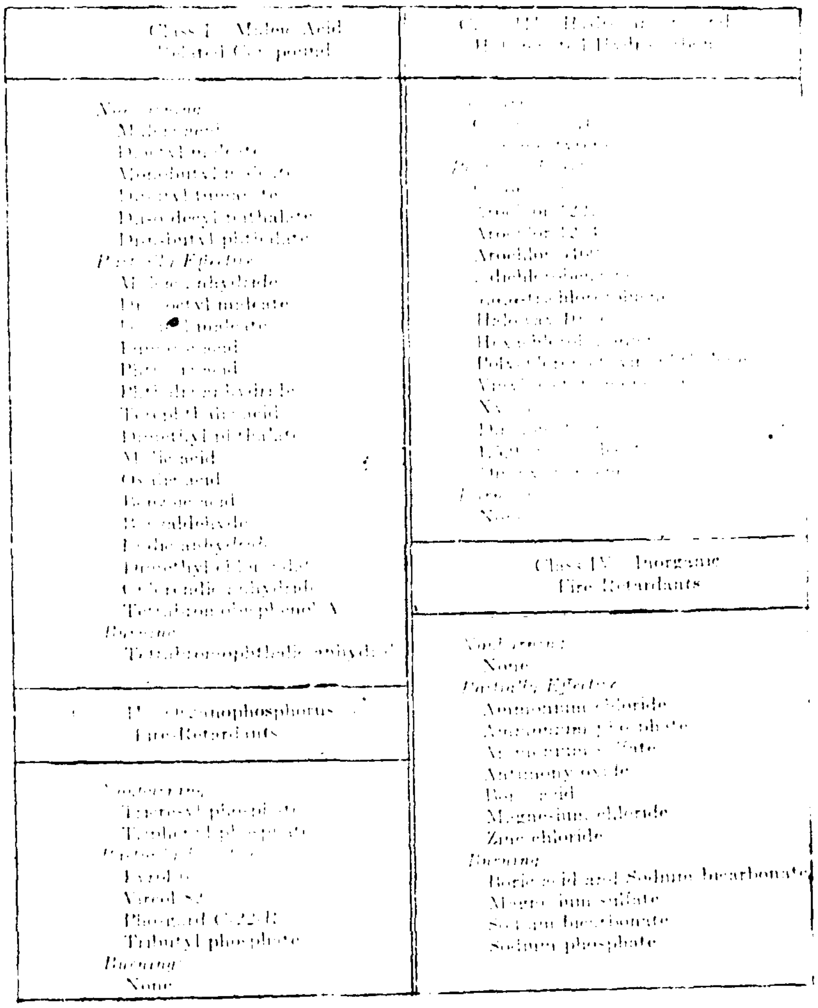
Flammability and heat susceptibility of sulfur concrete constitute a major area of concern. As previously mentioned, sulfur melts at about 239°F. A sulfur composite subjected to temperatures anywhere above this point will soften, melt, and lose all structural strength.[2] Sulfur will separate from the other mix components and simply "flow away." [13] There are no reported modifications or alterations to sulfur that will eliminate this problem (other than external techniques such as refrigeration). Raymont[2] does point out, however, that due to sulfur concrete's low conductivity and reasonable heat capacity, larger products should be able to withstand short exposure to melting temperatures with only "minor effects." Raymont gives one encouraging aspect of the situation: "the material can be remelted and re-used if desired."

As implied by its name "brimstone," sulfur will burn once ignited.[13] Furthermore, its combustion is self-sustaining, meaning that it continues burning until extinguished. As sulfur burns in the presence of oxygen, sulfur dioxide (toxic) is emitted. Efforts have been made to overcome the problem of burning, and fire retardants have been developed.[2] Dale and Ludwig[23] conducted an investigation to show that sulfur could, in fact, be fire retarded. In their studies, they tested many materials with sulfur to see which gave non-burning characteristics, which were partially effective, and which burned. Table 5 shows the materials initially tested and the results of the tests. Further detailed testing of the most promising materials was then accomplished (table 6). Dale and Ludwig concluded that sulfur can be fire retarded with small concentrations of inexpensive materials. The best formulation they tested was 3 parts dipentene dimercaptan to 3 parts Chlorowax 70S to 100 parts sulfur.

Raymont[2] added additional fire retardants to the list. Among these are organic phosphates and bromates, styrenes with other organics, and unsaturated hydrocarbon plasticizers, one of which is dicyclopentadiene, a widely studied sulfur plasticizer. One final point that Raymont makes is that "even with lean mixes (of sulfur concrete) containing fire retardants, sulfur binders will oxidize - albeit slowly - when exposed to a continuos source of heat . . . sulfur composites can never be rated as non-reactive on exposure to flame."[2]

Table 5

Burning Characteristics (ASTM D 635) of various materials mixed with sulfur (Ref. 23).



Class I – Maleic Acid Related Compound

Not effective
- Maleic acid
- Dioctyl maleate
- Monobutyl maleate
- Dioctyl fumarate
- Diisodecyl phthalate
- [illegible] phthalate

Partially Effective
- Maleic anhydride
- Di [illegible] octyl maleate
- [illegible] maleate
- [illegible] acid
- [illegible] acid
- Phthalic anhydride
- Terephthalic acid
- Dimethyl phthalate
- Malic acid
- Oxalic acid
- Benzoic acid
- Benzaldehyde
- [illegible] anhydride
- Dimethyl [illegible]
- Chlorendic anhydride
- Tetrabrom[illegible] A

Burning
- Tetrabromophthalic anhydride

[illegible] Organophosphorus Fire Retardants

Not effective
- Tricresyl phosphate
- [illegible] phosphate

[illegible]
- Fyrol 6
- Vircol 82
- Phosgard C-22-R
- Tributyl phosphate

Burning
- None

Class III [illegible]

[illegible]

- Aroclor [illegible]
- Aroclor [illegible]
- Aroclor [illegible]
- [illegible]
- Hexa[illegible]
- Poly[illegible]
- [illegible]

Class IV – Inorganic Fire Retardants

Not effective
- None

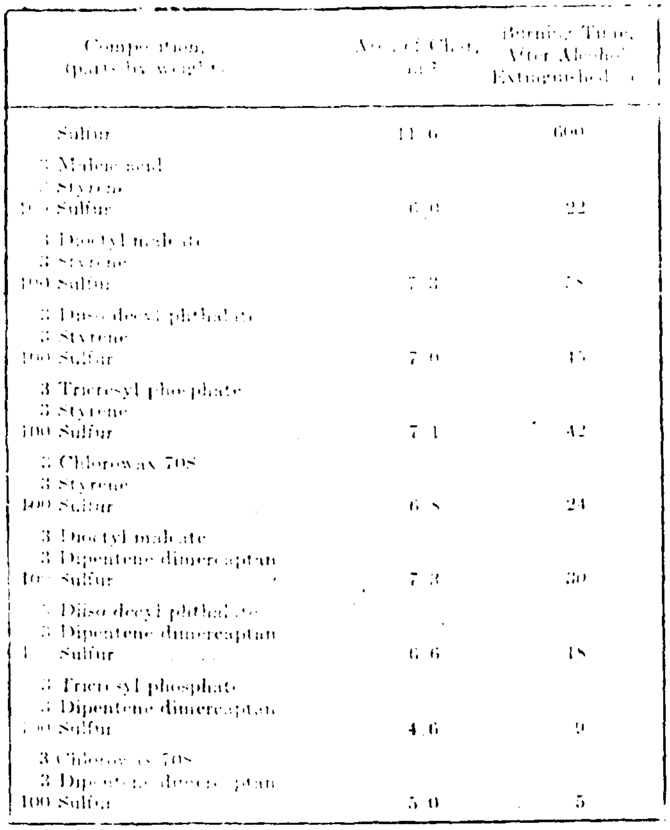
Partially Effective
- Ammonium chloride
- Ammonium phosphate
- Ammonium sulfate
- Antimony oxide
- Boric acid
- Magnesium chloride
- Zinc chloride

Burning
- Boric acid and Sodium bicarbonate
- Magnesium sulfate
- Sodium bicarbonate
- Sodium phosphate

Note: composition of mixtures was 3 parts of materials listed: 3 parts styrene monomer: 100 parts sulfur.

Table 6

Materials performance under ignition (ASTM C 209), including area of char and self-sustained burning time (Ref. 23)



Composition, (parts by weight)	Area of Char, in.²	Burning Time, After Alcohol Extinguished, s
Sulfur	11.6	600
3 Maleic acid 3 Styrene 100 Sulfur	6.0	22
3 Dioctyl maleate 3 Styrene 100 Sulfur	7.3	78
3 Diisodecyl phthalate 3 Styrene 100 Sulfur	7.0	15
3 Tricresyl phosphate 3 Styrene 100 Sulfur	7.1	42
3 Chlorowax 70S 3 Styrene 100 Sulfur	6.8	24
3 Dioctyl maleate 3 Dipentene dimercaptan 100 Sulfur	7.3	30
3 Diisodecyl phthalate 3 Dipentene dimercaptan 100 Sulfur	6.6	18
3 Tricresyl phosphate 3 Dipentene dimercaptan 100 Sulfur	4.6	9
3 Chlorowax 70S 3 Dipentene dimercaptan 100 Sulfur	5.0	5

Note: Alcohol is applied to the material and lighted. Once the alcohol is exhausted, the burning specimen is timed until it extinguishes itself. Area of char is measured after 1 minute of burning or when material extinguishes.

Thermal Expansion.

The coefficient of thermal expansion for raw sulfur is 55×10^{-6} per degree Centigrade.[20] With the addition of fillers, the value is reduced. Shrive[19] investigated the effects of thermal expansion using a sulfur concrete with a thermal coefficient of expansion of only 2×10^{-6} per °C. He inserted steel studs into the concrete samples (steel's coefficient is 12×10^{-6}) and subjected the samples to a 32.5 degree F. range of temperature cycling. He was unable to detect any signs of distress in the concrete around the studs. With pure sulfur cast with steel studs, however, he did observe cracks from sulfur-steel stresses caused by thermal cycling. Shrive also subjected sulfur concrete (without steel studs) to temperature cycling and did not observe any significant decrease in strength. He concluded that "although raw sulfur is susceptible to thermally induced stresses, sulfur-bound materials (concrete) are affected to a much smaller extent."

Thermal Conductivity.

Raymont reported the coefficient of thermal conductivity for sulfur concrete to be between 0.4 and 2.0 W/m°C (2.8 to 13.9 Btu in./ft.^{2} °F.).[2] Shrive[20] obtained a value of 13.5 Btu in./ft.^{2} °F. Table 7 gives thermal conductivity values for various materials. Due to the low thermal conductivity of sulfur composites, a great deal of interest exists in their use as insulating materials.[2]

Table 7

Values of thermal conductivity for various materials (Ref. 20).

Material	Thermal Conductivity (Btu in./ft.^{2} °F.)
Expanded polystyrenes	0.21 - 0.28
Raw sulfur	1.89
Sulfur-soil materials	2.1 - 4.2
Asbestos-cement board	5.2
Concrete	9.5
Steel (1% carbon)	300
Copper	2675

<u>Reinforcement of sulfur concrete</u>.

Raymont reports that steel can be used with sulfur concrete provided that moisture is not present. It was mentioned that sulfur oxidizes slowly in the presence of moisture, with sunlight accelerating the reaction. The results of the reaction, sulfuric and sulfurous acid, could cause catastrophic corrosion in steel.[2] Due to the low permiability of sulfur concrete (Diehl[24] found that samples absorbed only 1.02 percent water by weight compared to 2.00 percent for portland cement concrete), occasional wetting may not result in any water getting to the steel. Caution must be exercised, however, because if cracks develop in the sulfur concrete allowing moisture penetration, corrosion will occur.[2] The poor durability of most sulfur concretes in the presence of water must also be considered; ie., the formation of cracks is not unlikely if most sulfur concretes encounter water.

It has been mentioned that sulfur concrete's coefficient of thermal expansion is typically from 8 to 35 x 10^{-6} per °C, compared to portland cement concrete's coefficient of about 11 x 10^{-6} per °C.[2] In these regards, it appears that the same precautions used with portland cement concrete reinforcement would apply to sulfur concrete. Bond to steel should be no problem, having been reported to be 459 psi, compared to 427 psi for standard concrete.[24]

Thermal Contraction.

Sulfur increases in volume by 7.9 percent when cooled from its liquid state to solid.[3] Sulfur concrete, due to the presence of fillers, decreases only about 1 percent.[24] However, this 1 percent shrinkage causes problems. Loov[13] discussed the problems of thermal contraction. When liquid sulfur is placed on any cold surface, such as unheated mold material, a reduction in volume of the sulfur nearest the mold material occurs. The molten sulfur in the center of a specimen will try to fill the resulting surface voids. Thus, large voids can occur both near the surface and in the center of specimens of sulfur concrete. A solution to this problem is to keep the top part of the specimen from crystallizing by continual prodding, mixing, and adding additional molten sulfur as the remaining portion of the sample cools. Several investigators have observed this thermal shrinkage (1,19), and it is not uncommon to cut off the top couple of inches of a test sample in order to obtain a consistent surface.[1] Another problem caused by thermal shrinkage involves multiple pour operations. Sullivan and McBee[1] investigated this problem. They poured 6- by 6- by 30-inch beams with four horizontal lifts. Between pour each lift, the sulfur concrete was allowed to harden. Results showed that, due to more thermal contraction at lift surfaces for each lift, slightly lower modulus of rupture values occured than with single pour beams, plus there wa evidence of layering at pour junctions.

Shrive[19] has reported that it is possible to prevent internal shrinkage cavities by using concretes with low sulfur content (less than 20 percent by weight) and between 5 and 10 percent fines. Diehl found that with binder contents below 18 percent by weight, the volume shrinkage is almost negligible.[24] Thus, though thermal contraction is an inherent characteristic of sulfur, it can be minimized in sulfur concrete by careful selection of aggregate and by use of minimum binder. However, it may not be possible to be overly selective in aggregate choice, plus lesser binder amounts may not give adequate strengths.

Summary of Sulfur Concrete (unmodified) Properties.

Sulfur concrete demonstrates several favorable properties. Among these are its rapid strength gain, with the concrete reaching 90 percent of ultimate strength within about 6 hours after solidifying. Furthermore, its ultimate strength typically ranges from about 4000 to 10,000 psi in compression and from about 500 to 1500 psi in flexure. Sulfur concrete also exhibits favorable fatique properties. The material has been shown to withstand repeated loadings at a much higher percent modulus of rupture than portland cement concrete. Another favorable property is sulfur concrete's excellent resistance to acids, salts, and many organic materials.

Sulfur concrete also has unfavorable properties. Perhaps the most detrimental characteristic is its poor durability. When subjected to a wet environment or to cycles of freezing and thawing, there is generally drastic reduction in strength, frequently to the point of actual disintegration. Another problem area is sulfur's thermal contraction. When it cools, sulfur contracts; therefore, as sulfur concretes are cast, they tend to develop shrinkage voids. The above problems of durability and shrinkage are possible to control to some degree by aggregate choice, but it may be impossible to obtain the correct aggregates. Sulfur concrete, despite its excellent chemical resistance, is very susceptible to oxidation in the presence of water and sunlight, plus it can be damaged by certain bacteria. One additional limitation of sulfur concrete is its susceptibility to heat and fire, which can result in destruction of a product made from sulfur concrete.

MODIFIED SULFUR CONCRETE

In the previous section it was shown that sulfur concrete exhibits several undesirable properties, such as poor durability under certain conditions,[1] extreme brittleness,[2] and susceptibility to thermal cycling.[11] An explanation of these detriments is that when sulfur transforms upon cooling from the molten state to orthorhombic crystalline form, which is denser thus occupies less volume, a highly stressed product results. Any process that will then relieve the stresses, such as thermal cycling, will result in loss of strength.[11] Duecker[4] stated that by substituting plasticized sulfur for plain sulfur, ". . . these defects are overcome . . . the result . . . has admirable structural strength even when exposed to severe fluctuations in temperature." His work led to patents for cements containing plasticized sulfur, with the greatest success with olefin polysulfides as the modifiers. These materials were trademarked Thiokols. The use of these plasticizers allowed formulation of products with good durability and excellent resistance to thermal and mechanical shock.[4]

Diehl[24] perhaps best summarized the importance of using additives to modify the properties of sulfur.

> ". . . sulphur concrete displays a number of disadvantages as compared with cement

> concrete. . . there are . . . properties which are governed mainly by the binder content and which increase disadvantageously as the binder content increases. These are, the combustibility, the tendency of molten binder and aggregate to demix, the high linear thermal coefficient of expansion of the solid body and also the volume shrinkage of the binder when the melt sets. This latter feature results in considerable processing problems, for example cracking can occur when large quantities of sulphur concrete solidify.
>
> "All these properties and also the cost of sulfur mean that there is a constant demand to reduce the binder content. On the other hand, a high binder content is necessary in order to attain high compressive and flexural strength. Thus, if the properties of sulphur concrete are to be improved, its binder must be modified in such a way that high compressive and flexural strength is obtained with as low a sulphur content as possible."

Many recent investigators have attempted to plasticize sulfur. Plasticizers, in general, have tended to be expensive, making them non-feasible for common construction use.

There are, however, a few inexpensive plasticizers that are receiving a great deal of attention today.[17]

It has been discussed that as sulfur cools from the melt it goes through the monoclinic form to the stable (but stressed) orthorhombic state.[14] Plasticization, which is initiated by reacting additives with molten sulfur, modifies the sulfur to obtain in situ formations of polymeric polysulfides rather than orthorhombic crystals. The polymeric form of sulfur, incidentally, is reported to have a tensile strength of 12 times greater than that of orthorhombic sulfur.[17] Two materials that appear to have retarded orthorhombic crystal growth are dicyclopentadiene-modified sulfur concrete and Sulfurcrete.

<u>Dicyclopentadiene</u> (DCPD).

Blight, et. al.,[15] reviewed various sulfur additives and compared their effectiveness in retarding orthorhombic crystallization. One of the materials was DCPD, which is a colorless liquid hydrocarbon having unsaturated double bonds suitable for direct reaction with sulfur.[1] Blight found that with only 5 percent DCPD (5 percent of the binder was DCPD and the rest was sulfur), 54 percent of the sulfur converted to orthorhombic crystals. However, with 10 percent DCPD, there was no conversion to orthorhombic within 18 months. The resulting product was a mixture of polysulfides and free elemental sulfur. Furthermore, as the reaction time between molten sulfur and DCPD increased, the polysulfide content increased. Table 8 gives results from reacting different amounts of DCPD with sulfur to determine the polysulfide content of the product.

Table 8

DCPD-sulfur reaction results (Ref. 15).

DCPD %	Heating Time hrs.	Polysulfides* %	Unreacted Sulfur* %
5	3	13.4	86.6**
10	3	25.5	74.5***
25	3	54.7	45.3***
25	20	68.7	31.3***
40	10	64.3	35.7***

* at 18 months

** included 54% orthorhombic sulfur

*** no orthorhombic sulfur

Note that Blight's results cover only 18 months of testing. Currell[14] reports that typical products of DCPD (5 percent) have shown no formation of orthorhombic crystals for over four years.

Gregor and Hackl[16] investigated the effects of DCPD on sulfur concrete. They found that sulfur concrete with granulit and basalt aggregate and modified with 3 percent DCPD gave a 4 day compressive strength of 16,000 psi and a flexural strength of over 10,000 psi. To test for an optimum amount of DCPD, they conducted strength tests from samples with varying amounts of DCPD, from 1.5 to 10 percent (by weight of binder). Their results are shown in figure 17.

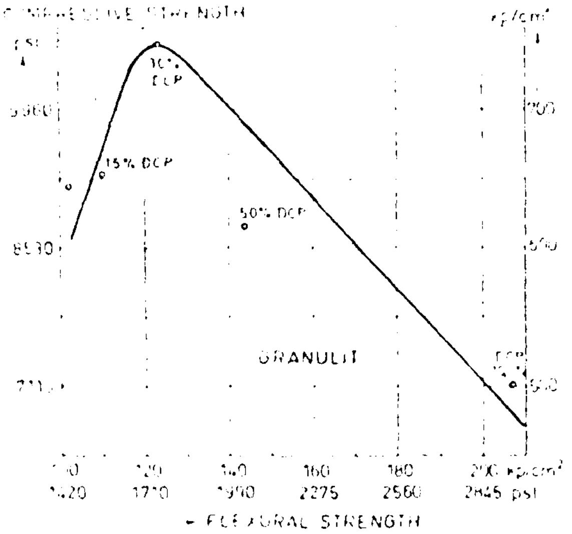


Figure 17. Compressive strength vs. flexural strength of sulfur concrete at different DCPD levels (Ref. 16).

The above results show that the optimum DCPD content is 3 percent for compressive strength. The results also show that as the DCPD content decreases, the flexural strength also decreases.

Gregor and Hackl also investigated the effects of storage time of DCPD-modified sulfur concrete. After 70 days storage at room temperature, the compressive strength had increased by 35 percent for the 10 percent DCPD mixture, and the 5 percent sample showed an increase of 15.5 percent. The flexural strengths, however, decreased 18 and 5.6 percent, respectively. These changes in strength were attributed to the presence of unreacted sulfur, part of which was initially in an amorphous form and then recrystallized over the 70 days.[16] No additional data on the loss of flexural strength were found.

Diehl[24] conducted extensive tests on DCPD and its use as a modifier for sulfur concretes. He reported that there is a functional relationship between DCPD-sulfur reaction temperature, reaction time, DCPD content of binder, and the attainable compressive strength of the modified concrete. During the reaction of DCPD and molten sulfur, there is a change in the combined ingredients: color goes from yellow through red to black with an enormous rise in viscosity. Figure 18a shows the relationship between viscosity and reaction time at different reaction temperatures. Figure 18b shows the relationship between viscosity and reaction time for different amounts of DCPD.

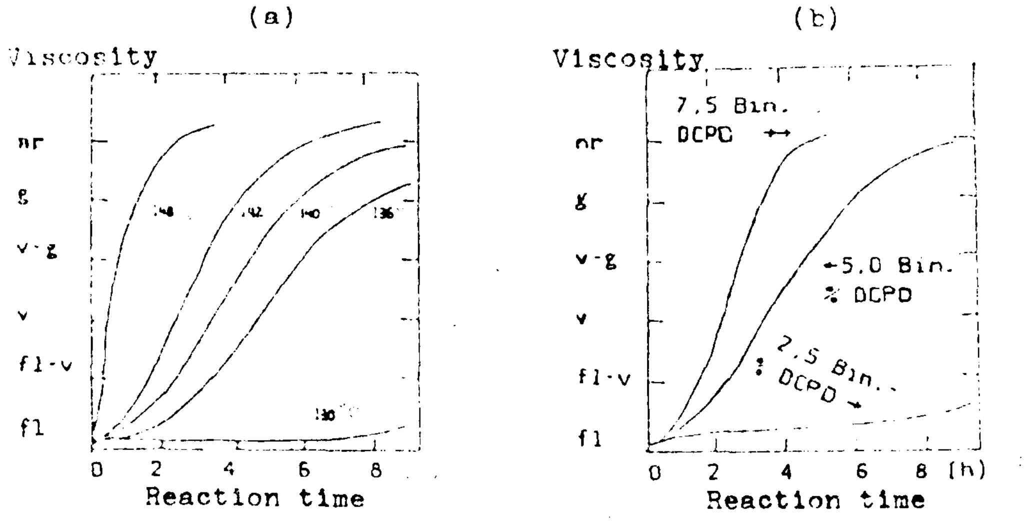


Figure 18. Viscosity vs. reaction time for

a. Constant 5% DCPD

b. Constant 140°C. (284°F) temperature

(Ref. 24).

Note: fl-viscosity of liquid sulfur;
v -highly viscous;
g -gel;
nr-black, glassy mass

Diehl stated that up to stage "g" the viscosity rise was reversible. Beyond that stage it was not.

To determine the optimum DCPD-sulfur reaction times and temperatures, Diehl measured compressive strength of sulfur concrete made from binders with differing reaction times and temperatures. He found that compressive strength of DCPD-modified sulfur concrete is dependent on the binder reaction time and temperature. These results are shown in figure 19. Since 5 percent DCPD gave the maximum compressive strength, Diehl used this value as a standard to obtain the relationship between differing DCPD-sulfur reaction times and temperatures required to obtain a given strength (figure 20). Curve 2 in figure 20 corresponds to Diehl's maximum compressive strength. Curves 1 and 3 represent the range of temperatures/times that will give compressive strengths within about 10 percent of the maximum. Diehl set 130°C. (266°F.) as the minimum reaction temperature because below this temperature the reaction time is too long. He set an upper limit of 145°C. (293°F.) because above this temperature reaction occurs so swiftly as to impare reproducibility. Thus, with 5 percent DCPD, Diehl showed that high compressive strength can be obtained if DCPD-sulfur reaction times and reaction temperatures are kept within a limit.[24]

Once Diehl had determined an optimum DCPD content for sulfur concrete, he then compared results of other properties of his modified concrete to properties of sulfur concrete and portland cement concrete (tables 9 and 10).

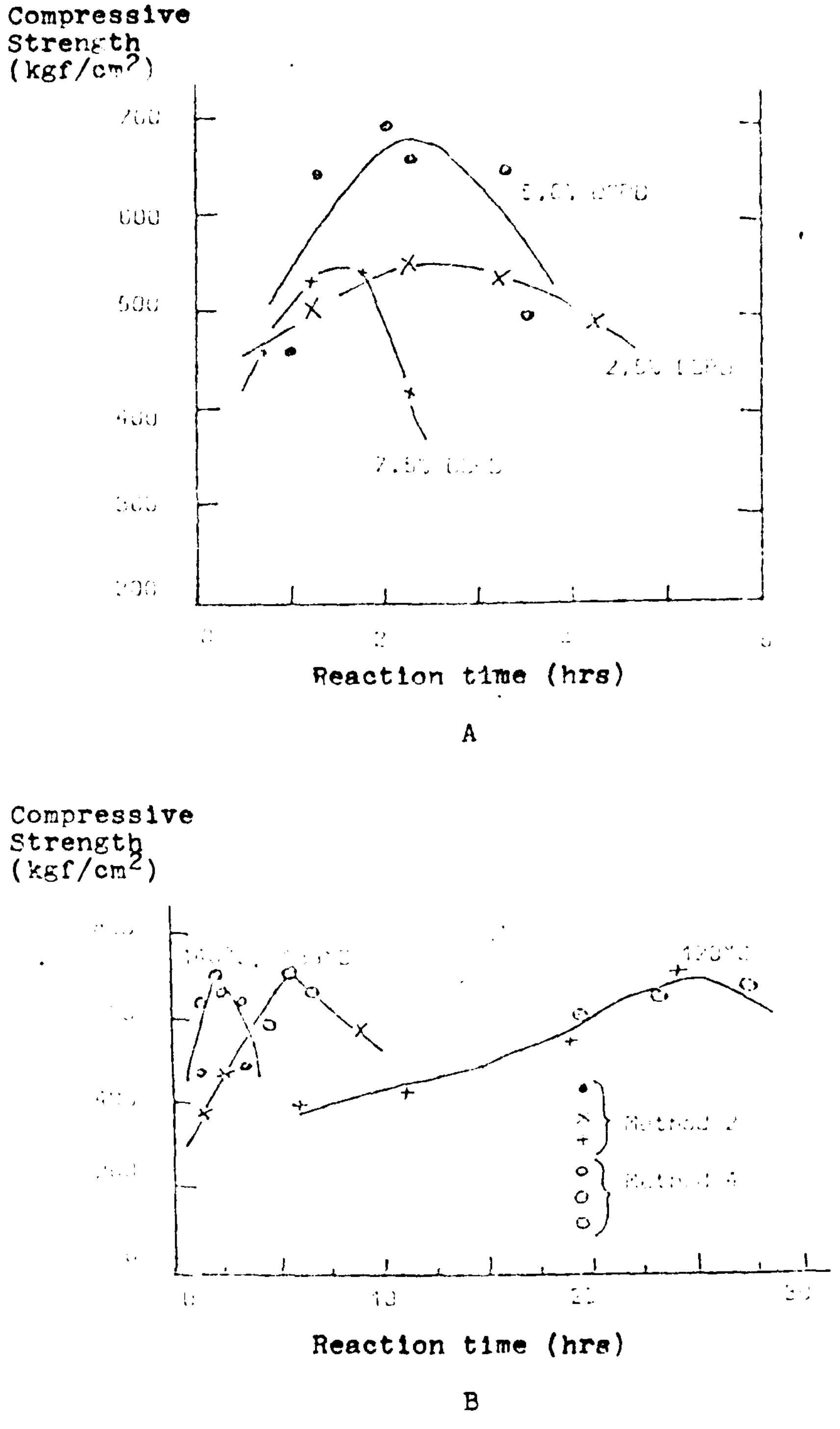


Figure 19. Compressive strength of DCPD-modified sulfur Concrete: A-varying DCPD content; B-varying temperatures. (Ref. 24).

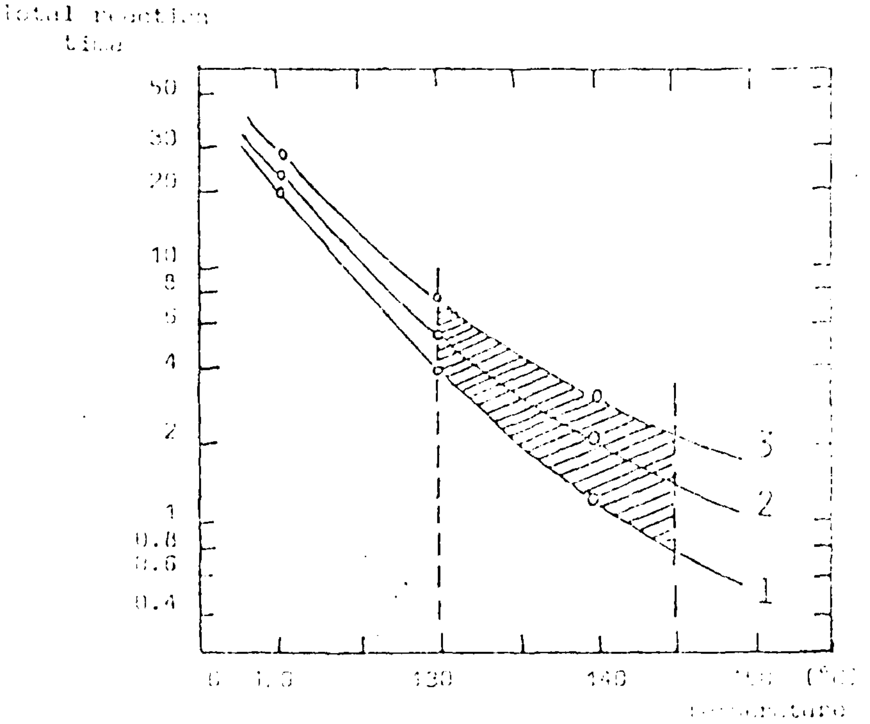


Figure 20. Functional connection between reaction time and temperature in making DCPD-modified sulfur concrete with constant compressive strength (Ref. 24).

Table 9

Properties of 5% DCPD-modified sulfur concrete compare to sulfur concrete and standard cement concrete (Ref. 24)

Property	DCPD-SC	SC	Standard concrete
Compressive strength (psi)	9656	6390	7810
Tensile strength (psi)	1988	1065	994
Volume shrinkage on setting (%vol)	0.3	0.9	< 0.13
Water uptake (% vol/% weight)	2.20/0.99	2.35/1.02	5.00/2.00
Bond to structural steel (psi)	639	459	427
Weathering erosion (in./yr.)	0.0012	0.0010	-

Table 10

Erosion (in./yr.) of sulfur concrete exposed to aggressive chemicals (Ref. 24)

Chemical	5%-DCPD SC	SC
Organic solvents		
Methanol	0.0012	0.0008
Acetone	0.0035	0.0024
Mineral spirits	0.0213	0.0335
Methyl chloride	0.710	0.107
Toluene	0.0937	0.170
Cyclohexane	0.102	0.193
Salt, NaCl (0.3%)	0	0.0008

(Continued)

Table 10 (continued)

Chemical	5%-DCPD SC	SC
Acid		
H_2SO_4 - 0.3% sol'n	0.0008	0.0008
3% sol'n	0.0012	0.0024
20% sol'n	0.0008	-
Alkalies		
NaOH - 0.3% sol'n	0.0004	0.0008
3% sol'n	0.0039	0.0110
20% sol'n	0.109	*

* Dissolved in 4 days

In addition to the high compressive strength obtained with the modified sulfur concrete, it is significant that the flexural strength was nearly double that of sulfur concrete. Another significant factor is that the volume shrinkage on setting is about a third that of sulfur concrete. Modified sulfur concrete showed resistance to organic solvents, salts and acids (Diehl did not have data on the effects of hydrogen sulfide, which as discussed earlier, affects sulfur). In the presence of concentrated alkalies, unmodified sulfur concrete dissolved; however, the modified sulfur concrete samples, although marked on the surface, were still intact.[24]

Sullivan and McBee[1] have conducted extensive tests on DCPD-modified sulfur concrete. It was previously mentioned that sulfur concrete boxes were cast, and when the boxes were filled with water, they all cracked. Boxes made from modified sulfur were also cast - none of these boxes cracked when filled with water (and had not for two years).

Sullivan and McBee used reaction times of 2 hours at 140°C. (284°F.) which, incidentally, is on the line of maximum compressive strength on Diehl's graph (figure20). The aggregates used to make sulfur concretes were different combinations of desert blow sand, commercial construction sand, volcanic rock, and limestone. A typical mix design was 23 percent sulfur (including 5 percent modifier), and equal parts of fine and coarse aggregate.[1]

Compressive strength results indicated that modified sulfur concrete with volcanic rock had slightly higher strengths than unmodified volcanic rock samples or limestone samples. The limestone aggregate samples were about the same for both modified and unmodified sulfur concrete. All the strengths were relatively high. The significance of the modifier was realized in compressive strength tests on samples that were aged for 28 days. When aged in wet (continuous fine mist) conditions, all the unmodified samples lost strength. The modified samples, however, did not, and even gained an average of14 percent. Under dry conditions, the unmodified samples showed a 6.1 percent increase in strength compared to a 19.5 percent increase for the modified samples.[1]

Sullivan and McBee also tested flexural strength. They found that flexural strength of the unmodified concrete, compared to its compressive strength, was in the range of that expected from portland cement concrete. The flexural strength of most of the modified sulfur concretes was greater than the comparable unmodified specimens. Samples modified with 5 percent DCPD had flexural strengths of about 20 percent of their compressive strengths, which was double that of the unmodified samples.[1]

In tests for modulus of elasticity, Sullivan and McBee obtained similar values to the modulus of elasticity for portland cement concrete. Samples with 5 percent DCPD in the binder had a modulus of 3.7×10^6 psi (versus $2\text{-}6 \times 10^6$ psi for portland cement concrete).[1] The stress-strain curves for the different sulfur concretes tested are shown in figure 21. One unmodified sample (curve 1 in figure 21) had the least yield before failure. DCPD or less sulfur decreased brittleness. One sample did not show a failure point because it exceeded the limits of the testing apparatus.[1]

In tests for freeze-thaw resistance of sulfur concrete, Sullivan and McBee[11] subjected prisms of sulfur concrete to 300 cycles of freeze-thaw. The flexural strength was measured after the cycling and was then compared to original strengths. Table 11 gives these results. It was found that for a given aggregate, residual flexural strength was greater for modified sulfur concrete than for unmodified samples. They also found that limestone aggregate samples showed higher strengths than silica aggregates. It was reported that the major damage occurred during the first 100 cycles of freeze-thaw, with little change between 100 and 300.

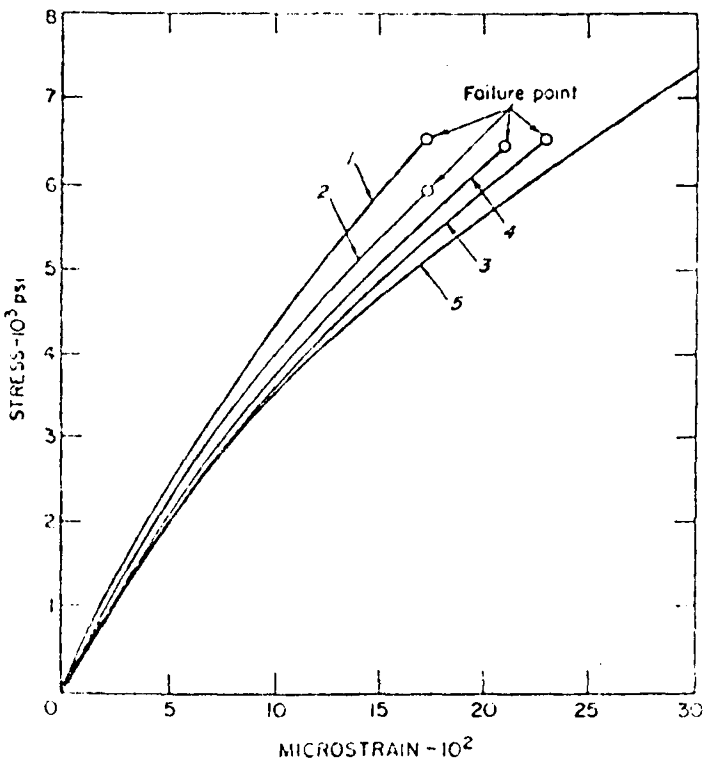


Figure 21. Stress-strain curves for sulfur concretes.

1- unmodified sulfur concrete, 30% sulfur
2- 2% DCPD, ½% dipentene, 21% sulfur
3- 2% DCPD, 21% sulfur
4- unmodified sulfur concrete, 26% sulfur
5- 5% DCPD, 21% sulfur

(Ref. 1).

Table 11

Flexural strengths after freeze-thaw testing (Ref. 11)

Aggregate	Sulfur, pct	Modulus of rupture, psi		Residual strength, pct
		Original	Final	
Silica......	24	845	125	14.8
Do........	26	905	140	15.5
Do........	22M	1,220	285	23.4
Do........	24M	1,335	310	23.2
Limestone...	22	700	235	33.6
Do........	24	810	285	35.1
Do........	21M	1,235	470	38.0
Do........	23M	1,330	400	30.1

M - sulfur concrete modified with 5% DCPD

To investigate the effects of multiple pour operations, Sullivan and McBee[1] performed the same tests previously described for unmodified sulfur concrete (pouring beams with 4 lifts, allowing solidification between each lift). With the modified sulfur concrete, there was no evidence of layering between lifts, plus the modulus of rupture was no less than modified concrete beams cast in single pours.[1]

Sullivan and McBee also conducted field tests with their modified sulfur concrete. One such test was the construction of a 4-inch thick, 3- by 7- foot slab using 5 percent DCPD modified sulfur concrete. The concrete was mixed in a heated mortar mixer. The average compressive strength of the concrete was 3880 psi, modulus of rupture was 1050 psi, specific gravity was 2.318, and the void content was 4.88 percent. As of 11 months after installation (in the entranceway to their laboratory), the slab had shown no sign of deterioration or cracking.[11]

Dicyclopentadiene has been shown to improve the properties of sulfur concrete. The modifier appears to increase both the flexural and compressive strengths of the concrete, plus it improves the durability of concrete exposed to wet and freeze-thaw conditions, with compressive strength even increasing. Thermal shrinkage, although still greater than with regular concrete, was shown to be reduced by about a third of that of unmodified sulfur concrete. Thus, it appears that DCPD-modified sulfur concrete may have the required properties to allow for increased acceptance of sulfur concrete as a construction material.

Sulfurcrete

"Sulfurcrete," a registered trademark in Canada and the U.S., is a term that describes sulfur concretes developed by Sulphur Innovations Ltd. of Alberta, Canada. Sulfurcrete paste consists of liquid sulfur, a viscosity increasing agent, and a proprietary polymer which prevents large crystal formations.[3] Normal concrete aggregates and even those not suited for portland cement may be used with Sulfurcrete. The material is extremely corrosion resistant, is essentially impermiable, has high strength, is quick setting, and may be used in freezing conditions. To make Sulfurcrete, liquid sulfur with additives is mixed with dry, heated aggregates. The hot mix can be transported in heated or insulated dump trucks or heated transit mix trucks. Since no chemical reaction is involved (cooling sets the mix), the material may be kept hot for many hours, and it may be placed under temperatures ranging from -40°F. to +140°F. Conventional reinforcement may be used, and due to low permiability, steel corrosion is minimized. The material bonds well to itself and to roughened concrete, Compressive strengths are usually about 5000 psi one hour after cooling and may reach 8000 to 10,000 psi in 24 to 48 hours. Typical tensile strengths range from 650 to 900 psi, and flexural strengths from 1300 to 1700 psi. The modulus of elasticity can be varied from 3.5 to 6.0 x 10^{-6} psi. The linear coefficient of expansion is close to that of normal concrete with the same aggregate. Sulfurcrete density is about 150 pcf with limestone aggregate. Corrosion resistance tests, where cylinders were immersed in 4 percent salt water brine, 10 percent sodium sulfate solutions, and saturated lime solution, revealed no significant deterioration. Sulfurcrete may be recycled after use by crushing the material and reheating, and no strength is lost. One limitation to Sulfurcrete is that it is not recommended as structural material where fire might occur.[26]

Sulfurcrete has been used in Canada for road repairs. Two patches were placed on a secondary highway with poor subgrade conditions; a third patch of normal patching material was also placed. Eight months after the repairs, and after a severe winter, both patches of Sulfurcrete were in excellent condition. The other patch had required continuous repatching.[26]

MIXING, CASTING, AND FINISHING
SULFUR CONCRETE

It has been found that the optimum temperature range for handling molten sulfur is between its melting point, 239°F., and 320°F. Above 320°F., the material becomes viscous and difficult to manipulate.[9] To insure that the viscosity limit is not exceeded inadvertently, most experimenters use a range of about 250 to 285°F. to prepare the molten sulfur. If modifiers are used, they are usually prereacted with the sulfur for a certain time at a given temperature (eg., Diehl's DCPD-sulfur reaction time/temperature graph). Aggregate is generally preheated to between 285 and 320°F. when introduced to the molten sulfur. The molten sulfur-aggregate mix is then thoroughly blended. Some experimenters use a heated or insulated mixer to maintain the temperature above sulfur's melting point until the material is cast. This method may, however, cause continued and undesirable reaction between modifiers and sulfur if not accounted for.[2]

A variety of equipment has been used to prepare sulfur concrete. The primary requirement is for good mixing capability and even heat distribution. The types of equipment that have been successfully used include standard laboratory equipment, heated hand operated concrete mixers, heated transit mix trucks, and asphalt pug mills. Sulfur concrete can be made in fixed or mobile units. For fixed mixing units, field pours can be accomplished by transporting the mix in heated[2] or insulated[9] trucks. Mobile mixing could incorporate a ready-mix type of operation, provided that the trucks were adapted with a heat source.[9]

An alternate approach to mixing molten modified sulfur with hot aggregate has been suggested by Saylak.[27] With this approach, sulfur and DCPD are reacted under appropriate controlled time and temperature conditions. The resulting modified sulfur is then allowed to cool and solidify. This solid mixture can then be crushed into dry powdery form and placed into bags for shipment to a site. At a site, the bags are emptied onto hot aggregate which melts the DCPD-sulfur mixture. The materials, melted sulfur, DCPD, and aggregate, are then mixed to form the concrete.[27] It may even be possible to introduce the powdered DCPD-sulfur to hot aggregate that has been preplaced, ie., already within the formwork, and then manually stir the materials as the sulfur melts. Thus, transportation of molten sulfur and aggregate is avoided.

Sulfur concrete can generally be poured into forms with relative ease.[2] The liquid sulfur will congeal on cold surfaces such as steel formwork, but the remaining mass will be workable to allow consolidation. Continued prodding, tamping, or even vibration may be required to prevent formation of voids within the mass.[13] Thermal shrinkage may cause difficulty in obtaining uniform sections of sulfur concrete if it is poured in lifts. Again, continued prodding, tamping, or vibration may minimize or eliminate this problem, and, if modified sulfur is used there may be no "lift" problem.[1]

Surface finishing is best accomplished with metal trowels and other standard finishers. It may be necessary to have this equipment preheated[10] which would retard the crystallization of the surface material being rapidly cooled by air.[13] Once the surface solidifies, it can still be reworked by applying direct heat to remelt the sulfur near the surface. Heat lamps or heated trowels may provide enough heat for some reworking.[2] Concerning the finished product, Loov[13] reports that sulfur concrete will "faithfully reflect the finish of a form . . . and it is easy to obtain . . . crisp details and corners."

COST AND USE OF SULFUR CONCRETE

Cost-wise, sulfur concrete is approximately the same as portland cement concrete.[28] A 1977 cost estimate showed the price of DCPD-modified sulfur concrete between $28.40 and $46.90 per cubic meter ($21.70 and $35.85 per cubic yard). These prices include the fuel costs in making the concrete. As a comparison, normal concrete costs were $29.20 per cubic meter ($22.30 per cubic yard). The reason for the large price range of sulfur concrete is that the price of sulfur varies considerably depending on location.[16] On the West coast of the U.S., sulfur currently costs about $20 per ton; whereas, on the East coast it is about $80 per ton. DCPD costs are between 10 and 15 cents per pound.[28]

Sulfur concrete has many potential uses. It has much similarity to regular cement concrete; thus, uses include many of the areas in which the regular concrete is now used. There are, however, limitations that must be dealt with. Sulfur concretes, being susceptible to heat and fire, should not be considered as a structural material in situations where fire is possible (eg., building construction).[2] Additional limitations are the brittleness and creep behavior of sulfur concrete.[8] Also, sulfur concrete is susceptible to damage caused by swelling clays in its aggregate if water is present.[6] Sulfur concrete exhibits several benefits over regular concrete. Its high early strength characteristics indicate potential for use in areas requiring rapid strength gain, such as highway and runway repair.[9] The ability of sulfur concrete to withstand repeated loadings at a higher percent modulus of rupture than conventional concrete also indicates potential in pavement construction.[18] Sulfur concrete may even be better suited for some pavement applications than conventional concrete because of its excellent resistance to salts, which have caused problems in many pavements. Also, sulfur concrete can be applied in lower temperatures than conventional concretes, meaning that it could be used to repair a pavement in weather too cold for conventional repairs.[2] The problems with deterioration caused by water appear to have been overcome with modifiers, so sulfur concrete has potential for use in wet environments for such things as breakwaters, piers, pilings, and even underwater construction.[2] With its excellent resistance to acids, salts, organics, and solvents, sulfur concrete could be used for construction and repair of acid tanks and industrial floors.[4] Other potential uses in areas susceptible to chemical attack are sewer treatment plants, sewer pipes, underground septic tanks, and catch basins.[2]

It is apparent that sulfur concrete has a wide variety of possible applications. Much testing is currently underway both for furthering present knowledge of the material's properties and for refining construction methods. With more widespread use of sulfur concrete, additional applications will develop.[2] There is yet much to be learned about sulfur concrete. Some will be learned in the laboratory, but much will come only through increased use.

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