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Development and Testing of Superior Sulfur Concretes

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DEVELOPMENT AND TESTING OF SUPERIOR SULFUR CONCRETES

by

T. A. Sullivan¹ and W. C. McBee²

ABSTRACT

The Bureau of Mines investigated modified sulfur concretes as one part of a program for utilizing sulfur in construction materials. The use of modified sulfur was studied as a means of preventing the stressing action in the concretes caused by the allotropic transformation of sulfur on solidification. Unmodified sulfur concretes have been prepared that have compression, flexural, and tensile strengths equivalent or better than Portland concretes. However, most of these concretes have been vulnerable to deterioration by weathering, temperature fluctuations, and freeze-thaw cycling. The sulfur was modified by reaction with dicyclopentadiene or dipentene before use as an aggregate binder. Sulfur concretes and modified sulfur concretes were prepared from acidic and basic type aggregates. Physical properties of the optimum mixtures were determined and compared with each other and with Portland cement concretes. The best results were obtained by reacting sulfur with 5 pct dicyclopentadiene to prepare modified sulfur concretes. Field testing of the concretes are in progress. Present results show that modified sulfur concretes are superior to unmodified sulfur concretes and equal or better than Portland concretes in compressive, flexural, and tensile strengths. Long-term aging characteristics of both modified and unmodified sulfur concretes are being determined.

INTRODUCTION

A Sulfur Utilization Program was initiated by the Bureau of Mines in 1972 to develop new uses for sulfur to take advantage of a projected sulfur surplus in the 1980's (22).³ Part of that program was to investigate concrete-type materials using sulfur instead of Portland cement as the binder for aggregate. Sulfur-aggregate concrete has been described by Dale and Ludwig as a thermoplastic mixture of sulfur, fine aggregate, and coarse aggregate that is heated to above the melting point of sulfur (240° F) and then cooled and allowed to solidify into a rigid, concretelike material (11). There are many potential speciality uses for sulfur concretes. As a corrosion resistant

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³Underlined numbers in parentheses refer to items in the list of references.

material, it can be used for acid-proof leach tanks, reaction vessels, thickeners, sumps, and for handling sewage and wastes that contain acid and salts. Since the material is thermoplastic, it can be placed in freezing temperatures without damage. Sulfur concrete attains 90 pct of its ultimate strength within a few hours after solidifying and would be useful in the paving industry for base or surface material which can be placed in service quickly. It is also resistant to salt solutions that damage normal concrete paving. While sulfur concretes have advantages in selected application, the replacement of cement by sulfur in all concrete is not feasible on a resource basis alone as the production of cement is roughly 10 times that of sulfur. Cement production in 1974 declined 8 pct principally from shortages of natural gas, low-sulfur coal, and modernization and improvements of dust collection facilities to conform to environmental pollution standards. Saving of cement and of the energy used in its production will result by utilizing sulfur for preparing concretes.

The projected use of sulfur as a construction material is not new. During World War I the demand for sulfur grew enormously and led to development of the Texas sulfur deposits. This resulted in more than a doubling of the U.S. annual sulfur production. A potential surplus of sulfur similar to the present day situation existed at the end of the war. At that time, Bacon and Davis reported on projected use of sulfur in the construction industry (2). They found that many additives had been suggested to modify the sulfur to enhance its properties and tested most of the proposed additives and found them unsuitable. They did, however, develop an acid-resistant mortar containing 40 pct sulfur and 60 pct sand, and it was this work that led to the industrial production of acid-resistant sulfur mortar for the chemical industry. Duecker, in 1934, found that the sulfur mortars grew on thermal cycling with a loss of flexural strength which resulted in failure of the mortars (14). He modified the sulfur cements by the addition of an olefin polysulfide to the sulfur. This resulted in retarding both the tendency to grow and the loss in flexural strength on thermal cycling of the mortar. The use of additives to modify the sulfur to prepare more stable mortars led to industrial acceptance of the material.

Dale and Ludwig's research work on the physical properties of sulfur has led to a better understanding of its potential use in construction materials (5-13, 16-17). Their work using sulfur as a binder for aggregate to prepare concretes showed that such materials could be prepared having compressive, flexure, and tensile strengths comparable to Portland cement concretes, which for building purposes average 2,500 to 3,500 psi compressive strengths and when prestressed will average up to twice these values. For pavements, Portland concretes are used with compressive strengths of 3,000 to 4,000 psi. In general, these concretes have flexural strengths of 10 to 15 pct and tensile strength of 10 pct of their compressive strengths. Sulfur concretes of various strengths have been prepared by using various aggregates and mix designs (10-11). Crow and Bates used sulfur and basalt aggregates to prepare high-strength sulfur concretes with compressive strengths ranging to 10,000 psi (4). Malhotra, in 1973, reported that elemental sulfur could be combined with mineral aggregate to produce high-strength concrete (18).

While it has been demonstrated that high-strength sulfur concrete can be prepared, several detrimental properties have appeared. Sulfur on solidifying undergoes an allotropic transformation from the monoclinic to the orthorhombic form which is more dense and occupies less volume. This results in a concrete that is highly stressed. Both Malhotra (18) and Dale and Ludwig (11) have commented on the low freeze-thaw resistance of sulfur mortars. Temperature variations have caused some sulfur concretes to self-destruct and they are vulnerable to melting at fairly low temperatures and require additives to prevent flammability problems.

The research reported in this paper was aimed at the development of a modified sulfur binder that prevented formation of a highly stressed product and at determining the physical properties of the modified sulfur concrete. The investigation was limited to the use of relatively low-cost modifiers that are commercially available in large quantities. Under these criteria, the olefin polysulfide modifiers used by Duecker would probably be too expensive.

ACKNOWLEDGMENTS

The assistance of Professor Bob Galloway and Dr. Donald Saylak of the Texas Transportation Institute in the freeze-thaw testing of sulfur concretes; metallographic examination and modulus of elasticity determination by Peter Romans and Ronald Lowery of the Albany Metallurgy Research Center, Bureau of Mines; and mineralogical examination of aggregate materials by Howard Heady of the Reno Metallurgy Research Center, Bureau of Mines, are gratefully acknowledged.

EXPERIMENTAL PROCEDURE

Preliminary Tests

Sulfur concrete was first investigated for its suitability in constructing such things as acid leach tanks and containment ponds for waste acid and salt solutions. Previous researchers had reported that sulfur concrete had strength characteristics that should be suitable for such uses (4, 11).

Preliminary tests were made to determine workable mixtures of sulfur with various aggregate materials. The aggregates used were construction sand, silica sand, 1/4- to 3/8-inch volcanic rock, and waste copper mill tailings. The sulfur concrete was made in a small, bucket concrete mixer by heating the mixing bucket and aggregate to 160° C, adding liquid sulfur at 150° C and mixing for 2 minutes. The mixture was poured and tamped into a heated metal mold (135° C) with a demountable center mold. This produced 7-1/2- by 15-1/2- by 7-3/4-inch sulfur concrete boxes with 1-1/2-inch thick bottoms and walls. On cooling, the molds were removed and the boxes were aged for at least 24 hours.

It was found that initially sound boxes of various mixes all developed cracks when filled with water. Figure 1 shows some of the test boxes. Some cracked immediately while others took up to a week to develop cracks large enough for the water to leak through.

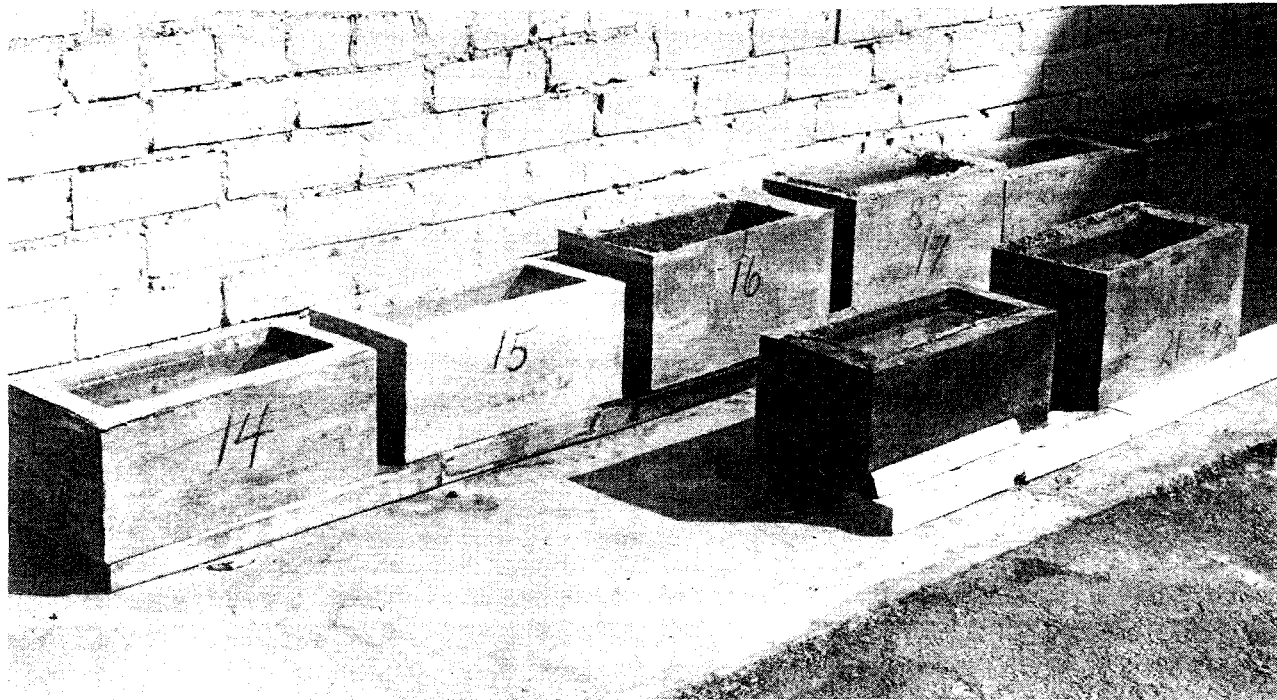


FIGURE 1. - Sulfur concrete test boxes.

In the development of sulfur coatings the authors (20) found that two unsaturated hydrocarbons, dicyclopentadiene (DCPD) and dipentene (DP), were useful in modifying sulfur to prevent cracking of the coatings. These chemicals are available in commercial quantities at relatively low cost (8 to 12 cents per pound). It was found that reacting the sulfur with 2 or 5 pct dicyclopentadiene for 1 hour before mixing with the aggregate produced sulfur concrete boxes that did not crack when filled with water; however, the use of dipentene for the same purpose was not successful. A summary of the composition and test results is given in table 1. The unmodified boxes all failed while those made with modified sulfur have contained water for 2 years without any signs of cracking.

TABLE 1. - Sulfur concrete boxes

| Box | Sulfur, pct | Sand, pct | Type sand | Rock, pct ¹ | DCPD modifier, pct ² | Results after filling with water |
|---------|-------------|-----------|--------------|------------------------|---------------------------------|----------------------------------|
| 1..... | 29.4 | 39.2 | Silica..... | 31.4 | None | Cracked after 3 days. |
| 2..... | 33.4 | 37.0 | ...do..... | 29.6 | None | Do. |
| 3..... | 29.4 | 39.2 | Construction | 31.4 | None | Cracked immediately. |
| 4..... | 33.4 | 37.0 | ...do..... | 29.6 | None | Cracked after 3 days. |
| 5..... | 36.4 | 63.6 | Tailings.... | None | None | Cracked after 1 week. |
| 6..... | 30.0 | 39.1 | Silica..... | 30.9 | 2 | Sound, no cracking. |
| 7..... | 30.3 | 38.9 | ...do..... | 30.8 | 5 | Do. |
| 8..... | 30.0 | 39.1 | Construction | 30.9 | 2 | Do. |
| 9..... | 30.3 | 38.9 | ...do..... | 30.8 | 5 | Do. |
| 10..... | 50.0 | 50.0 | Tailings.... | None | 5 | Do. |

¹Volcanic rock, 1/4- to 3/8-inch.

²The modified sulfur contained the indicated amount of dicyclopentadiene.

The failure of the unmodified sulfur concrete boxes was believed to be caused by stresses developed during the allotropic transformation from the monoclinic to the orthorhombic form of sulfur in cooling. In this regard, Dale reported that sulfur has a 13 pct shrinkage from the liquid to the solid state, but that the sulfur concretes shrink only 1 pct on solidification (11). Monoclinic sulfur has a density of 1.96 g/ml at 20° C and an atomic volume of 16.4 ml while the orthorhombic form has a density of 2.07 g/ml at 20° C and an atomic volume of 15.5 ml. Conversion of the sulfur from the monoclinic to the orthorhombic form on cooling and aging induces stresses because the physical nature of the sulfur concrete prevents it from shrinking.

With the successful demonstration of the use of modified sulfur to prevent stress cracking of the sulfur concrete, the testing program was extended to determine the optimum conditions for preparing modified sulfur concretes and to determine the effect that the modified sulfur had on the physical properties of the material as compared with Portland cement concrete and unmodified sulfur concrete.

Materials

The materials used in preparing the sulfur concretes were sulfur, unsaturated hydrocarbons for modifiers, and fine and coarse aggregates. The sulfur was commercial high-purity grade (99.9 min) secondary sulfur. It was in flake form which made it convenient for handling without dusting.

The chemical modifiers were commercial grades of dicyclopentadiene ($C_{10}H_{12}$)--a colorless liquid with a specific gravity of 0.976, a boiling point of 200° C, and a melting point of 33.6° C, and dipentene ($C_{10}H_{16}$)--a colorless liquid with a specific gravity of 0.860, a boiling point of 176° C, and a melting point of -40° C. Both of these hydrocarbons have unsaturated double bonds suitable for direct reaction with sulfur. In a previous investigation involving sulfur spray coatings, it was found that reaction of sulfur with 13 pct dicyclopentadiene or 26 pct dipentene would result in a fully plasticized sulfur product (20). Smaller additions of dicyclopentadiene were found to retard or prevent crystallization of the sulfur, while providing comparable physical properties. In this investigation, dicyclopentadiene was chosen as a plasticization agent in the modification of sulfur and the dipentene was used in conjunction with dicyclopentadiene as a viscosity control agent. Small additions (\cong 1 pct) of dipentene to sulfur were found to retard the formation of viscous sulfur in the 160° to 200° C range and also improved the ability of the sulfur to wet the aggregate.

Four types of aggregate materials were investigated. These were desert blow sand, commercial construction sand, volcanic rock, and limestone.

The fine desert blow sand consisted of subrounded to subangular grains 0.2 to 0.5 mm in diameter. Most grains consisted of one mineral with about equal amounts of plagioclase, feldspar, quartz, and microcline feldspar. About 25 pct of the desert sand consisted of very fine-grained lithic fragments of granitic rock, cryptocrystalline silicified rocks, limestone, and volcanic rocks. The construction sand was 1- to 3-mm angular grains of medium to

fine-grained granitic rock. The volcanic rock was sized 3/8-inch rock of intermediate to basic intermediate composition and fell on either side of the andesite-basalt composition boundary and was quite vesicular as shown by its lower specific gravity. The 3/8-inch limestone was principally calcite with minor amounts of dolomite, quartz, and feldspar. The physical properties of the aggregates are shown in table 2.

TABLE 2. - Physical properties of aggregates

| Aggregate | Specific gravity | Voids, pct | Unit weight, lb/cu ft |
|------------------------|------------------|------------|-----------------------|
| Desert sand..... | 2.683 | 37.5 | 104.6 |
| Construction sand..... | 2.679 | 37.3 | 104.8 |
| Volcanic rock..... | 2.518 | 40.7 | 93.2 |
| Limestone rock..... | 2.731 | 35.0 | 110.8 |

Preparation of Test Samples

A standard procedure was developed for preparing test specimens for strength measurements. This was necessary to insure sound samples for comparing the properties of various sulfur-concrete mixtures. Sulfur concrete cast into standard concrete compression molds develops a porous shrinkage area in the top of samples even with good tamping and refilling of the mold as it cools. Malhotra has reported on the differences he obtained in compressive strengths with 4- by 8-inch and 6- by 12-inch samples of sulfur concrete (19). The following procedure was used to obtain sound samples and minimize the difference between samples.

Standard cylindrical compression molds 3 by 6 and 6 by 12 inches long were fitted with 3-inch extensions on the top of the molds. Both modified and unmodified sulfur concretes were prepared by mixing together sulfur (140°-150° C) and aggregate (160°-170° C) in a heated mixing bowl (150° C) for 2 minutes with a Hobart or Triumph mixer.⁴ When modified sulfur concrete was prepared, the sulfur was first reacted with the modifier before mixing with the aggregate. Sulfur and dicyclopentadiene were reacted for 2 hours at 140° C. Sulfur and dipentene were reacted for 2 hours at 170° C. Sulfur and a mixture of the two were made by reacting with dipentene first for one-half hour at 170° C and then adding the dicyclopentadiene and reacting for 2 hours at 150° C. The sulfur concrete after mixing was tamped into the molds. The molds and tamper were preheated to 120° C. The tamper was a 3/4-inch steel rod with a hemispherical tip. After tamping, the samples were cooled to room temperature and removed from the molds. The top 3 inches of the samples were cut off and discarded. The compression samples were capped with a standard sulfur capping compound before testing. The results of all test measurements reported are for samples aged 1 day unless otherwise specified.

Sulfur concrete beam samples were prepared in a similar manner. Beams 3 by 3 by 14 and 3 by 4 by 16 inches were cast in vertical molds with tamping.

⁴Reference to specific brands is made for identification only and does not imply endorsement of the Bureau of Mines.

All molds and tampers for beam samples were preheated to 150° C. The molds were 3 inches longer than the desired length and the top 3 inches were cut off before testing. Larger beam samples, 6 by 6 by 30 inches, were cast into horizontal molds with tamping. Some of the larger beams were cast in one pouring and others in four lifts allowing each lift to solidify before adding the next lift. On the large beam samples additional material was added to the top of the beam surface as shrinkage occurred to obtain a level surface.

The purpose of preheating the sample molds and tamping rods was to prevent segregation of sulfur in the test specimens. When sulfur concrete is poured into a cold steel mold, the mold acts as a heat sink and freezes the sulfur at the surface of the specimens. This action tends to draw sulfur from the core of the sample. The use of heated molds and extensions on the molds resulted in sound test specimens. The various molds used in preparing the test samples are shown in figure 2.

Sulfur Concrete Mixture Design

A workable mixture of sulfur with fine and coarse aggregates is desired in preparing sulfur concretes that have good strength properties. A workable mixture may be described as one that is fluid enough to pour and tamp easily into forms or molds without separation of the sulfur on solidification of the concrete. The strength of sulfur concrete is principally dependent on the strength of the aggregates used, the strength of the sulfur, and the bonding developed between the two on the thermosetting of the sulfur. It would seem feasible that the highest compressive strength sulfur concretes would be obtained by completely filling the voids in the large aggregate with a mixture of sulfur and fine aggregate.

No standard methods of mix design have been developed for sulfur concrete. The most extensive work on characterizing sulfur concrete mixtures is that of Dale and Ludwig (11). They investigated the blending of standard concrete aggregates with fine aggregate and determined the amount of sulfur needed to obtain workable mixes that gave products with acceptable strengths. They also investigated how the type of aggregate used affected strength characteristics and developed a maximum density gradation to obtain highest comprehensive strength. Crow and Bates (4), in their investigation using basalt aggregate to prepare high compressive strength sulfur concretes, utilized the average grain size of the mixture and the coefficient of uniformity in determining their best mixtures. Malhotra used variations of standard aggregate blends in determining his sulfur concrete mixtures and also made use of added silica flour as a workability aid in holding the sulfur in suspension in the mix (18).

In this investigation, 10 aggregate blends were used and the mixture of each blend with the optimum amounts of both sulfur and modified sulfur was found. This was based on the compressive strength of the workable mixtures containing varying amounts of sulfur mixed with the aggregates. The void content of each aggregate blend was determined and used as a guide for the amounts of sulfur needed for each blend to obtain maximum compressive strength

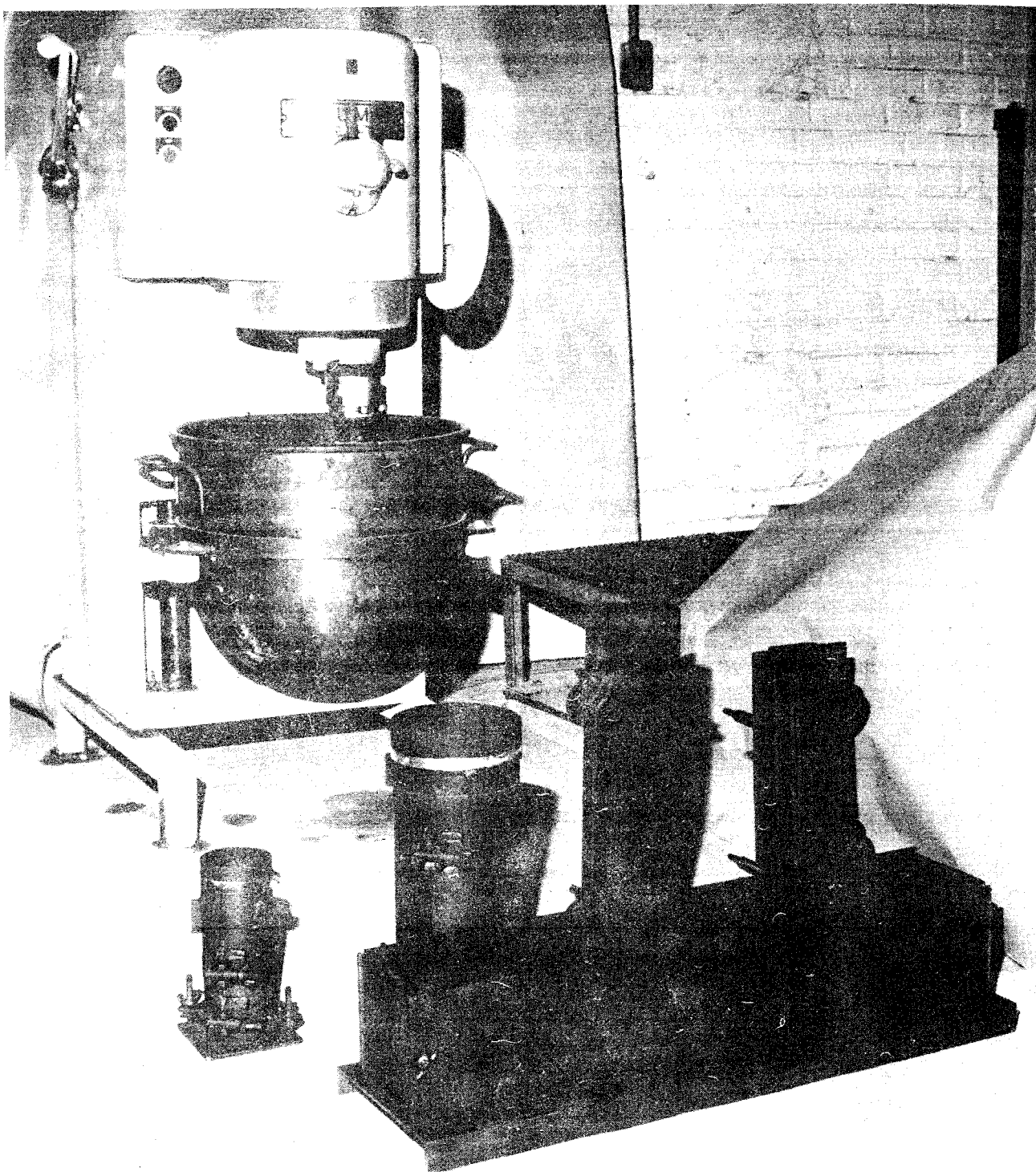


FIGURE 2. - Sulfur concrete test specimen molds.

products. The blends used are listed in table 3. The grain size distribution of the blends is shown in figure 3. Mixtures of the individual blends with varying amounts of sulfur were made and 3- by 6-inch compressive samples cast of the sulfur-blend mixtures that produced workable mixes. The compressive strengths were determined in accordance with ASTM Method C-39-49 "Compressive

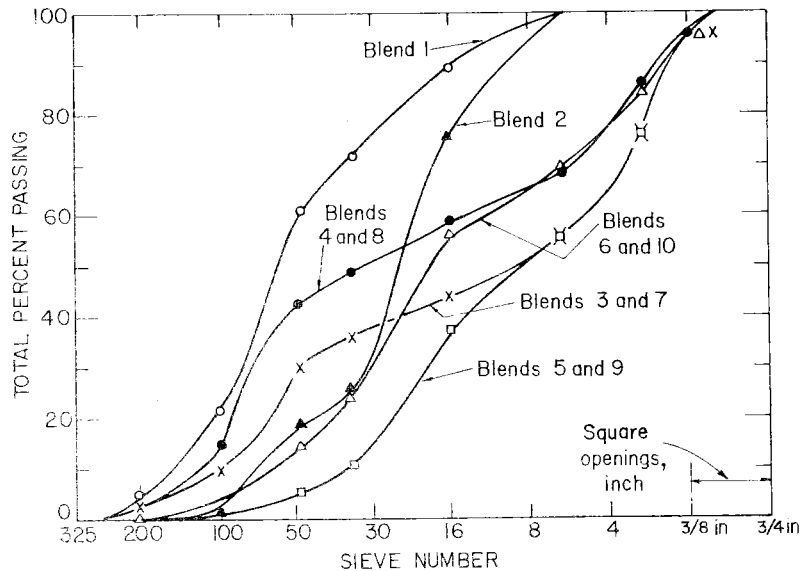


FIGURE 3. - Aggregate gradation chart.

Strength of Molded Concrete Cylinders" (1). The unmodified sulfur concentration giving the highest compressive strength mixture for each blend was established. After the optimum sulfur-aggregate value was found, the amount of modified sulfur needed to give maximum compressive strength was determined. The sulfur was modified by reaction with dicyclopentadiene or a mixture of dicyclopentadiene and dipentene before adding to the aggregate blends and mixing. Mixtures of aggregates and sulfur modified with dipentene alone were

found unsuitable because of low compressive strengths.

TABLE 3. - Aggregate blends

| Composition | Average particle size, mm ¹ | VMA, pct |
|--|--|----------|
| 1. Desert sand..... | 0.24 | 37.5 |
| 2. Construction sand..... | .78 | 37.3 |
| 3. 1:1 Desert sand and 3/8-inch volcanic rock ² | 2.40 | 26.0 |
| 4. 2:1 Desert sand and 3/8-inch volcanic rock..... | .50 | 29.7 |
| 5. 1:1 Construction sand and 3/8-inch volcanic rock. | 2.80 | 31.0 |
| 6. 2:1 Construction sand and 3/8-inch volcanic rock. | .94 | 32.7 |
| 7. 1:1 Desert sand and 3/8-inch limestone rock..... | 2.40 | 29.0 |
| 8. 2:1 Desert sand and 3/8-inch limestone rock..... | .50 | 30.0 |
| 9. 1:1 Construction sand and 3/8-inch limestone rock | 2.80 | 34.0 |
| 10. 2:1 Construction sand and 3/8-inch limestone rock | .94 | 34.0 |

VMA--Voids in the mineral aggregate.

¹The particle size, in mm, below which is half of the sample weight.

²Weight ratio of sand and 3/8-inch rock.

Metallographic Examination of Sulfur-Bonded Aggregates

The role of sulfur in bonding aggregates in sulfur concretes and modified sulfur concretes was studied using scanning electron microscopy. Three types of sulfur-bonded aggregates were prepared. These were (1) sand and sulfur, (2) sand and sulfur modified with 5 pct dicyclopentadiene; and (3) sand and sulfur modified with 2 pct dipentene. Samples of each type were prepared using construction sand and desert blow sand.

The samples were mounted in epoxy, polished and etched with 30 pct carbon disulfide (CS₂) in ethanol (C₂H₅OH). The etching was purposely severe to

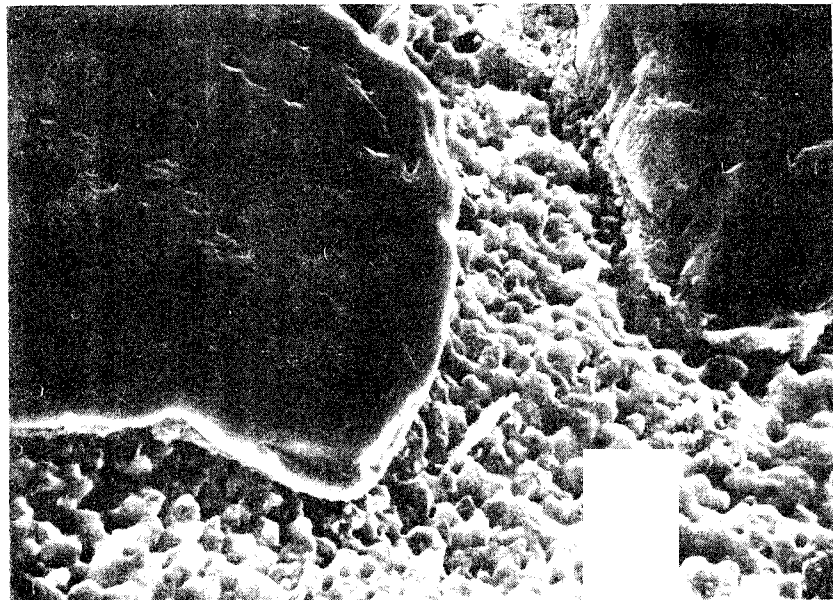
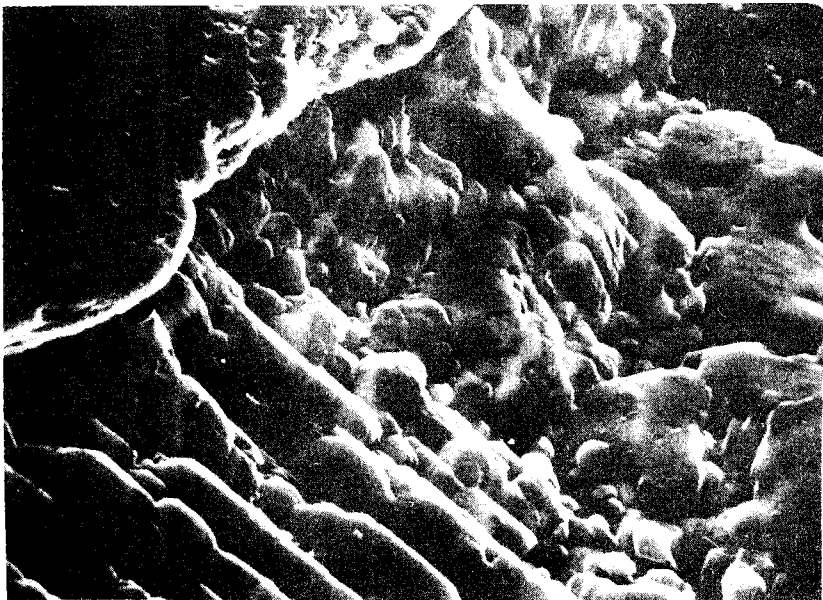
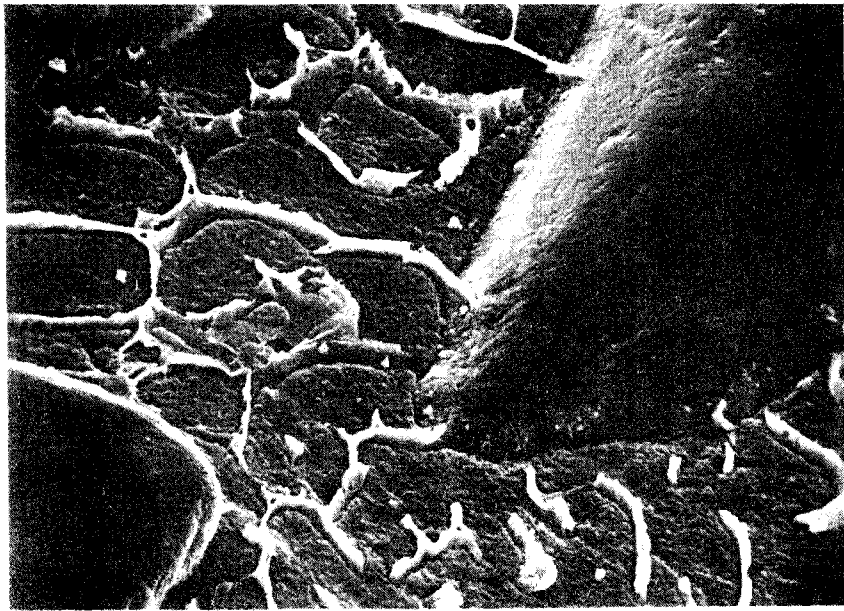


FIGURE 4. - Metallographs of sulfur-sand-aggregate concretes (X 1,000).

provide relief for scanning electron microscopy. Photomicrographs of three of the samples at $\times 1,000$ made with a Cambridge scanning electron microscope are shown in figure 4. The top photo is of desert sand and unmodified sulfur. The sulfur matrix consists of a stable phase of rather large equiaxed grains with an intergranular S_u phase which appear as stringers and which were virtually unattacked by the CS_2 etch.

The right photo is of construction sand bonded with sulfur modified by reaction with 5 pct dicyclopentadiene. It shows a noncrystalline continuous phase with small amounts of S_u present as stringers. The continuous phase is presumed to be a sulfur-organic compound.

The left photo is of desert sand bonded with sulfur which was modified by reaction with 2 pct dipentene. A mixture of noncrystalline and crystalline sulfur is present. The crystalline phase exhibits a lathlike matrix. Stringers of S_u were also present.

These studies indicated that dicyclopentadiene could be used to retard or eliminate the crystallization of sulfur used in sulfur concretes.

EXPERIMENTAL RESULTS

Compressive Strength

The compressive strength of the 10 aggregate material blends listed in table 3 mixed with varying amounts of sulfur were determined on 3- by 6-inch test cylinders. After the amount of sulfur required to give maximum compressive strengths was determined, comparative values were determined for each blend using modified sulfur as the binder material. From the results given in table 4, it is apparent that less modified sulfur was required to obtain optimum mixtures. The 1-day strength of the modified sulfur concretes was generally not as high as those for sulfur concrete in blends 1 to 6 which are principally acidic rock aggregates. However, the strengths of both types of mixtures were similar for the blends 7 to 10 which were made with basic rock. All compressive strength values of the modified sulfur concretes increased more with aging than those of the sulfur concretes. This will be shown in the section that follows.

TABLE 4. - Compressive strengths of optimum sulfur concrete mixtures

| Blend | Unmodified sulfur | | Sulfur-5DCPD ¹ | | Sulfur-2DCPD | |
|---------|--------------------|---------------------------|---------------------------|---------------------------|----------------|---------------------------|
| | Sulfur, wt-pct | Compressive strength, psi | Sulfur, wt-pct | Compressive strength, psi | Sulfur, wt-pct | Compressive strength, psi |
| 1..... | 38 | 6,380 | 26 | 4,990 | 38 | 5,735 |
| 2..... | 35 | 6,000 | 23 | 2,620 | 33 | 3,830 |
| 3..... | 30 | 7,190 | 23 | 4,580 | 23 | 7,300 |
| 4..... | 30 | 7,275 | 23 | 4,800 | 24 | 5,915 |
| 5..... | 30 | 5,190 | 20 | 5,090 | 24 | 7,120 |
| 6..... | 29 | 6,320 | 20 | 3,700 | 23 | 6,140 |
| 7..... | 26 | 5,350 | 23 | 6,000 | - | - |
| 8..... | 26 | 5,990 | 23 | 5,900 | - | - |
| 9..... | 26 | 5,700 | 23 | 5,600 | - | - |
| 10..... | 30 | 5,355 | 23 | 4,990 | - | - |
| | Sulfur-2DCPD-1/2DP | | Sulfur-2DCPD-1DP | | | |
| | Sulfur, wt-pct | Compressive strength, psi | Sulfur, wt-pct | Compressive strength, psi | | |
| 1..... | 26 | 4,800 | 28 | 4,540 | | |
| 2..... | 28 | 5,690 | 28 | 4,100 | | |
| 3..... | 21 | 6,170 | 21 | 7,340 | | |
| 4..... | 26 | 6,470 | 20 | 5,940 | | |
| 5..... | 21 | 6,030 | 21 | 5,380 | | |
| 6..... | 26 | 5,960 | 23 | 4,970 | | |
| 7..... | - | - | - | - | | |
| 8..... | - | - | - | - | | |
| 9..... | - | - | - | - | | |
| 10..... | - | - | - | - | | |

¹The modifier was either 2 or 5 wt-pct of the sulfur with DCPD and 1/2 wt-pct DP in the combined modifiers.

The differences in compressive strength measurements of small and large test cylinders were investigated. Before the standard procedure for preparing test samples was adopted, higher compressive strength values were obtained on 3- by 6-inch test cylinders than on 6- by 12-inch cylinders. The values were similar to those reported by Malhotra who obtained lower compressive strength values on the large cylinders (19). Where the standard procedure was used for preparing test specimens, no large differences in compressive strength values were found between the two sizes of cylinders. To confirm this, a series of tests were made in which 300-lb batches of sulfur concrete were prepared in a heated mortar mixer. Five each, compressive strength test cylinders 3 by 6 and 6 by 12 inches with 3-inch extension on top were cast from the mix. The excess 3 inches was cut from the top after solidification. Five sulfur concrete mixtures (aggregate blends 7, 8, 9, 13, and 14) were investigated using both sulfur and modified sulfur as the binding agent. Mixtures using aggregate blends 13 and 14 are similar to the sulfur concrete mixtures prepared by Malhotra (19) and consisted of blends 9 and 10 (table 3) in which 6 wt-pct silica flour was substituted for an equivalent amount of construction sand. The results obtained are summarized in table 5. The

values show that the compressive strength values of sound sulfur concrete cylinders of 3- by 6- and 6- by 12-inch size are comparable. In the 10 comparative tests, 6 tests exhibited an increase and 4 a decrease in strength upon increasing the cylinder size. The magnitude of the change was generally small and within the limit of error of the test method. The average compressive strength value of the 50 3- by 6-inch test cylinders was 5,890 psi compared with 5,870 psi from the average of the 50 6- by 12-inch cylinders.

TABLE 5. - Influence of cylinder size on compressive strength values

| Blend | Sulfur, wt-pct | Test cylinder, inches | Compressive strength, psi | Deviation, pct |
|---------|-----------------------|-----------------------|---------------------------|----------------|
| 7..... | 26 | { 3 by 6 | 6,080 | 3.0 |
| | | { 6 by 12 | 5,590 | 3.9 |
| 7..... | 23-5DCPD ¹ | { 3 by 6 | 3,070 | 1.4 |
| | | { 6 by 12 | 3,730 | 2.9 |
| 8..... | 26 | { 3 by 6 | 5,890 | 2.2 |
| | | { 6 by 12 | 5,020 | 6.7 |
| 8..... | 23-5DCPD | { 3 by 6 | 5,890 | 1.9 |
| | | { 6 by 12 | 6,160 | .4 |
| 9..... | 26 | { 3 by 6 | 6,070 | 18.5 |
| | | { 6 by 12 | 6,720 | 12.3 |
| 9..... | 23-5DCPD | { 3 by 6 | 6,350 | 14.2 |
| | | { 6 by 12 | 6,730 | 6.0 |
| 13..... | 26 | { 3 by 6 | 6,720 | 7.4 |
| | | { 6 by 12 | 6,970 | 2.8 |
| 13..... | 23-5DCPD | { 3 by 6 | 6,880 | 5.5 |
| | | { 6 by 12 | 6,080 | 6.1 |
| 14..... | 26 | { 3 by 6 | 7,700 | 24.7 |
| | | { 6 by 12 | 7,300 | 1.0 |
| 14..... | 23-5DCPD | { 3 by 6 | 4,260 | 2.6 |
| | | { 6 by 12 | 4,480 | 2.0 |

¹Sulfur modified with 5 wt-pct dicyclopentadiene.

The test values obtained are contrary to those reported by Malhotra; probably as a result of the different methods used in preparing test specimens. Malhotra prepared his samples by continuous filling and rodding the concrete in a standard mold and placing extra concrete on top to allow for shrinkage. The extra concrete was removed by cutting off the top 1/4-inch of the cylinder before testing.

Shrinkage cavities up to 3 inches deep in 6- by 12-inch samples were observed after employing Malhotra's filling technique. To insure sound test samples, provisions were made to cast longer cylinders and the top 3 inches of concrete were cut off and discarded in order to obtain standard size cylinders for testing. The results obtained are in general agreement with the Tucker "Summation Strength Theory," which states that (a) the strength of material is independent of the area of the specimen upon which the tests are made provided the length-diameter ratio is constant in compression tests and (b) the standard deviation of the compressive strength decreases with increasing diameter (21).

Specific Gravity and Voids Content of Sulfur Concrete

The specific gravity of the sulfur concretes was determined on 3- by 6-inch compressive strength test cylinders using a saturated surface-dry method similar to ASTM Method D 2726-73 for Asphaltic Concrete. The values obtained on various compositions of 10 blends of aggregates are given in table 6 along with their calculated voids content. The voids content of the various mixes was generally lowest for unmodified sulfur concretes. The optimum strength values for modified sulfur concretes were for those mixtures that had voids in the range of 3 to 7 pct. Inspection of broken, compressive strength samples of unmodified sulfur concretes showed that the voids were present as discreet bubbles in the binder rather than void layers between pieces of aggregate from nonwetting of the aggregate. The discreet bubbles present in the modified sulfur concretes may act as a stress relief agent in the concrete, thereby lessening its tendency to crack on aging in moist conditions.

TABLE 6. - Specific gravity and voids content of sulfur concretes

| Blend | Sulfur, pct ¹ | Theoretical specific gravity | Actual specific gravity | Voids content, pct |
|---------|--------------------------|------------------------------|-------------------------|--------------------|
| 1..... | 38 | 2.375 | 2.189 | 7.8 |
| 1..... | 26-5DCPD | 2.399 | 2.094 | 12.7 |
| 1..... | 26-2DCPD, 1/2DP | 2.439 | 2.090 | 14.1 |
| 2..... | 35 | 2.394 | 2.193 | 8.4 |
| 2..... | 23-5DCPD | 2.442 | 2.096 | 14.2 |
| 2..... | 26-2DCPD, 1/2DP | 2.436 | 2.149 | 11.8 |
| 3..... | 30 | 2.384 | 2.349 | 1.5 |
| 3..... | 23-5DCPD | 2.390 | 2.289 | 4.2 |
| 3..... | 21-2DCPD, 1/2DP | 2.424 | 2.288 | 5.6 |
| 4..... | 30 | 2.401 | 2.273 | 5.3 |
| 4..... | 23-5DCPD | 2.408 | 2.241 | 6.9 |
| 4..... | 26-2DCPD, 1/2DP | 2.404 | 2.154 | 10.4 |
| 5..... | 30 | 2.383 | 2.397 | None |
| 5..... | 23-5DCPD | 2.389 | 2.316 | 3.1 |
| 5..... | 26-2DCPD, 1/2DP | 2.385 | 2.290 | 4.0 |
| 6..... | 30 | 2.399 | 2.295 | 4.3 |
| 6..... | 20-5DCPD | 2.433 | 2.218 | 8.8 |
| 6..... | 26-2DCPD, 1/2DP | 2.402 | 2.211 | 8.0 |
| 7..... | 26 | 2.479 | 2.437 | 1.7 |
| 7..... | 23-5DCPD | 2.460 | 2.359 | 4.1 |
| 8..... | 26 | 2.474 | 2.324 | 6.1 |
| 8..... | 23-5DCPD | 2.455 | 2.274 | 7.6 |
| 9..... | 26 | 2.478 | 2.441 | 1.5 |
| 9..... | 23-5DCPD | 2.458 | 2.338 | 4.9 |
| 10..... | 30 | 2.441 | 2.326 | 4.7 |
| 10..... | 23-5DCPD | 2.453 | 2.286 | 6.8 |

¹ 5DCPD = sulfur containing 5 wt-pct dicyclopentadiene; 2DCPD, 1/2DP = sulfur containing 2 wt-pct dicyclopentadiene and 1/2 wt-pct dipentene.

Aging in Dry and Humid Conditions

As previously mentioned, the small tanks constructed of unmodified sulfur concrete in the preliminary tests had all cracked or disintegrated on filling with water. As a means of determining the durability of sulfur concretes when exposed to moisture and weathering, a test was developed to measure the loss or gain of compressive strength when exposed to humid conditions over a period of time.

In the method, 10 samples of sulfur concrete were cast in elongated 3-by 6-inch compression cylinder molds from one batch of the mixture. After cooling to room temperature, the cylinders were removed from the molds and cut to length (6 inches). One group of five samples were stored in the laboratory at ambient conditions and the other group of five samples was stored in a wet room, equipped with a multiple spray head which gave a continued fine mist spray over the samples. The humidity in the wet room was 95 ± 5 pct and the temperature was maintained at 80° F. One sample from each group was removed after 1, 7, 14, 21, and 28 days, capped with a standard sulfur capping compound and their compressive strengths were determined. Capping the samples before exposure in the wet room was not feasible as the capping compound cracked and disintegrated on exposure to these conditions. The method was developed to compare aging under wet and dry conditions and to give a means of evaluating the compressive strengths of sulfur concrete mixtures using sulfur and modified sulfur as the binding agent. A total of 56 sulfur concrete mixtures were tested. Fourteen were unmodified sulfur concrete blends and the remainder were the same aggregate blends using various modified sulfur formulations as binders. The blends tested were those shown in table 3 for which the sulfur contents were established that gave workable mixtures with optimum compressive strengths. In addition, a new set of blends (11 to 14) were prepared by substituting minus 325-mesh silica flour, amounting to 6 pct of the aggregate mix, for an equivalent amount of the sand in blends 7 to 10.

The results are given in table 7. The values shown are the initial compressive strength value of the mixture and the compressive strength at 28 days for both the dry control samples and the wet room samples. The percent increase or decrease of compressive strength after 28 days aging is shown. The intermediate sample values generally fell on a straight line plot drawn from the original to the 28-day compressive strength values.

Some unmodified concrete samples are shown in figure 5 after aging in the wet room. The cracking of the specimens on exposure to wet conditions is quite evident.

The results of the tests demonstrated that deterioration in compressive strength occurred with all the unmodified sulfur concrete blends aged under moist conditions. In some cases the samples disintegrated so completely that compressive strength determinations could not be made. In contrast, the compressive strengths of the dry samples increased over the aging period.

TABLE 7. - Compressive strengths of control and wet-aged sulfur concrete cylinders

| Blend | Sulfur, pct | Modifier, ¹ pct | Compressive strength, psi | | | Compressive strength, pct of gain | |
|-------|-------------|----------------------------|---------------------------|---------|-------|-----------------------------------|-------|
| | | | Initial | 28 days | | Dry | Wet |
| | | | | Dry | Wet | | |
| 1... | 38 | - | 6,030 | 6,200 | 4,400 | 2.8 | -27.0 |
| 1... | 27 | 5DCPD | 3,800 | 4,580 | 4,510 | 20.5 | 18.7 |
| 1... | 26 | 2DCPD | 5,100 | 6,080 | 5,550 | 19.2 | 8.8 |
| 1... | 28 | 2DCPD, 1/2DP | 4,310 | 4,860 | 4,730 | 12.8 | 9.7 |
| 1... | 28 | 2DCPD, 1DP | 4,380 | 4,700 | 4,355 | 7.3 | -.6 |
| 2... | 35 | - | 6,000 | 6,180 | 4,000 | 3.0 | -33.3 |
| 2... | 23 | 5DCPD | 2,680 | 2,820 | 2,780 | 5.2 | 3.7 |
| 2... | 26 | 2DCPD | 4,560 | 5,520 | 5,050 | 21.0 | 10.8 |
| 2... | 28 | 2DCPD, 1/2DP | 5,080 | 5,695 | 5,100 | 12.1 | .4 |
| 2... | 26 | 2DCPD, 1DP | 4,600 | 5,300 | 4,930 | 15.0 | 7.2 |
| 3... | 30 | - | 7,125 | 7,325 | 0 | 2.8 | -100 |
| 3... | 20 | 5DCPD | 4,960 | 6,100 | 5,980 | 23.0 | 20.6 |
| 3... | 26 | 2DCPD | 6,320 | 7,180 | 6,430 | 13.6 | 1.7 |
| 3... | 21 | 2DCPD, 1/2DP | 6,420 | 6,970 | 6,680 | 8.6 | 4.0 |
| 3... | 21 | 2DCPD, 1DP | 6,170 | 7,160 | 6,420 | 16.0 | 4.0 |
| 4... | 30 | - | 6,715 | 6,930 | 0 | 3.2 | -100 |
| 4... | 23 | 5DCPD | 4,850 | 5,520 | 5,690 | 13.8 | 17.3 |
| 4... | 26 | 2DCPD | 6,100 | 7,160 | 6,730 | 17.4 | 10.3 |
| 4... | 26 | 2DCPD, 1/2DP | 5,610 | 6,320 | 6,140 | 12.7 | 9.4 |
| 4... | 26 | 2DCPD, 1DP | 5,610 | 6,105 | 5,900 | 8.8 | 5.2 |
| 5... | 26 | - | 6,460 | 6,990 | 0 | 8.2 | -100 |
| 5... | 20 | 5DCPD | 5,070 | 5,510 | 5,100 | 8.7 | .6 |
| 5... | 21 | 2DCPD | 5,880 | 7,170 | 6,110 | 21.9 | 3.9 |
| 5... | 21 | 2DCPD, 1/2DP | 5,625 | 6,620 | 6,560 | 17.7 | 16.6 |
| 5... | 21 | 2DCPD, 1DP | 5,380 | 6,100 | 5,550 | 13.4 | 3.2 |
| 6... | 29 | - | 5,980 | 6,280 | 3,060 | 5.0 | -48.8 |
| 6... | 20 | 5DCPD | 2,680 | 3,690 | 3,140 | 37.7 | 17.2 |
| 6... | 26 | 2DCPD | 5,815 | 6,520 | 5,900 | 12.1 | 1.5 |
| 6... | 26 | 2DCPD, 1/2DP | 5,300 | 5,960 | 5,830 | 12.4 | 10.0 |
| 6... | 26 | 2DCPD, 1DP | 5,845 | 6,390 | 5,970 | 9.3 | 2.1 |
| 7... | 26 | - | 5,500 | 6,200 | 800 | 12.7 | -85.4 |
| 7... | 23 | 5DCPD | 5,030 | 5,985 | 5,210 | 19.0 | 3.6 |
| 8... | 26 | - | 5,400 | 5,720 | 1,240 | 5.9 | -77.0 |
| 8... | 23 | 5DCPD | 5,810 | 6,920 | 6,910 | 19.1 | 18.9 |
| 9... | 26 | - | 5,200 | 5,610 | 2,680 | 7.9 | -48.5 |
| 9... | 23 | 5DCPD | 5,600 | 6,100 | 6,020 | 8.9 | 7.5 |
| 10... | 30 | - | 5,300 | 5,870 | 2,800 | 10.8 | -47.2 |
| 10... | 23 | 5DCPD | 4,900 | 6,930 | 6,610 | 41.4 | 34.9 |
| 11... | 26 | - | 5,985 | 6,000 | 2,615 | .2 | -56.3 |
| 11... | 23 | 5DCPD | 4,490 | 5,480 | 5,510 | 22.0 | 22.7 |
| 12... | 26 | - | 5,705 | 6,100 | 2,600 | 6.8 | -54.4 |
| 12... | 23 | 5DCPD | 4,395 | 5,100 | 5,085 | 16.0 | 15.7 |
| 13... | 26 | - | 5,655 | 6,185 | 0 | 9.4 | -100 |
| 13... | 23 | 5DCPD | 4,415 | 5,585 | 5,570 | 26.5 | 26.2 |
| 14... | 30 | - | 5,845 | 6,200 | 0 | 6.1 | -100 |
| 14... | 23 | 5DCPD | 4,685 | 5,195 | 5,170 | 10.9 | 10.4 |

¹DCPD = Dicyclopentadiene; DP = Dipentene.



FIGURE 5. - Unmodified concrete cylinders after aging in humid conditions;

The compressive strengths of wet and dry samples of modified sulfur concretes increased over the 28-day period. In general, the values for both wet and dry samples were similar with possibly a slightly greater gain in compressive strengths of the dry samples during the test period. The average gain in compressive strengths expressed as the percent of initial compressive strength for the dry samples was as follows:

| Blends of-- | <u>Pct</u> |
|---------------------------------------|------------|
| 14 unmodified sulfur..... | 6.1 |
| 14 5 DCPD modified sulfur..... | 19.5 |
| 6 2 DCPD modified sulfur..... | 17.5 |
| 6 2 DCPD, 1/2 DP modified sulfur..... | 12.7 |
| 6 2 DCPD, 1 DP modified sulfur..... | 11.6 |

The modifiers were 2 and 5 pct dicyclopentadiene and mixtures of 2 pct dicyclopentadiene with 1/2 and 1 pct dipentene.

The percentage gain in compressive strength was highest for concretes made with the 5 pct dicyclopentadiene modified sulfur blends, and lowest for the unmodified sulfur concretes.

Sulfur concretes made with modified sulfur and volcanic rock had compressive strengths equal to or less than those made with unmodified sulfur. With limestone rock, the compressive strengths of modified sulfur concretes were equal to or greater than those made with unmodified sulfur. These results indicate that there is a better bonding between sulfur concretes made with limestone aggregate than those made with volcanic type rocks.

In summary, the aging tests in dry and humid conditions have demonstrated the vulnerability of unmodified sulfur concretes to loss of compressive strength and to disintegration on weathering in moist atmospheres. It also demonstrated that the use of modified sulfur prevents compressive strength loss. Less modified sulfur than unmodified sulfur was required as the binding agent to give workable mixes. The cost of the modifier could be offset at least partially by the lower sulfur requirement. The modified sulfur concretes did not develop their maximum compressive strengths as rapidly as unmodified sulfur based on comparison of their initial and 28-day strengths.

Flexural Strength of Sulfur Concrete

A series of tests was made on both the sulfur concrete and modified sulfur concrete using the 10 aggregate blends listed in table 3 to determine their modulus of rupture. Their flexural strengths were determined in accordance with ASTM Method C 78-64 "Flexural Strength of Concrete (Using Simple Beam With Third-Point Loading)" using either 3- by 4- by 16- or 6- by 6- by 30-inch bars of the materials. The modulus of rupture values obtained along with their percentage of the compressive strength values are given in table 8. In general the flexural strengths of the unmodified sulfur concretes compared to their compressive strengths were in the range of what would be expected with regular Portland concretes. The flexural strengths of most of the modified concretes were greater than those of comparable unmodified concretes. The most notable examples of this were the sulfur concretes prepared using 5 pct dicyclopentadiene modified sulfur. These products had flexural strengths of approximately 20 pct of their compressive strengths which was double the values for unmodified concretes. The development of higher flexural strengths in sulfur concretes is important in making sulfur concretes more desirable for structural usage where greater flexural strength is more important than higher compressive strengths.

TABLE 8. - Transverse rupture testing of sulfur concrete

| Blend | Composition, pct ¹ | | | Modulus of rupture | Pct of compressive strength |
|---------|-------------------------------|------|-----|--------------------|-----------------------------|
| | S | DCPD | DP | | |
| 1..... | 38 | - | - | 650 | 10.2 |
| 1..... | 28 | 5 | - | 1,050 | 21.0 |
| 1..... | 28 | 2 | - | 550 | 10.1 |
| 1..... | 26 | 2 | 1/2 | 455 | 9.5 |
| 2..... | 35 | - | - | 375 | 6.3 |
| 2..... | 23 | 5 | - | 575 | 21.9 |
| 2..... | 26 | 2 | - | 750 | 21.2 |
| 2..... | 26 | 2 | 1/2 | 900 | 16.0 |
| 3..... | 30 | - | - | 850 | 11.8 |
| 3..... | 20 | 5 | - | 975 | 17.1 |
| 3..... | 21 | 2 | - | 900 | 15.0 |
| 3..... | 21 | 2 | 1/2 | 1,260 | 18.0 |
| 4..... | 30 | - | - | 750 | 10.3 |
| 4..... | 23 | 5 | - | 950 | 25.4 |
| 4..... | 26 | 2 | - | 1,125 | 17.6 |
| 4..... | 26 | 2 | 1/2 | 800 | 12.4 |
| 5..... | 30 | - | - | 700 | 13.5 |
| 5..... | 20 | 5 | - | 950 | 18.7 |
| 5..... | 24 | 2 | - | 900 | 12.6 |
| 5..... | 21 | 2 | 1/2 | 600 | 10.0 |
| 6..... | 30 | - | - | 565 | 9.4 |
| 6..... | 20 | 5 | - | 675 | 18.2 |
| 6..... | 24 | 2 | - | 750 | 12.2 |
| 6..... | 26 | 2 | 1/2 | 725 | 12.1 |
| 7..... | 26 | - | - | 520 | 9.7 |
| 7..... | 23 | 5 | - | 925 | 15.4 |
| 8..... | 26 | - | - | 430 | 7.2 |
| 8..... | 23 | 5 | - | 1,065 | 18.1 |
| 9..... | 26 | - | - | 430 | 7.5 |
| 9..... | 23 | 5 | - | 925 | 17.2 |
| 10..... | 30 | - | - | 580 | 10.8 |
| 10..... | 23 | 5 | - | 980 | 19.6 |

¹Wt-pct of sulfur in the blends. The sulfur was either unmodified or contained the amounts of dicyclopentadiene (DCPD) and dipentene (DP) as shown.

Modulus of Elasticity

The modulus of elasticity of modified and unmodified sulfur concretes composed of sulfur and 1 to 1 desert sand and volcanic rock as well as sulfur and 1 to 1 desert sand and limestone rock was determined using a Baldwin Universal Test Machine. The modulus values were calculated from strain gage measurements and loads taken from the testing machine when loading the specimens in compression to approximately 50 pct of their ultimate strengths. Specimens, 3 inches in diameter by 6 inches high, were used as shown in figure 6 with the strain gages attached. The modulus values obtained are

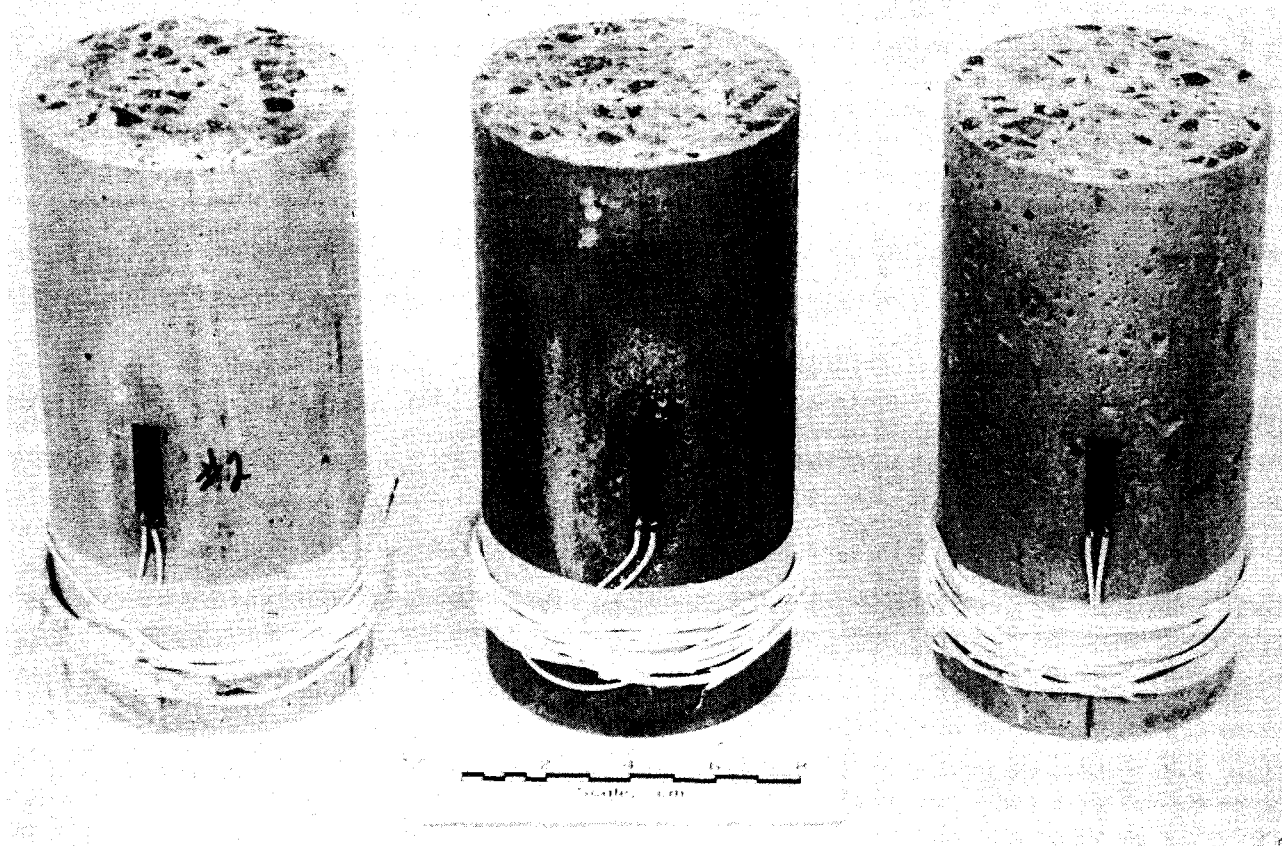


FIGURE 6. - Sulfur concrete cylinders for modulus of elasticity testing.

listed in table 9 and are comparable to published values for Portland cement concretes which normally range from 2 to 6×10^6 psi.

TABLE 9. - Modulus of elasticity of sulfur concretes

| Sample | Aggregate blend | Sulfur content, pct ¹ | Modulus of elasticity, psi $\times 10^6$ |
|--------|-----------------|----------------------------------|--|
| 1..... | 3..... | 30 | 3.9 |
| 2..... | 3..... | 21-2 DCPD, 1/2 DP | 4.1 |
| 3..... | 3..... | 21-2 DCPD | 4.1 |
| 4..... | 7..... | 26 | 4.7 |
| 5..... | 7..... | 21-5 DCPD | 3.7 |

¹The modified sulfur binders contained the indicated amounts of DCPD and DP modifiers.

The stress-strain relationship between unmodified and modified sulfur concretes is quite similar. The materials did not undergo significant yielding before failure. The stress-strain curves for the five types of sulfur concrete are shown in figure 7. Specimen number 5 did not fail within the load capacity (60,000 lb) of the test machine.

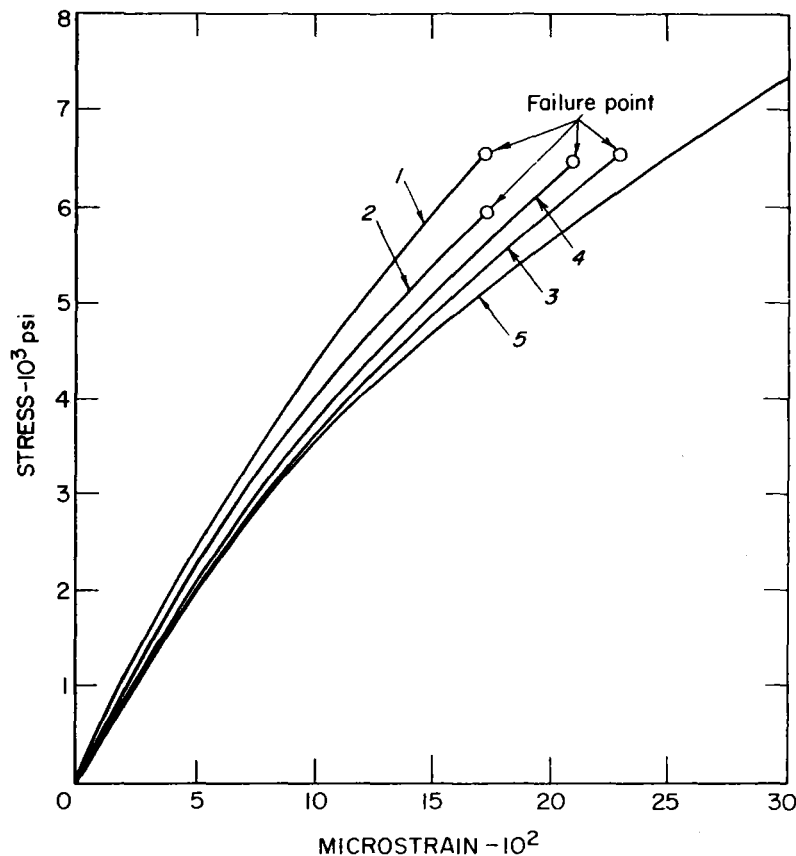


FIGURE 7. - Stress-strain curves for sulfur concretes.

question on whether rapid freeze-thaw cycling is deleterious to sulfur concretes and does not represent freeze-thaw conditions found in nature.

Two methods of freeze-thaw testing have been used in this investigation. The first utilizes six cycles per day in a water-ice media at 40° to 0° F in accordance with ASTM Method C 215-60 "Test for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water." The second method was identical except only one freeze-thaw cycle per day was made. Testing of both modified and unmodified sulfur concretes are still in progress. Results obtained so far show that sulfur concretes made with aggregate blends 1 to 6 all had poor freeze-thaw properties. The vesicular volcanic rock with desert sand and sulfur had the lowest resistance to the freeze-thaw cycling used. Desert blow sand and sulfur mixtures were not as resistant as those of construction sand and sulfur. Modified sulfur used as the binder for these blends improved their durability under freeze-thaw conditions. Using these blends and modified sulfur, the maximum number of freeze-thaw cycles before failure was 60 cycles.

Blends of desert sand or construction sand with dense limestone aggregate (blends 7 to 10) gave concretes with improved freeze-thaw properties. The best freeze-thaw resistance was for blend 9 with 26 pct sulfur; blend 9 with 23 pct sulfur modified with 5 pct dicyclopentadiene; and blend 10 with 23 pct sulfur modified with 5 pct dicyclopentadiene. Using six freeze-thaw cycles

Freeze-Thaw Testing of Sulfur Concretes

The ability of sulfur concrete to withstand freezing and thawing conditions has been measured by various methods. Beaudoin and Sereda used a freezing cycle of 6 hours in air at 0° F and a thawing cycle of 6 hours in water at 45° F in testing a large number of concretes made with sulfur and sands (3). They also tested some samples by freezing in air to minus 10° F for 16 hours and thawing for 8 hours at 70° F. Malhotra used eight freeze-thaw cycles per day in accordance to ASTM Method C 661-71 in testing sulfur concretes (18). He suggested additional work be done on slow freeze-thaw cycling in testing sulfur concretes, because of the

per day, these three blends went 165 cycles before failure. Results of testing using one freeze-thaw cycle per day in water gave similar results. In general, the use of modified sulfur as the binder improved the freeze-thaw properties of sulfur concretes made with aggregate blends 7 to 10. Blend 9, composed of construction sand and limestone rock, had the greatest durability of the unmodified sulfur concretes.

LARGER SCALE AND FIELD TESTING

Preparation of Sulfur Concrete Beams

As a means of determining potential problems when multiple pours of the sulfur concrete are made in practice, beams 6 by 6 by 30 inches were cast in one and four lifts. Aggregate blend 8 composed of 2 to 1 desert blow sand and 3/8-inch limestone rock was used with sulfur and modified sulfur as the binders. The beams poured with four lifts were allowed to solidify between additions of the next batch of sulfur concrete. Flexural strength determinations and compressive strength measurements were made on the beams, after aging 1 month, in accordance with ASTM Methods C 78-64 and C 116-49, respectively. The results listed in table 10 are the average of two determinations. Beams from test number 2 made with multiple lifts of unmodified sulfur concrete showed an indication of layering at the pour junctions on the fractured specimens. This was similar to the results reported by Loov (15). There was no indication of layering on the fractured surface of the beams from tests 4 and 6. The unmodified sulfur concrete beams poured in multiple lifts had slightly lower modulus of rupture values than the beams made with one pour. Slightly higher flexural strengths were obtained with multilift beams made with modified sulfur compared to single lift beams. Higher flexural strengths were obtained with the beams made with the 5 pct dicyclopentadiene modified sulfur.

TABLE 10. - Sulfur concrete beam data

| Test | Composition | | Type beam, pours | Modulus of rupture, psi | Compressive strength, psi ² | |
|-------|-------------|--------------------------|---------------------|----------------------------|---|-------|
| | Blend | Sulfur, pct ¹ | | | S | T |
| | | | | | 1.... | 8 |
| 2.... | 8 | 26 | 4 | 535 | 6,530 | 5,410 |
| 3.... | 8 | 23-5 DCPD | 1 | 920 | 6,180 | 6,090 |
| 4.... | 8 | 23-5 DCPD | 4 | 1,025 | 6,320 | 5,470 |
| 5.... | 8 | 23-2 DCPD | 1 | 800 | 7,440 | 5,610 |
| 6.... | 8 | 23-2 DCPD | 4 | 835 | 7,140 | 5,070 |

¹The wt-pct of dicyclopentadiene used in modifying the sulfur is 2 and 5 DCPD.

²Compressive strength values: S = side loading; T = top loading.

Based on the results obtained in these tests, there should be no problems in making multiple pours of modified sulfur concretes. Unmodified sulfur concrete beams had a tendency to layer at the junction of the lifts and delamination might be a problem.

Sulfur Concrete Slab

A 4-inch thick, 3- by 7-foot slab of modified sulfur concrete was poured in the service entryway of the laboratory building. The concrete was mixed in the heated mortar mixer using aggregate blend 9 (1 to 1 construction sand and 3/8-inch limestone rock) and 23 pct sulfur modified with 5 pct dicyclopentadiene. Three batches of mix were required and samples were taken from each batch for 3- by 6-inch compressive strength cylinders and 3- by 4- by 16-inch flexural strength bars. The average compressive strengths of the slab was 3,880 psi, modulus of rupture was 1,050 psi, specific gravity was 2.318, and the void content was 4.88 pct. The slab is shown in figure 8, and after 11-month service it has shown no signs of cracking or deterioration.

Sulfur Concrete Wall Sections

An 18-foot retaining wall was built of sections composed of six different blends of both modified and unmodified sulfur concrete to determine the behavior of the materials under weathering conditions typical of desert climates. The wall consisted of six footer sections (3- by 1.5- by 1-foot in depth) and six-wall sections (3- by 3-foot and 8 inches in thickness) and both were poured using reinforcing steel to meet city building code specifications.



FIGURE 8. - Sulfur concrete paving slab.

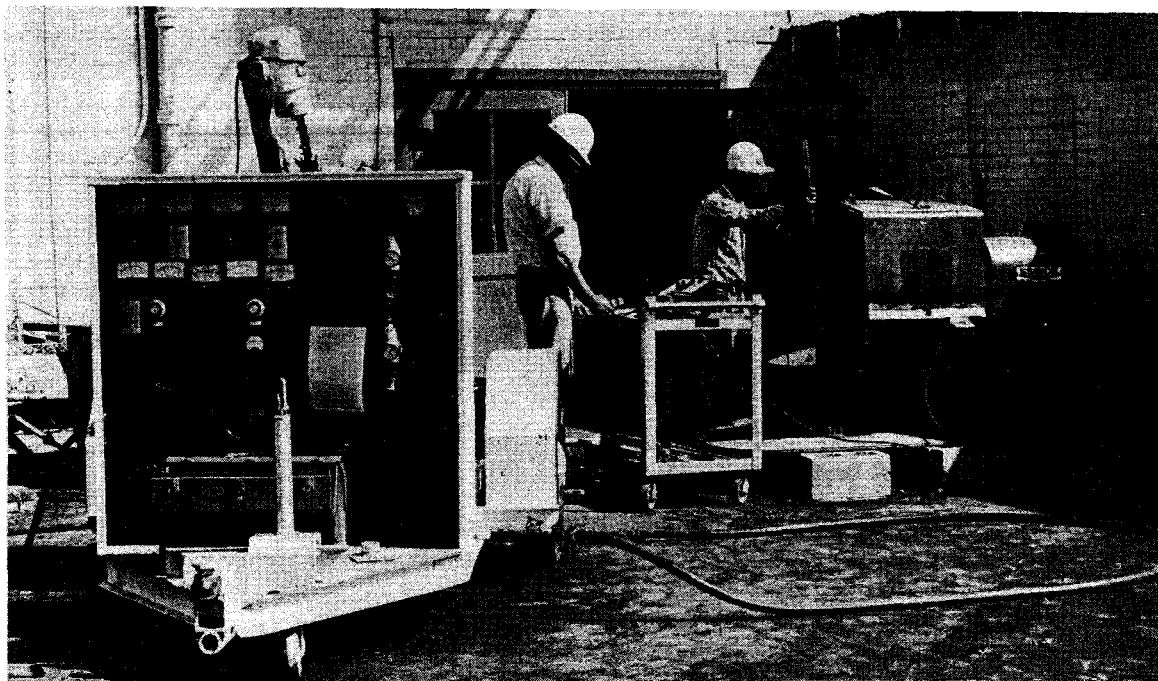


FIGURE 9. - Equipment for mixing sulfur concrete.

Each section consisted of a footer and a wall made with the same blend of sulfur concrete. The material was mixed in the heated mortar mixer shown in figure 9. Three batches of 300 lb each were used in each wall. Samples for strength determination were taken from each batch. Figure 10 shows the pouring of the second section footing with the reinforcing steel for both footer and wall in place. Footers were poured on one day and the wall section was poured the following day. The footers were poured next to each other without an expansion joint, but a 2-inch gap was left between each wall section for inspection purposes. After completion of this work, the back side of the retaining wall was filled and the footers were covered. The completed sections are shown in figure 11. The aggregate blends and the sulfur used are shown in table 11 along with averaged test values obtained for each wall section. From the data it is evident that the sulfur concretes have strength properties equal to or better than Portland cement concretes.

TABLE 11. - Sulfur concrete wall demonstration, test data

| Wall section | Composition | | Specific gravity | Voids, pct | Compressive strength, psi | Modulus of rupture | | Tensile strength | |
|--------------|-------------|-------------|------------------|------------|---------------------------|--------------------|------------------|------------------|------------------|
| | Blend | Sulfur, pct | | | | Psi | Pct ¹ | Psi | Pct ² |
| 1..... | 9 | 23-5 DCPD | 2.338 | 4.88 | 4,340 | 820 | 18.9 | 845 | 19.5 |
| 2..... | 7 | 23-5 DCPD | 2.460 | 4.10 | 5,735 | 935 | 16.3 | 860 | 15.0 |
| 3..... | 5 | 23-5 DCPD | 2.316 | 3.05 | 4,756 | 1,115 | 23.4 | 860 | 18.1 |
| 4..... | 3 | 23-5 DCPD | 2.367 | 1.00 | 5,645 | 1,345 | 23.8 | 940 | 16.7 |
| 5..... | 5 | 27 | 2.366 | 1.29 | 6,320 | 765 | 12.1 | 875 | 13.8 |
| 6..... | 9 | 26 | 2.441 | 1.49 | 6,320 | 785 | 11.8 | 790 | 11.9 |

¹Modulus of rupture expressed as percentage of compressive strength.

²Splitting tensile strength expressed as percentage of compressive strength.



FIGURE 10. - Pouring sulfur concrete footer.

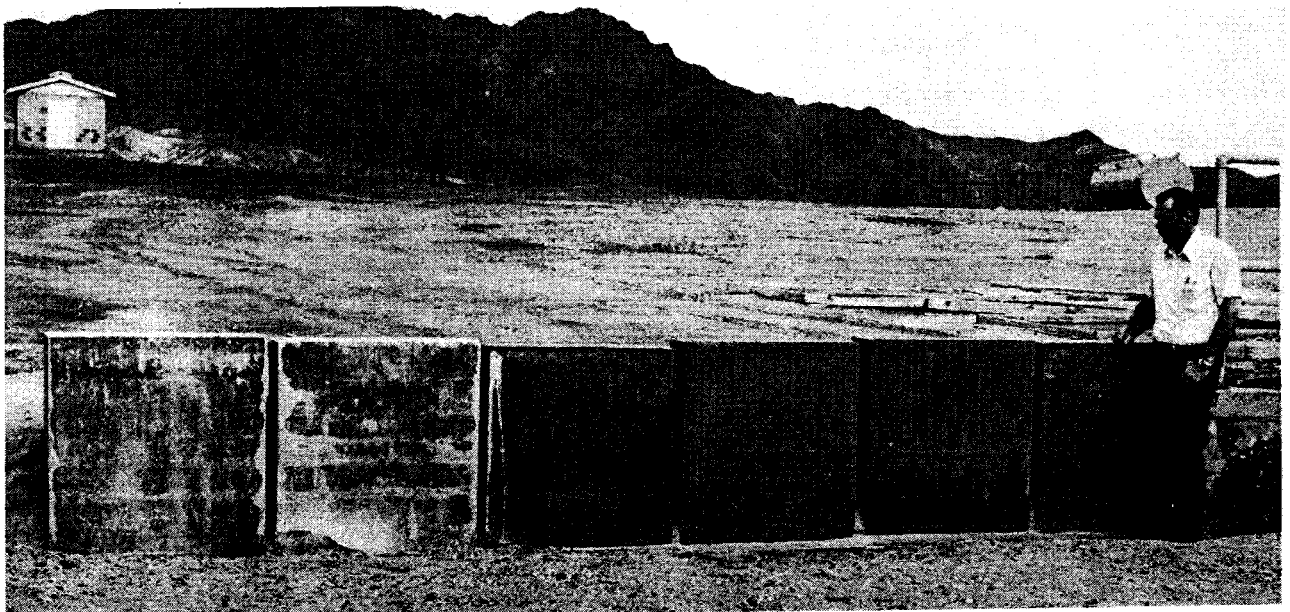


FIGURE 11. - Retaining wall of sulfur concrete sections.



FIGURE 12. - Unmodified sulfur concrete wall section.

All of the sections of modified concrete are sound after 8 months of exposure. Section No. 5, composed of volcanic rock, construction sand, and unmodified sulfur cracked 3 days after pouring. The other concrete section of limestone, construction sand, and unmodified sulfur cracked after 6 months of exposure. The wall part of No. 5 is shown in figure 12 illustrating the cracking that can take place when unmodified sulfur concrete is used. The wall sections will be monitored to observe any further effects of weathering on their stabilities.

CONCLUSIONS

The use of modified sulfur as the binder in sulfur concretes has solved some of the problems associated with these concretes such as cracking and disintegration caused by temperature fluctuation and weathering. The optimum mix design, based on compressive strength, for both modified and unmodified sulfur concretes was dependent on the type of aggregate, voids content and size of aggregate mixture, and the amount of sulfur used to prepare modified concretes with about 5 pct voids and unmodified concretes with 1.5 pct voids.

The compressive strength of sulfur concretes can be tailored to required specifications by choice of aggregates and mix design. The use of modified sulfur binders for volcanic rock aggregate produce concretes with equal or lower compressive strengths than those with sulfur binders. In contrast, limestone aggregates bonded with modified sulfur resulted in materials with equal or higher compressive strength values compared to unmodified sulfur binders.

The flexural and tensile strength values of modified sulfur concretes compared to their compression strength were higher than those of sulfur concretes. The flexural strengths ranged from 18 to 25 pct of their compressive strength for modified concretes. This compares to a range of 10 to 15 pct for sulfur concretes and Portland concretes. This same relationship held true for tensile strengths of the three types of concrete.

The modulus of elasticity values for both modified and unmodified sulfur concretes was in the area of 4×10^6 psi which is similar to the value for normal Portland concretes.

A new test method was developed for determining the weatherability of sulfur concretes which was based on the change of compressive strength of test cylinders on aging in a humid atmosphere. All samples of unmodified sulfur concretes tested had lower compressive strengths or disintegrated completely over a period of 4 weeks. Modified sulfur concretes tested under the same conditions gained in compressive strength.

The freeze-thaw resistance of modified and unmodified sulfur concretes is still being investigated. Preliminary results indicate that some blends of each have resistance to the effects of freeze-thaw cycling equivalent to or better than normal Portland concretes.

A further study of methods of testing freeze-thaw properties of sulfur concrete is needed to establish a standard procedure for evaluating these products. More information is necessary on the influence of types of sand and aggregate used, the effects of fast and slow freeze-thaw cycling times, and the influence of freezing and thawing in air or in water on the freeze-thaw properties of sulfur concretes.

Larger scale testing has shown that modified sulfur concrete beams can be prepared by pouring in lifts with good bonding between lifts. Slightly higher flexural strengths were obtained in beams poured in four lifts compared with similar beams poured in one lift. Unmodified sulfur concretes poured in lifts did not bond as well between lifts and were susceptible to delamination. Concrete retaining wall sections were constructed of optimal blends of four types of modified sulfur concretes and two types of unmodified sulfur concretes to investigate their durability on exposure to temperature cycling and weathering. Both sections of unmodified sulfur concrete have cracked while the remaining four sections are sound after 8 months in service.

A modified sulfur binder prepared by reacting 5 pct dicyclopentadiene with sulfur was successfully used to prepare sulfur concretes that were resistant to loss of strength on exposure to moisture and temperature cycling. Further investigation is needed on the long-term aging properties of both modified and unmodified sulfur concretes.

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