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Corrosion-Resistant Sulfur Concretes

By William C. McBee, Thomas A. Sullivan,
and Bing W. Jong



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8758

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

° C	degree centigrade	min	minute
cp	centipoise	pct	percent
ft	foot	ppm	part per million
ft ²	square foot	psi	pound per square inch
hr	hour	sec	second
in	inch	t/day	ton per day
in/hr	inch per hour	t/hr	ton per hour
in/in ° C	inch per inch per degree centigrade	wt-pct	weight-percent
lb	pound		

CORROSION-RESISTANT SULFUR CONCRETES

By William C. McBee,¹ Thomas A. Sullivan,² and Bing W. Jong³

ABSTRACT

Sulfur concretes have been developed by the Bureau of Mines as construction materials with physical and mechanical properties that suit them for use in acid and salt corrosive environments where conventional concretes fail. Mixture design methods were established for preparing sulfur concretes using different types of aggregates and recently developed mixed-modified sulfur cements. Bench-scale testing of the sulfur concretes has shown their potential value. Corrosion resistance, strength, and durability of sulfur concrete are superior to those of conventional materials. Field in situ evaluation tests of the sulfur concretes as replacement for conventional concrete materials are in progress in corrosive areas of 24 commercial chemical, fertilizer, and metallurgical plants.

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INTRODUCTION

The Bureau of Mines sulfur utilization project was conceived in 1972 to develop new uses for sulfur. A large increase in byproduct sulfur production was expected to start in the 1980's from sour gas, petroleum refining, utilization of coal as an alternate energy source, and control of air pollution sources, such as emissions from smelters and powerplants (23).⁴

The project was implemented to find new uses for sulfur in materials of construction and to take advantage of an abundant domestic commodity which had the possibility of replacing energy-intensive and imported products. Asphalt obtained from Middle Eastern crude oil is a good example. The utilization of sulfur as an extender for asphalt and in the recycling of old asphaltic pavements in the asphalt paving industry has been demonstrated (10-12, 14).

Another potential area for utilizing sulfur in construction materials is as a binder for aggregate in concrete. Sulfur concrete materials can be prepared with excellent strength properties (5, 8). The historical development of sulfur concrete materials was described by Raymont (19), and the present state-of-the-art of sulfur concrete materials was reported by The Sulphur Institute (17). While sulfur concrete materials made using unmodified sulfur have good initial strength characteristics, their durability and life in

commercial applications have frequently proven unsatisfactory. Many of the failures are related to the thermal history and handling of elemental sulfur. Davis (6) describes how the thermal expansion of unmodified sulfur varies with the rate of cooling and age. The use of bond-altering agents with sulfur has been reported by Shrive as a method of producing "ductile" sulfur concrete (21); however, use of these agents does not appear to alter the expansion variation noted by Davis. Previous Bureau of Mines research in the development of specialized sulfur concrete materials (5, 9, 13, 22) was directed toward solving the durability problems associated with unmodified sulfur concrete materials. Development of modified-sulfur cements (13) for sulfur concrete products with improved properties has led to the preparation of good-quality sulfur concrete materials with excellent resistance to salt and acid corrosive environments.

The technology developed for the production of stable sulfur cements and mixture designs for preparing sulfur concrete products will be discussed. These second-generation cements and concretes are amenable to commercial-scale production and have exhibited excellent durability in more than 3 years of in situ testing in corrosive environments in commercial plants. The sulfur concretes described are "rigid" types similar to portland cement concretes.

ACKNOWLEDGMENT

The assistance of Harold Fike of The Sulphur Institute in the industrial evaluation of sulfur concretes is gratefully acknowledged, as are differential scanning calorimetry examination by

Arthur Petty, supervisory ceramic engineer, at the Bureau of Mines Tuscaloosa (Ala.) Research Center, and stress-strain determinations and carbon, sulfur, and hydrogen analysis by Mike Burrus, engineering technician, and Dean Bollman, research chemist, at the Bureau of Mines Albany (Oreg.) Research Center.

⁴Underlined numbers in parentheses refer to items in the list of references at the end of this report.

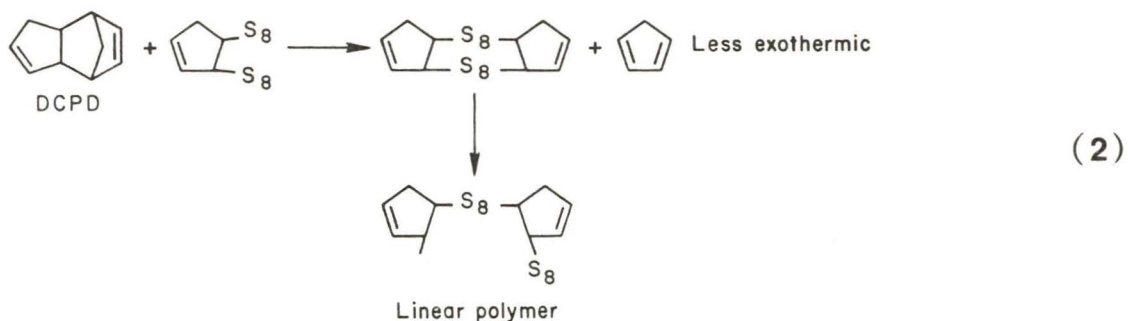
MODIFIED-SULFUR CEMENTS

In earlier work, commercial-grade dicyclopentadiene (DCPD) was used in the preparation of sulfur cement; the sulfur cements described in this report were developed to eliminate problems in the preparation of DCPD-modified-sulfur cement and to improve the durability of concretes prepared with them (13). The

chemistry of the reaction between sulfur and DCPD has been described by Bordoloi (4). DCPD will spontaneously depolymerize to cyclopentadiene (CPD) at the reaction temperature for polymerization with sulfur (120° to 140° C) and results in the highly exothermic reaction 1:



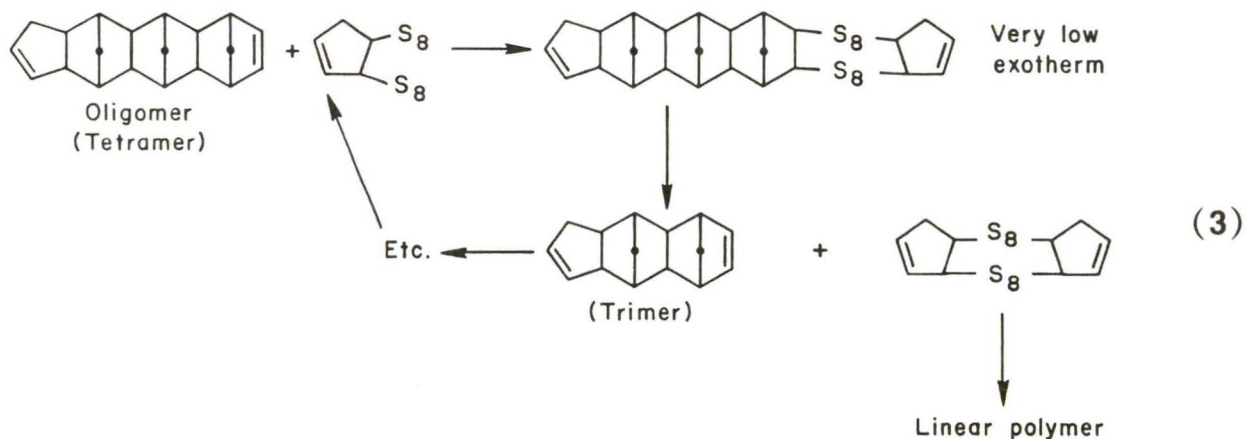
The DCPD in the reaction mixture reacts with the polysulfide product formed in 1, as shown in reaction 2:



When sulfur reacts with DCPD to form long-chain linear polymers, the reaction temperature must be carefully controlled at approximately 120° C to prevent a runaway exothermic reaction. Commercially it is believed to be impossible to prepare DCPD-modified-sulfur cement with specific properties, such as viscosity, that do not vary from batch to batch. If the DCPD-modified-sulfur cement is maintained in the liquid state, the chemical reaction between sulfur and DCPD continues with a corresponding increase in the

viscosity of the material. When using DCPD-modified-sulfur cement to prepare concrete, close control of the aggregate temperature and mixing temperature is necessary to prevent further exothermic reaction between the sulfur and DCPD which occurs above 140° C and results in a viscous unworkable mass of concrete.

A mixed-modifier system was developed to moderate the polymerization reaction between sulfur and the modifiers, as shown in reaction 3:



By reacting sulfur at 130° to 150° C with a 5-wt-pct mixture of DCPD and a cyclopentadiene oligomer product, hereafter referred to as oligomer, stable modified-sulfur cements were routinely prepared. The cements can be prepared with reproducible viscosity properties and are less thermosensitive in the temperature ranges used in preparing both the cement and concrete. The oligomer products are obtained from the commercial production of DCPD resins, as steam sparge oils, and contain less than 5 pct CPD. Major oligomer components are approximately 10 pct dimer, 10 pct trimer, 20 pct tetramer, 45 pct pentamer, and 10 pct higher polymers. While different proportions of DCPD and oligomer have been used to prepare modified-sulfur cements, the best results were obtained with a 5-wt-pct mixture of 50 pct DCPD and 50 pct oligomer. Unless otherwise indicated, the sulfur concrete properties in this report will be those of concretes prepared using this modified-sulfur cement and indicated as 50-50 cement.

Differential scanning calorimetry (DSC) thermograms for sulfur and modified-sulfur cements are shown in figure 1. The thermograms were made on samples aged for 14 months at ambient temperature. The 50-50 cement (B) remained in the monoclinic phase $S\beta$. The DCPD-modified cement (C), originally in the $S\beta$ phase, was transformed to the orthorhombic phase $S\alpha$, similar to unmodified sulfur (A). A DSC thermogram on the 50-50 cement (B) after 21 months of aging was identical to the 14-month curve. These results show that the 50-50 cement does not undergo a rapid phase transformation from $S\beta$ to $S\alpha$ on solidification, and durability of sulfur concretes made with the 50-50 cement will be improved by eliminating internal stress caused by the phase transformation.

Thermal expansion measurements were made in the solid state on samples of elemental sulfur and 50-50 cement freshly prepared and aged 1 month before testing. The linear thermal expansion of the materials with increasing temperature is shown in figure 2. Sulfur goes through a

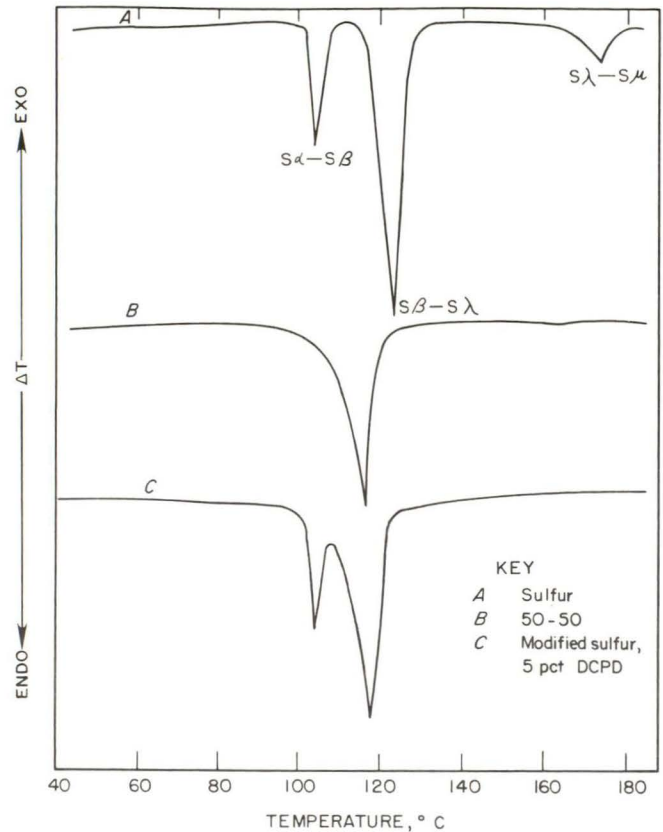


FIGURE 1. - Differential scanning calorimetry (DSC) thermograms for sulfur cements after 14 months of aging.

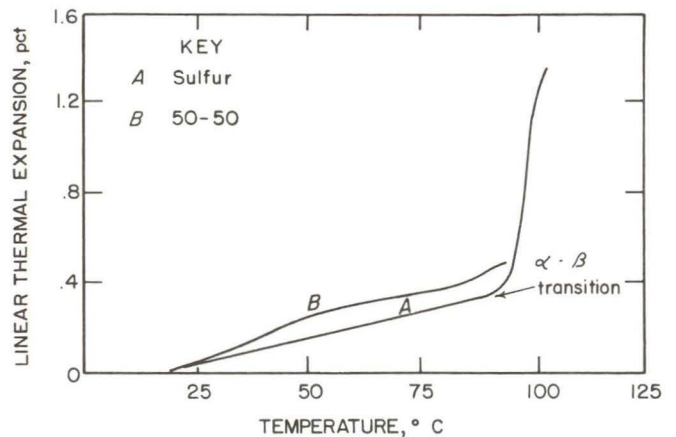


FIGURE 2. - Linear thermal expansion data for sulfur and sulfur cement.

$S\alpha$ to $S\beta$ transformation with a rapid increase in volume. The 50-50 cement was heated to its softening point and did not go through the $S\alpha$ to $S\beta$ transition. For unmodified-sulfur cement, a 13-pct volume contraction occurs on solidification of

the liquid and through the $S\beta$ to $S\alpha$ transformation. Since the stable $S\alpha$ phase is more dense and occupies less volume (6 pct) than the solid $S\beta$ phase first formed on solidification, there is a resultant stressing of the sulfur binder in the solid state. The 50-50 cement does not go through this allotropic transition on solidification. Its expansion or contraction is approximately one-third that of unmodified-sulfur cement and results in less shrinkage of the sulfur concrete and less stressing of the binder. The thermal expansion coefficients of the two materials are given in table 1.

TABLE 1. - Thermal expansion coefficients of sulfur cements

Sulfur cement	Thermal expansion coefficient, 10^{-6} in/in $^{\circ}$ C
Sulfur:	
25 $^{\circ}$ to 95 $^{\circ}$ C.....	46
95 $^{\circ}$ to 108 $^{\circ}$ C.....	1,000
50-50 cement: 25 $^{\circ}$ to 100 $^{\circ}$ C.....	59

The composition and properties of the 50-50 cement prepared by reacting sulfur with DCPD and oligomer at 145 $^{\circ}$ C for 6 hr has been determined. A typical analysis is shown in table 2.

TABLE 2. - Composition and properties of 50-50 cement

Composition or property	Value
Sulfur.....pct..	94.8
Carbon.....pct..	4.4
Hydrogen.....pct..	0.45
Viscosity at 135 $^{\circ}$ C.....cp..	50
Specific gravity.....	1.8999

As with portland cement concrete (PCC) and asphaltic concrete (AC), the optimum mixture design for sulfur concretes must take into consideration the properties desired for specific uses. Just as certain bag mixes, water content, and aggregate proportions are used for PCC to obtain specific strength properties, the

The 50-50 cements are being produced on a commercial scale (approximately 50 t/day) by Chemical Enterprises, Inc., at Odessa, Tex. The commercial reactor system is similar in design to the 500-lb pilot-scale reactor used in the initial development research (13).

The system at the Chemical Enterprises plant consists of two steam-heated reactor units, each with a capacity of 9 tons of molten sulfur. One reactor is located above the other, with the upper one discharging into the lower. Both units are equipped with stirrers to agitate the molten sulfur. Sulfur at 140 $^{\circ}$ C is pumped from a storage tank into the top reactor, and the chemical modifier mixtures are injected under the surface of the sulfur in the vicinity of the vortex formed by stirring. A 2-hr retention time is sufficient in the top reactor to mix the sulfur and modifiers and initiate the reaction. Reactants are discharged into the bottom reactor for approximately 2 additional hours to complete the reaction. The temperature in both reactors is maintained at 140 $^{\circ}$ \pm 5 $^{\circ}$ C.

Upon completion of the reaction, the modified sulfur is pumped from the bottom reactor to a storage tank which feeds the product onto dual Sandvik belt flaking machines. The solidified, water-cooled 1/16-in sheet of material falls off the end of the belt and is chopped and screened into 1/8-in-diameter flakes. Fines from the screening operation are recycled to the lower reactor. Flaked material is stored in a bin prior to packaging in 50- to 3,000-lb bags. While a dual-reactor system was used because of the plant layout, a single reactor could be used to prepare the 50-50 cement.

MIXTURE DESIGN

strength properties of sulfur concrete are influenced by the amount and types of sulfur cement binder and the type of aggregate gradation. The mixture designs for sulfur concrete materials are suitable for construction of floors, foundations, tiles, sumps, and electrolytic cells in acid or salt environments.

These uses require materials with good mechanical strength properties, chemical resistance, minimum moisture absorption, and durability.

AGGREGATE GRADATION

Aggregates are obtained from two sources. One source is sand and gravel deposits produced by natural weathering and abrasion from running water; these aggregates consist primarily of silica. The second source is quarried rock which is crushed and screened; stone quarry products include limestone, granite (all coarse-grained igneous rock), traprock (all-fine grained igneous rock), and sandstone. Aggregates for corrosion-resistant sulfur concretes must be clean, hard, tough, strong, durable, and free from any swelling constituents. In addition, they must resist chemical attack and absorption from exposure to acid and salt solutions. Moisture absorption and

acid dissolution losses should not exceed 1 pct. The highest quality concretes produced have been formulated with a homogeneous source of mineral aggregate. In developing mixture designs for sulfur concrete, aggregates with chemical resistance consistent with their use must be selected. For example, in acidic environments quartz aggregates are suitable, whereas either quartz or limestone aggregates may be used where salt corrosion is the problem.

In previous work, aggregate gradations, shown in figure 3, that were suitable for PCC were used in preparing sulfur concretes (9). These materials had excellent corrosion resistance and mechanical properties where sufficient binder was used to fill the voids in the mineral aggregate. Disadvantages of this gradation were the large amount of binder required (22 to 26 wt-pct) and the amount of shrinkage upon cooling and solidification

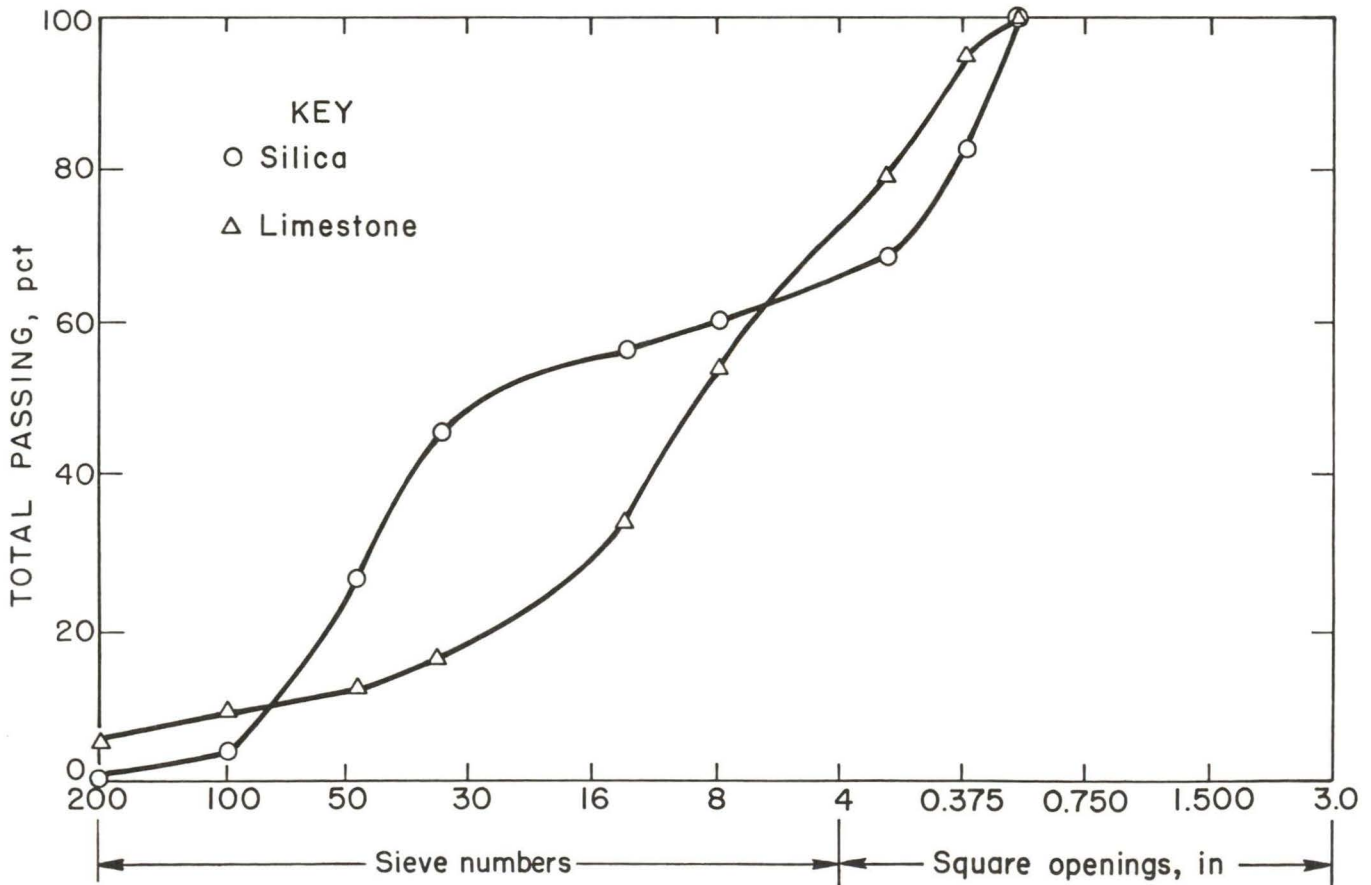


FIGURE 3. - Aggregate gradation curves, open-graded.

of the concrete. Crushed aggregates produced superior-strength sulfur concretes compared with rounded sand and gravel aggregates. The sulfur concrete properties referred to in this report are for sulfur concrete made with crushed aggregates.

Mechanisms involved in preparing sulfur concretes are different from those of portland cement concretes (PCC). Sulfur concrete is a thermoplastic material which is mixed and cast hot and solidifies upon cooling to ambient temperatures. The liquid sulfur binder on solidification binds the aggregate together and forms rigid sulfur concrete. PCC is prepared at ambient temperatures and relies on a chemical hydration reaction to form the concrete.

New aggregate gradation designs for sulfur concrete were developed based on technology for another thermoplastic material, AC. The gradation design was aimed at developing aggregate mixtures with maximum density and minimum voids in the mineral aggregate (VMA). With this design, less sulfur would be required to fill the voids in the aggregate mixture. In most cases, this results in higher strength materials because of improved aggregate contact and in less shrinkage on solidification because of decreased sulfur binder requirements.

Suitable aggregate gradation designs for sulfur concretes were achieved based on Fuller maximum density curves (3), shown in figure 4, for materials having a

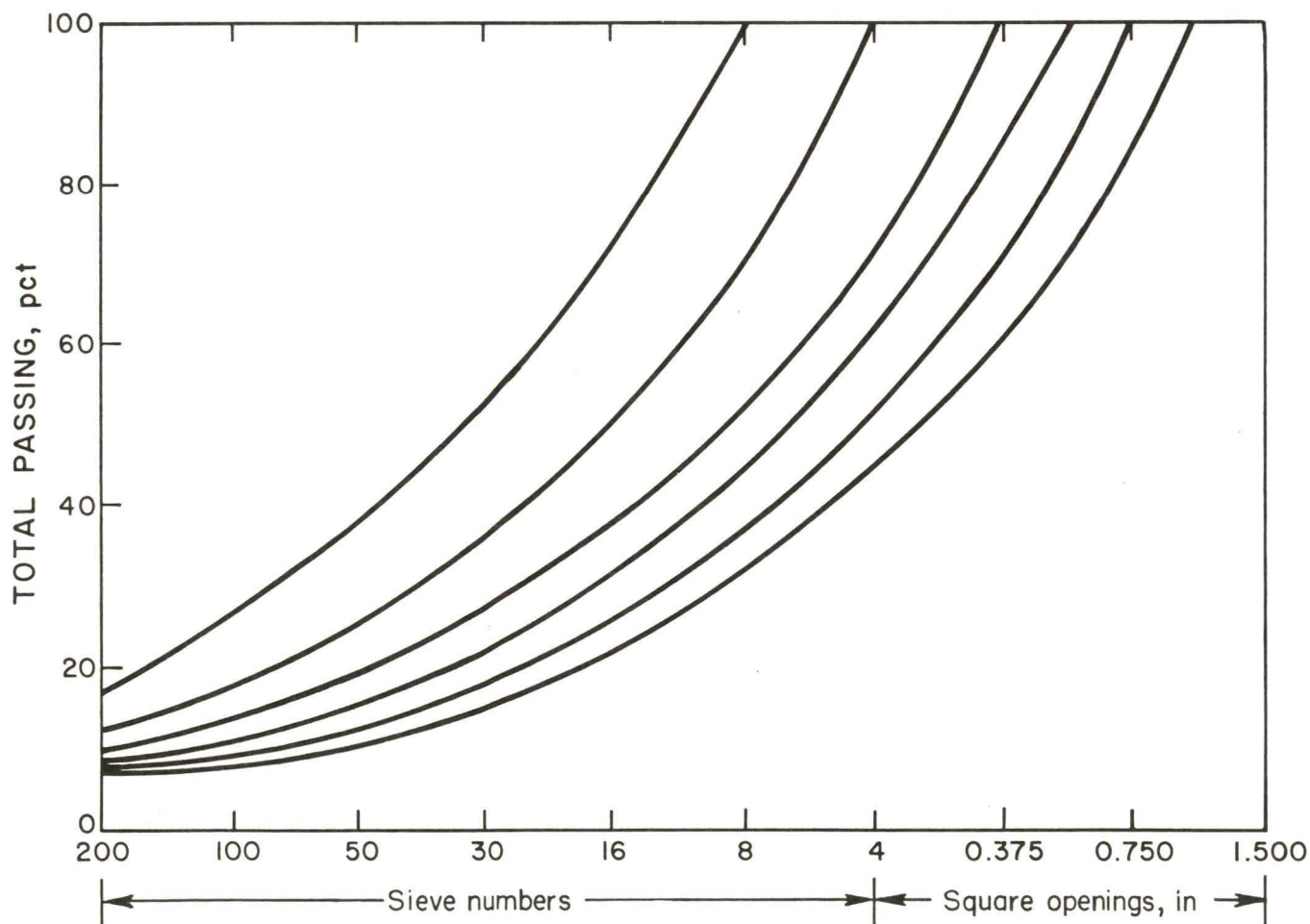


FIGURE 4. - Aggregate gradation curves, dense-graded.

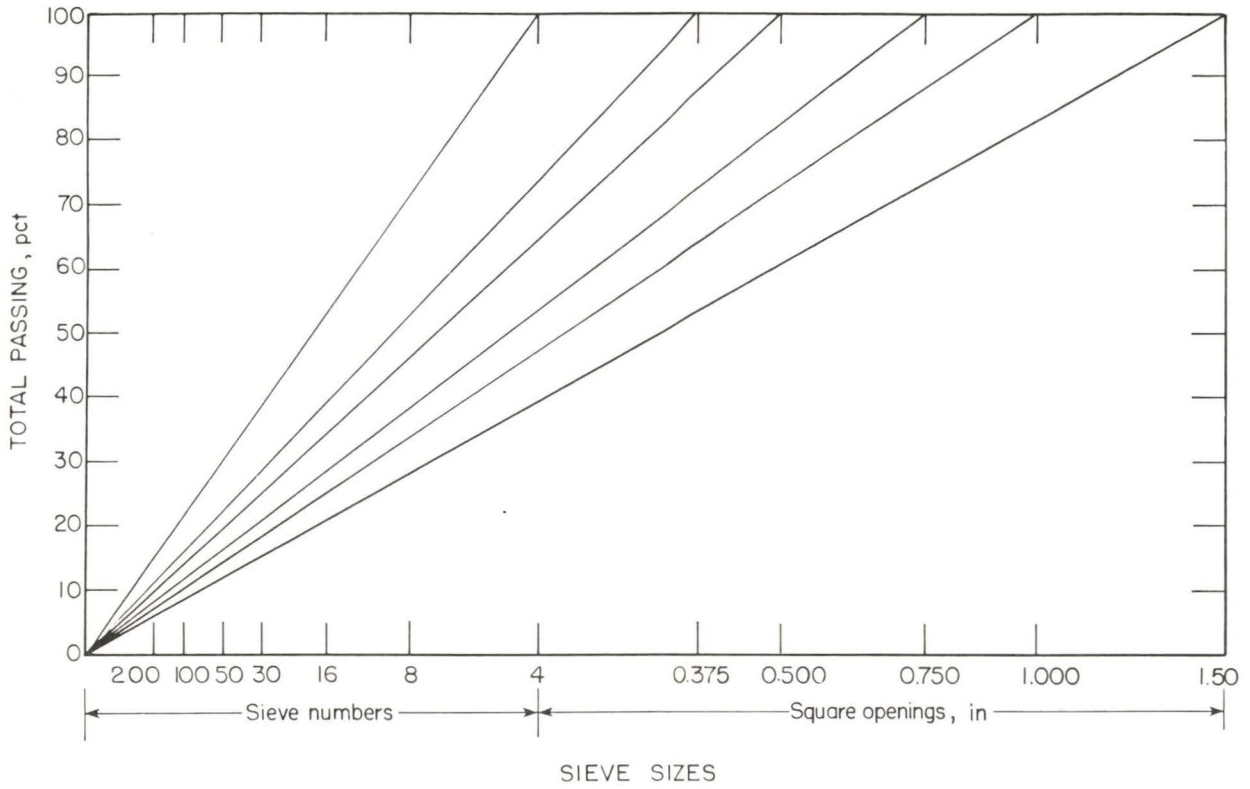


FIGURE 5. - Maximum density curves on Federal Highway Administration 0.45-power gradation chart.

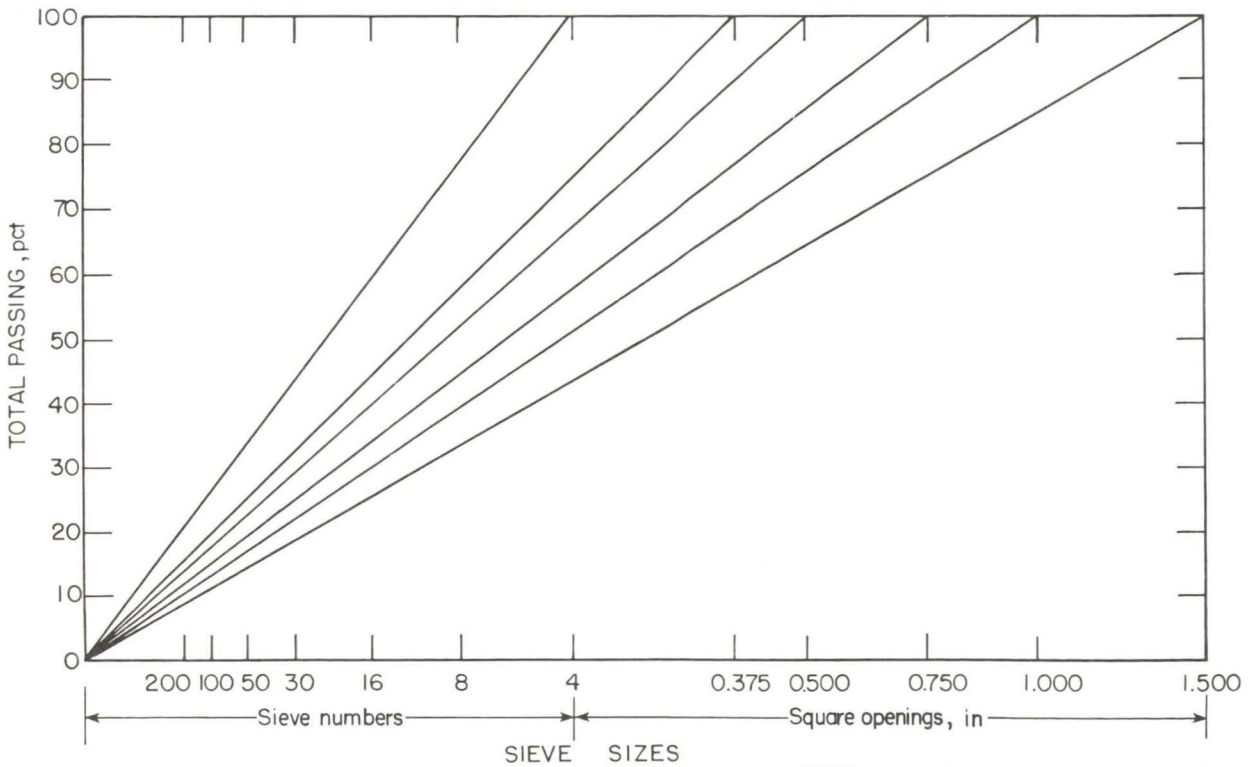


FIGURE 6. - Maximum density curves on a 0.40-power gradation chart.

maximum size ranging from 8 mesh to 1 in. The Fuller maximum density relationship

$$P = 100 \left(\frac{d}{D} \right)^{0.5},$$

where P = total percent passing given sieve,

d = size of sieve opening,

and D = largest size (sieve opening) in gradation,

was used as the starting point for designing optimum sulfur concrete aggregate gradations. The Asphalt Institute reported (3) that better aggregate gradations for AC were obtained with the Fuller maximum density relationship raised to the 0.45 power instead of the 0.5 power and plotted on the Federal Highway Administration's 0.45-power gradation curve shown in figure 5. The main difference was a higher proportion of fines in the gradation.

For sulfur concretes, an optimum aggregate gradation was developed with the Fuller maximum density relationship raised to the 0.4 power instead of the 0.5 power. A 0.4-power gradation chart (fig. 6) was developed for use in dense-grading aggregates for sulfur concretes. Good-quality sulfur concretes have been prepared with aggregate gradation ranges between the 0.4- and 0.5-power gradation curves.

BINDER REQUIREMENTS

The role of the modified-sulfur cement binders in corrosion-resistant sulfur concrete technology is threefold: (1)

They bond together the aggregate particles, (2) they fill the voids in the mineral aggregate to minimize moisture absorption, and (3) they provide sufficient fluidity in the mix to give a workable sulfur concrete mixture.

In previous work (9), when sulfur cements containing 5 wt-pct modifier were used to prepare sulfur concretes, less binder was required to fill the voids in the mineral aggregate than was required for an unmodified-sulfur binder. Since modified-sulfur cements are more viscous than sulfur, when they are mixed with aggregate, 4 to 8 pct air voids are entrained in the binder, increasing the volume. The entrained air occurs as discrete bubbles which are not interconnected; thus, the moisture absorption into the material is negligible. This is in contrast to portland cement concrete, which forms interconnected voids that increase susceptibility to absorption and decrease resistance to corrosion and freeze-thaw damage.

To obtain corrosion-resistant sulfur concrete with good strength and durability, the mix is designed for moisture absorption less than 0.1 wt-pct and preferably below 0.05 wt-pct. Criteria used to determine the optimum mix design are based on adjusting the binder level to provide the best balance between maximum compressive strength, maximum specific gravity, minimum absorption, and a workable mixture. To illustrate the development of a mix design, properties obtained by varying the sulfur and 50-50 cement contents using 3/8-in dense-graded quartz and limestone aggregates are given in table 3.

TABLE 3. - Mixture design data for sulfur concretes using 3/8-in dense-graded aggregates

Aggregate, wt-pct	Binder, wt-pct	Specific gravity	Voids, wt-pct	Compressive strength, psi	Absorption, wt-pct	Workability
QUARTZ AGGREGATE--SULFUR CEMENT						
90.0	10.0	2.1329	16.6	830	5.75	Dry.
87.5	12.5	2.2449	11.7	1,500	1.93	Dry.
85.0	15.0	2.3531	6.9	5,740	.60	Stiff.
82.5	17.5	2.4183	3.7	7,710	.08	Fluid.
80.0	20.0	2.4238	2.9	7,640	.03	Soupy.
QUARTZ AGGREGATE--50-50 CEMENT						
90.0	10.0	2.2087	13.7	2,960	1.06	Dry.
87.5	12.5	2.2971	9.7	6,100	.54	Dry.
85.0	15.0	2.3695	6.2	7,360	.07	Stiff.
82.5	17.5	2.3725	5.5	7,455	.02	Fluid.
80.0	20.0	2.3664	5.1	6,530	.01	Soupy.
LIMESTONE AGGREGATE--SULFUR CEMENT						
88.0	12.0	2.2809	14.5	1,560	2.41	Dry.
86.0	14.0	2.3227	13.2	2,570	1.46	Dry.
84.0	16.0	2.3756	10.0	3,690	.58	Stiff.
82.0	18.0	2.3868	9.1	4,270	.49	Do.
80.0	20.0	2.4433	6.3	6,990	.07	Fluid.
78.0	22.0	2.4194	6.7	6,820	.04	Soupy.
LIMESTONE AGGREGATE--50-50 CEMENT						
88.0	12.0	2.3015	13.8	4,020	1.59	Dry.
86.0	14.0	2.4428	7.9	8,710	.22	Stiff.
84.0	16.0	2.4920	5.5	8,870	.04	Fluid.
82.0	18.0	2.4840	6.0	8,410	.02	Do.
80.0	20.0	2.4230	7.1	6,210	.06	Soupy.

Maximum compressive strength and specific gravity and minimum water absorption were obtained using 50-50 cement with a binder range of 16 to 18 pct. A fluid, workable mix was obtained with both types of aggregates in that same range. Figures 7 and 8 show the changes in compressive strength and in specific gravity in the sulfur concretes prepared with varying 50-50 cement binder levels. On scale-up from laboratory to 500-lb batch size, the optimum binder content

for the 3/8-in quartz aggregate was 17 wt-pct; for the 3/8-in limestone aggregate, it was 18 wt-pct. Independent mix designs should be made for each new type and gradation of aggregate. For example, when a 1-in dense-graded silica aggregate was used, the optimum binder level of 50-50 cement was 14 wt-pct, and the concrete product had approximately the same strength values as the 3/8-in dense-graded silica aggregate.

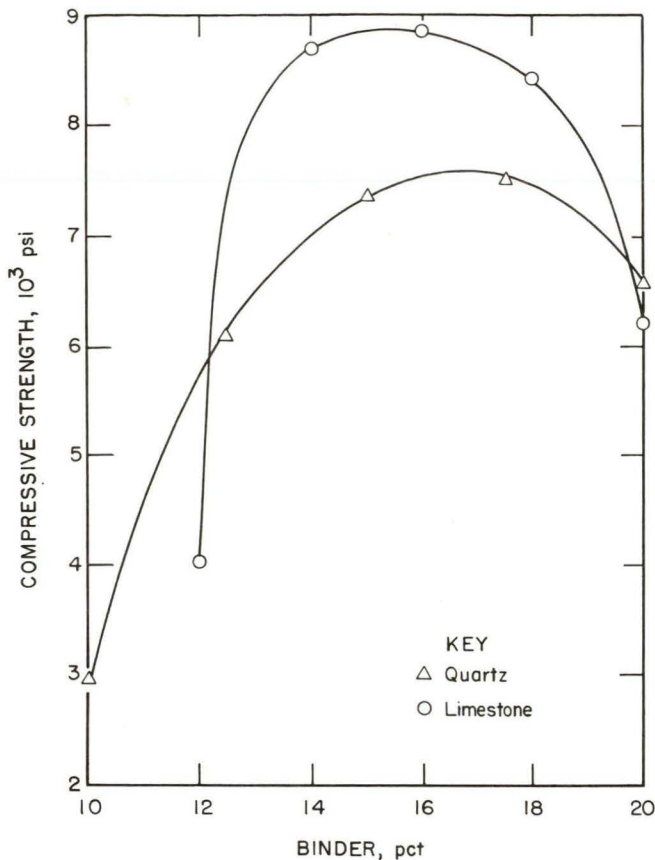


FIGURE 7. - Variation of sulfur concrete compressive strength with sulfur cement content.

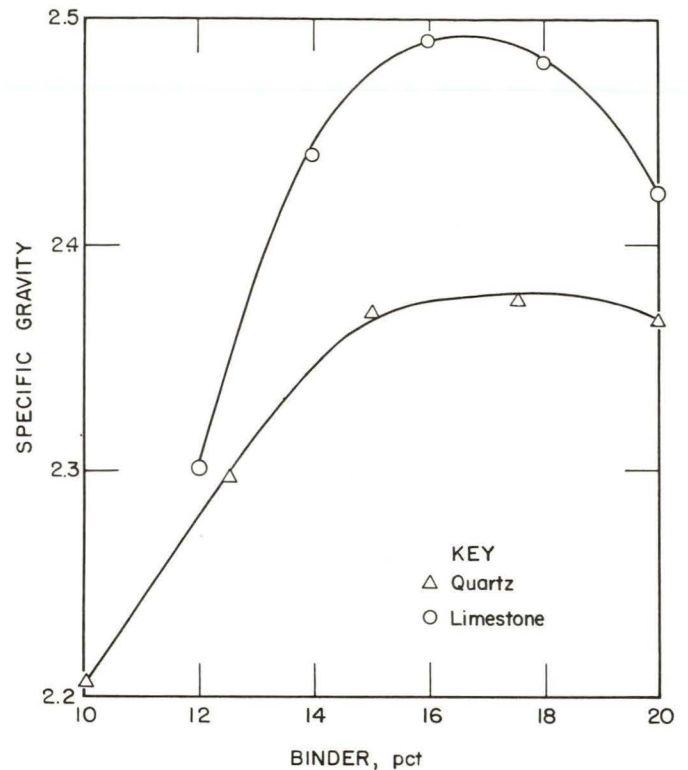


FIGURE 8. - Variation of sulfur concrete specific gravity with sulfur cement content.

PROPERTIES OF SULFUR CONCRETE

MECHANICAL PROPERTIES

Strengths of typical modified-sulfur concretes are given in table 4. The measurements were determined in accordance with Standard ASTM Methods for concrete and mineral aggregates (2). Compressive strength was determined in accordance with ASTM Method C 39-72, "Compressive

Strength of Cylindrical Concrete Specimens;" tensile strength measurements were made in accordance with ASTM Method C 496-71, "Splitting Tensile Strength of Concrete Cylinders;" and flexural strength measurements were in accordance with ASTM Method C 78-75, "Flexural Strength of Concrete Using Single Beam with Third-Point Loading."

TABLE 4. - Properties of typical sulfur concretes

Aggregate		Sulfur cement, wt-pct	Strength, psi		
Type	Wt-pct		Compressive	Tensile	Flexural
QUARTZ					
3/8-in:					
Open-graded.....	77	23	5,030	730	1,130
Dense-graded.....	84	16	7,720	1,040	1,440
1-in: Dense-graded....	86	14	8,710	1,030	1,330
LIMESTONE					
3/8-in:					
Open-graded.....	79	21	9,100	1,050	1,480
Dense-graded.....	82	18	8,710	1,050	1,720
1/2-in: Dense-graded..	86	14	8,800	1,100	1,530

Strength measurements were made 1 day after casting the sulfur concrete test specimens. Compressive and tensile strength measurements were made on 3- by 6-in cylinders of the sulfur concrete. Flexural strength and freeze-thaw durability measurements were made on 3- by 3- by 14-in cast bars of sulfur concrete. All measurements were made in triplicate.

Approximately 80 pct of the ultimate mechanical strength of the modified sulfur concrete was attained in 24 hr. The ultimate strength was achieved after aging between 6 and 12 months. Aging changes are attributed to nucleation and growth of monoclinic sulfur crystals in the binder.

LOAD DEFLECTION IN COMPRESSION

The stress-strain behavior of modified-sulfur concrete prepared with quartz aggregate was studied as a function of time for a 1-year period using the procedure described by Sullivan (22). A bond-altering agent (0.75 pct asphalt) was also included in the testing for comparison with the rigid concrete and was used to alter the mode of failure, because the rigid materials were reported to fail by a brittle catastrophic mode (21). Bond-altering agents, such as selected blends of crude oil, have been described by Shrive as important in preparing "ductile" concretes, or concretes that fail in a noncatastrophic mode. The

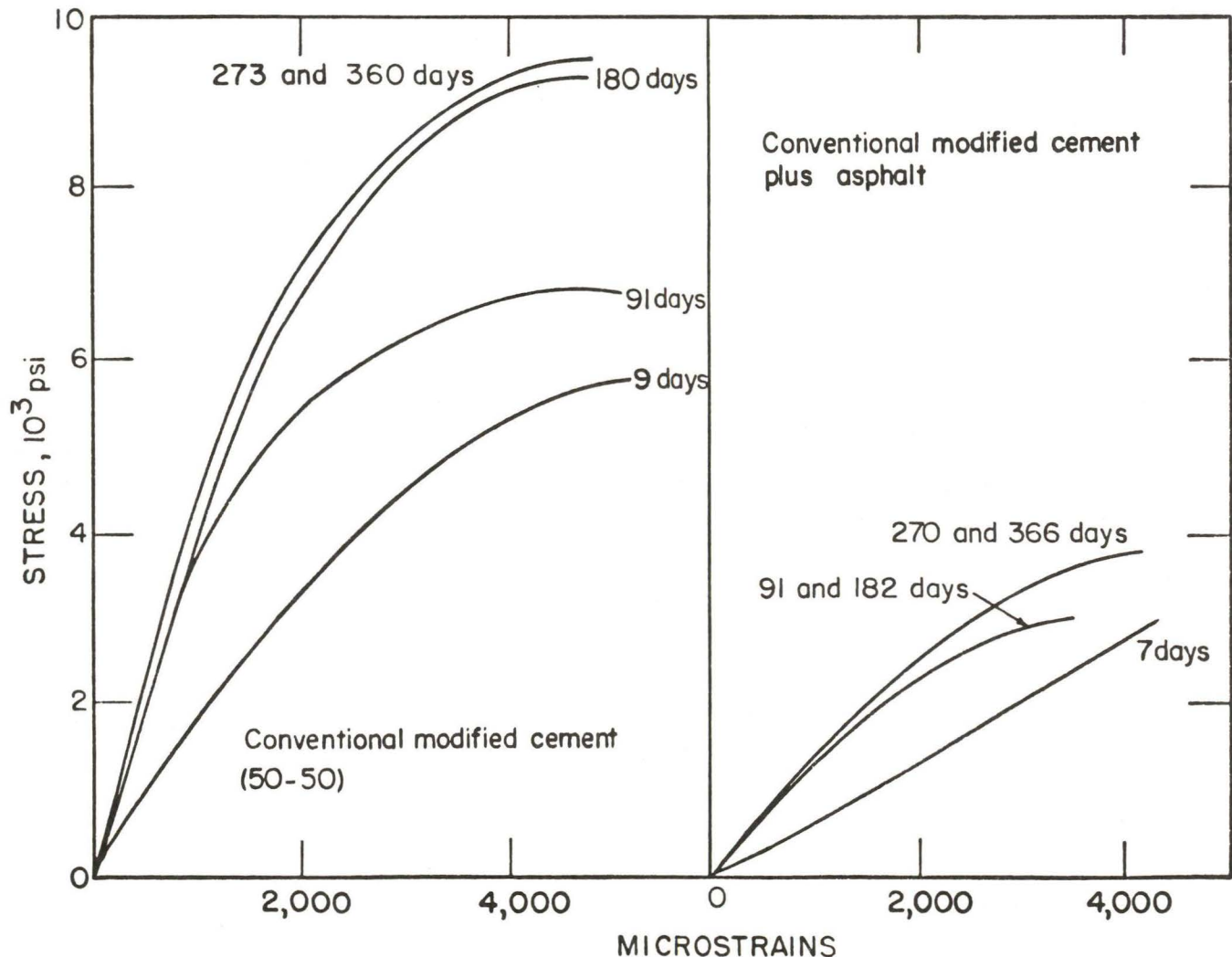


FIGURE 9. - Stress-strain curves for modified-sulfur concretes.

cylindrical samples were tested initially and at 3-month intervals for 1 year. Data for the tests are plotted in figure 9. Using the conventional modified cement, the load deformation curves indicate that aging increases the stress-to-failure values significantly during the first 180 days. Initially, the materials exhibit some plastic yielding when the load increases. After 91 days, the curves approach a more elastic position and show some plastic yielding occurring at stress levels above 7,000 psi.

Failure mode of the material is by transgranular rupture of the aggregate and indicates that the bond strength exceeds the aggregate strength. The aggregate was quartz rock, which is an elastic brittle material. When the bond was altered by adding 0.75 pct AR 2000 asphalt to the hot aggregate before addition of binder, the materials exhibited very low stress to failure values and concurrently lower strain values. The failure mode was 100 pct intergranular and indicated a very weak bond between cement and aggregates. The materials were all extremely brittle.

Figure 10 contains ultimate compressive strength and modulus values calculated from the load deflection curves. The higher strength concrete increased in modulus and strength during a 180-day period in a manner similar to portland cement concrete. The strength increase was attributed to nucleation and growth of monoclinic sulfur crystals in the matrix. When the bond was altered, the materials exhibited a considerably lower initial strength and modulus, showed no effects of aging, and indicated that the limiting factor for strength was the bond strength between aggregate and sulfur.

According to Davis (7), "ductility is that property of a material which enables it to be drawn out to a considerable extent before rupture and at the same time to sustain appreciable load. Mild steel is a ductile material. A nonductile

material is said to be brittle; i.e., it fractures with relatively little or no elongation. Cast iron and concrete are brittle materials." Usually the tensile strength of brittle materials is only a fraction of their compression strength. For sulfur concrete, tensile values were 10 to 20 pct of compressive value.

MOISTURE ABSORPTION

Porosity is an important factor in preparing corrosion-resistant concrete materials. This is especially true if reinforcing steel is used in the concrete. Air voids in modified-sulfur concretes are not interconnected. In properly designed sulfur concretes, the porosity measured by moisture absorption can be maintained at less than 0.05 pct.

Moisture absorption was determined on 3- by 6-in cylinders of sulfur concrete. The cylinders were weighed, immersed in water at 20° C for 24 hr, surface-dried, and reweighed. Moisture absorption was calculated as follows:

$$A = [(C-B)/B] \times 100,$$

where A = percent moisture absorption,

B = weight of dry cylinder,

and C = weight of immersed cylinder, surface-dried.

Figure 11 shows the variation of moisture absorption with binder content on sulfur concretes using sulfur and 50-50 cement binder and a dense-graded 3/8-in quartz aggregate. To obtain less than 0.05 moisture absorption would require 17 wt-pct 50-50 cement or 20 pct sulfur. The lower binder requirements for 50-50 cement result from natural entrainment of discrete air voids during the mixing cycle because of the higher viscosity of the cement. Entrained air voids are not normally generated on mixing sulfur and aggregate.

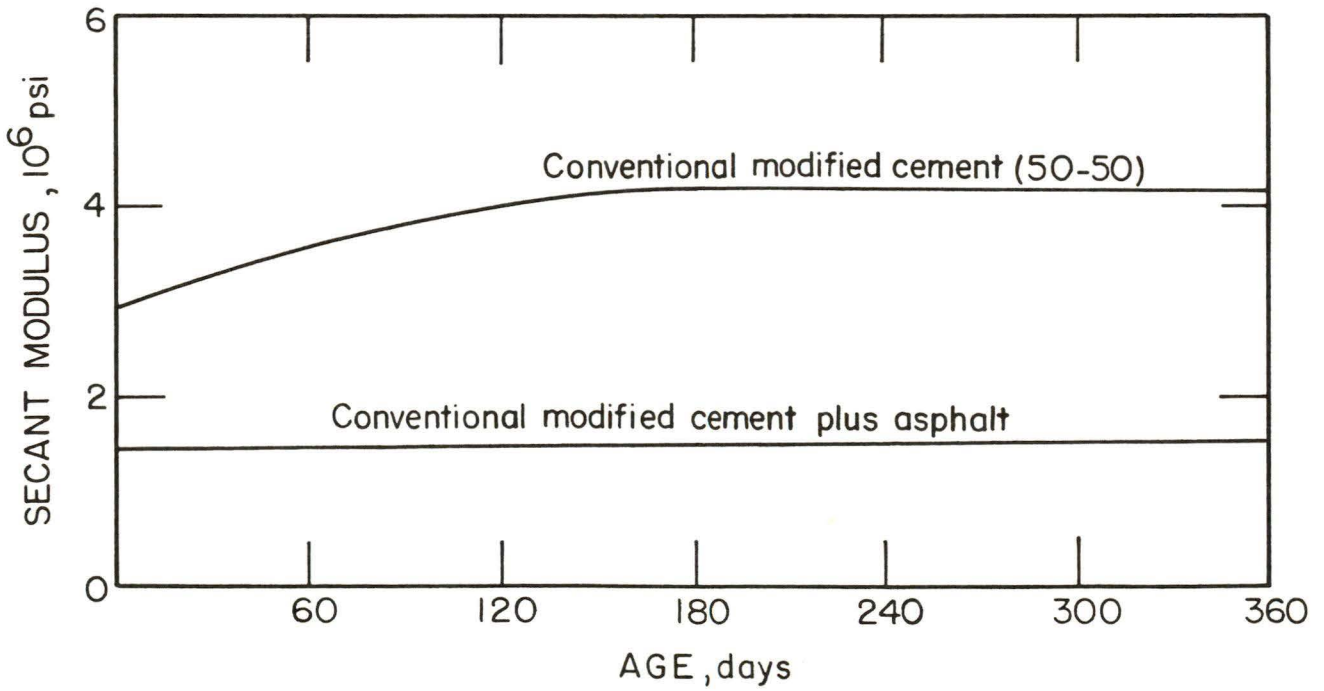
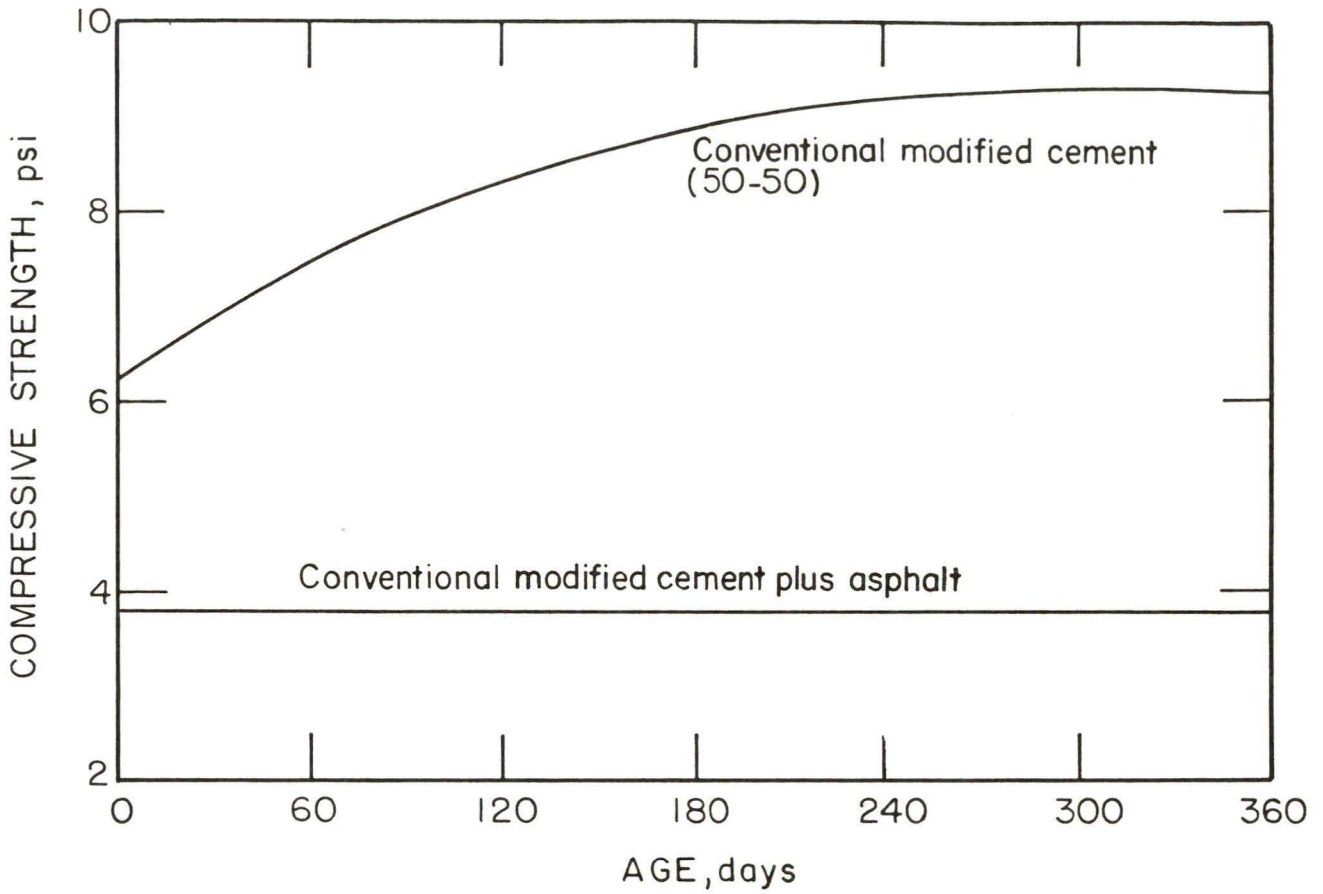


FIGURE 10. - Compressive strength and modulus value calculated from load deflection curves.

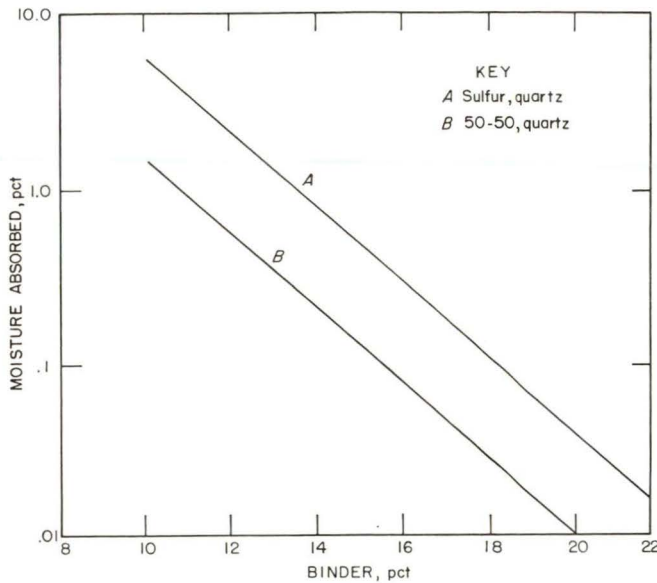


FIGURE 11. - Moisture absorption versus binder content of sulfur concrete.

Static water permeation tests were made comparing the permeability of the sulfur concrete and portland cement concrete. Five-foot sections of 6-in-diameter plastic pipe were bonded to the surface of 2-in-thick slabs of sulfur concrete and portland cement concrete. A 51-in column of water was placed in each pipe section to provide a 1.84-psi water pressure on the surface of the slabs. The sulfur concrete has shown no loss in water height after 6 months, while the portland cement concrete slab has shown more than

1-in/hr loss of water height by permeation through the more porous portland cement concrete material. Figure 12 shows a test unit of sulfur concrete after 6 months. There was no penetration of water through the sulfur concrete slab.

SPECIFIC GRAVITY AND AIR VOIDS

The specific gravity of sulfur concretes was determined on 3- by 6-in cylinders of the cast material. The measurements were made in accordance with ASTM Method C 642-75, "Specific Gravity, Absorption, and Voids in Hardened Concrete." The variation of specific gravity with binder content using 3/8-in dense-graded quartz and limestone aggregates is shown in figure 8. Air voids were determined in two ways: by calculation of the void content from the actual specific gravity of the sulfur concrete sample and the theoretical specific gravity of the aggregate-binder mixture, and by microscopic determination in accordance with ASTM Method C 457-71, "Microscopic Determination of Air-Void Content," using the linear traverse method (Rosiwal). The microscopic method is useful when the specific gravity of the aggregate materials is not available. Table 5 compares the results obtained by the two methods for different sulfur concrete formulations with 50-50 cement.

TABLE 5. - Air-void content of different sulfur concrete formulations

Sulfur concrete formulation, pct		Air-void content, pct	
Quartz aggregate	Cement	Microscopic method	Specific gravity method
3/8-in:			
90.....	10	12.7	11.6
84.....	16	7.8	6.3
81.....	19	7.3	7.0
1-in:			
87.....	13	2.6	4.2
86.....	14	2.2	3.3
85.....	15	3.6	3.7
84.....	16	3.3	3.7

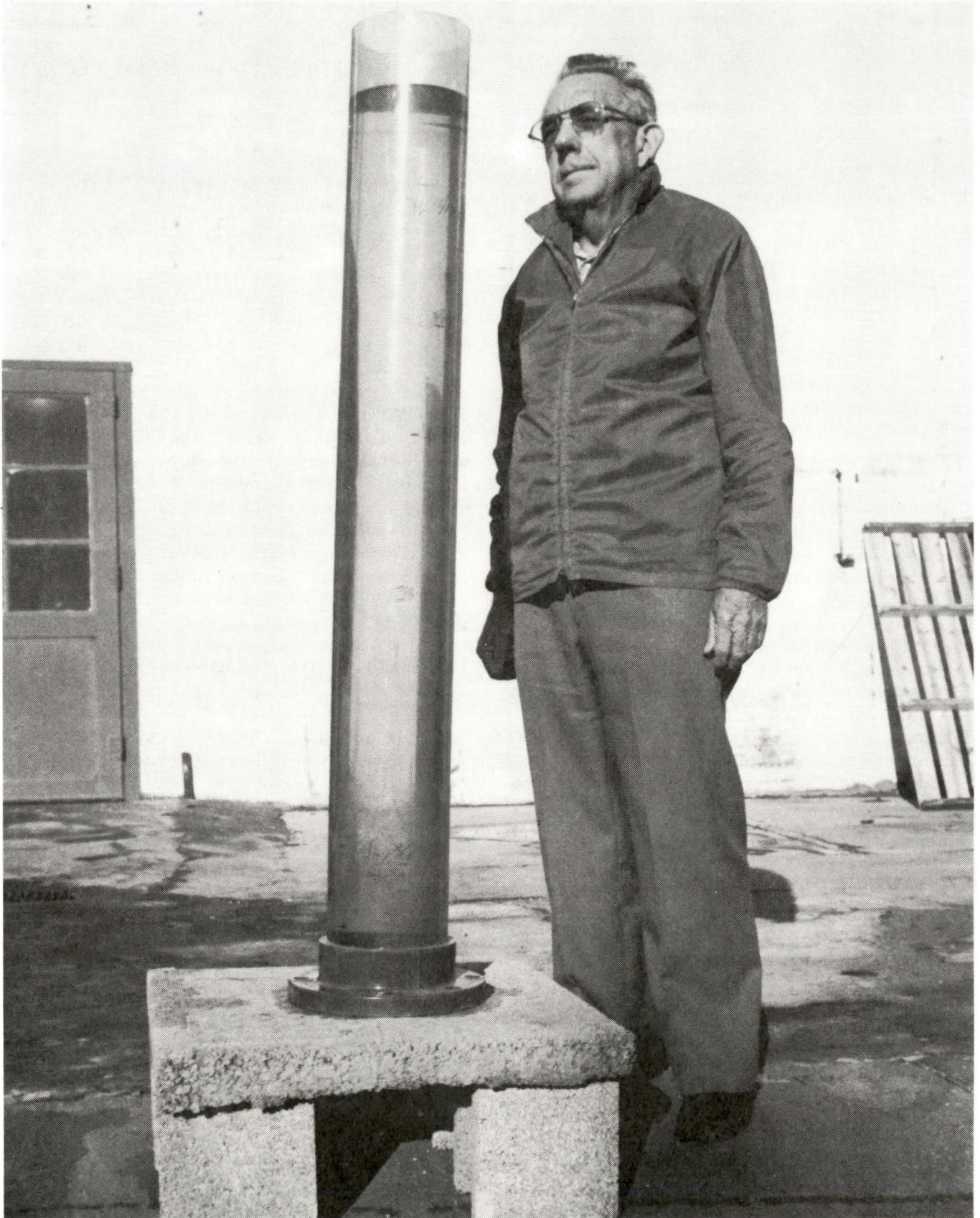


FIGURE 12. - Water permeation test unit.

THERMAL EXPANSION OF
MODIFIED-SULFUR CONCRETE

Linear thermal expansion values for specific aggregates and the concrete materials were determined on samples 1/2 by 1/2 by 1 in long. The expansion was measured over a 25° to 100° C temperature range, at a constant heating rate of 3° C per minute. Values obtained are plotted in figure 13, and thermal expansion coefficients are shown in table 6. The thermal expansion coefficient of the 50-50 cement is given for comparison purposes.

The values shown in table 6 indicate that thermal expansion of modified-sulfur concrete is a direct function of the amount of cement used. In decreasing the sulfur binder content from 22 to 14 pct, a 1-pct decrease in the coefficient of thermal expansion is obtained for every percent decrease in sulfur binder concentration.

Coefficients of thermal expansion values for sulfur concrete materials are important in designing for specific uses because of compatibility with other materials. For comparison, the

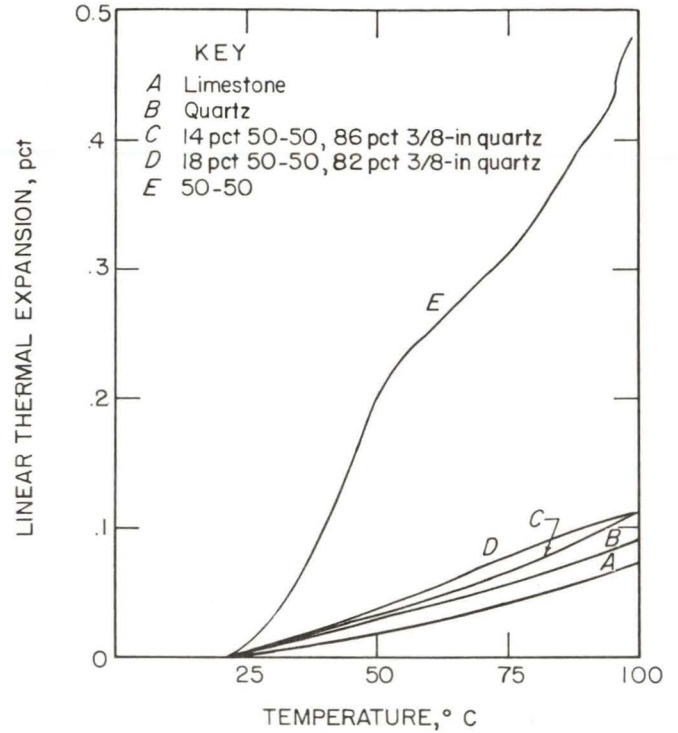


FIGURE 13. - Linear thermal expansion of sulfur cements and concretes and aggregate materials.

coefficient of thermal expansion for quartz portland cement concrete is $11.9 \times 10^{-6}/^{\circ}C$ and for steel about $12 \times 10^{-6}/^{\circ}C$ (18).

TABLE 6. - Thermal expansion coefficients of 50-50 cement, aggregate, and sulfur concrete between 25° and 100° C

Sample	Coefficient of thermal expansion, per ° C ($\times 10^{-6}$)
Limestone aggregate.....	9.3
Quartz aggregate.....	12.0
50-50 cement.....	59.0
14 pct sulfur cement; 86 pct 3/8-in quartz aggregate.....	14.0
18 pct sulfur cement; 82 pct 3/8-in quartz aggregate.....	14.7
22 pct sulfur cement; 78 pct 3/8-in quartz aggregate.....	15.3

FREEZE-THAW DURABILITY

A useful method for predicting long-range durability of sulfur concrete is its ability to withstand damage by rapid freeze-thaw cycling. Testing was performed on modified-sulfur concrete prisms cast vertically to a 3- by 3- by 14-in size. ASTM Method C 666-76, "Resistance of Concrete to Rapid Freezing and Thawing, Procedure A, Rapid Freezing and Thawing in Water," was followed. Figure 14 shows a typical quartz aggregate, modified-sulfur concrete behavior on undergoing 300 freeze-thaw cycles between -18° and 4.4° C while retaining 80 pct of the relative dynamic modulus of elasticity. This is typical behavior for materials prepared with the optimum mix procedure and a moisture absorption of less than 0.05 wt-pct. ASTM criteria require 60 pct modulus retention after 300 cycles. Figure 14 includes behavior of the

sulfur concrete formulated with an asphalt bond-altering component. The material failed the freeze-thaw durability test after approximately 60 freeze-thaw cycles because of the decrease in bond strength between the aggregate and the cement. This behavior is typical of unmodified-sulfur concrete (9).

The influence of the moisture absorption of sulfur concretes on their freeze-thaw durability is shown in figure 15. The relative dynamic modulus of elasticity is plotted against initial water absorption of different quartz aggregate, modified-sulfur concrete formulations. When the moisture absorption of a sulfur concrete formulation exceeds 0.05 pct, its resistance to freeze-thaw damage decreases dramatically. The data indicate that good quality control is essential in producing durable sulfur concrete materials.

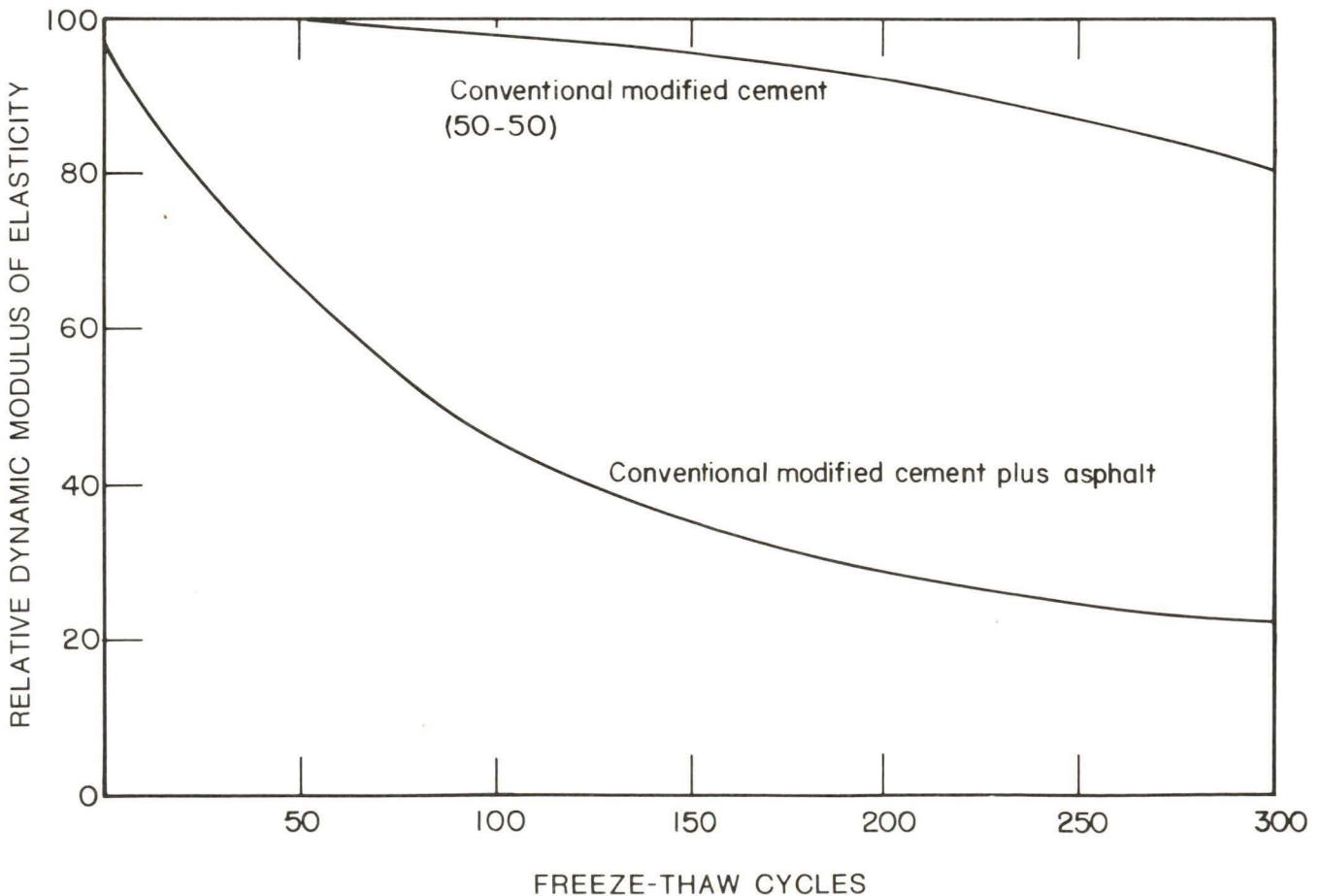


FIGURE 14. - Freeze-thaw durability of modified-sulfur concrete.

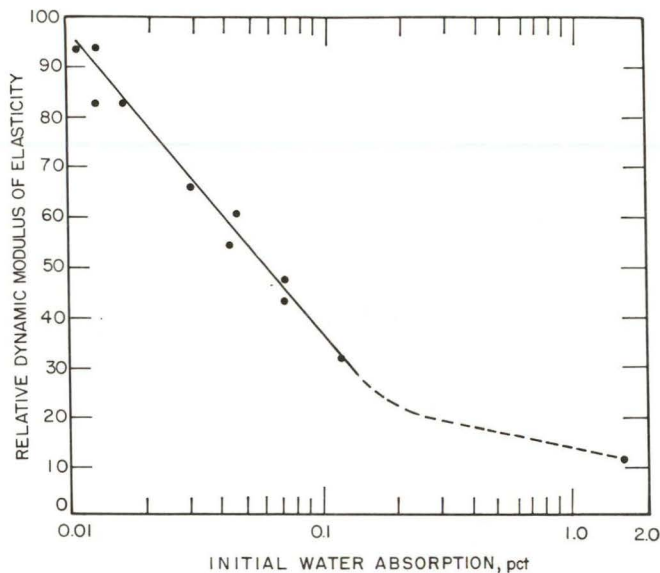


FIGURE 15. - Influence of moisture absorption of sulfur concretes on their freeze-thaw durability.

RESISTANCE TO ACID AND SALT CORROSION

Previous corrosion testing of sulfur concrete in different corrosive environments has been reported (9, 22).

SULFUR CONCRETE PREPARATION

Corrosion-resistant sulfur concretes are prepared by hot-mixing aggregate and 50-50 cement at 130° to 150° C. Any type of mechanical mixer may be used that can maintain the mixture at the required temperature and produce a well-coated homogeneous mixture. It is preferable to mix at the higher end of the temperature range to allow more time for transporting and casting the mixture before solidification. The 50-50 cement may be added either in the liquid or the solid form. When using liquid cement, it is added at about 140° C to aggregate at about 160° C to obtain a mixture in the 140° to 150° C range. Solid flake 50-50 cement can be added to aggregate heated to 170° to 190° C to melt the cement and obtain the desired mixture temperature. Mixing time to obtain homogeneous materials depends on the equipment used. Small batch mixtures require 1 to 2 min.

Recently, acid corrosion tests were made on 3- by 6-in cylinders of sulfur concrete prepared from 3/8-in dense-graded quartz aggregate and 17 pct 50-50 cement. The test cylinders were immersed in 10-, 20-, 60-, and 96-pct-strength H_2SO_4 solutions for 1 year. Samples were removed every 3 months to determine any change in weight, specific gravity, or chemical damage. Some samples were evaluated quarterly for compressive strength measurements.

No signs of spalling or corrosion of the materials were observed during the 1-year program. A slight weight gain was shown, with the absorption increasing from 0.05 to 0.18 pct for the samples in 10-pct H_2SO_4 and from 0.02 to 0.10 pct for those in the more concentrated H_2SO_4 solutions. The small change in absorption over the 1-year period indicated that solution penetration was very small and would not reach any reinforcing materials used in the sulfur concrete. Compressive strength measurements showed an increase in strength similar to that shown in figure 10.

Preparation of bench-scale batches of sulfur concrete for design and test purposes was done by heating the aggregate in an oven and mixing the concrete in a Hobart bakery-type mixer or heated mortar mixer (9, 22). Where in situ testing of components in commercial applications was desired, a small plant was set up that was capable of preparing up to 3 tons of sulfur concrete per hour in 500-lb batches. The unit consisted of a propane-heated kiln and a heated mortar mixer. Aggregate was fed into the feed hopper, heated, and discharged into the mortar mixer. After a batch of aggregate was discharged into the mixer, the 50-50 cement, either liquid or flake, was added, and the contents were mixed and then discharged into an insulated hopper for conveyance to the casting area. A pilot-scale sulfur concrete plant is shown in figure 16, and representative test components are shown in figures 17 and 18.

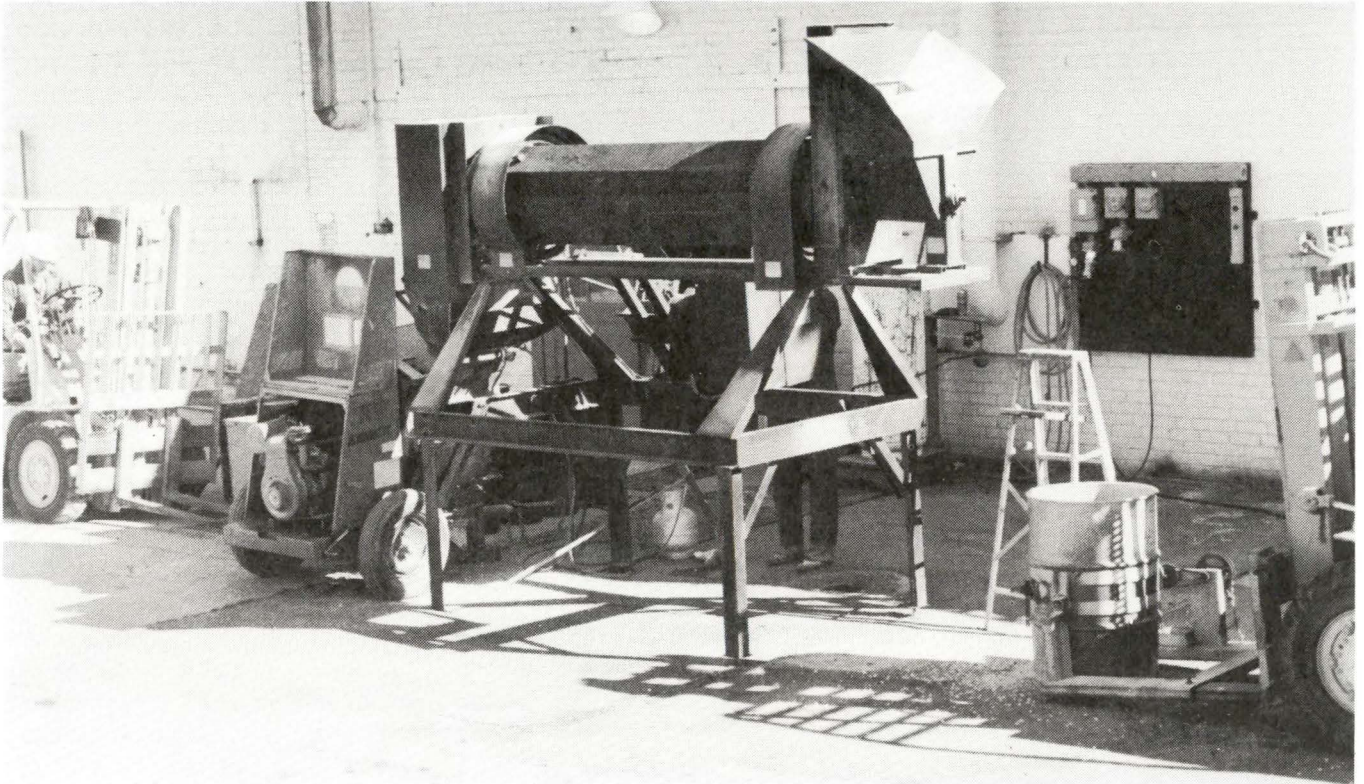


FIGURE 16. - Pilot-scale sulfur concrete plant.

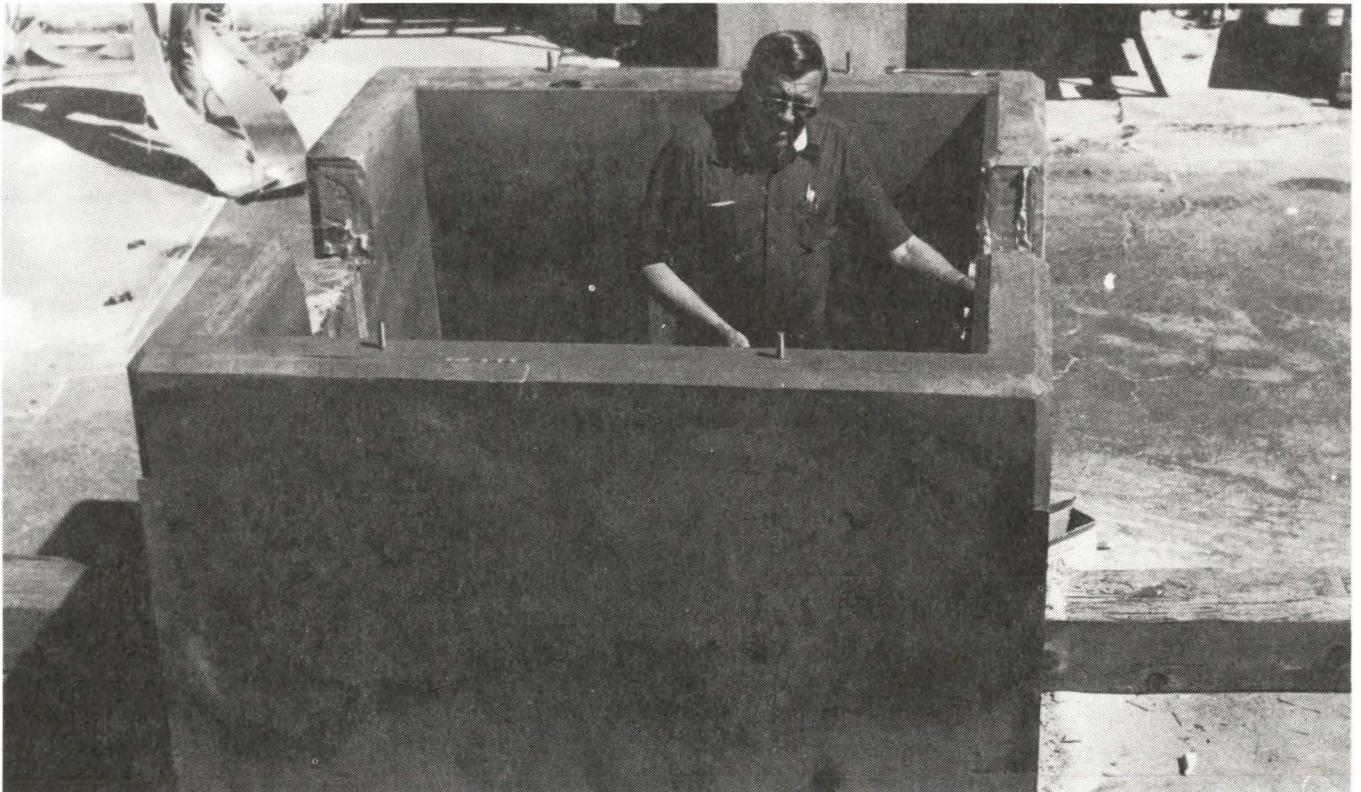


FIGURE 17. - Sulfur concrete sump unit.

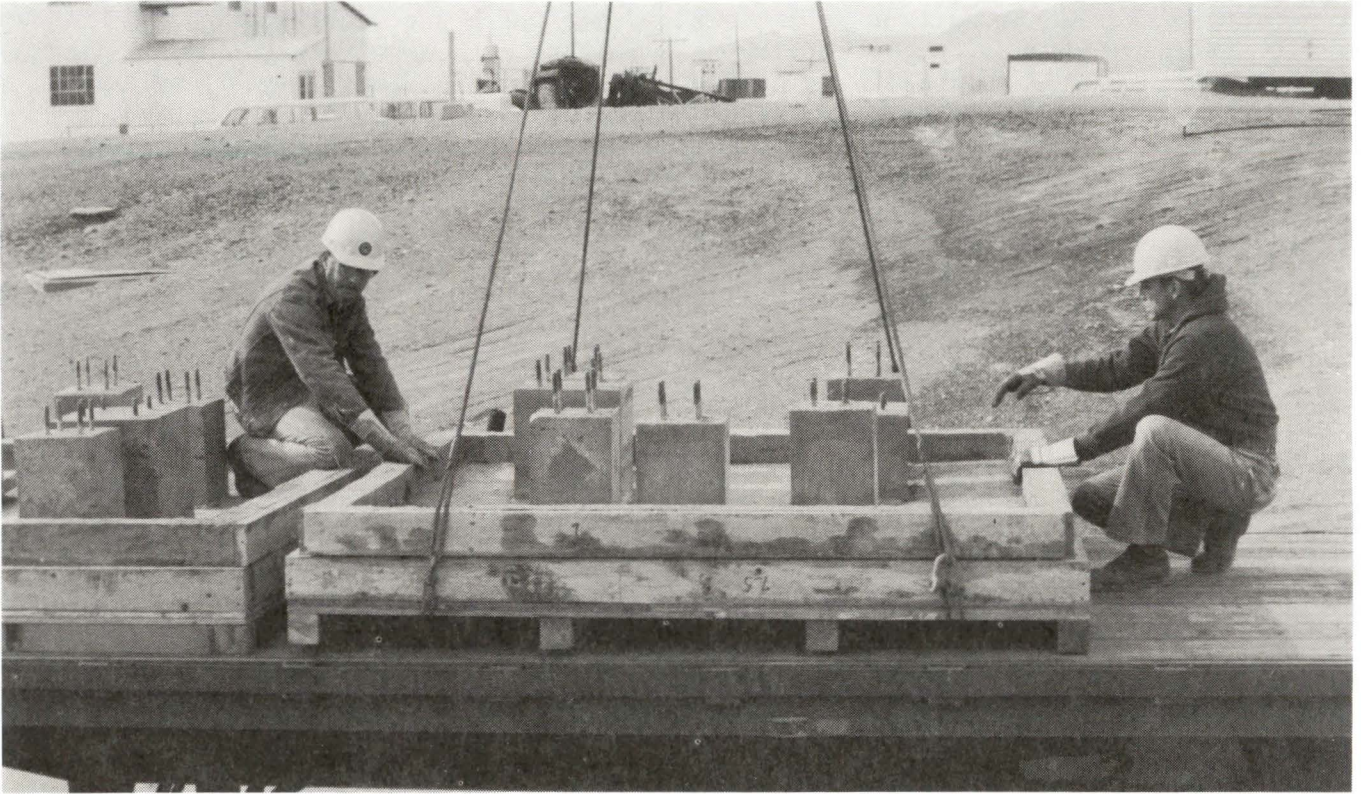


FIGURE 18. - Sulfur concrete base for mounting H_2SO_4 pumps.

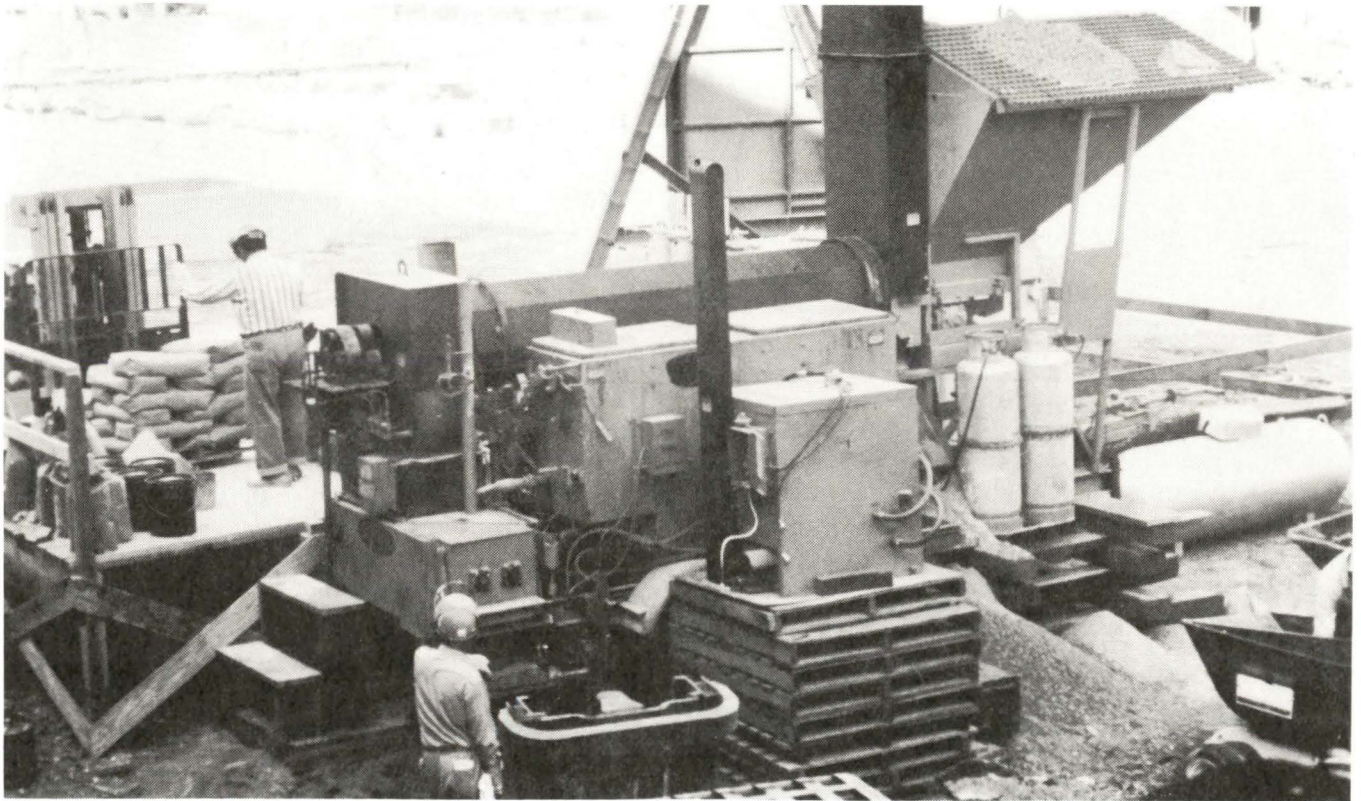


FIGURE 19. - Sulfur concrete production unit.

A larger scale production unit was built by The Wylie Co. by modifying an asphalt patchmobile. Aggregate is heated in a propane-fired kiln and falls into a hot-oil jacked pugmill, where 50-50 cement is added and the concrete is mixed and discharged. The unit can continuously produce up to 12 t/hr of sulfur concrete and has been used to produce larger scale test components, such as slabs and tanks. The machine, in operation at ASARCO's Corpus Christi zinc refinery, is shown in figure 19 and was used to produce 21,000 ft² of 4-in-thick sulfur concrete to replace a corroded PCC floor. The effect of the corrosive environment in the plant on test slabs of sulfur concrete and PCC is shown in figure 20. The sulfur concrete remains unaffected after 4 years of exposure. The control samples of PCC were destroyed within 1 year. Installation of the sulfur concrete floor is illustrated in figure 21. The Wylie unit was also used to prepare 4,500 ft² of sulfur concrete

floor which was overlaid on existing PCC in the nickel sulfate plant at ASARCO's Amarillo copper refinery.

Modified sulfur concrete has been prepared in regular hot-mix asphalt batch plants and heated transit mixers. A similar technique was used at Cities Service Co.'s Pinto Valley copper operation to pour a sulfur concrete floor for an electrolytic copper cellhouse. Seven-yard batches of sulfur concrete were prepared by adding 50-50 cement to preheated aggregate in a transit mixer. The heated aggregate was supplied by a hot-mix asphalt plant. Propane burners mounted on the transit mixer were used to maintain the sulfur concrete at the desired temperature. Figure 22 shows the 50-50 cement being loaded into the mixer. The sulfur concrete was used to construct approximately 10,000 ft² of acid-resistant floor and a drain system underneath the electrolytic cells and cathode stripping area of the cellhouse.

PLACEMENT OF SULFUR CONCRETE

Sulfur concrete is handled like PCC concrete, except that the material must be transported and cast without undue heat loss. Metal or wooden forms may be used in casting sulfur concretes. Metal molds or forms should be heated to about 110° C before use to prevent freezing out a skin of sulfur cement on contacting a cold metal mold. Depending on the type of casting, sulfur concrete can be rodded, vibrated, or screeded during compaction and finishing. All working of sulfur concrete should be concluded before it starts to set and a crust forms. Sulfur concrete floors should be poured on dry, compacted base material. If there is moisture in the base, the heat in the sulfur concrete will vaporize the moisture, forming channels through the sulfur concrete during setting and increasing susceptibility to moisture penetration.

Sulfur concrete may be transported in hoppers or motorized concrete buggies from the preparation plant to the pouring

area. These types of containers should be insulated by welding a steel inner liner with 1 to 2 in of fiberglass insulation in the hopper or buggy. The rapid chilling of the material that takes place when sulfur concrete is transported in uninsulated containers will be prevented. Heated trucks or transit mixers may also be used to transport sulfur concrete. When sulfur concrete is prepared in the 140° to 150° C range, the time available for transportation and placing is about 30 min. In casting floors and slabs, wooden vibratory screeds can be used to compact and level off the section being poured. Some of the material should always be in front of the screed to obtain best results. Touchup finishing may be made with metal or wooden trowels. Working of the sulfur concrete should stop when a crust is formed. Reworking of the surface is possible with the application of indirect heat while the material is still hot.



FIGURE 20. - Sulfur concrete test slabs in electrolytic zinc plant.



FIGURE 21. - Pouring a sulfur concrete floor.



FIGURE 22. - Sulfur concrete preparation in a heated concrete mixer.

Since sulfur concrete is a new material of construction, techniques for placing and finishing it are still being developed. Individual applications must be evaluated independently, based on the prevailing conditions such as the degree of thermal cycling, type of exposure, new construction, or renovation of existing structures. For example, when overlaid on PCC, it is important to isolate the sulfur concrete from the PCC to prevent any corrosive penetration from reaching the PCC. Materials such as PVC sheeting

and bitumastics are being evaluated for this purpose in industrial environments. Since sulfur concrete is poured hot and contracts on cooling to ambient temperatures, expansion joints must be installed between adjacent pours of a floor. The shrinkage of sulfur concrete on cooling must also be taken into consideration on pouring monolithic castings, such as tanks or sumps. Provisions must be made for the shrinkage to prevent inside molds from being locked into place.

INDUSTRIAL EVALUATION

To evaluate the durability, longevity, and performance of sulfur concretes under operating conditions, a program was developed for testing the materials in chemical and metallurgical plants. Different forms of sulfur concrete components were supplied to industrial plants for installation in severe corrosion

areas. Initial installation was in a potash plant in December 1977, where eight 4- by 4-ft by 4-in test sections were installed in the floors of two processing plants in which salt corrosion of concrete was a major problem. Figure 23 shows one of the installations. Since 1977, materials have been installed in

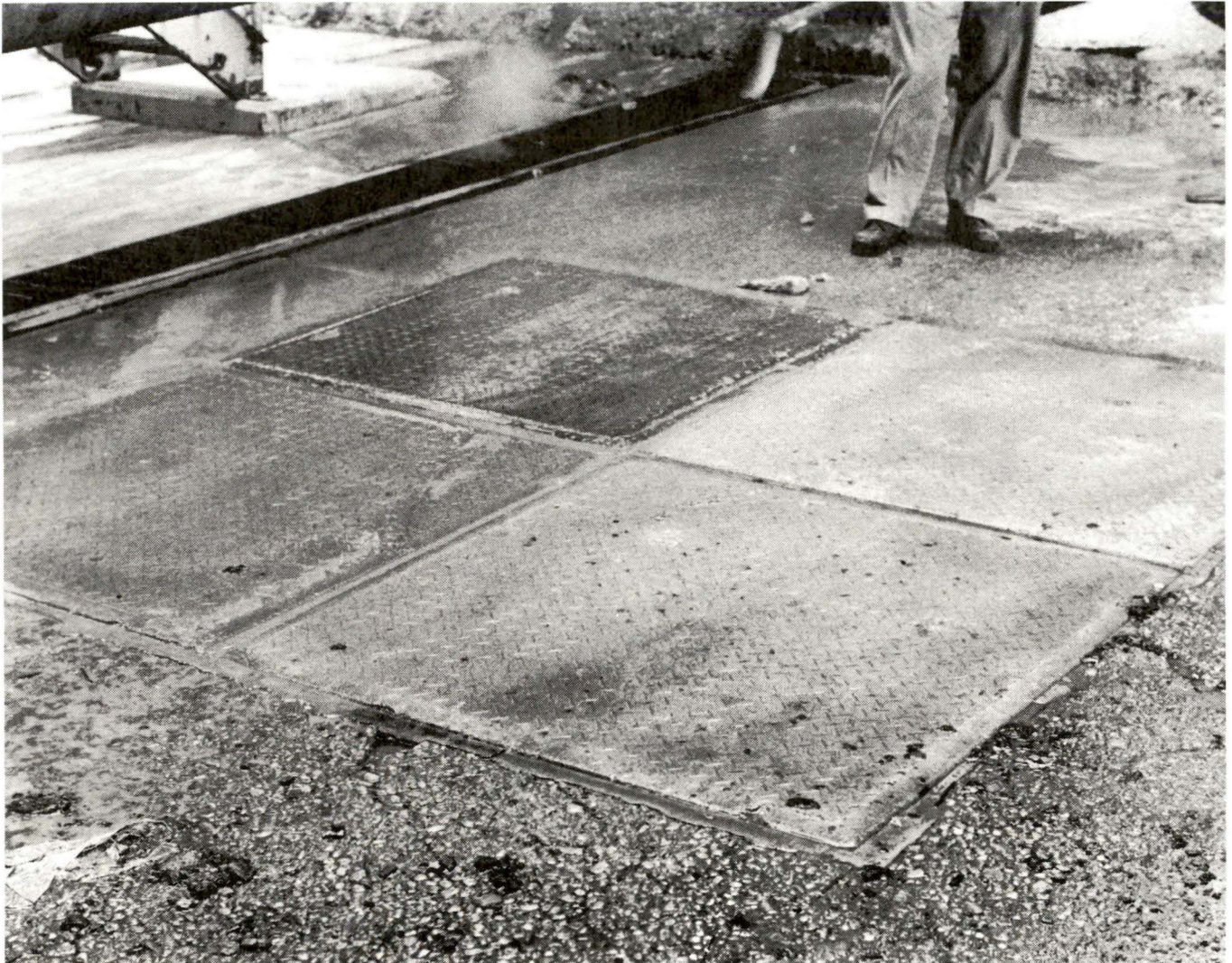


FIGURE 23. - Sulfur concrete test slabs in a potash plant.

24 industrial plants for evaluation in 30 types of corrosive environments. The plants include metal production and refining operations for aluminum, copper, lead, magnesium, titanium, uranium, zinc, and precious metals and chemical production plants for sodium and potassium salts, mineral acids, and electrolytic manganese dioxide. Other evaluation areas are in a citrate process plant used

for removing SO_2 from powerplant emissions and in sewer and septic tank environments. Components being tested include sections inserted into present plant floors, sump and weir tanks, cast pump foundations, electrolytic cells, and various sized test bars, cylinders, and boxes. Units containing reinforcing and coated reinforcing steel are included in the test program.

SAFETY

Preparation and handling of hot sulfur concrete materials pose problems similar to those encountered in the hot-mixed asphaltic concrete industry. In preparing sulfur concrete, a mixture of hot aggregate and liquid sulfur cement is produced, and precautions for handling

hot liquid materials must be observed. Practices for handling both solid and liquid sulfur, including its haulage and safety, have been established by the National Safety Council (15-16) and should be followed in preparing sulfur concretes.

Emissions of sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) may be generated during the mixing and placing of sulfur concrete mixtures. When sulfur concrete materials are prepared in the recommended range of 120° to 150° C, emissions of SO_2 and H_2S are well below their threshold limit values. The values for SO_2 are 5 ppm for short term exposure and 2-ppm for the time-weighted average concentration for an 8-hr exposure. Corresponding values for H_2S are 15 ppm and 10 ppm, respectively (1).

The preparation of sulfur concrete on a bench scale was monitored with continuous-recording, commercial detection units for SO_2 and H_2S with inlets 1 ft above the mixing units. Emission values obtained were 0 to 2 ppm SO_2 and 0 to 1 ppm H_2S . The higher values for both SO_2 and H_2S were momentary values and occurred during the first 15 sec of a 2-min mixing cycle after which the emissions decreased to zero or trace values. Similar results for these emissions were obtained in manufacturing larger batches (500 lb) of sulfur concrete in the small-scale production plant. Monitoring SO_2 and H_2S emissions in the work

areas when the larger scale pugmill mixer (12 t/hr) was used to pour sulfur concrete floors gave values similar to those obtained in the laboratory tests and met all safety requirements.

Sulfur vapor may be given off during the mixing and placing of sulfur concrete mixtures. It crystallizes into small dustlike particles on cooling to ambient temperatures. Sulfur is considered non-toxic, and there has been no evidence of systemic poisoning resulting from the inhalation of sulfur dust. Sulfur dust may irritate the inner lining of the eyelids. This problem is minimized by requiring that goggles be worn in areas where sulfur vapors may be encountered.

An environmental impact study (20) on possible emissions and pollutants from the use of sulfur in paving materials, including sulfur concrete, stated that evolved gases and pollutants could be maintained within safe limits if mix temperatures were kept below 149° C, and recommended a maximum allowable mixing temperature of 149° C for hot sulfur paving materials.

SUMMARY AND CONCLUSIONS

A corrosion-resistant-sulfur-concrete technology was developed to prepare durable construction materials for use in acidic or salt environments where PCC materials fail. A modified-sulfur cement was developed in which sulfur is reacted with dicyclopentadiene and oligomers of cyclopentadiene to form a stable cement product. Mixture designs utilizing corrosion-resistant aggregates and 50-50 cements were developed to prepare stable sulfur concretes for use as corrosion-resistant materials of construction. Sulfur concretes were produced with excellent resistance to damage by most acid and salt environments, good mechanical

strength properties, and resistance to damage by freeze-thaw cycling; coefficients of expansion were compatible with those of other materials of construction such as PCC and reinforcing steel.

The technology has been demonstrated on a commercial scale both in the manufacture of the 50-50 cement and in its utilization in producing sulfur concrete construction materials. Cooperative evaluation with industry on testing in corrosive environments indicates that sulfur concrete has the potential for widespread applications in the chemical, metallurgical, and fertilizer industries.

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