

Sulfur Construction Materials

By W. C. McBee, T. A. Sullivan, and H. L. Fike



UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS BULLETIN

°C	degree Celsius	lb	pound
cP	centipoise	min	minute
°C/min	degree Celsius per minute	mm	millimeter
c/min	cycle per minute	μm	micrometer
°F	degree Fahrenheit	mt	metric ton
ft	foot	pct	percent
ft ²	square foot	psi	pound per square inch
gal	gallon	r/min	revolution per minute
h	hour	st	short ton
in	inch	st/h	short ton per hour
in/h	inch per hour	vol pct	volume percent
in/(in·°C)	inch per degree Celsius	wt pct	weight percent
kcal/mol	kilocalorie per mol	yd ³	cubic yard
kg	kilogram	yr	year

(To convert degrees Celsius to degrees Fahrenheit, multiply the Celsius temperature by 1.8, then add 32.)

SULFUR CONSTRUCTION MATERIALS

By W. C. McBee,¹ T.A. Sullivan,² and H. L. Fike³

ABSTRACT

This Bureau of Mines bulletin summarizes both Government and private sector research related to the use of sulfur in construction materials through 1984. Byproduct sulfur has been investigated for use in concretes, coatings, and paving materials as part of a Bureau research program to utilize abundant minerals. Material properties, mixture design procedures, and applications for these materials are described.

INTRODUCTION

Increasing amounts of sulfur and sulfur products are being produced from secondary (involuntary) sources, in-

cluding sour gas, crude oil, metal sulfide ores, and coal. In 1972, the Bureau of Mines initiated a research program to investigate new uses for sulfur, a commodity whose major use is in the production of sulfuric acid, a chemical with relatively inelastic use patterns. This bulletin summarizes the Bureau's research on sulfur construction materials and related research by other organizations. It is divided into three chapters covering sulfur concretes, sulfur spray coatings, and sulfur-extended asphalt as a paving material.

¹Supervisory metallurgist, Albany Research Center, Bureau of Mines, Albany, OR.

²Research chemist, Boulder City Engineering Laboratory (now closed), Bureau of Mines, Boulder City, NV (now consultant for The Sulphur Institute, Washington, DC).

³President, The Sulphur Institute, Washington, DC.

CHAPTER 1.—SULFUR CONCRETES

HISTORY

The use of sulfur as a hot-melt bonding agent and sealer for water vessels has been known since prehistoric times (1).⁴ A technique developed in the 17th century that uses sulfur to anchor metal to stone is still used in Latin America (2). In 1919, the demand for sulfur led to the opening of the Big Dome sulfur deposit near Matagorda, TX. This doubled the production of sulfur in the United States, resulting in a surplus. Bacon and Davis (3) in 1921 reported on projected uses of sulfur in construction materials to utilize the surplus sulfur. They tested many suggested additives for modifying the properties of sulfur for specific uses and found almost all of them unsuitable. However, they found that a mixture of 60 wt pct sand and 40 wt pct S produced an acid-resistant product of excellent strength. Kobbe (4), in 1924, reported on the acid-resistant properties of materials prepared from sulfur and coke. Duecker (5), in 1934, found that the sand-and-sulfur product originated by Bacon and Davis grew on thermal cycling with a loss in flexural strength. Duecker was able to retard both the tendency to grow and loss of strength on thermal cycling by modifying the sulfur with addition of an olefin polysulfide (Thiokol).⁵ The use of additives to prepare more stable sulfur cements and other sulfur products led to greater industrial acceptance of sulfur products and more research and development on means for improving sulfur products such as acid-resistant mortars and grouts. In 1940, McKinney (6) outlined testing methods for sulfur materials that have been found satisfactory through his research at the Mellon Institute. Many of these methods were adopted and are found in specifications established by the American Society for Testing and Materials (ASTM) for chemical-resistant sulfur mortar (7).

CURRENT TECHNOLOGY

The development of modern corrosion-resistant sulfur concrete (SC) has taken place in the last decade. Research in this area was based on the premise that for SC to be a viable construction material, its durability would have to be improved, new sulfur cements would have to be developed, and mixture designs would have to be developed for the production of uniform products on a routine basis. Impetus for improved sulfur construction materials was provided by the rapid rise of sulfur production in the early 1970's from secondary sources such as sour natural gas and crude oil (8). In 1971, the Bureau of Mines and The Sulphur Institute launched a cooperative research program to develop new uses for sulfur. In 1973, the Sulphur Development Institute of Canada (SUDIC), jointly funded by the Canadian Government and Canadian sulfur producers, was established to develop new uses for Canadian-produced sulfur (9). Both the U.S. and Canadian programs were primarily concerned with research to develop sulfur construction materials.

Earlier work by Dale and Ludwig (10-11) and Crow and Bates (12) had shown that SC with excellent strength properties could be prepared from sulfur and aggregate mix-

tures. Their work indicated the necessity for aggregate gradation to obtain the best strength properties. While SC may be prepared by hot-mixing unmodified sulfur and aggregate, durability is a problem. Early SC failed during normal temperature cycling when exposed to humid conditions, and on immersion in water.

When unmodified sulfur and aggregate are hot-mixed, cast, and cooled to prepare SC products, the sulfur binder crystallizes from the liquid state (S_8) as monoclinic sulfur (S_8) at 119° C, with a decrease of 7 vol pct. On cooling to below 114° C, the S_8 starts to transform to orthorhombic sulfur (S_8), which is the stable form of sulfur at ambient temperatures. The transformation is rapid and occurs in less than 24 h. Since S_8 is denser than S_8 , high stress is induced in the material as the solid sulfur shrinks. The sulfur in SC products may be highly stressed, and anything that changes this stress, such as temperature cycling, can cause failure in the sulfur binder and result in disintegration of the SC. The swelling of sulfur mortars observed by Duecker is an example of the failure of a sulfur product through stress relief by thermal cycling.

The Bureau directed its research on SC toward two goals. The first was to develop an economic means for modifying the sulfur so that the SC products would not be highly stressed and would have good durability. While olefinic polysulfide additives showed promise, their costs were prohibitive with respect to large-scale construction uses of SC. By reacting sulfur with an unsaturated hydrocarbon, dicyclopentadiene (DCPD), stable sulfur cements were prepared by the formation of long-chain polymeric polysulfides (13-16). The second goal was the development of mixture designs and specifications for the preparation of durable, corrosion-resistant SC. This goal also was achieved (17-23).

Other methods for treating sulfur for use in SC have been reported. Vroom (24-25) used olefinic hydrocarbon polymer materials; Luetner and Diehl (26) used DCPD; Gillott (27) used crude oil and polyol additives; Schneider and Simic (28) used DCPD or a glycol; Woo (29) used phosphoric acid to improve freeze-thaw resistance; and Nimer and Campbell (30) used organosilane to improve water stability. In addition, Gregor and Hackl (31) have reported on laboratory design tests for DCPD-modified SC products; Bright (32) reported on modified sulfur systems; and Bordoloi and Pearce (33) reported on stabilizing sulfur with DCPD.

While modification of sulfur by reaction with DCPD has been investigated by many researchers, its use in commercial applications has been limited because the reaction between sulfur and DCPD in preparing sulfur cement is exothermic and requires close control. Also, the cement is unstable when exposed to high temperatures (140° C), such as those encountered in mixing with hot aggregate, and may react to form an unusable SC product. The Bureau devised methods for preparing modified sulfur cements that are stable, can be manufactured easily, and are not temperature-sensitive at mixing temperatures used for producing SC (17). These methods are based on a controlled reaction of cyclopentadiene (CPD) with sulfur in mixtures of DCPD and oligomers of CPD, hereafter referred to as "oligomer."

Commercial production of the sulfur cements devised by the Bureau was initiated by Chemical Enterprise, Inc., of Houston, TX, in 1979, after a successful pilot production

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

⁵Reference to specific products does not imply endorsement by the Bureau of Mines.

of 300 st by the company in a joint project with the Bureau and The Sulphur Institute. Since then, commercial production and installations of corrosion-resistant SC have increased continually. Currently sulfur concretes are being precast or installed directly in industrial plants where Portland cement concrete (PCC) materials fail from acid and salt corrosion. Typical installations are floors, sumps, electrolytic cells, drainage ditches, sidewalls, and foundations for columns and pumps. Limited commercial application of a proprietary SC technology developed by Vroom (24-25) has also been made in the United States.

The descriptions of corrosion-resistant SC materials in this chapter are based on commercial applications that use the Bureau's technology.

SULFUR CEMENTS

The need to plasticize sulfur for use as cement was recognized during the 1930's. Many types of organics have been employed in efforts to produce durable cements, but only a few organics are used commercially.

A mixed modifier system of DCPD and oligomers (of CPD) developed by the Bureau is currently being used commercially to produce uniform durable cements (17). The oligomers are obtained from the production of DCPD resins, such as steam sparge oils, and contain less than 5 wt pct CPD. The major oligomer components are approximately 10 wt pct dimer, 10 wt pct trimer, 20 wt pct tetramer, 45 wt pct pentamer, and 10 wt pct higher polymer. Generally, a 5-wt pct-modifier content was the best for producing rigid types of concrete.

A generalized reaction employing the mixed modifier is illustrated in figure 1. The initial CPD for sulfuration is supplied by DCPD, which spontaneously depolymerizes at room temperature.

The percentage of DCPD in the mixture can be varied in the range of 40 to 50 wt pct to produce cements with stable and reproducible viscosity characteristics. As illustrated in figure 2, chemical mixtures with less than 40 wt pct oligomer result in unstable cements that are too reactive for subsequent concrete production. These cements exhibit increasing viscosity with age at elevated temperatures and are similar in behavior to DCPD-modified sulfur.

The cements are prepared in the temperature range of 140° to 150° C at ambient pressure in a sealed, jacketed reactor. Normal reaction times are 4 to 6 h, after which the molten cement can be solidified for future use or used directly as a liquid.

Differential scanning calorimetry (DSC) thermograms for sulfur and modified sulfur cements are shown in figure 3. The thermograms were made on samples aged for 14 months at ambient temperature. Cement B was prepared using a 50-50 mixture of DCPD and oligomer, at 5 wt pct. This cement, hereafter referred to as "50-50 cement," remained in the S_β phase. The DCPD-modified cement (C), originally in the S_β phase, transformed to the S_α phase resulting in a curve similar to the curve for unmodified sulfur (A). A DSC thermogram for the 50-50 cement after 21 months of aging was identical to the 14-month curve (B). The thermograms show that the 50-50 cement does not undergo a phase transformation from S_β to S_α on solidification. Because there is no phase transformation, internal stress is eliminated; therefore, SC made with the 50-50 cement has greater durability than SC made with the other cements represented in figure 3.

Linear thermal expansion values as a function of temperature are shown in figure 4 for plasticized sulfur. Unmodified sulfur goes through an S_α -to- S_β transformation with a rapid increase in volume. The 50-50 cement was heated to its softening point, but did not go through a S_α -to- S_β transition. For unmodified sulfur cement, a 13-vol-pct contraction occurs on solidification of the liquid and through the S_β -to- S_α transformation. Since the stable S_α phase is denser and occupies 6 pct less volume than does the solid S_β phase first formed on solidification, there is a resultant stressing of the sulfur binder in the solid state. The 50-50 cement, however, 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 SC and less stressing of the binder. The thermal expansion coefficients of the two materials are given in table 1.

Composition and properties were determined for 50-50 cement prepared by reacting sulfur with DCPD and oligomer at 145° C for 6 h. A typical analysis is shown in table 2.

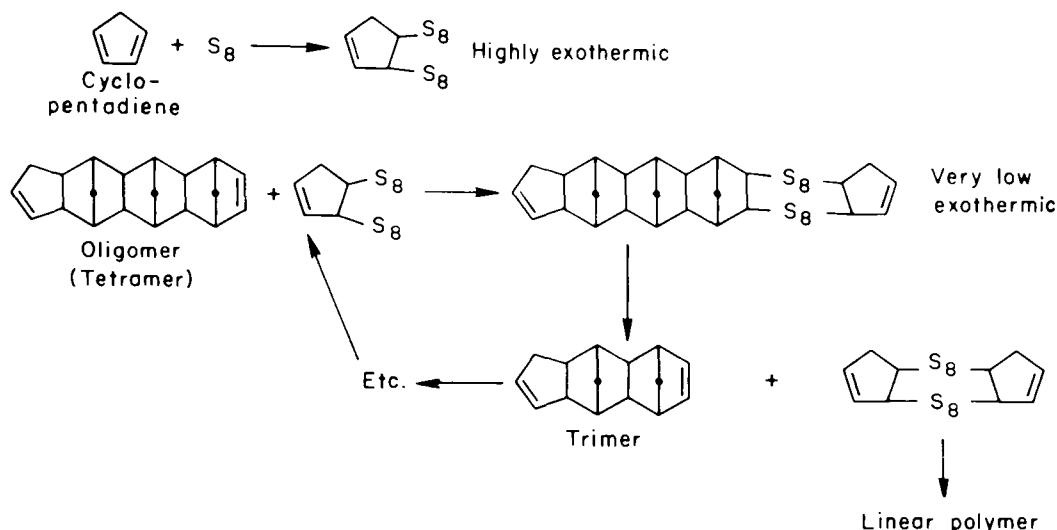


Figure 1.—Generalized reaction for sulfur cement production employing mixed modifier.

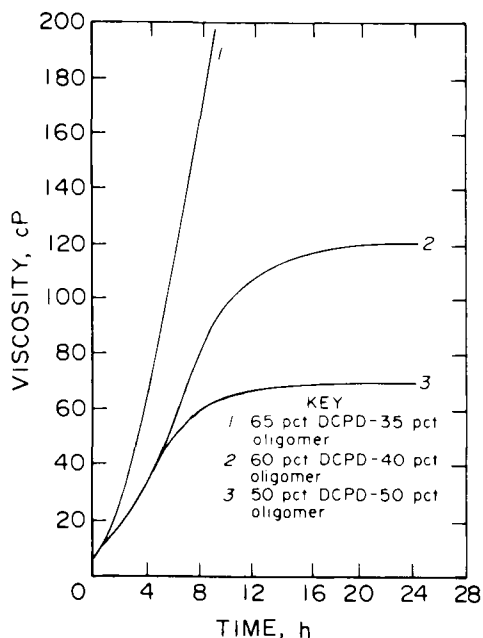


Figure 2.—Viscosity of modified sulfur cements versus time at reaction temperature of 140° C.

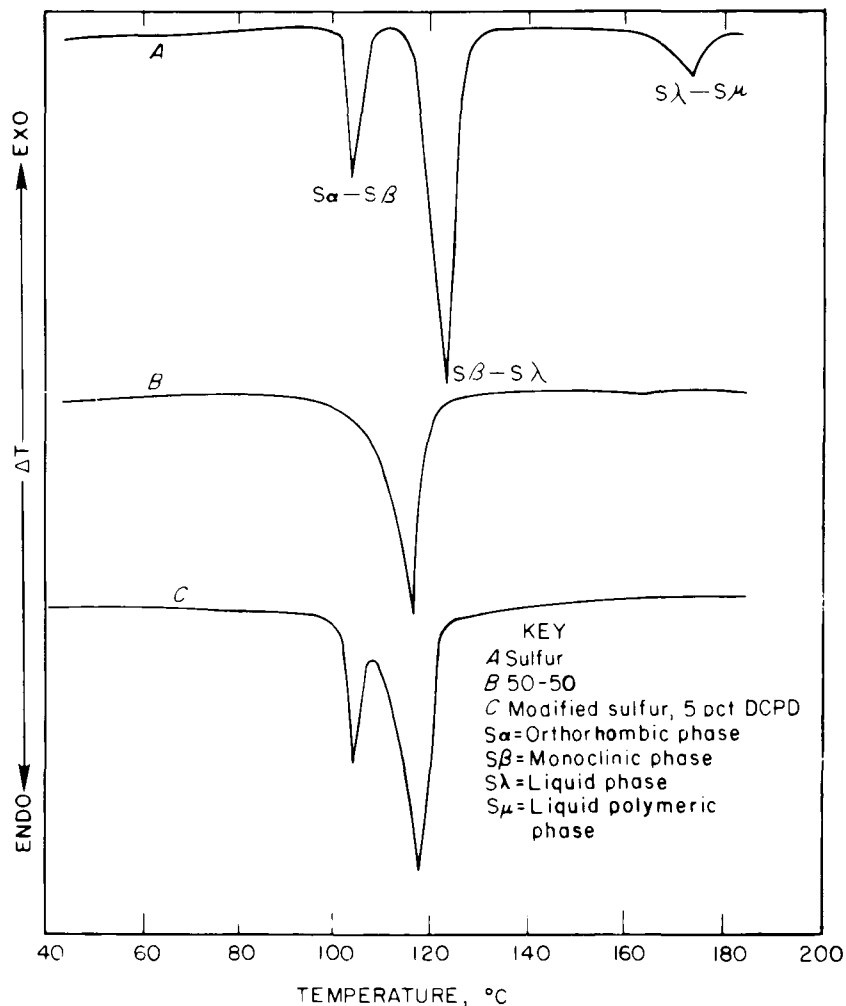


Figure 3.—Differential scanning calorimetry thermograms for sulfur cements after 14 months of aging.

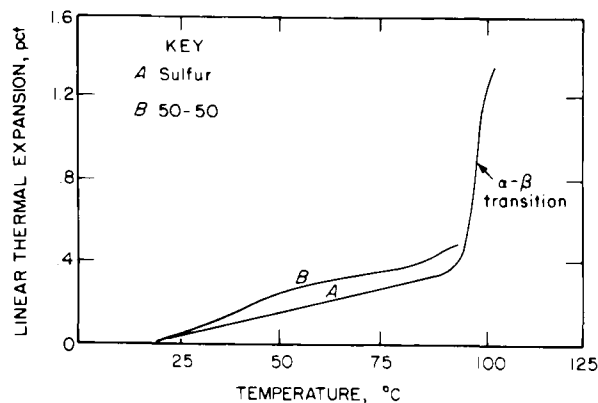


Figure 4.—Linear thermal-expansion data for sulfur and sulfur cement.

TABLE 1.—Thermal-expansion coefficients of sulfur cements

	Coefficient, 10 ⁻⁶ in/(in·°C)
Sulfur:	
25° to 95° C	46
95° to 108° C	1,000
50-50 cement ¹ at 25° to 100° C	59

¹Testing was limited to 100° C maximum because of softening of the sample.

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

	Value
Sulfur	pct 94.8
Carbon	pct 4.4
Hydrogen	pct 0.45
Viscosity at 135° C	cP .50
Specific gravity	1.90

MIXTURE DESIGN

As with PCC and asphaltic concrete (AC), the best mixture design for SC must take into consideration the properties desired for specific uses. The strength properties of SC are influenced by the amount and types of sulfur cement binder and the aggregate gradation, just as cement and water contents and aggregate proportions are used to obtain specific PCC strength properties. The mixture designs for SC materials discussed below are suitable for construction of floors, foundations, tiles, sumps, and electrolytic cells for use in acid or salt environments. These uses require materials with acceptable mechanical strength, chemical resistance, and durability and a minimum capacity for moisture absorption.

Aggregate Gradation

Aggregates generally are obtained from two sources. One is sand and gravel deposits produced by natural weathering and abrasion caused by running water. These aggregates are primarily silica. The second source is quarried rock, which is crushed and screened for use as aggregate. Quarry stone products include limestone, granite (all coarse-grained igneous rock), traprock (all fine-grained igneous rock), and sandstone. Aggregates for corrosion-resistant SC must be clean, hard, tough, strong, durable, and free from any swelling constituents. In addition, they must resist chemical attack and absorption of water 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 homogeneous sources of mineral aggregate. In developing mixture designs for SC, aggregates with chemical resistance consistent with the intended SC use must be selected. For example, quartz aggregates are suitable in acidic environments, whereas either quartz or limestone aggregates may be used where salt corrosion is a problem.

In previous work, SC's were prepared using aggregate gradations that were suitable for PCC (15). These gradations are shown in figure 5. These SC's had excellent corrosion resistance and mechanical properties when sufficient binder was used to fill the voids in the mineral aggregate. However, disadvantages were the large amount of binder required (22 to 26 wt pct) and the amount of shrinkage on cooling and solidification of the concrete. Crushed aggregates produced superior-strength SC compared to SC made with rounded sand and gravel aggregates. The properties of SC referred to in this chapter are for SC made with crushed aggregates.

Mechanisms involved in preparing SC are different from those used in PCC preparation. Sulfur concrete is a thermoplastic material that is mixed and cast hot. On solidification and cooling to ambient temperatures, the liquid sulfur binds the aggregate and forms a rigid SC. Portland cement concrete is prepared at ambient temperatures and relies on a chemical hydration reaction to form the concrete.

New aggregate gradation designs were devised for SC, based on technology for AC, another thermoplastic material

(34). The gradation design was aimed at developing aggregate mixtures with maximum density and a minimum volume of voids in the mineral aggregate. With this design, less sulfur is required to fill the voids in the aggregate mixture. In most cases, this results in stronger materials because of improved aggregate contact and in less shrinkage on solidification because of decreased sulfur binder requirements.

Suitable aggregate gradation designs for SC were achieved based on Fuller maximum density curves (34), shown in figure 6, for materials having a maximum size ranging from 8 mesh to 1 in. The Fuller maximum density relationship used for designing SC aggregate gradations was

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

where P = total aggregate passing given sieve size, pct,
 d = size of sieve opening,
 and D = largest size (sieve opening) in gradation.

Binder Requirements

The role of the modified sulfur cement binders in corrosion-resistant SC technology is threefold: (1) they bond the aggregate particles together; (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 SC mixture.

In previous work (15), when sulfur cements containing 5 wt pct modifier were used to prepare SC, less binder was required to fill the voids in the mineral aggregate than was required when an unmodified sulfur binder was used. Since modified sulfur cements are more viscous than unmodified sulfur when they are mixed with aggregate, 4 to 8 pct air voids are entrained in the binder and increase the volume. The entrained air occurs as discrete bubbles that are not interconnected; thus, moisture absorption into the material is negligible. In contrast, PCC forms interconnected voids that increase moisture absorption and decrease resistance to corrosion and freeze-thaw damage.

To obtain corrosion-resistant SC with good strength and

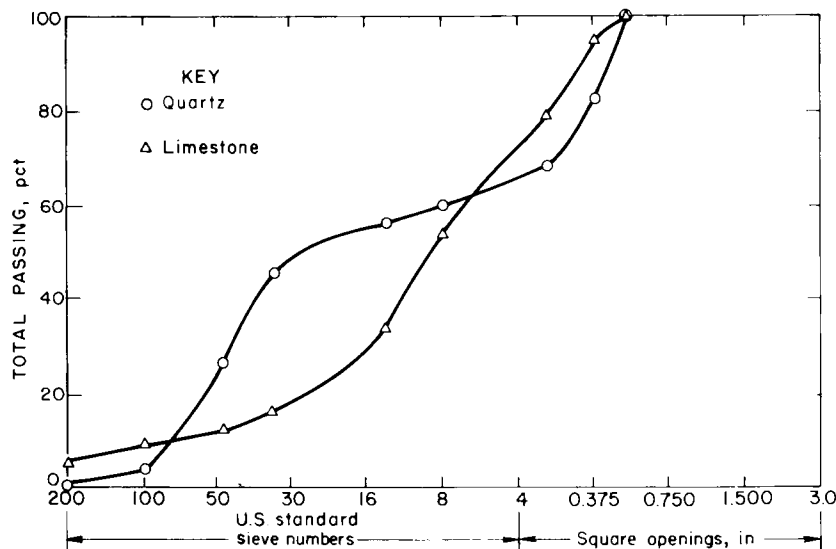


Figure 5.—Aggregate gradation curves, open graded.

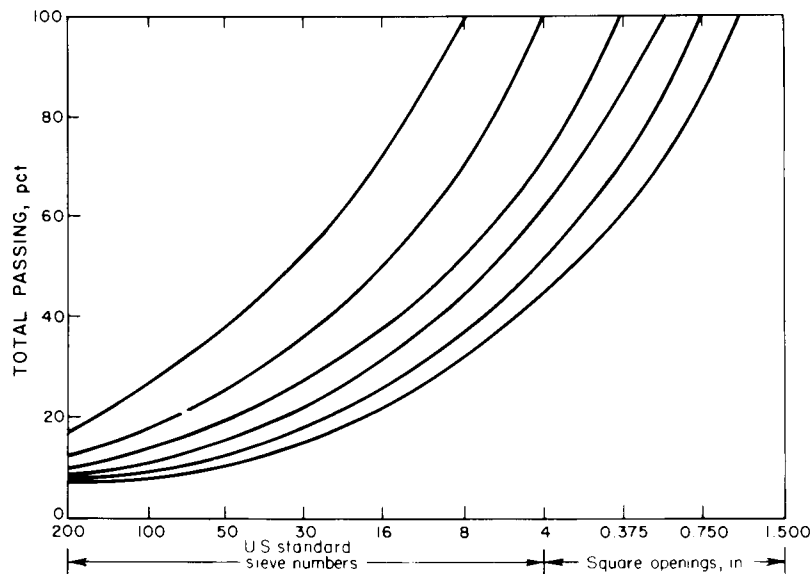


Figure 6.—Aggregate gradation curves, dense graded.

durability, the mix is designed for moisture absorption of less than 0.1 pct and preferably below 0.05 pct. To determine the best mix design, the binder level is adjusted to provide the best balance between maximum compressive strength, maximum specific gravity, minimum absorption, and a workable mixture.

The best mix design was found to consist of a binder range of 16 to 18 wt pct using a 3/8-in aggregate. For both quartz and limestone aggregates, binder levels within this range produced fluid, workable mixtures that yielded SC

with maximum compressive strength and specific gravity and a minimum capacity for water absorption. Figures 7 and 8 show the changes in compressive strength and in specific gravity, respectively, in SC prepared with 3/8-in aggregate and various 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 and for the 3/8-in limestone aggregate was 18 pct. Independent mix designs should be made for each type and gradation of aggregate. For example, when a 1-in, dense-graded quartz aggregate was used, the optimum binder level of 50-50 cement was 14 wt pct, and the SC product had approximately the same strength values as SC made with 3/8-in, dense-graded quartz aggregate.

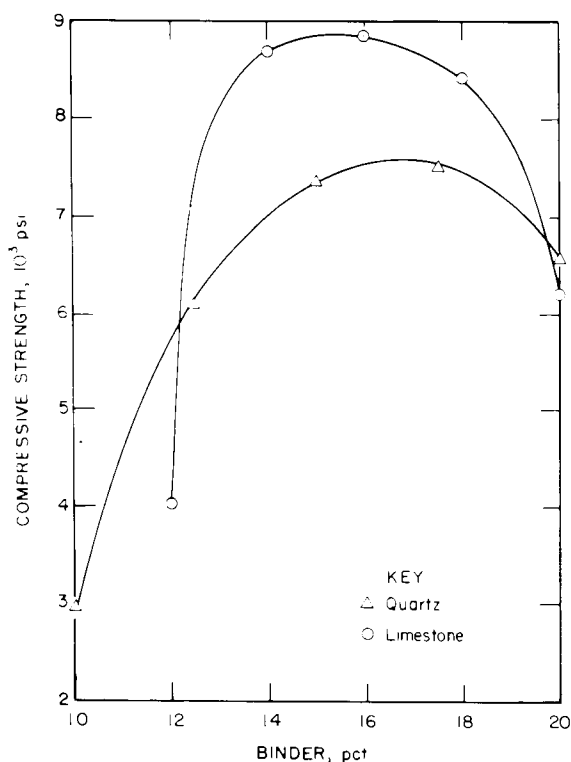


Figure 7.—Variation of SC compressive strength with sulfur cement content.

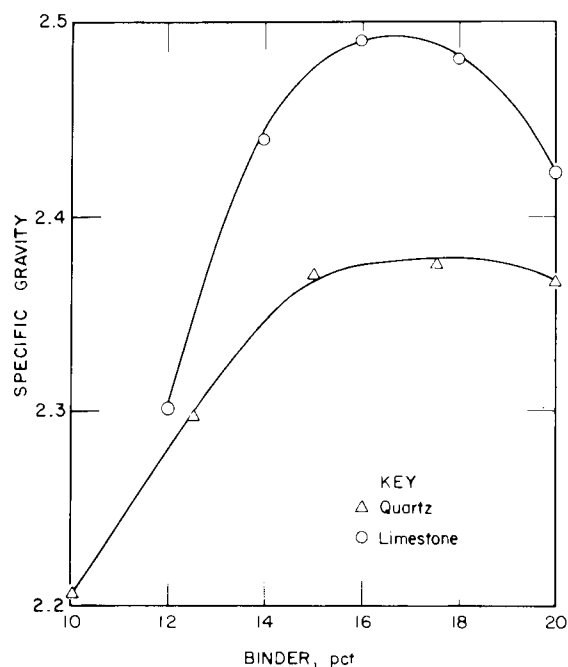


Figure 8.—Variation of SC specific gravity with sulfur cement content.

PROPERTIES

Mechanical Properties

Strengths of typical modified SC's are given in table 3. The measurements were determined in accordance with standard ASTM methods for concrete and mineral aggregates (7). Compressive strength was determined in accordance with ASTM Method C 39, "Compressive Strength of Cylindrical Concrete Specimens;" tensile strength measurements were made in accordance with ASTM Method C 496, "Splitting Tensile Strength of Cylindrical Concrete Specimens;" and flexural strength measurements were made in accordance with ASTM Method C 78, "Flexural Strength of Concrete (Using Single Beam With Third-Point Loading)."

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

Approximately 80 pct of the ultimate mechanical strength of the modified SC was attained within 24 h after casting, and the ultimate strength was achieved after 6 to 12 months of aging. Changes in strength from aging were attributed to nucleation and growth of S_p crystals in the binder.

Load Deflection in Compression

Stress-strain behavior of modified SC prepared with quartz aggregate and a conventional modified cement (50-50) was studied as a function of time for a 1-yr period, using a procedure described previously (14). Cylindrical samples were tested initially and at 3-month intervals. Data for the tests are plotted in figure 9. The load-deformation (stress-strain) curves indicate that aging increased the stress-to-failure values significantly during the first 180 days. Initially, the materials exhibited some plastic yielding when the load increased. After 91 days, the curves approached a more elastic position and showed some plastic yielding occurring at stress levels above 7,000 psi.

The failure mode of the material was transgranular rupture of the aggregate, indicating that the bond strength exceeded the aggregate strength. The aggregate was quartz rock, which is brittle material.

Figure 10 shows ultimate compressive strength and modulus of elasticity values calculated from the load-deflection curves. The SC increased in modulus of elasticity and strength during a 180-day period in a manner similar

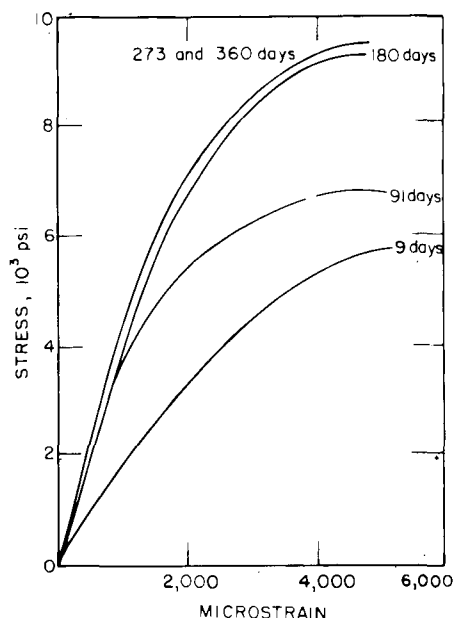


Figure 9.—Stress-strain curves for modified SC made with 50-50 cement.

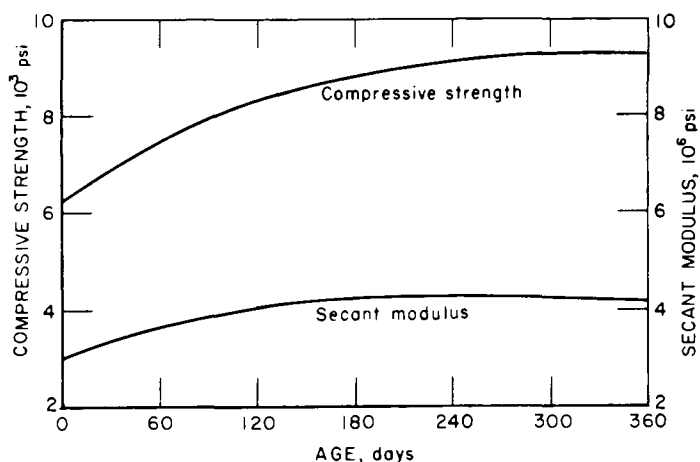


Figure 10.—Compressive strength and modulus values calculated from load-deflection curves for modified SC made with 50-50 cement.

to the behavior of PCC. The strength increase was attributed to nucleation and growth of S_p crystals in the matrix.

TABLE 3.—Strengths of typical SC's

Aggregate		Sulfur cement, pct	Strength, psi		
Type	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

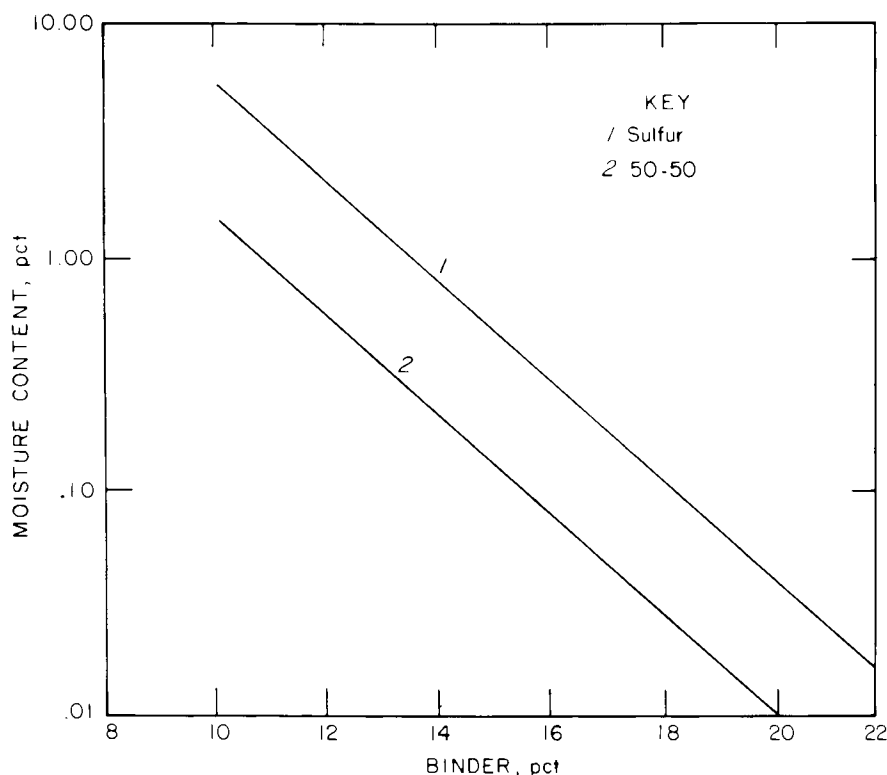


Figure 11.—Moisture absorption versus binder content of SC.

Moisture Absorption, Specific Gravity, and Air Voids

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

Figure 11 shows the variation of moisture absorption with binder content in SC using a sulfur or 50-50 cement binder and dense-graded 3/8-in quartz aggregate. To obtain less than 0.05 pct moisture absorption would require 17 pct 50-50 cement or 20 pct S. The lower binder requirements for modified sulfur result from natural entrainment of discrete air voids during the mixing cycle because of the higher viscosity of the cement. Fewer entrained air voids are generated when unmodified sulfur and aggregate are mixed.

Static water-permeation tests were made to compare the permeability of SC and PCC. Five-foot sections of 6-in-diam plastic pipe were bonded to the surface of 2-in-thick slabs of SC and PCC. A 51-in column of water was placed in each pipe section to provide 1.84 psi water pressure on the surface of the slabs. The SC showed no loss in water height after 6 months, while the PCC slab showed more than a 1-in/h loss of water height by permeation through the more porous PCC material. There was no penetration of water through the SC slab.

The specific gravity of SC was determined on 3- by 6-in-high cylinders of the cast material. The measurements were made in accordance with ASTM Method C 642, "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 calcula-

TABLE 4.—Air-void content of various SC formulations, percent

SC formulation		Air-void content	
Quartz aggregate content	Cement content	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	16	2.2	3.3
85	15	3.6	3.7
84	16	3.3	3.7

tion of the void content from the actual specific gravity of the SC sample and the theoretical specific gravity of the aggregate-binder mixture, and by microscopic determination in accordance with ASTM Method C 457, "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 4 compares the results obtained by the two methods for various SC formulations with 50-50 cement.

Thermal Expansion of Modified-Sulfur Concrete

Linear thermal-expansion values for specific aggregates and the concrete materials were determined on 1/2- by 1/2- by 1-in samples. The expansion was measured over a 25° to 100° C temperature range at a constant heating rate of 3° C per minute. The values obtained are plotted in figure 12, and thermal-expansion coefficients are shown in table 5. The thermal-expansion coefficient of the modified-sulfur cement is given for comparison purposes.

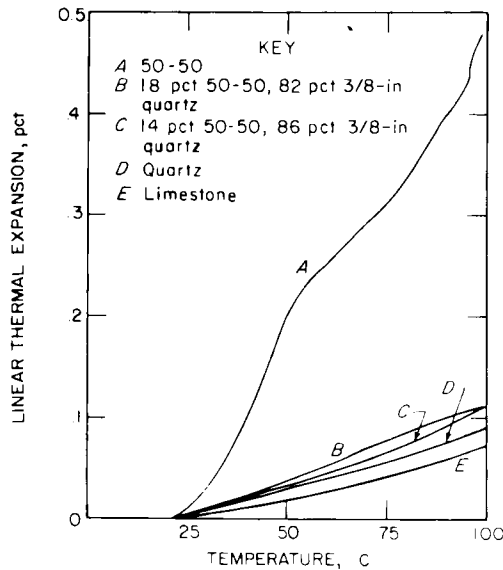


Figure 12.—Linear thermal expansion of sulfur cement (A), SC's (B and C), and aggregate materials (D and E).

The values shown in table 5 indicate that thermal expansion of modified SC increased with the amount of cement used in the mix. For SC's containing sulfur binder content from 22 to 14 pct, there is a 1-pct decrease in the coefficient of thermal expansion for every percent decrease in binder content.

Coefficients of thermal expansion for SC materials are important in designing for specific uses because of their usefulness in determining compatibility with other materials. For comparison, the coefficient of thermal expansion for a quartz-aggregate PCC is 11.9×10^{-6} in/(in·°C) and for steel is about 12×10^{-6} in/(in·°C).

TABLE 5.—Thermal-expansion coefficients of sulfur cement, aggregates, and SC's between 25° and 100° C

	Coefficient, 10 ⁻⁶ in/(in·°C)
Limestone aggregate	9.3
Quartz aggregate	12.0
50-50 sulfur 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 the long-range durability of SC is to determine its ability to withstand damage by rapid freeze-thaw cycling. Testing was performed on modified SC cast vertically into 3- by 3- by 14-in prisms. ASTM Method C 666, "Resistance of Concrete to Rapid Freezing and Thawing, Procedure A, Rapid Freezing and Thawing in Water," was followed. Figure 13 shows the typical behavior of a quartz-aggregate modified SC during freezing and thawing at temperatures between -18° and 4.4° C. After 300 freeze-thaw cycles, the concrete retained 80 pct of the relative dynamic modulus of elasticity. This is typical behavior for SC prepared with the best mix procedure and having a moisture absorption value of less than 0.05 pct. ASTM criteria require 60 pct modulus retention after 300 cycles.

The effect of SC moisture absorption on freeze-thaw durability is shown in figure 14. The relative dynamic modulus of elasticity is plotted against initial water absorption of different quartz-aggregate modified SC formulations. When the moisture absorption capacity of an SC 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 SC materials with a uniformly low absorption potential.

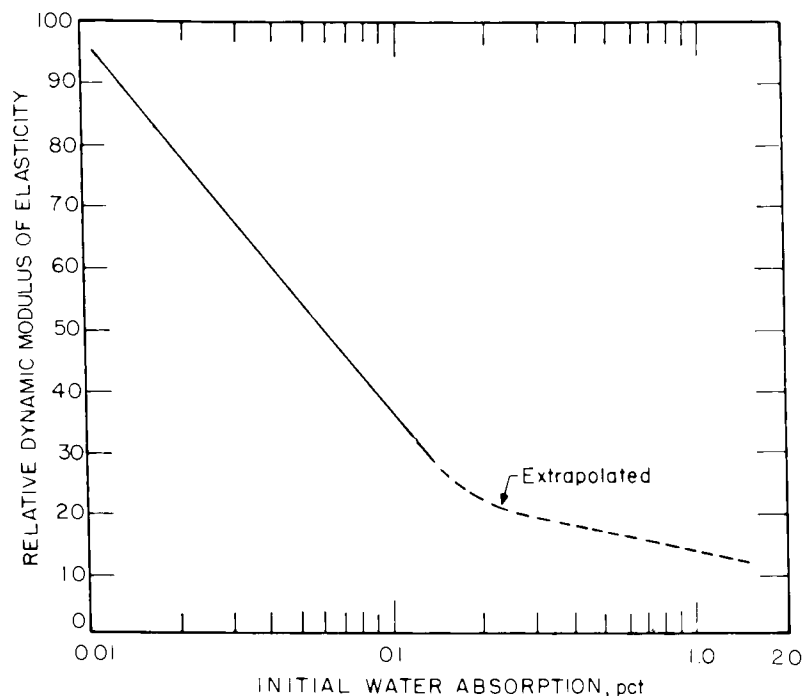


Figure 13.—Freeze-thaw durability of modified SC made with 50-50 cement.

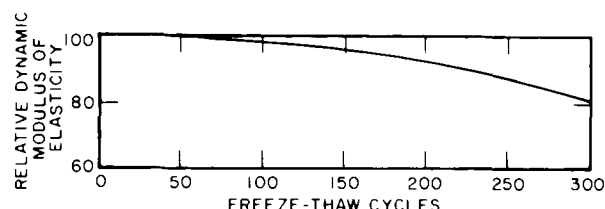


Figure 14.—Effect of moisture absorption of SC on relative dynamic modulus of elasticity.

Resistance to Acid and Salt Corrosion

Previous corrosion testing of SC in different corrosive environments has been reported (14-15). Recently, acid corrosive tests were made on 3- by 6-in cylinders of SC prepared from 3/8-in dense-graded quartz aggregate and 17 pct modified-sulfur cement. The test cylinders were immersed in 10-, 20-, 60-, and 96-pct- H_2SO_4 solutions for a 1-yr period. The samples were removed every 3 months to determine if any changes in weight or specific gravity or if any chemical damage had occurred. Some samples were evaluated quarterly for compressive strength measurements.

No signs of spalling or corrosion of materials were observed during the 1-yr program. A slight weight gain was noted, and absorption increased 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 sulfuric acid solutions. The small change in absorption over the 1-yr period indicated that solution penetration into the SC was very slight and that it would not reach any reinforcing materials used in the SC. Compressive strength measurements showed an increase in strength similar to that shown in figure 10.

Industrial Evaluation

The Bureau and The Sulphur Institute initiated a cooperative test program in 1977 to evaluate the performance of SC under operating conditions in industrial cor-

rosive environments (22). The program involved testing SC in 40 commercial plants in 56 corrosive environments. The major objectives of the program were to establish the feasibility of using SC in large-scale applications and to determine the ultimate longevity of SC under actual operating conditions in problem environments. Initially, precast components such as tiles, slabs, tanks, and pump foundations were cast at a Bureau laboratory and subsequently transported and placed in industrial plants. When larger scale prototype equipment was developed for SC production, larger scale projects were conducted at the industrial sites. A summary of the tests is listed in table 6. The results obtained from exposing SC to different chemical environments are listed in table 7.

Figure 15 illustrates the destruction of a PCC floor in an electrolytic zinc plant. The entire floor area of the plant was later replaced with SC. An SC support pier was installed to replace a deteriorated PCC support pier in a potash plant (fig. 16). Some other types of test components are shown in figures 17-19. An in situ installation of SC is illustrated in figure 20.

TABLE 6.—Summary of industrial tests of SC performance

	Number of tests
Precast tests:	
Sump tank, 1,000 gal	3
Basin, 400 gal	2
Slab:	
4 by 4 ft by 4 in	8
3 by 3 ft by 3 in	17
2 by 2 ft by 3 in	45
Foundation unit, 8 by 8 ft by 4 in	2
Weir tank, 4 by 4 by 4 ft	3
Pump foundation, 2 by 4 ft	2
Tile loading dock	1
Tile drain ditch	1
Mechanical tests	18 ¹
In situ tests:	
Floor, 37,000 ft ²	4
Pump foundations	6
Sumps	3
Acid loading dock	1

¹Number of specimens.

TABLE 7.—Results of exposing SC to various chemical environments

Environment	Number of different environments	Status of SC as of June 1, 1984 ¹
Sulfuric acid	12	3, 2, 1.
Copper sulfate-sulfuric acid	5	1.
Magnesium chloride	4	1.
Hydrochloric acid	3	3, 2, 1.
Nitric acid	3	1.
Zinc sulfate-sulfuric acid	3	2, 3.
Copper slimes	2	Attacked by slimes.
Nickel sulfate	2	1.
Vanadium sulfate-sulfuric acid	2	1.
Uranium sulfate-sulfuric acid	2	1.
Potash brines	2	1.
Manganese oxide-sulfuric acid	2	1 for slabs, but coupon deteriorated in cell at 95° C.
Hydrochloric acid-nitric acid	2	1.
Mixed nitric-citric acid	1	2.
Ferric chloride-sodium chloride-hydrochloric acid	1	2 at 90° C.
Boric acid	1	1.
Sodium hydroxide	1	Attacked by > 10 pct NaOH.
Citric acid	1	1.
Acidic and biochemical	1	2.
Sodium chlorate-hypochlorite	1	Attacked by solution at 50°-60° C.
Ferric-chlorate ion	1	1.
Sewage	1	3.
Hydrofluoric acid	1	3. Only graphite-aggregate SC held up.
Glyoxal-acetic acid-formaldehyde	1	1.
Chromic acid	1	Deteriorated at 82° C and 90 pct concentration; marginal at lower temperature and concentration.

¹Numbers 1-3 indicate that test results showed no sign of corrosion or deterioration for (1) > 5 yr, (2) 3-5 yr, and (3) < 3 yr.



Figure 15.—Corrosion of PCC by acid electrolytes in electrolytic zinc plant.



Figure 16.—SC support pier used to replace deteriorated PCC pier in potash storage facility. Disintegration of PCC wall behind pier is evident.

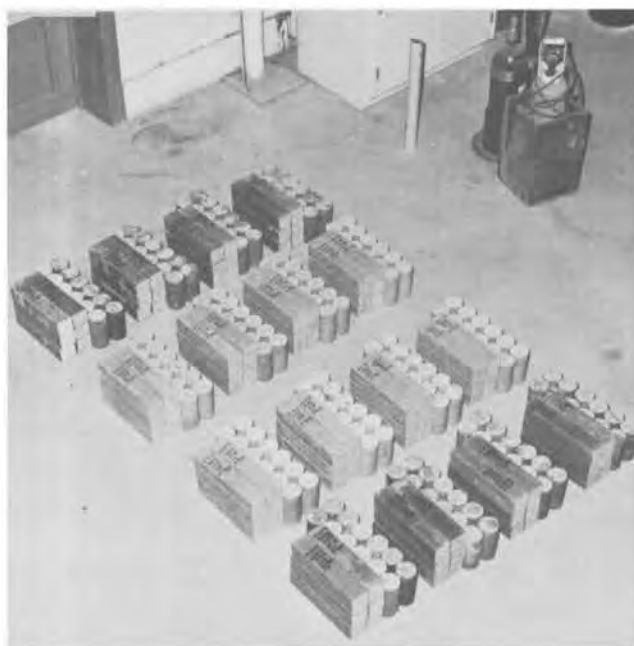


Figure 17.—Test cylinders and bars for corrosion testing.



Figure 18.—SC pump support unit installed with a chlorine gas pump.



Figure 19.—SC sump unit for containing waste acidic solutions.



Figure 20.—Installing SC floor in electrolytic copper plant.

Major industrial corrosion problems are caused by mineral acids or metallic ion species that contain mineral acids. Therefore, many replicate tests were conducted in areas exposed to mineral acids. Test components included materials fabricated with and without the use of reinforcing steel.

The plants used in the corrosion-testing program included metal production and refining operations for aluminum, copper, nickel, lead, manganese, magnesium, titanium, uranium, vanadium, zinc, and precious metals, and chemical and fertilizer production plants for phosphoric, sulfuric, chromic, and nitric acids and sodium and potassium salts.

While the evaluation of corrosion-resistant SC in industrial applications is continuing, the results to date have shown that this has potential for use in many corrosive environments where other materials fail. The use of SC is most promising in areas that are exposed to corrosive electrolytes and acid and salt solutions, which cause major damage to cells, floors, foundations, and equipment. For specific types of corrosion, such as that from hydrofluoric acid, a specialized SC using dense graphite aggregate and modified sulfur cement is required.

The test results showed that SC performed well in the majority of corrosive atmospheres. Deterioration of SC was observed in hot chromic acid solutions, sodium chlorate-hypochlorite, copper slimes, and hot organic solvent solutions. Failures also resulted where SC was exposed to temperatures in excess of 110° (230° F).

The durability and longevity of SC is being established. The oldest corrosion-resistant SC materials under test are components in sulfuric acid solutions and copper electrolytic solutions. These units have shown no evidence of corrosion or deterioration after 9 yr of service. Additional long-term testing will be necessary to fully establish the service life of SC.

After 6 yr of testing SC in chemical processing environments, there was essentially no evidence of material degradation or loss of strength. Conventional concrete materials, however, were attacked and in some cases completely destroyed under the same conditions. Minor degradation, similar to that encountered with PCC, occurred when SC was exposed to strong alkali, hot chromic acid, and copper slimes solutions. Although long-term aging characteristics of SC materials are still being determined, these materials already are finding widespread use in metallurgical, chemical, and fertilizer processing plants.

MANUFACTURING PROCESS

Commercial preparation and installation of corrosion-resistant SC is a new industry which has developed in the last 3 yr. Techniques for SC manufacture and installation are still being improved. Present technology is based upon techniques and equipment used in PCC and AC production.

Equipment

Production of SC requires equipment for measuring, blending, and heating aggregate materials to specifications. Mixing of the hot aggregate with modified sulfur cement will produce a homogeneous SC in the temperature range of 127° to 149° C (260° to 300° F). Equipment that has been successfully used to prepare SC includes the following:

1. A small-scale unit capable of preparing 500-lb

(288-kg) batches of SC and consisting of a propane-heated kiln feeding into a electrically heated mortar mixer (fig. 21).

2. Heat-jacketed concrete transit-mixers with SC capacities up to 16 st per batch. Aggregate may be heated in the unit or added hot before mixing with the sulfur cement. Two commercial SC mixing units are shown in figures 22 and 23, respectively.

3. Modified mobile asphalt batch plants with SC capacities of 12 to 30 st/h. A 12-st/h unit is shown in figure 24.

4. Modified hot-mix asphalt batch plants. Plants of various capacities have been converted to SC production.

The mixing time for preparing homogeneous SC mixtures may vary from less than 1 min to considerably longer and depends on the type of equipment used.

Preparation, Casting, and Finishing

Production of SC is accomplished by mixing hot aggregate and modified-sulfur cement to produce a concrete material in the 127° to 149° C (260° to 300° F) range. Either molten or flaked cement may be used to prepare SC. When using flaked instead of molten cement, an aggregate temperature of 171° to 193° C (340° to 380° F) is necessary to obtain the desired SC temperature range.



Figure 21.—Small-scale (500-lb) batch plant for SC.



Figure 22.—Mobile mixing unit for SC.



Figure 23.—SC transporter with heating and mixing system (10-yd³ capacity).



Figure 24.—Mobile 12-st/h SC mixing unit.

Casting the SC is accomplished either by discharging it directly from a mixing unit into forms or by transporting it from the mixing unit in concrete buggies with insulated hoppers. Sufficient SC should be prepared or available to make a complete pour; this is necessary to obtain a homogeneous slab. Sulfur concrete must be poured on a dry base, because moisture will be vaporized by the hot concrete, form minute channels through the casting, and render it susceptible to penetration by corrosive liquids. When SC is cast over existing PCC, a barrier, such as a bituminous mastic coating, should be installed over the PCC to prevent moisture vaporization from the PCC and to provide a corrosion barrier between the two materials. The development of construction practices for commercial SC installation has been described by Yarbrough (34) and Pickard (35). Yarbrough reported on the use of a slip-plane membrane to provide both a barrier between PCC and SC and an effective

stress-relief plane between the two materials. He described the use of polyvinylchloride (PVC) waterstops and different types of sealant materials to waterproof joints between adjacent SC pours.

When casting a horizontal slab of SC, a continuous pour should be made from one end to the other. A vibratory probe may be used in casting SC; however, mold-release agents should be used on the forms. Metal forms also should be preheated to approximately 95° C (203° F) to prevent premature freezing of a skin of sulfur cement on the surface of a cold mold.

Consolidation of SC castings may be accomplished by rodding, using a vibratory probe, or casting on a vibratory table. Finishing SC is generally accomplished by screeding with a wood vibratory screen to consolidate and level the concrete. If further finishing is necessary, it may be done with wood or metal trowels. All finishing of SC should cease

when any of the concrete solidifies. When finishing an SC surface using trowels, the trowels should be kept in contact with the hot SC to prevent solidification of the concrete on the trowel.

Safety

Construction of SC materials involves precautions and practices similar to those encountered in paving operations with hot-mixed AC. Normal precautions for handling hot fluid materials must be observed, such as wearing proper protective clothing, safety glasses, goggles or face shields, gloves, and hard hats. Practices for safe handling of both solid and liquid sulfur have been established by the National Safety Council (37-38), and these practices should be observed in preparing and handling SC.

When using SC as a construction material, its limitations and its advantages must be recognized. Sulfur concrete, like wood or plastic materials, will burn on exposure to a direct flame source, but properly prepared SC using dense-graded aggregate will cease burning on removal of the heat source. If exposed to temperatures above 96° C (205° F), SC will lose strength. If the temperature exceeds the melting point of the sulfur cement, the cement will start to melt and lose its integrity. Also, SC must be used in applications consistent with its strength and thermoplastic properties.

When SC materials are produced in the recommended mixing temperature range of 127° to 149° C (260° to 300° F), gaseous emissions of sulfur dioxide and hydrogen sulfide will not exceed the allowable threshold limit values, and sulfur vapor emissions will be minimized. The threshold values established for sulfur dioxide are 5 ppm for a short-term exposure and 2 ppm (time-weighted average concen-

tration) for an 8-h exposure. The corresponding values for hydrogen sulfide are 15 and 10 ppm, respectively (39). These gases can be monitored and measured with commercially available instruments (fig. 25).

Sulfur vapor crystallizes on cooling into fine dustlike particles. Sulfur dust may cause eye irritation, but this problem can be minimized if workers are required to wear goggles in areas where there is a potential for exposure to sulfur vapors and/or dust.

The toxicity of modified sulfur cements (sulfur reacted with 5 pct mixed DCPD and oligomer) has been investigated (40). The results were similar to those for sulfur. Two-hour inhalation tests of vapor from cement heated to 141° C (285° F) showed no toxic effects.

ADVANTAGES AND DISADVANTAGES

The main advantage of SC is that it can be used in applications where state-of-the-art materials fail. It is a corrosion-resistant construction material with excellent mechanical properties. So far, the main use of SC has been as a replacement for PCC in industrial plant areas where acid and metallic salt environments result in the destruction of PCC. In new construction, SC installations would cost less, compared with replacement installations (21), and quality control would be simplified. While the ultimate life or durability of SC has not been completely established in many end-use applications, enough evidence of its corrosion resistance and durability has been accumulated to show that it has at least three times the life of most of the construction materials presently being used in corrosive environments (22).

Another advantage of SC is its fast setting time. Since



Figure 25.—Recording instruments for measuring hydrogen sulfide and sulfur dioxide concentrations.

it achieves most of its mechanical strength in less than 1 day, forms can be removed and it can be placed in service without a long curing period.

The in-place cost of SC is considerably higher than that of PCC and varies according to the size of the project. However, the initial higher cost of SC is offset by elimination of the need for protective coatings, plant downtime, and repair and/or replacement costs for corroded concrete.

A disadvantage in using SC is that, like wood and plastics, it will burn if exposed to open flame. If exposed to prolonged temperatures above the melting point of the sulfur cement, it will lose structural integrity. However, since SC is a poor thermal conductor, it will not be destroyed on short exposures to elevated temperatures. Potential interaction with oxidant chemicals such as ammonium nitrate could promote fire hazard (41).

Production and placement techniques for SC are still in the developmental stage, but are being improved as more experience is gained. Currently, there is a lack of standard specifications for SC materials. However, the American Concrete Institute has established a new subcommittee on SC with the purpose of developing a state-of-the-art report and user's guide (42).

SUMMARY

Technology has been developed to prepare corrosion-resistant SC. A modified sulfur cement has been developed in which sulfur is reacted with DCPD and oligomers (of CPD) to form a stable cement product. Mixture designs utilizing corrosion-resistant aggregates and modified sulfur cements have been developed to prepare stable SC for use as a corrosion-resistant construction material. Sulfur concretes have been produced with excellent resistance to damage by most acid and salt environments, good mechanical strength properties, resistance to damage by freeze-thaw cycling, and coefficients of expansion compatible with those of other construction materials such as PCC and reinforcing steel.

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

CHAPTER 2.—SULFUR SPRAY COATINGS

HISTORY

Sulfur spray coatings were originated in the early 1950's. Marian Barnes (43) of The Sulphur Institute conceived the idea of using sulfur coatings as a replacement for mortar in construction. The technique that resulted, known as surface-bond construction (44), uses sulfur coatings to bond bricks or blocks stacked without mortar to achieve the desired wall configuration. The coatings are applied to both surfaces of the wall. The strength of sulfur bonding compared with conventional mortar and other building techniques has been reported by Hubbard (45), Testa and Anderson (46), and Dale and Ludwig (47). Hubbard's work indicated that sulfur is superior to conventional mortar in all important aspects. In some cases, walls made with blocks joined by sulfur surface bonding were 10 to 20 times stronger. In 1963, a sulfur-surface-bonded building was constructed at the Southwest Research Institute, San Antonio, TX (48). The sulfur coating was applied to both sides of stacked blocks by hot application with paint brushes. The building is still in use and demonstrates the technical feasibility of the technique. In 1973, a sulfur-surface-bonded building was built by the Bureau at Boulder City, NV (fig. 26) (13). Spray equipment was used to apply the hot sulfur-fiber formulation. Surface-bond construction techniques have also been used to construct an addition to a house in New Mexico and low-cost housing in Colombia, and demonstrations have been conducted in Tanzania and Botswana (44).

Other uses of sulfur spray coatings have also been developed. In 1972, Dale and Ludwig (49) reported on a sulfur spray coating for mine support. In 1975, Sullivan, McBee, and Blue (13) discussed the use of sulfur coatings for structural materials, pollution abatement, and the stabilization of fine tailings materials. In 1976, Fike (50) reviewed the status of sulfur coating technology. Recent emphasis has been on the development and commercialization of sulfur spray coatings for use as canal, pond, and basin linings; in land, slope, and tailings stabilization; and as protective coatings for concrete and masonry surfaces that are exposed to corrosive acid and salt solutions (13, 51-56). Sulfur spray coatings have also been developed for use as traffic marking paints (57). This chapter discusses the corrosion-resistant and surface-bonding types of sulfur coatings.



Figure 26.—Surface-bonded block building.

MIXTURE DESIGN

The design of sulfur spray composites has developed according to the requirements for their use. Dale (49) designed a sulfur spray coating to seal and support mine walls. It consisted of 100 parts sulfur, 10 parts talc, 3 parts milled glass fibers, and 2 parts DCPD. This formulation was also used as a sprayable surface-bonding composition for mortarless construction of block buildings.

Mixture design technology to modify and control the properties of sulfur spray composites has advanced significantly in recent years. The beneficial effects of sulfur plasticizers such as olefins and polysulfides have been demonstrated. Various fillers, reinforcing agents, and other modifiers have been developed to improve the properties of the composites, such as durability and thermal shock resistance.

Components of sulfur spray coating mixtures are generally used in the following (percent) ranges:

Sulfur	75-95
Fillers	5-15
Fibers	0-10
Chemical modifiers	2-15

The proportion of each component depends on its properties and on the intended use of the spray coating. Increasing the proportions of fillers increases viscosity and decreases the coefficient of thermal expansion. Flexural strength improves with increases in fiber content. Chemical modifiers are used to increase durability, decrease reversion of the sulfur to the orthorhombic allotrope, decrease the coefficient of thermal expansion, and impart fire-retardant properties to the spray mixtures.

Sulfur spray coatings are prepared by reacting liquid sulfur (120° to 150° C) with the modifiers, adding the fillers and fibers, and blending to a homogeneous mixture.

SULFUR MODIFIERS

Chemical modifiers perform several functions, such as retarding reversion to the orthorhombic allotrope and imparting fire-retardation qualities by polymerization and cross-linkage of the sulfur (49). Currel (58) has described the reactions of sulfur with limonene; myrcene; alloocimene; DCPD; cyclododeca-1,5,9-triene; cycloocta-1,3,-diene; styrene and polymeric polysulfides; and Thiokol LP-31, -32, and -33 to give mixtures of polysulfides. Limonene, myrcene, and DCPD were particularly effective in retarding reversion to the orthorhombic allotrope. By retarding this reversion, these modifiers can decrease the thermal expansion of sulfur by about half. This decreases the tendency of sulfur coatings to craze or crack when exposed to extreme changes in temperature. Sullivan (13) has described the use of a sulfur spray coating composed of sulfur and modified with DCPD and dipentene for use in stabilizing fine mill tailings. In this application, the dipentene assists in wetting the surfaces and allows more rapid penetration of the spray into the tailings. Modifiers also improve the ability of the sulfur to wet the fillers and fibers. Proper wetting is essential to obtain full benefits from the additives.

FILLERS AND FIBERS

Fillers are used to increase the viscosity of the spray mixture and to prevent running of the spray. Fillers that have been used include talc, silica flour, and mica.

Fibers are used to increase the flexural and shear strength of the coating. Fiberglass, asbestos, and mica have been used for this purpose; they also decrease crazing and cracking.

USES

Many uses for sulfur spray coatings have been reported. These include surface-bond construction techniques, mine-wall sealing and support, and sulfur coatings for land stabilization and dust prevention. Other uses are in containment reservoirs and ponds and as corrosion-resistant coatings used to protect vats, tanks, sumps, silos, storage pads, foundations, pilings, equipment bases, floors, and walls. In general, sulfur coatings are used most intensively

in chemical, metallurgical, and food processing plants where commonly used materials are subject to corrosion.

MANUFACTURE AND APPLICATION

Preparation and Spraying Equipment

Sulfur coating materials are prepared in a heated pressure tank that can be sealed and pressurized for spraying the mixture. A small-scale unit is shown in figure 27. It consists of an electrically heated, insulated tank with a capacity of 400 lb, equipped with a stirring unit and mounted on a trailer. A heated pressure hose with a spray nozzle is bottom-connected to the tank. The unit is capable of operating at up to 200° C and 30 psi.

Commercial units are available that have a capability for preparing and spraying up to 20,000-lb batches of spray mixtures. A 9,000-lb-capacity trailer-mounted unit for applying protective sulfur coating to a concrete floor is shown in figure 28. This unit is equipped with a hot-oil jacket and



Figure 27.—Laboratory-scale sulfur spray machine (13).



Figure 28.—Commercial-scale sulfur spray machine (55).

internal coils for melting the sulfur spray mixture components and has a stirring unit for mixing. Air pressure of 20 to 30 psi is used to force the mixture through two 100-ft heated spray hoses.

To prepare a mixture, sulfur is first reacted with chemical modifiers at 120° to 150° C (248° to 302° F) in the spray unit. Then, on completion of the reaction, the fillers and fibers are added, and the components are mixed until homogeneous. The reactor is sealed, and air pressure is applied to force the mixture through the heated spray hoses.

APPLICATION

The prepared coating is applied molten at 130° to 150° C (266° to 302° F), at spray rates up to 200 lb of coating per minute, using the heated, pressurized hoses mentioned previously. Several thin coatings are applied to insure coating continuity. Each coating is applied about 1/16 in thick, and a total thickness of 1/8 to 1/4 in (1.3 to 2.6 lb of coating per square foot) is applied. The coatings set rapidly and almost immediately attain sufficient strength for use.

Several precautions should be taken in applying the coatings. If applied over concrete, the concrete should be cured and the surface either acid-etched or sandblasted to remove any weak lime coating on the concrete. All materials to be spray coated must be clean and dry to insure good adhesion of the coating. Moisture condensed on the surface will cause poor bonding between coating layers.

Therefore, successive layers should be applied as soon as possible.

Safety

The same safety precautions should be observed in working with sulfur spray coatings as are described in the chapter on SC. Additional precautions such as proper clothing, shoes, gloves, and masks are needed to protect workers from the hot spray. Vapors or mists of sulfur spray coatings may cause eye and skin irritation and allergic skin reactions. In addition, the flammability of the fine overspray material presents a hazard, and precautions must be taken to prevent ignition. Information on the safe handling of spray coatings is available from the producers (55).

PROPERTIES

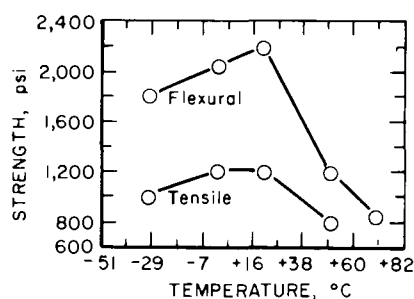
Physical and Mechanical Properties

Recent emphasis on sulfur spray coatings has been on their use as high-strength, sprayable materials for protective coatings. The reported properties of a commercially available spray coating (55) for corrosion-resistant applications are listed in table 8. The properties shown may be altered by changes in the coating formulation, depending on the use of the material. For example, a more flexible coating may be obtained by increasing the amount of plasticizer in the mixture.

TABLE 8.—Typical properties of SUCOAT¹ sulfur spray coating

	Value
Softening point	°C 98
Viscosity (Brookfield) at 140° C	cp 600
Specific gravity	2.0
Coefficient of thermal expansion	°C 35×10^{-6}
Thermal conductivity	Low
Electrical conductivity	Low
Acid and salt resistance	High
Application temperature	°C 120-150
Measurements at 23° C, psi:	
Tensile strength (modified ASTM D 638)	1,000
Flexural strength (ASTM D 790)	2,100
Flexural modulus (ASTM D 790)	6×10^5
Compressive strength (ASTM D 695)	4,000
Compressive modulus (ASTM D 695)	2×10^5
Shear strength (ASTM D 732)	1,100

¹SUCOAT (56), registered trademark, Chevron Chemical Co.

**Figure 29.—Typical strength of sulfur composites versus temperature.**

Paulson (52) determined the effect of temperature variations on the tensile and flexural strengths of a typical sulfur spray material. The results are plotted in figure 29.

Chemical Resistance

One advantage of sulfur spray coatings is their corrosion resistance to most salt and acid solutions. Sulfur spray coatings have many potential uses in chemical, metallurgical, and fertilizer plants as protective coatings on materials that are attacked easily by corrosive solutions, for example, PCC and other materials used in structural supports. Listed below are a number of chemical substances that are compatible with sulfur spray coatings (59).

Salt solutions:

Alum
Aluminum chloride, nitrate, and sulfate
Ammonium chloride, nitrate, and sulfate
Barium chloride, nitrate, and sulfate
Calcium chloride, nitrate, and sulfate
Cupric chloride and sulfate
Iron chlorides, nitrates, and sulfates
Lead acetate, chloride, and nitrate
Magnesium chloride, nitrate, and sulfate
Nickel chloride, nitrate, and sulfate
Potassium chloride and dichromate
Potassium nitrate and sulfate
Sea water
Silver nitrate
Sodium chloride, chromate, and dichromate
Sodium nitrate and sulfate
Sodium sulfite and thiosulfate
Tin chlorides and sulfates
Zinc chloride, nitrate, and sulfate

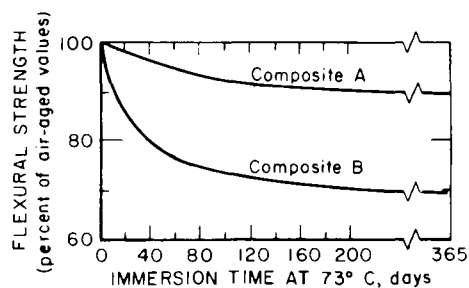
Acid solutions:

Acetic
Benzoic
Boric
Citric
Hydrochloric
Hypochlorous
Lactic
Nitric
Oxalic
Sulfuric

Other:

Animal wastes
Ethyl alcohol
Food wastes
Formaldehyde
Glycerine
Methyl alcohol
Saturated lime (at 20° C)
Some vegetable oils
Urea

The chemical resistance of typical sulfur spray coating formulations to selected acid and salt solutions is shown in figure 30. Sulfur spray coatings may not be resistant to solutions above pH 12, some oxidizing materials, and some organic hydrocarbons. Sulfur spray coatings are rapidly attacked by sodium and potassium hydroxide and other strong bases.

**Figure 30.—Chemical resistance of two proprietary sulfur composites to water, seawater, sodium sulfate (saturated), 2N sulfuric acid, and 2N hydrochloric acid (52).**

Durability

The durability of a sulfur spray coating is dependent on both its composition and the environment in which it is used. Excellent results have been obtained with coatings used in areas where temperature variations are small and where the coatings are protected from exposure to direct sunlight (48, 51). As with many other protective coatings, sulfur coatings are subject to failure if corrosive materials penetrate the coating and attack the substrate material. Penetration by a corrosive liquid can occur if the coating is fractured by mechanical means or cracked by thermal expansion and contraction. Durable sulfur spray coatings can be achieved by designing individual coatings for both the degree of corrosion and the physical environment to which they will be subjected. In addition, good maintenance practices in repairing any fracture of the coating are necessary.

ADVANTAGES AND DISADVANTAGES

There are several advantages in using sulfur spray coatings as protective, corrosion-resistant coatings for other construction materials. They can be applied easily and then put into service almost immediately, without a long curing period to attain full strength. Sulfur spray coatings can be installed on both horizontal and vertical surfaces. Correctly designed coatings are strong and durable. Pigments may be used to prepare colored coatings. Costs of installed sulfur spray coatings should be less than those of other durable coating materials (52). The strength of mortarless block buildings constructed with surface bonding by sulfur spray coatings has exceeded that of buildings constructed with mortar joints.

Like all protective coatings, sulfur spray coatings are vulnerable to penetration by corrosive materials if the coating is chipped or cracked, which leaves the base

material open to corrosive attack. This can result in failure of the substrate-coating bond. Surface-bond construction for residential construction may not meet existing building or fire codes in many areas.

SUMMARY

Sulfur spray materials have been developed primarily as protective coatings for construction materials exposed to corrosive acid and salt environments. This development has included laboratory design and testing and scale-up to large-scale field installations using special equipment and application techniques.

Surface-bond construction using sulfur spray coatings has been shown to be technically feasible. Block buildings constructed by this method have structural properties that exceed those of buildings constructed with mortar joints.

Chapter 3.—Sulfur-Extended Asphalt as a Paving Material

HISTORY

The process for treating asphalt with sulfur dates back to more than a century ago when the concept was first disclosed by A. G. Day (60). Later, Dubbs (61) heated Pennsylvania, Lima, and Ohio residuums with 20 to 25 wt pct S, at a temperature of 260°C (500° F) until the evolution of gas ceased to occur. The result was an asphalt with improved weathering characteristics. Dubbs' asphalt was only slightly susceptible to temperature changes, but was lacking in ductility. The early sulfur-treated asphalts were introduced commercially under a variety of trade names, such as Pittsburg Flux, Dubbs Asphalt, and Ventura Flux (62). However, with the advent of air-blown asphalt, which provided better durability at lower cost, the marketability of the sulfurized asphalt products was virtually eliminated.

Although some of the more pertinent developments of sulfur-asphalt paving materials are summarized below, the reader is referred to references 63-67 for a more comprehensive discussion of the chemical reactions and technological properties of sulfurized asphalt. Because of the similarity between rubber vulcanization and sulfurization of asphalt, much of this former technology was employed in the curing of bituminous mixtures (68). Attempts to alter the viscosity, ductility, and flow properties, as well as blending characteristics, toughness, and stability of road-building asphalts were made, using natural and synthetic rubbers as additives (69). Burning the surface of sulfur-asphalt pavements was claimed to improved hardness, skid resistance, and resistance to organic solvents (70).

Substitution of sulfur for part of the asphalt binder of asphalt concrete (AC) pavements was described by Bencowitz and Boe (71) in 1938. They reported that stable mixtures of 25 pct S in asphalt could be prepared by mixing the two at 149° C (300° F) for 2 h with a stirrer at 325 r/min. With some asphalts they achieved stable mixtures containing up to 40 pct S. Their report also indicated that the sulfur lowered the binder viscosity at the mixing temperature and improved the performance of the pavement. Increasing the

sulfur content of the binder resulted in increased stability of the compacted pavement when the sulfur content exceeded 25 pct.

Although Bencowitz's work laid the groundwork for sulfur-extended-asphalt (SEA) binder pavements, additional development of the process did not take place until the early 1970's. Then, concern over the increasing cost and decreasing availability of asphalt, coupled with a forecast of ever-increasing supplies of sulfur, revived interest in SEA pavements. Development of SEA has followed two basic approaches, which differ in the role sulfur plays in the final paving mixture. One approach uses sulfur as a partial replacement for asphalt to form SEA. In the other approach, sulfur is used primarily as a structuring agent, thus permitting use of lower quality or locally available aggregates, such as sands (72).

This chapter discusses only SEA paving materials. As a spin-off of the SEA concept, sulfur's unique properties have been shown to produce good-quality mixtures of sulfur-recycled Bituminous pavements (73-74).

The Bureau (75-77), Société Nationale Elf-Aquitaine (SNEA) (78-80), Gulf Canada Ltd. (81-83), and F. E. Pronk of R. M. Hardy and Associates of Calgary, Alberta, Canada (84-85), have developed and demonstrated technologies based on the SEA concept.

The SNEA, Gulf, and Pronk processes are proprietary and rely on high-shear mixing units to preblend the sulfur and asphalt prior to their entry into the mixing plant. The Bureau's method utilizes the shearing action produced within the mixing plant to produce SEA binders, thus requiring a considerably smaller capital investment for plant equipment. This method can be used with either solid or liquid sulfur.

All four of the SEA processes have been tested in the field. The first SEA test pavement on U.S. public roads was made in Texas in 1975 using an SNEA emulsified SEA binder (86-87). A second test section was laid in Nevada in 1977 using the Bureau's direct-mixing procedure (77). Since that time, other test sections of SEA pavement have been laid in 30 States (fig. 31), including two recent pro-

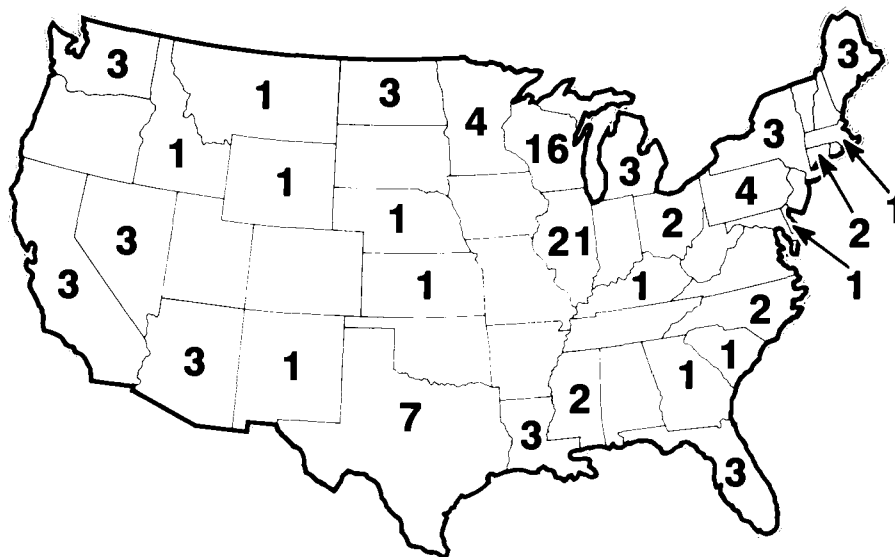


Figure 31.—Number of SEA projects in individual States.

TABLE 9.—Number of SEA paving trials to 1984

Year	United States	Canada	Europe	Other	Total
Pre-1977 ..	1	4	7	0	12
1977	2	3	4	2	11
1978	5	2	8	1	16
1979	15	3	9	2	29
1980	27	2	11	3	43
1981	26	2	4	2	34
1982	17	3	4	1	25
1983	4	4	2	1	11
1984 ¹	4	3	1	0	10

¹Mexico: 2 trials in 1984.

jects that used solid sulfur feed for both a batch plant and a drum mixing plant (88-89). As shown in table 9, 191 SEA paving tests were conducted in the United States, Europe, Canada, and the Middle East through 1984.

The Federal Highway Administration (FHWA) is encouraging State highway agencies to construct SEA pavements so they can be evaluated in the field under typical operating conditions. The Bureau and The Sulphur Institute are cooperating with the FHWA in the endeavor. The Bureau prepared a manual in 1980 under a contract with the FHWA to acquaint potential users of SEA paving materials with state-of-art guidelines for the design, quality control, and construction of SEA pavements (90). These guidelines are based on knowledge and experience gained in the design, construction, and evaluation of test sections of SEA pavement that have been constructed in the United States and Canada.

This chapter deals with design, preparation, placement, and performance evaluation of SEA mixtures. The Bureau's direct-mixing technology is emphasized, since this technique has been employed in the majority of U.S. field trials. The

preparation techniques described can be used with either liquid or solid sulfur.

GENERAL MIX CHARACTERISTICS

Before a pavement is designed, the general characteristics of sulfur, asphalt, and SEA should be understood by the practitioner. Of prime importance is the role of sulfur in SEA mixture. The solubility of sulfur in asphalt varies according to the source and grade of the asphalt and as a general rule averages approximately 5 wt pct at ambient temperatures (91). At elevated temperature, the solubility increases, into the range of 30 to 35 wt pct. Figure 32 illustrates the solubility versus temperature relationship for several asphalts.

Initially, most of the sulfur in the SEA binder is soluble in the asphalt at the hot mixing temperature. Any sulfur in excess of the solubility limit disperses as immiscible droplets that are generally in the 5- μ m-diam size range. As the material cools to ambient temperature, sulfur in excess of the solubility threshold precipitates within the asphalt phase to form an ultrafine dispersion of crystalline sulfur. Since the activation energy required for diffusion of sulfur in asphalt is low (15 kcal/mol) (91), the precipitates grow readily at ambient temperatures. This growth normally occurs in the void regions, forming sulfur needles that serve as a structuring source similar to reinforcing fiber within the material. Figure 33 shows scanning electron photomicrographs that illustrate the sulfur distribution within the asphalt phase in a solid section cut from a roadway. The lower photomicrographs illustrate the typical structure obtained from a freshly fractured section of pavement at both low and high magnification. The upper

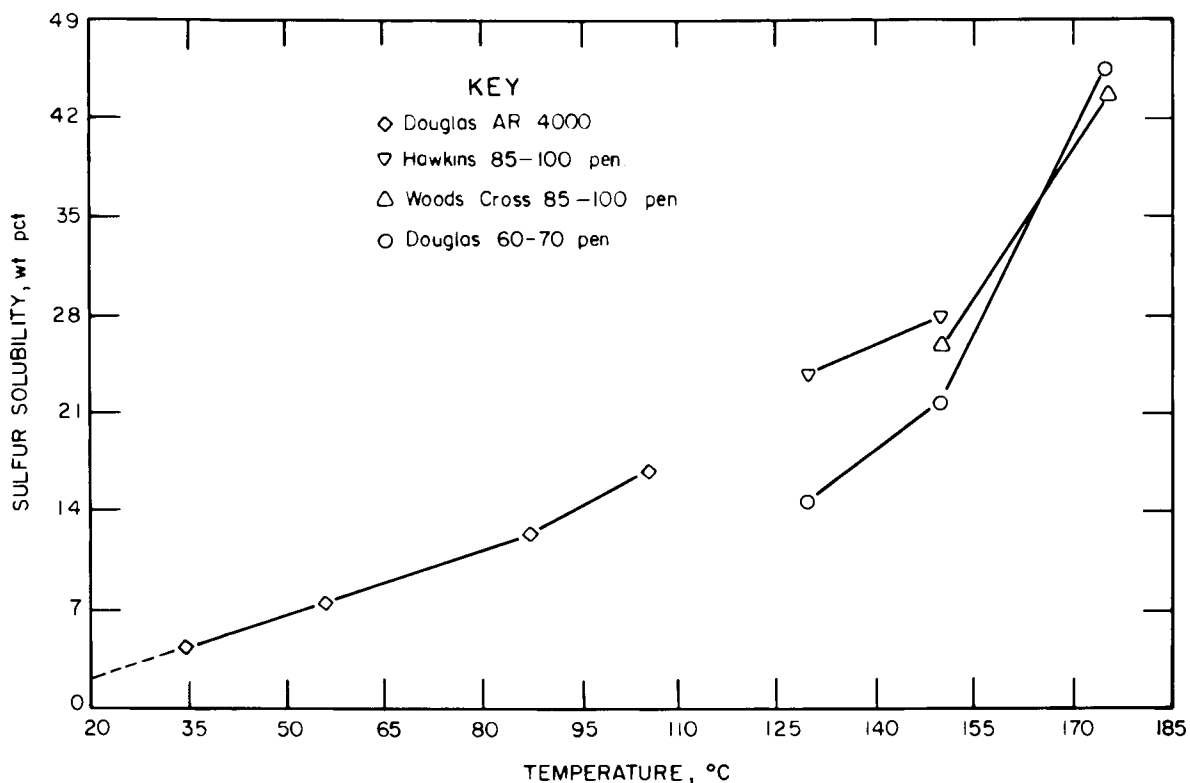


Figure 32.—Solubility of sulfur measured in several asphalts. ("Pen." indicates penetration grade.)

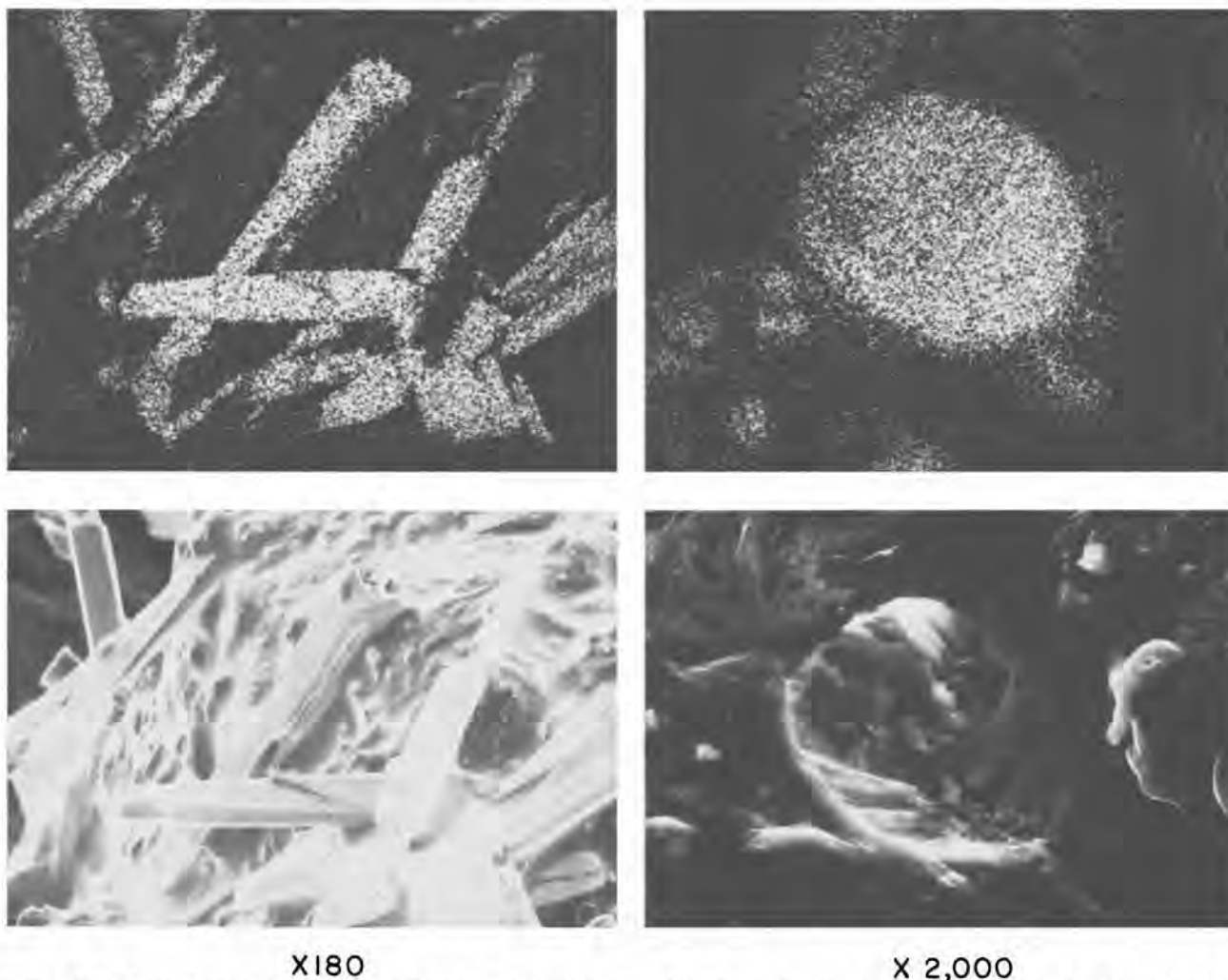


Figure 33.—Photomicrographs of sulfur distribution in asphalt: Typical structures (bottom panels) and sulfur $K\alpha$ X-ray scans (top panels).

micrographs are sulfur $K\alpha$ X-ray scans that show sulfur dispersements obtained using an energy-dispersive X-ray system. The faceted needles are characteristic of crystals formed through unconfined growth and were observed to increase in size as the pavement aged. The spherical particles, which were initially an immiscible liquid, also showed growth with age; they ranged in size from 3 to 10 μm diam.

Figure 34 illustrates fine crystals growing into the void regions at both low and high magnification. The needles extend across void spaces, forming an important structuring mechanism similar to fiber reinforcement in composite materials.

The role of sulfur in SEA materials is two fold: It is an integral part of the binder and also a structuring agent.

MATERIAL CHARACTERISTICS

Binder

As the name "sulfur-extended asphalt" implies, sulfur is used to extend asphalt in paving materials as a means of conserving asphalt. To successfully accomplish this extension, the SEA design must be related directly to the con-

ventional asphalt design; the amount of sulfur that should be used in the SEA can then be determined.

Sulfur at ambient conditions of temperature and pressure exists as a friable yellow solid, in contrast to asphaltic cement, which exists as a viscoelastic solid. Because of its unique properties, sulfur can significantly alter the basic physical properties of the binder. Therefore, a thorough knowledge of these properties is essential for formulating a cost-effective mix design with good structural integrity.

Table 10 shows specific gravity data for sulfur, grade AR 2000 asphalt, and SEA blends. At ambient temperatures, sulfur is twice as dense as asphalt and occupies one half the volume of asphalt per unit weight. At elevated temperatures, the density ratio decreases to approximately 1.8 to 1. When combined with asphalt to form SEA, the sulfur increases the specific gravity in proportion to the volume of sulfur added. Figure 35 illustrates the temperature-viscosity relationship for the materials listed in table 10 over mixing temperature range. As indicated, between 115° and 154° C, sulfur exists as a very low viscosity liquid, compared to asphalt. Below 115° C, sulfur solidifies, and above 154° C, it becomes extremely viscous. Blends of sulfur and asphalt exhibit lower viscosities than asphalt. The lowest viscosity occurred when 15 vol pct (26

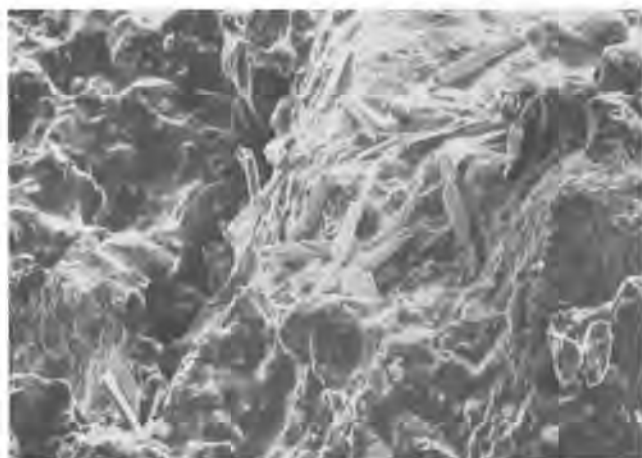


Figure 34.—Sulfur crystal growth in void regions of asphalt. Top, X 45; bottom, same region at X 4,000 magnification.

TABLE 10.—Specific gravity data for sulfur, asphalt, and SEA

	At 16° C	At 121° C	At 149° C
Sulfur.....	1.96-2.07	1.80	1.78
AR 2000 asphalt.....	1.01	.97	.96
SEA, vol pct S in binder:			
15.....	1.16	1.10	1.09
25.....	1.26	1.17	1.15
35.....	1.34	1.24	1.22

SEA Sulfur-extended asphalt.

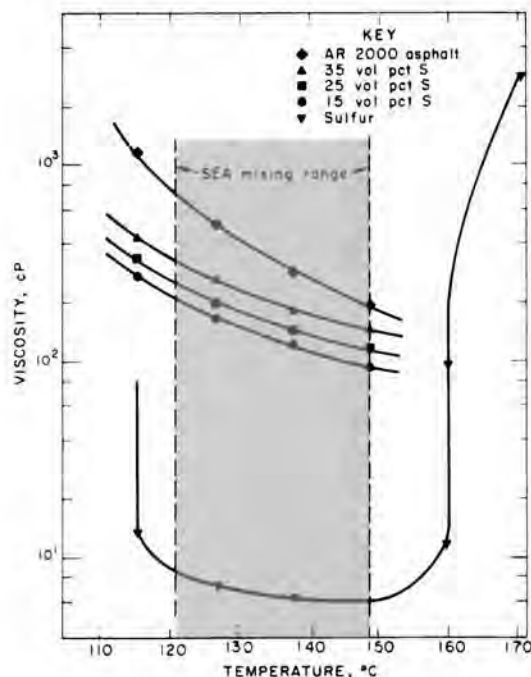


Figure 35.—Temperature-viscosity chart (mixing temperature range) for SEA blends.

wt pct) S was substituted. (Here and in the next section, volume-percent values indicate percentage of total binder components whereas weight-percent values indicate percentage of the total mix.)

Concrete Material

The effects of equal volume substitutions of sulfur for asphalt in a typical material prepared using 7.0-wt-pct grade AR 2000 asphalt (100-vol-pct-asphalt binder) as the optimum design concentration are illustrated in table 11.

TABLE 11.—Effects of sulfur substitution on SEA material properties

(Volcanic aggregate)

Composition ¹				Specific gravity	Voids, pct	Marshall properties		Dynamic stiffness, ³ 10 ⁶ psi
Sulfur		Asphalt				Stability, lb	Flow, 0.01 in	
vol pct ¹	wt pct ²	vol pct ¹	wt pct ²					
0	0	100	7.0	2.288	2.4	2,580	12	0.653
15	2.0	85	5.9	2.300	2.8	2,230	10	.980
25	3.4	75	5.2	2.307	3.2	3,085	11	1.542
35	4.7	65	4.4	2.321	3.2	5,520	10	2.040
50	6.7	50	3.4	2.320	4.4	9,605	12	ND
75	9.9	25	1.7	2.343	4.9	9,910	6	ND

ND Not determined. SEA Sulfur-extended asphalt.

¹Volume percentage of binder.

²Weight percentage of total mix.

³Determined using Schmidt method at ambient temperature.

Equal volume substitutions were used to eliminate binder volume variations. The mineral aggregate was graded to meet type-IVb Asphalt Institute specifications. As this table shows, at the 15-vol-pct (26-wt-pct) substitution level, the Marshall properties were essentially unchanged, and the extended material was virtually indistinguishable from the original (0-vol-pct-S) material.

As sulfur substitution was increased beyond 15 vol pct, uniform increases in stability, density, and stiffness were obtained with little change in the flow and void levels. These data illustrate (1) the potential latitude in stability tailor-

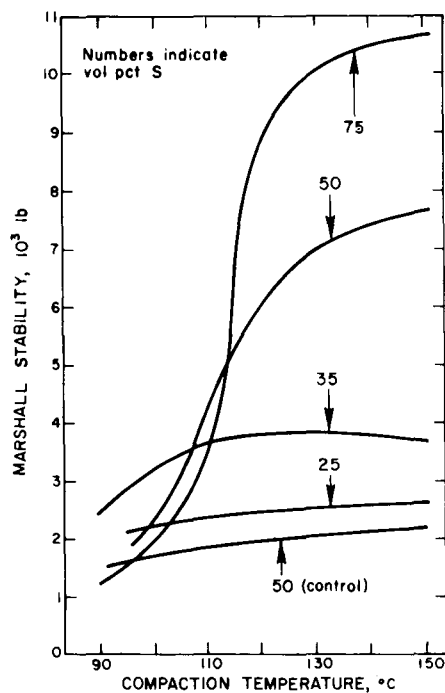


Figure 36.—Marshall stability versus temperature for SEA blends.

ing that can be obtained through variations of the sulfur substitution percentage and (2) the dual role of sulfur as a binder component and structuring agent.

Figure 36 illustrates typical stability variations for the SEA materials listed in table 11 over the entire working range of 85° to 149°. The curve for the control material was identical to the curve for the material made with a 15-vol-pct-S substitution. These materials were mixed at 149° and compacted at successively lower temperatures down to 85°. Sulfur substitution up to 25 vol pct (40 wt pct) resulted in materials that were essentially insensitive to compaction temperature. Sulfur substitution of 25 vol pct produced higher stabilities. Above 25 to 35 vol pct (40 to 50 wt pct), slight sensitivity to compaction was observed; however, the materials exhibited higher stabilities than the control material when compacted at temperatures as low as 85°. At sulfur substitution levels of more than 35 vol pct (50 wt pct), the materials were very sensitive to compaction below 115° (the sulfur solidification temperature) and sustained considerable reduction in stability when compacted at the lower temperatures. Figure 37 illustrates the effect of compaction temperature on void levels for the same materials. These data parallel the stability relationships and indicate that the upper allowable limit for asphalt replacement in SEA materials is 25 vol pct. Also, sulfur substitution in the range of 15 vol pct and lower results in materials with essentially the same properties as the conventional binder. These considerations should be used in selecting sulfur substitution percentages for construction projects.

Figure 38 illustrates the viscosity-temperature relationship for the same SEA blends and asphalt over the compaction temperature range. The similarity of these relationships to those in figure 35 is apparent, again indicating viscosity reduction for the SEA binders over the entire range. Lower viscosities for SEA binders should result in enhanced workability for SEA materials in the field and are the reason sulfur has been considered for use in recycling age-hardened bituminous pavements (92).

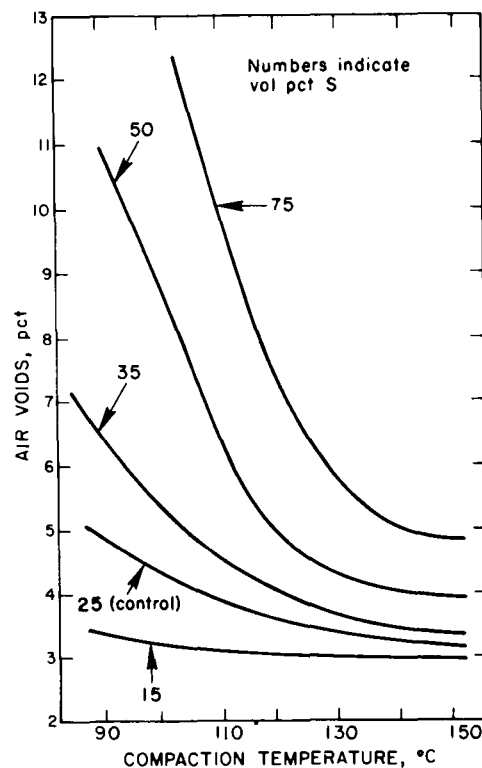


Figure 37.—Void levels versus compaction temperature for SEA blends.

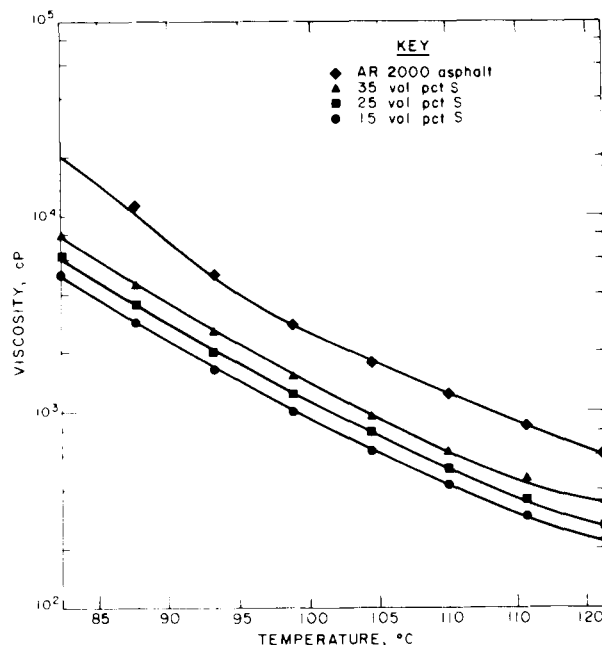


Figure 38.—Temperature-viscosity chart (compaction temperature range) for SEA blends.

Figure 39 presents the results of laboratory flexural fatigue tests of four SEA materials prepared using volcanic aggregate (table 11) and evaluated under constant stress-amplitude conditions. These data reflect the influence of sulfur content in tailoring the fatigue characteristics of SEA mixes.

From the general characteristics discussed in this sec-

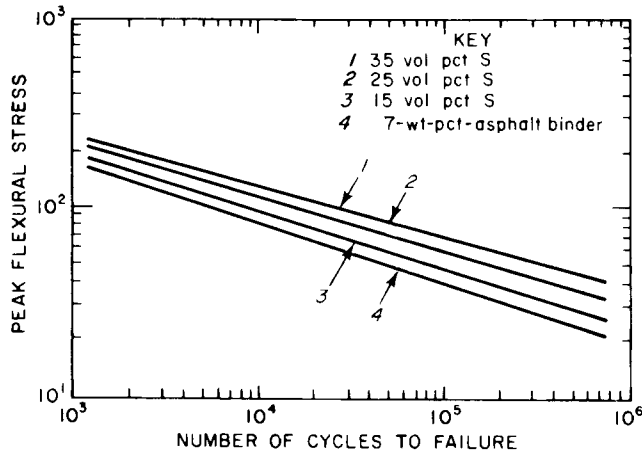


Figure 39.—Flexural fatigue results for SEA blends.

tion, the following conclusions can be drawn concerning SEA materials versus conventional AC:

1. Binder viscosities are lower for SEA over the mixing and working temperature range, which should result in enhanced workability.
2. Marshall stabilities are a function of the sulfur substitution percentage. Levels around 15 vol pct (26 wt pct) S yield a material comparable to conventional AC, while higher levels result in significant stability increases.
3. Substitution levels above 25 vol pct (40 wt pct) result in materials that are sensitive to compaction temperature.
4. A 2-to-1 density difference exists between sulfur and asphalt at ambient temperature.
5. Sulfur additions enhance fatigue durability.

Mix Design Procedure

If an SEA binder is to be used in a conventional all-asphalt mix design, the equivalent binder content for the new mix is established using the following relationship:

Equivalent SEA binder content (weight percent)

$$= A \left(\frac{100R}{100R - S(R - G)} \right), \quad (1)$$

where A = Asphalt content in conventional design, wt pct,
 R = sulfur-to-asphalt substitution ratio,
 S = sulfur to be used in SEA binder, wt pct,
 and G = specific gravity of the asphalt.

This calculation requires a knowledge of the optimum asphalt content (A) in the conventional mix. Theoretically, at ambient temperatures, the relative specific gravities of sulfur and asphalt suggest a substitution ration (R) of 2 to 1. However, construction experience obtained in the United States and Canada indicates that, due to the inherently lower viscosity of SEA binders, substitution ratios as low as 1.4 may be feasible.

The following example illustrates this design procedure indicated in equation 1:

Consider a conventional mix design with a pure asphalt content of 5.3 wt pct and a specific gravity (G) of 1.03. To determine the amount of 30-70 SEA binder (S = 30) required

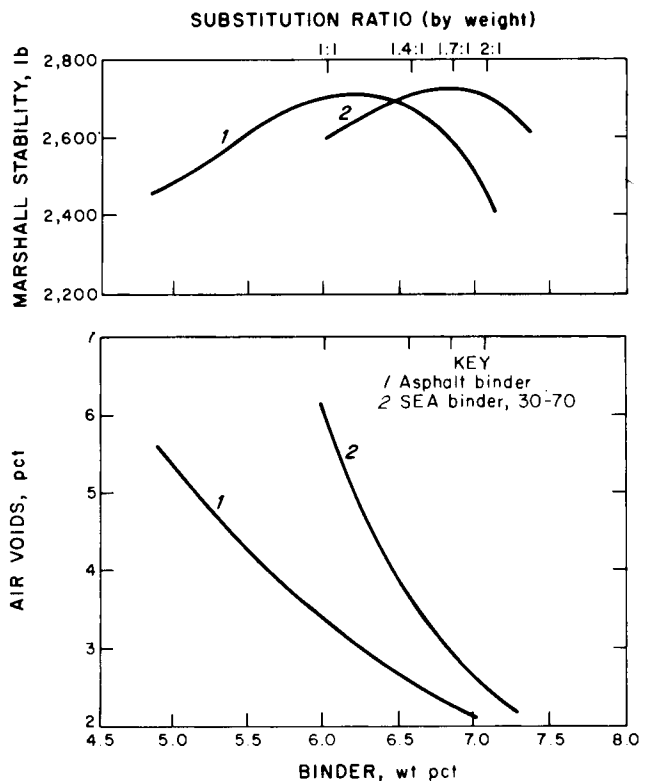


Figure 40.—Justification test data for 30-70 SEA blends.

to replace the binder in the control on an equal-volume basis (i.e., R = 2), substitutions are made in equation 1 as follows:

$$\text{SEA binder content} = 5.3 \left(\frac{100(2)}{100(2) - 30(2 - 1.03)} \right) \quad (2)$$

or 6.2 wt pct.

Similarly, if the replacement is to be made using a 40-60 SEA binder, S becomes 40, and

$$\text{SEA binder content} = 5.3 \left(\frac{100(2)}{100(2) - 40(2 - 1.03)} \right) \quad (3)$$

or 6.6 wt pct.

Conformation justification tests should then be made in the laboratory to establish the optimum sulfur substitution ratio. Typical data for a 30-70 SEA binder along with control data for a 5.3 wt pct conventional design are plotted in figure 40. As indicated, an optimum substitution ratio of 1.5 to 1 yields a material with properties comparable to those of the control, such as void levels in the same range equivalent or greater stabilities. By minimizing the substitution ratio, it should be possible to achieve optimum economic benefits in substituting sulfur for asphalt.

MANUFACTURING PROCESS AND EQUIPMENT

As discussed earlier, various methods have been developed for preblending the sulfur and asphalt. These methods include the use of colloid mills, high-shear mix-

ers, and static in-line blenders. Figure 41 is a generalized illustration of these methods. The constituents are metered in the proportions desired and charged into the hot mixing plant, either by direct volume or through the weighing system. The direct-mixing method used by the Bureau utilized the shearing action produced within the mixing plant, together with the relatively high solubility of sulfur in asphalt at the mixing temperature, to disperse the sulfur within the asphalt phase. This method is illustrated in figure 42, which indicates how the components are metered in the proportion desired and charged into the hot mixing plant. In batch-plant operations, this method can be used without proportionating pumps by weighing the constituents individually into the weigh bucket. Figure 43 illustrates direct feed using solid sulfur, the newest method in use. Using this method, solid sulfur and asphalt cement are weighed cumulatively into the weigh bucket at batch plants and then introduced into the pug mill for mixing. In drum-mix plants, solid sulfur and asphalt cement are independently metered into the drum mixer through separate piping systems.

Actual use of the direct-mixing method to prepare SEA paving is shown in figure 44. This figure shows the Industrial Asphalt Co. plant at Henderson, NV, which was

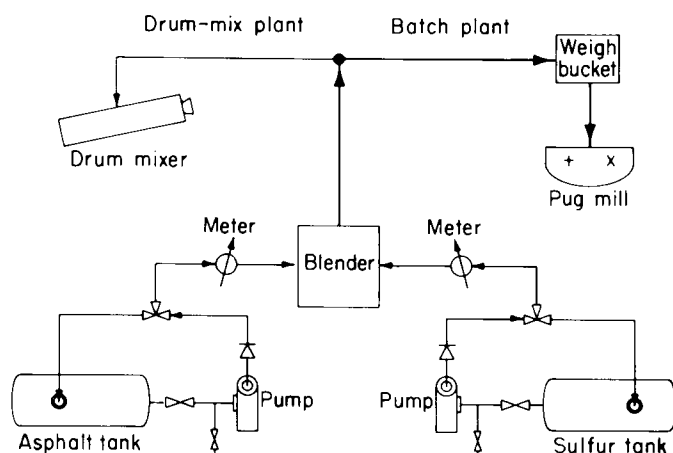


Figure 41.—Flowsheet for preblending sulfur and asphalt.

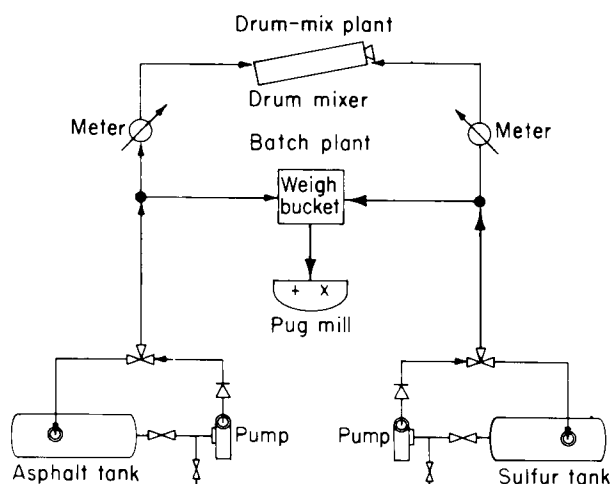


Figure 42.—Flowsheet for direct mixing of sulfur in asphalt.

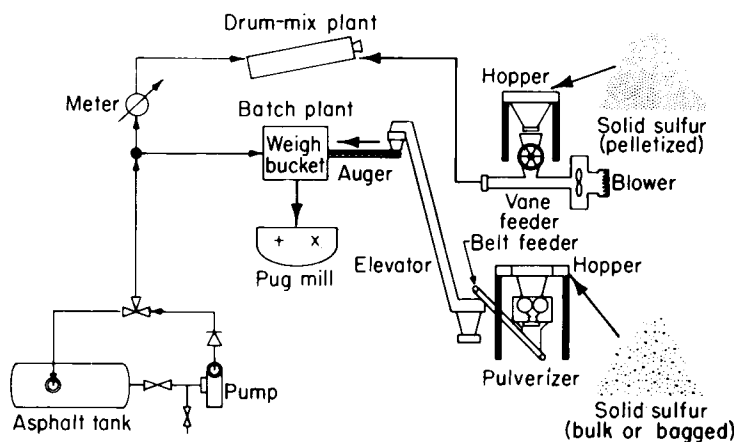


Figure 43.—Flowsheet for direct feed of solid sulfur into liquid asphalt.

modified to allow the direct addition of sulfur into the pug mill weigh bucket. This plant was used to prepare SEA material for use in constructing an experimental test section on U.S. 95 near Boulder City, NV, in 1977. Figure 45 illustrates an asphalt-sulfur preblending unit used to prepare SEA for a test section on road MH 153 near Bryan, TX, in 1978. This unit disperses the sulfur in asphalt prior to discharge into the pug mill. After the SEA material is prepared all further construction is accomplished using conventional equipment and techniques.

SAFETY

The normal precautions taken in the preparation and placement of AC must also be observed with sulfur-asphalt concretes. In addition, certain operating precautions are necessary because of several potentially hazardous properties of sulfur and asphalt. Both asphalt and sulfur are flammable materials with flashpoints in the same temperature range (205° to 250° C). Sulfur burns in air to form sulfur dioxide and also reacts with asphalt at elevated temperatures (above 150° C) to form hydrogen sulfide. Research (91) has shown that at the normal operating temperatures used to mix sulfur-asphalt concretes (132° to 150° C), there is only slight evolution of hydrogen sulfide at mix temperatures below 155°.

Sulfur-asphalt binder should not be stored—it should be used as it is made—to prevent toxic gas buildup. Similarly, the pavement mixture should be laid down shortly after manufacture; it should never be stored overnight in silos.

ADVANTAGES AND DISADVANTAGES

The use of sulfur as an additive in paving mixtures provides materials with new engineering properties while replacing part of the asphalt used and thus conserving energy. Mixtures employing up to 30 wt pct S exhibit equivalent mechanical properties (compared with all asphalt), while 40 wt pct S results in superior stability, resistance to rutting, and fatigue durability. The substituted sulfur allows the stability to be tailored according to the specific needs of the designing agency. Conventional equipment can be used for preparation and placement of SEA materials.



Figure 44.—Modified asphalt mix plant for preparing SEA pavement using direct-mix method.



Figure 45.—Modified asphalt mix plant for preparing SEA pavement using colloid mill to disperse sulfur in asphalt.

Field tests of SEA pavements installed in Nevada (1977) and Texas (1975) have shown that these 8- and 10-yr-old pavements are outperforming control sections of normal AC paving in normal highway use.

The disadvantages are that binder requirements (in weight percent) are greater for SEA than for conventional AC because of the approximate 2-to-1 specific-gravity ratio between sulfur and asphalt. Slightly more SEA materials by weight will be required to pave a given depth because of the higher specific gravity of the pavement.

SUMMARY

Sulfur-extended-asphalt materials have proven to be technically feasible as alternative paving materials. The substitution of sulfur for up to 40 wt pct of the asphalt produces materials with properties equal or superior to those of normal AC. These materials can be prepared in conventional hot-mix plants and placed and compacted with conventional paving equipment. Properties of SEA pavements containing up to 30 pct S in the binder are similar to those of AC. Sulfur substitution at higher levels results in pavements with increased stability. Field performance results obtained to date indicate equivalent or superior results (in comparison with normal AC) throughout the U.S. and Canada.

REFERENCES

1. Sheppard, W. L., Jr. Sulphur Mortars: A Historical Survey. *Sulphur Inst. J.*, v. 11, No. 3-4, 1975, pp. 15-17.
2. Rybczynski, W., A. Ortega, and W. Ali. Sulphur Concrete and Very Low Cost Housing. Paper in Canadian Sulphur Symposium (Univ. Calgary, Calgary, Alberta, Canada, May 30-June 1, 1974). Sulphur Dev. Inst. Can., Calgary, Alberta, Canada, 1974, pp. P1-P9.
3. Bacon, R. F., and H. S. Davis. Recent Advances in the American Sulphur Industry. *Chem. and Metall. Eng.*, v. 24, No. 2, 1921, pp. 65-72.
4. Kobbé, W. H. New Uses for Sulfur in Industry. *Ind. and Eng. Chem.*, v. 16, No. 10, 1924, pp. 1026-28.
5. Duecker, W. W. Admixtures Improve Properties of Sulfur Cements. *Chem. and Metall. Eng.*, v. 41, No. 11, 1934, pp. 583-586.
6. McKinney, P. V. Provisional Methods for Testing Sulfur Cements. *ASTM Bull.* 96-107, 1940, pp. 27-30.
7. American Society for Testing and Materials. 1983 Annual Book of ASTM Standards: Sec. 4, v. 04.05, Chemical-Resistant Nonmetallic Materials. Philadelphia, PA, 1983, 864 pp.
8. U.S. Department of the Interior. Mining and Mineral Policy Act of 1970. Public Law 91-631, 1972, pp. 34, 104.
9. Vroom, A. H. Sulfur Utilization. *Natl. Res. Council Can., NRC 12241*, 2d ed., 1971, 80 pp.
10. Dale, J. M., and A. C. Ludwig. Feasibility Study for Using Sulfur-Aggregate Mixtures as a Structural Material. Southwest Res. Inst. Tech. Rep. AFWL-TR-66-57, Sept. 1966, 40 pp.
11. _____. Advanced Studies of the Sulfur-Aggregate Mixtures as a Structural Material. Southwest Res. Inst., Tech. Rep. AFWL-TR-68-21, Oct. 1968, 69 pp.
12. Crow, L. J., and R. C. Bates. Strength of Sulfur-Basalt Concretes. *BuMines RI 7349*, 1970, 21 pp.
13. Sullivan, T. A., W. C. McBee, and D. D. Blue. Sulfur in Coating and Structural Materials. Ch. 4 in *New Uses of Sulfur*, ed. by J. R. West. *Adv. Chem. Ser.* 140, 1975, pp. 55-74.
14. Sullivan, T. A., and W. C. McBee. Development and Testing of Superior Sulfur Concretes. *BuMines RI 8160*, 1976, 30 pp.
15. McBee, W. C., and T. A. Sullivan. Development of Specialized Sulfur Concretes. *BuMines RI 8346*, 1979, 21 pp.
16. _____. Modified Sulfur Cement. U.S. Pat. 4,311,826, Jan. 19, 1982.
17. McBee, W. C., T. A. Sullivan, and B. W. Jong. Modified Sulfur Cements for Use in Concretes, Flexible Pavings, Coatings, and Grouts. *BuMines RI 8547*, 1981, 24 pp.
18. McBee, W. C., and T. A. Sullivan. Concrete Formulations Comprising Polymeric Reaction Products of Sulfur/Cyclopentadiene, Oligmer/Dicyclopentadiene. U.S. Pat. 4,348,313, Sept. 7, 1982.
19. McBee, W. C., T. A. Sullivan, and B. W. Jong. Modified-Sulphur Concrete Technology. Paper in *Proc. SULPHUR-81* (Calgary, Alberta, Canada, May 25-28, 1981). Sulphur Dev. Inst. Can., 1981, pp. 367-388.
20. _____. Corrosion-Resistant Sulfur Concretes. *BuMines RI 8758*, 1983, 28 pp.
21. Funke, R. H., Jr., and W. C. McBee. An Industrial Application of Sulfur Concrete. Ch. 12 in *Sulfur: New Sources and Uses*, ed. by M. E. D. Raymont. *Adv. Chem. Ser.* 183, 1981, pp. 195-208.
22. McBee, W. C., T. A. Sullivan, and B. W. Jong. Industrial Evaluation of Sulfur Concrete in Corrosive Environments. *BuMines RI 8786*, 1983, 15 pp.
23. Sullivan, T. A. Corrosion-Resistant Sulphur Concretes—Design Manual. *The Sulphur Inst.*, 1982, 18 pp.
24. Vroom, A. H. Sulfur Cements, Process for Making Same and Sulfur Concretes Made Therefrom. U.S. Pat. 4,058,500, Nov. 15, 1977.
25. _____. Sulfur Cements, Process for Making Same and Sulfur Concretes Made Therefrom. U.S. Pat. 4,293,463, Oct. 6, 1981.
26. Leutner, B., and L. Diehl. Manufacture of Sulfur Concrete. U.S. Pat. 4,025,352, May 24, 1977.
27. Gillott, J. E., I. J. Jordaan, R. E. Loov, and N. G. Shrive. Sulfur Concretes, Mortars and the Like. U.S. Pat. 4,188,230, Feb. 12, 1980.
28. Schneider, R. A., and M. Simic. Plasticized Sulfur Composition. U.S. Pat. 4,308,072, Dec. 29, 1981.
29. Woo, G. L. Phosphoric Acid Treated Sulfur Cement-Aggregate Compositions. U.S. Pat. 4,376,831, Mar. 15, 1983.
30. Nimer, E. L., and R. W. Campbell. Sulfur Cement-Aggregate-Organosilane Composition and Methods for Preparing. U.S. Pat. 4,376,830, Mar. 15, 1983.
31. Gregor, R., and A. Hackl. A New Approach to Sulfur Concretes. Ch. 4 in *New Uses of Sulfur—II*, ed. by D. J. Bourne. *Adv. Chem. Ser.* 165, 1978, pp. 54-78.
32. Bright, L., B. R. Currell, B. J. Nash, R. A. M. Scott, and C. Stillo. Preparation and Properties of Modified Sulfur Systems. Ch. 2 in *New Uses of Sulfur—II*, ed. by D. J. Bourne. *Adv. Chem. Ser.* 165, 1978, pp. 13-30.
33. Bordoloi, B. K., and E. M. Pearce. Plastic Sulfur Stabilization by Copolymerization of Sulfur With Dicyclopentadiene. Ch. 3 in *New Uses of Sulfur—II*, ed. by D. J. Bourne. *Adv. Chem. Ser.* 165, 1978, pp. 31-53.
34. Asphalt Institute (College Park, MD). Mix Design for Asphalt Concrete. MS-2, Mar. 1979, pp. 17-32.
35. Yarbrough, R. L. Specialized Construction Practices for Sulfur Concretes. Pres. at Sulfur in Concrete Symposium (Los Angeles, CA, Mar. 23, 1983). *Am. Concrete Inst.*, 1983, 15 pp.
36. Pickard, S. C. Sulfur Concrete at AMAX Nickel: A Project Case History. *SULCON, Inc.*, Champaign, IL, 1983, 15 pp.
37. National Safety Council (Chicago, IL). Handling and Storage of Solid Sulfur. Data Sheet 612, 1968, 4 pp.
38. _____. Handling Liquid Sulfur. Data Sheet 1-592-78, 1979, 9 pp.
39. American Conference of Governmental Industrial Hygienists. TLVs, Threshold Limit Values for Chemical and Physical Agents in the Workroom Environment With Intended Changes for 1981. Cincinnati, OH, 4th ed., 1980, 94 pp.
40. Fike, H. L. New Materials for Building and Civil Engineering. Paper in *Proc. Inst. Natl. Sci. Appliques* (Rennes, France, Sept. 13-15, 1983). pp. 109-114.
41. Mason, C. M., D. R. Forshey, and F. J. P. Perzak. Fire Hazards of Ammonium Nitrate Sulfur Systems. *Agric. and Food Chem.*, v. 15, No. 6, 1967, pp. 954-66.
42. *SULCON, Inc.* (Champaign, IL). Roadshow Report. Newsletter, June 1983, 6 pp.
43. Barnes, M. D. Construction Method. U.S. Pat. 3,306,000, Feb. 28, 1967.
44. Fike, H. L., and M. Conitz. Surface Bond Construction. Sec. in *New Horizons in Construction Materials*, ed. by Hsai-Vang Fang. *Env. Publ. Lehigh Valley, PA*, 1967, pp. 377-390.
45. Hubbard, S. J. Feasibility Study of Masonry Systems Utilizing Surface-Bond Materials. U.S. Dep. Army, Tech. Rep. 4-43, 1966, pp. 20-22, 33-35.
46. Testa, R. B., and G. B. Anderson. The Use of Sulfur in Housing Construction: An Exploratory Study. *Dep. Civil Eng. and Eng. Mech.*, Columbia Univ., 1969, 48 pp.
47. Dale, J. M., and A. C. Ludwig. Mechanical Properties of Sulfur Allotropes. *Materials Research and Standards. Bull. Am. Chem. Soc.*, v. 5, No. 8, 1965, pp. 411-417.
48. Dale, J. M. Sulfur-Fibre Coating. *Sulphur Inst. J.*, v. 1, No. 1, 1965, pp. 11-13.
49. Dale, J. M., and A. C. Ludwig. Sulfur Coatings for Mine Support (contract H0210062, Southwest Res. Inst. BuMines OFR 31-73, 1972, 46 pp.; NTIS PB 220 408).
50. Fike, H. L. Sulphur Coatings - A Review and Status Report. Paper in Symposium on New Uses for Sulphur and Pyrites (Madrid, Spain, May 17-19, 1976). *The Sulphur Inst.*, 1976, pp. 215-230.
51. Dale, J. M. Utilizing Sulfur-Based Spray Coatings. *Min. Eng.* (Littleton, CO), v. 25, no. 9, 1973, pp. 49-52.
52. Paulson, J. E., M. Simic, R. W. Campbell, and J. W. Ankers. Sulfur Composites as Protective Coatings and Construction Materials. Ch. 12 in *New Uses of Sulfur—II*, ed. by D. J. Bourne. *Adv. Chem. Ser.* 165, 1978, pp. 215-226.
53. Pickering, I. G., J. A. Watson, J. M. Dale, and A. C. Ludwig. A Sprayable Sulfur Coating for Protection of Concrete Leaching

- Vats. Proceedings of the 78th National Meeting (Salt Lake City, UT, Aug. 18-21, 1974). AIChE, 1974, pp. 17-21.
54. Chevron Chemical Co. (San Francisco, CA). Chevron SUCOAT Coating Compounds, General Products Guide. Sulfur Products Div., P.O. Box 3744 (not dated), 4 pp.
55. Chemical Enterprise, Inc. (Houston, TX). SUCOAT Coating for Concrete Protection. 8582 Katy Freeway, Suite 202 (not dated), 4 pp.
56. Schneider, R. A., and M. Simic. Plasticized Sulfur Composition. U.S. Pat. 4,308,072, Dec. 29, 1981.
57. Barnes, N. C., and J. M. Dale. Marking Composition. U.S. Pat. 3,316,115, Apr. 25, 1967.
58. Currell, B. R., A. J. Williams, A. J. Mooney, and B. J. Nash. Plasticization of Sulfur. Ch. 1 in *New Uses of Sulfur*, ed. by J. R. West. Adv. Chem. Ser. 140, 1975, pp. 1-17.
59. Raymont, M. E. D. Sulfur Concrete and Coatings. *New Uses for Sulphur Technology*, Series 4. SUDIC, Calgary, Alberta, Canada, 1978, 43 pp.
60. Day, A. G. A Process for Treating Asphalt With Sulfur. U.S. Pat. 58,615, Oct. 9, 1866.
61. Dubbs, J. A. Sulfur Treatment of Asphalt. Can. Pat. 38,929, May 12, 1892; 41,025, Nov. 26, 1892; and 41,101, Nov. 29, 1892.
62. Abraham, H. Asphalts and Allied Substances. Van Nostrand, 6th ed., 1960, v. 1, p. 80; v. 2, pp. 178-179; and v. 3, pp. 12, 87.
63. Bocca, P. L., U. Petrossi, and V. Piconi. Heavy Hydrocarbons and Sulfur: Reactions and Reaction Products. *Chim. Ind. (Milan)*, v. 55, No. 5, 1973, pp. 425-431.
64. Tucker, J. R., and H. E. Schwyer. Distribution and Reactions of Sulfur in Asphalt During Air Blowing and Sulfurizing Processes. *Ind. and Eng. Chem., Prod. Res. and Dev.*, v. 4, No. 1, 1965, p. 51.
65. Petrossi, U., P. L. Bocca, and P. Pacor. Reactions and Technological Properties of Sulfur-Treated Asphalt. *Ind. and Eng. Chem., Prod. Res. and Dev.*, v. 11, No. 2, 1972, p. 214.
66. Lee, D. Y. Modification of Asphalt and Asphalt Paving Mixtures by Sulfur Additives. *The Sulfur Inst.*, 1974, 26 pp.
67. _____. Modifications of Asphalt and Asphalt Paving Mixtures by Sulfur Additives. *Ind. and Eng. Chem., Prod. Res. and Dev.*, v. 14, No. 3, 1975, p. 171.
68. Nicolau, A., C. Garrigues, and M. Brossel. Bitumen Binders Containing Sulfur for Road Surfacing. *Fed. Rep. Ger. Pat.* 2,016,568, Oct. 5, 1970.
69. Welborn, J. Y., and J. F. Babashak, Jr. A New Rubberized Asphalt for Roads. *Proc. ASCE*, v. 84, 1958, p. 1651.
70. Bacon, R. F., and I. Bencowitz. Method of Paving. U.S. Pat. 2,182,837, Dec. 12, 1939.
71. Bencowitz, I., and E. S. Boe. Effect of Sulfur Upon Some of the Properties of Asphalt. *Proc. ASTM*, v. 38, No. 2, 1938, p. 539.
72. Hammond, R., I. Deme, and D. McManus. The Use of Sand-Asphalt-Sulfur Mixes for Road Base and Surface Applications. *Proc. Can. Tech. Asphalt Assoc.*, v. 16, 1971, p. 27.
73. McBee, W. C., T. A. Sullivan, and D. Saylak. Recycling Old Asphalt Payments With Sulfur. Ch. in *Recycling of Bituminous Pavements*, ed. by L. E. Wood. ASTM STP 662, 1978, pp. 123-141.
74. Strand, D. L. Recycling with Sulfur-Extended Asphalt in Wisconsin. *Sulfur Res. and Dev.*, v. 5, 1982, pp. 6-9.
75. McBee, W. C., and T. A. Sullivan. Utilization of Secondary Sulfur in Construction Materials. Paper in Proceedings of the Fifth Mineral Waste Utilization Symposium (cosponsored by BuMines and ITT Res. Inst., Chicago, IL, Apr. 13-14, 1976). ITT Res. Inst., Chicago, IL, 1980, pp. 39-52.
76. _____. Sulfur Utilization in Asphalt Paving Materials. Ch. 8 in *New Uses of Sulfur—II*, ed. by D. J. Bourne. Adv. Chem. Ser. 165, 1978, pp. 135-160.
77. _____. Direct Substitution for Asphalt in Paving Materials. BuMines RI 8303, 1978, 23 pp.
78. Garrigues, C., and P. Vincent. Sulfur/Asphalt Binders for Road Construction. Ch. 8 in *New Uses of Sulfur*, ed. by J. R. West. Adv. Chem. Ser. 140, 1975, pp. 130-153.
79. Société Nationale de Petroles d'Aquitaine. Properties of Sulfur Bitumen Binders. Paper in International Road Federation World Meeting (Munich, Fed. Rep. Ger., Oct. 1973). Int. Road Federation, 1973, p. 39.
80. Vincent, P. Sulfur in Road Construction Technology. Paper in Symposium on New Uses for Sulfur and Pyrites (Madrid, Spain, May 17-19, 1976). *The Sulfur Inst.*, 1976, pp. 32-52.
81. Kennepohl, G. J. A. The Gulf Canada Sulfur-Asphalt Process for Pavements. Paper in Symposium on New Uses for Sulfur and Pyrites (Madrid, Spain, May 17-19, 1976). *The Sulfur Inst.*, 1976, pp. 66-79.
82. Kennepohl, G. J. A., A. Logan, and D. C. Bean. Conventional Paving Mixes With Sulfur-Asphalt Binders. *Proc. Assoc. Asphalt Paving Technol.*, v. 44, 1975, pp. 485-497.
83. _____. Sulfur-Asphalt Binders in Paving Mixes. Paper in Canadian Sulfur Symposium 1974 (Univ. Calgary, Calgary, Alberta, Canada, May 30-June 1, 1974). *Sulfur Dev. Inst. Can.*, Calgary, Alberta, Canada, 1974, pp. Q1-Q16.
84. Pronk, F. E., A. F. Soderberg, and R. T. Frizzell. Sulfur Modified Asphaltic Concrete. *Proc. Can. Tech. Asphalt Assoc.*, v. 20, 1975, p. 135.
85. Pronk, F. E., and A. F. Soderberg. Sulfur in Asphalt Paving. Paper in Sulfur in Construction (Proc. Int. Conf., Ottawa, Ontario, Canada, Sept. 12-15, 1978). *Sulfur Dev. Inst. Can.*, Calgary, Alberta, Canada, 1978, pp. 299-320.
86. Izatt, J. O. Sulfur-Extended Asphalt Paving Project. Construction Report. *The Sulfur Inst.*, Dec. 1977, 20 pp.
87. The Free Press (Diboll, TX). Sulfur Being Tested as Road Asphalt Substitute. v. 22, No. 37, Sept. 11, 1975, p. 1.
88. Mahoney, J. P., W. A. Liddle, R. G. Hicks, and S. Kidwa. Sulfur Extended Asphalt Pavement Evaluation for Baker River Highway, Washington: Design and Construction Report. U.S. Fed. Highway Admin., FHWA-DP-54-7, June 1983, 84 pp.
89. Galloway, B. M., and F. C. Benson. SEA Production with Pelletized Sulfur in a Drum Dryer Plant. Paper in Proc. SULPHUR-84 (Calgary, Alberta, Canada, June 3-6, 1984). *Sulfur Dev. Inst. Can.*, 1985 (in press).
90. McBee, W. C., T. A. Sullivan, and J. O. Izatt. State-of-the-Art Guideline Manual for Design, Quality Control, and Construction of Sulfur Extended Asphalt (SEA) Pavements. U.S. Fed. Highway Admin., FHWA-IT-80-14, Aug. 1980, 57 pp.
91. McBee, W. C., P. A. Romans, T. A. Sullivan, and R. R. Uhde. Role of Sulfur in SEA Pavements. *Sulfur Res. and Dev.*, v. 4, 1981, pp. 5-12.
92. Sullivan, T. A., W. C. McBee, and K. L. Rasmussen. Studies of Sand-Sulfur-Asphalt Paving Materials. BuMines RI 8087, 1975, 19 pp.