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Modified-Sulfur Cements for Use in Concretes, Flexible Pavings, Coatings, and Grouts

By W. C. McBee, T. A. Sullivan, and B. W. Jong

UNITED STATES DEPARTMENT OF THE INTERIOR

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MODIFIED-SULFUR CEMENTS FOR USE IN CONCRETES, FLEXIBLE PAVINGS, COATINGS, AND GROUTS

by

W. C. McBee,[1] T. A. Sullivan,[2] and B. W. Jong[3]

ABSTRACT

A family of modified-sulfur cements has been developed by the Bureau of Mines for the preparation of construction materials with improved properties. Various types of sulfur cements were prepared by reacting sulfur with mixtures of dicyclopentadiene (DCPD) and oligomers of cyclopentadiene (CPD). Durable cements were prepared with structural characteristics ranging from rigid to flexible. These cements were used to prepare corrosion-resistant materials for use in a wide variety of industrial applications where resistance to acidic and salt conditions is needed. These materials were prepared as rigid concretes, flexible pavings, spray coatings, and grouts. Production of modified-sulfur cements in a commercial-size plant was demonstrated.

INTRODUCTION

In order to take advantage of a potential sulfur surplus forecast for the 1980's (8),[4] the Bureau of Mines initiated research to develop new beneficial uses for sulfur. The project included development of construction materials where sulfur replaces energy-intensive materials such as asphalt and portland cement. Part of the program was to develop and evaluate specialized concrete materials in which sulfur replaces portland cement as the aggregate binder. These materials resist acid and salt corrosion for applications where portland cement concretes are not adequate. Epoxy and polymer concretes have been used in acid environments, but performance has not been consistently good, and the materials are comparatively expensive. Sulfur concretes have important potential uses as construction materials in chemical and metallurgical processing plants, as well as in pollution control applications involving acidic and salt wastes such as sewage, scrubber waters, and leach solutions. Sulfur concretes may also be used as road paving and bridge decking where salt corrosion problems are encountered.

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

The historical development of sulfur concrete materials has been described recently by Raymont (5). Previous Bureau of Mines research (2-3, 6-7) on the development of specialized sulfur concretes has shown that sulfur concrete materials can be prepared using an aggregate binder of sulfur, modified by reaction with DCPD. The present state of the art for sulfur concrete materials has been described by The Sulphur Institute (4).

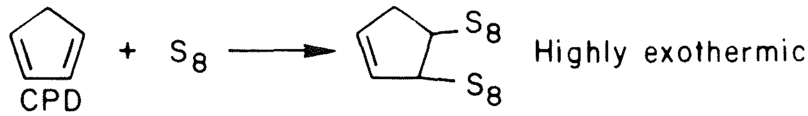
Sulfur concrete products may be produced using a binder of DCPD-modified sulfur, but the products exhibit marginal durability, and there are many disadvantages in its use in commercial-scale concrete production. For one thing, close temperature control is necessary to prevent a runaway exothermic reaction between sulfur and DCPD that can result in a rubbery, unusable polymeric product that is almost impossible to remove from the reactor. As such, this limits both variation in reaction temperature and the rate of DCPD addition to the sulfur in a reactor. Second, since a reaction time of at least 24 hours is generally required to ensure obtaining a modified-sulfur product using DCPD, maintaining a consistent quality for the DCPD-modified sulfur binder is difficult because its viscosity increases with prolonged reaction time. Third, the temperature of the aggregate as it is added to the DCPD-modified sulfur must also be carefully controlled during preparation of the sulfur concrete. Further reactions occur if the hot aggregate creates a sulfur concrete mixture at a temperature exceeding 145° C; the result is a viscous mass of sulfur and aggregate that may even set up inside the mixer. Although DCPD has been reported to stabilize monoclinic sulfur, the concentration required for modified-sulfur binders in concrete production (5 pct DCPD) is insufficient to prevent reversion of the modified sulfur to the orthorhombic structure. As a result of the transformation, the sulfur concrete is stressed such that there is a corresponding loss in its durability.

This report describes the development of a new family of modified-sulfur cements that eliminates the disadvantages noted above. These materials exhibit a wide range of structural characteristics, and the properties can be tailored to specific applications through variation of the individual constituents. Laboratory development and scaling up of the process in a commercial plant to produce tonnage amounts of a modified-sulfur cement are described along with typical properties of materials prepared with these new modified-sulfur cements.

DEVELOPMENT OF MODIFIED-SULFUR CEMENTS

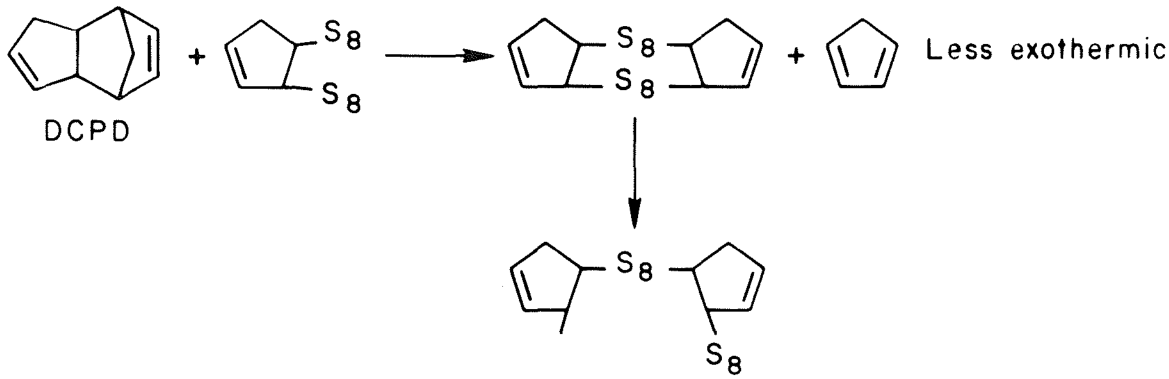
Background

Previous reports (2-3, 7) described the reacting of DCPD with sulfur to form long-chain linear polymers, with the resultant product being used as the binder to prepare sulfur concretes, spray coatings, and mortars. The chemistry of the sulfur-DCPD system has been reported by Bordoloi (1). Reaction between sulfur and DCPD to form the modified-sulfur cement must be carefully controlled because of its exothermicity. Commercial DCPD contains stabilizers to prevent spontaneous depolymerization to the monomer CPD at room temperature, but the presence of sulfur at elevated temperatures, 120° to 140° C, accelerates the depolymerization of DCPD even with the use of stabilizers. Because of the exothermicity of reaction 1



(1)

and because the higher temperatures increase the rate of reaction, this depolymerization is difficult to control. The DCPD in the reaction mixture reacts with the polysulfide product formed in reaction 1 as shown below in reaction 2:



(2)

Linear polymer

Reaction 2 between the DCPD and the polysulfide-CPD product is significantly less exothermic than reaction 1, but still difficult to control. The combined exothermicity of reactions 1 and 2 poses significant control problems. If the rates of these reactions are not controlled, highly viscous rubberlike polymers are formed that may damage extensively the reaction apparatus.

Even if the DCPD-modified sulfur can be prepared, it is difficult to use in making concrete or mortar because of its sensitivity to the aggregate temperature. If the temperature of the aggregate and binder mixture is too high, above 145° C, further reaction in the binder will take place, resulting in a viscous unworkable mass of concrete.

A less thermal sensitive sulfur cement binder that alleviates the above problems was prepared by reacting a mixture of sulfur, DCPD, and an oligomer of CPD, primarily higher order molecules of trimer through pentamer, hereafter referred to as "oligomer." Use of the oligomer reduces the depolymerization to CPD and thereby modulates the reaction. Temperatures are more easily controlled, and the linear polymeric polysulfides formed are more useful in preparing durable sulfur cements. In addition, the sulfur is stabilized in the monoclinic form.

Materials

Commercial-grade flake sulfur (99.9-pct minimum purity) from a secondary source was used in the research described in this report. Technical-grade DCPD was used to modify the sulfur, together with an oligomer of CPD. Virtually any source of oligomer may be used. Generally, the oligomer is obtained from the production of DCPD resin as steam sparge oils. A typical oligomer starting material may contain the following constituents: 5 pct CPD, 10 pct each of dimer and trimer, 20 pct tetramer, 45 pct pentamer, and 10 pct traces of higher polymers such as alkyl naphthalenes and of vinyl DCPD aromatic copolymers. Two types of DCPD products have been used; commercial DCPD containing approximately 77 to 80 pct DCPD and a purified 97 pct DCPD. In most of the development work, the cheaper commercial DCPD type product was used.

Laboratory Studies

Initial laboratory tests were made by reacting 1,000-g quantities of liquid sulfur with various mixtures of DCPD and oligomer in a sealed and vented glass laboratory reactor, stirring until complete reaction was achieved. Reaction temperatures were in the 120° to 180° C range for times up to 48 hours. The test matrix for these screening tests is shown in table 1. All percentage values expressed are in weight-percent.

TABLE 1. - Reactor test matrix for 1,000-g batches

Modifier mixture, pct		Modifier concentration, pct	Reaction temperature, ° C
DCPD	Oligomer		
0	100	2-10	140-180
34	66	2- 8	140-155
50	50	2- 8	140-155
50	50	10	140-150
65	35	2- 5	140-150
75	25	2- 5	140-150
40	60	10-20	120-135
25	75	20-30	120-150
25	75	40	125-140
15	85	35	125-140

The more promising compositions of modified-sulfur cements were selected for further larger scale investigations along with a sulfur cement modified with 5 pct DCPD. These are listed in table 2. Preparation of 1,000 lb of each binder in two batches was accomplished in the vented laboratory reactor, shown in figure 1.

TABLE 2. - Laboratory reactor tests, 500-lb batches

Modifier mixture, pct		Modifier concentration, pct	Modifier mixture, pct		Modifier concentration, pct
DCPD	Oligomer		DCPD	Oligomer	
100	0	5	25	75	20
50	50	5	25	75	30
40	60	10	25	75	40

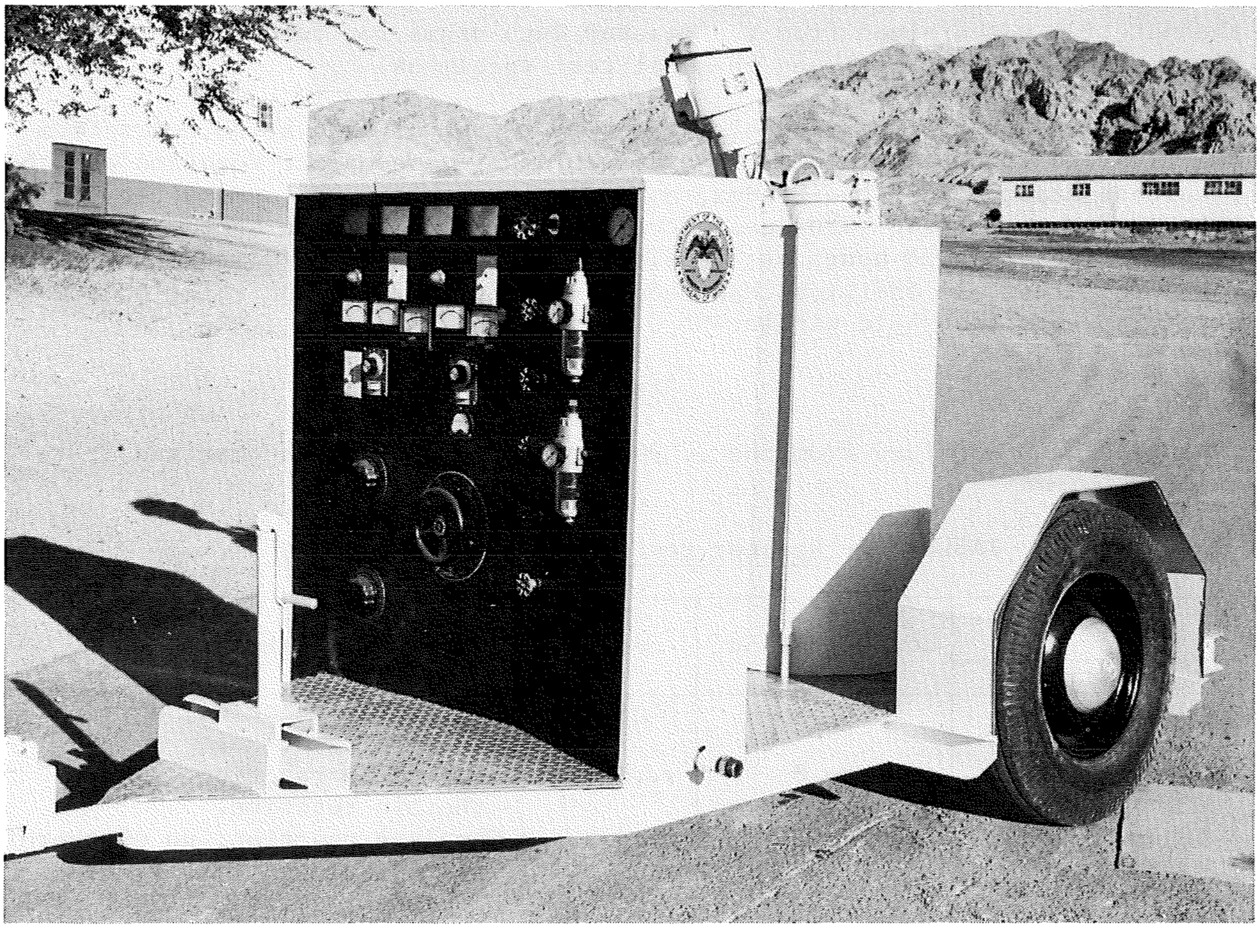


FIGURE 1. - Laboratory reactor for preparing modified-sulfur cements.

The general procedure used in preparing the 500-lb batches was first to heat the sulfur in the reactor to 135° to 140° C. Because it was found that the reaction between modifiers and sulfur proceeded more rapidly if some reacted material was present, it was seeded with 25 lb of starter. The oligomer was then added in three increments. Each addition caused the temperature to drop to about 125° C, so that it had to be raised to 135° C before the following addition. Next, the DCPD (commercial-grade, 80 pct pure) was introduced in two increments, raising the temperature to 135° C after each addition. Normal safety precautions were followed in handling the DCPD chemicals to comply with OSHA and NIOSH regulations. After completion of the reaction, the material was drained from the reactor into drums for future use in preparing physical, mechanical, and chemical test specimens.

Total reaction time for this series of tests was held at 30 hours from the first addition of oligomer in order to assure a complete reaction and the resultant stability of the binder, as well as to obtain uniformity between batches for comparison purposes. However, the data indicate that reaction times of less than 24 hours are possible. Viscosity of the mixture was monitored after all additions had been made in each test, and reaction temperatures were then held within ±5° C until completion.

Results

The data obtained from the 1,000-g reactor tests are summarized in table 3.

TABLE 3. - Reactor test data, 1,000-g batches

Modifier mixture, pct		Modifier concentration, pct	Type cement	Comments
DCPD	Oligomer			
0	100	2-10	Rigid....	Negligible reaction, no exothermic reaction.
34	66	2- 8	...do....	Incomplete reaction, no exothermic reaction.
50	50	2- 8	...do....	Complete reaction, no exothermic reaction.
50	50	10	...do....	Complete reaction, slight exothermic reaction.
65	35	2- 5	...do....	Do.
75	25	2- 5	...do....	Complete reaction, significant exothermic reaction.
40	60	10-20	Flexible.	Complete reaction, no exothermic reaction.
25	75	20-30	...do....	Do.
25	75	40	...do....	Incomplete reaction, slight exothermic reaction.
15	85	35	...do....	Do.

From these tests the following conclusions were made:

1. Oligomer alone does not react with sulfur at temperatures up to 180° C at concentrations under 10 pct. Above 10 pct oligomer, there is an incomplete reaction.

2. When modifiers are added in concentrations of less than 10 pct, at least half the modifier must be DCPD to obtain a complete reaction. The modifier must contain at least 35 pct oligomer to control the exothermic reaction.

3. If modifier concentrations are between 10 pct and 20 pct, at least 60 pct of the modifier must be oligomer to adequately control temperature.

4. At modifier concentrations above 20 pct, at least 75 pct of the modifier must be oligomer.

5. A brittle-to-flexible transition is observed at modifier concentrations above 20 pct, indicating potential plastic or viscoelastic properties.

Data from the larger scale tests are summarized in table 4, and viscosity profiles are plotted in figure 2.

TABLE 4. - Laboratory reactor test data, 500-lb batches

Curve, figure 2	Modifier mixture, pct		Modifier concentration, pct	Softening point, ° C	Specific gravity	Viscosity at 135° C, cp
	DCPD	Oligomer				
1	100	0	5	>82	1.905	>450
2	50	50	5	>82	1.899	28
3	40	60	10	>82	1.818	40
4	25	75	20	>82	1.765	92
5	25	75	30	35	1.667	108
6	25	75	40	38	1.498	155

Modifier compositions used in these tests were based on data from the 1,000-g reactor tests. With 5 pct DCPD alone as the sulfur modifier, the viscosity of the sulfur cement continues to increase almost exponentially during the reaction, as indicated in figure 2. This behavior results in a cement product that is almost impossible to use because of thermal behavior. The curves indicate that sulfur cements of low thermal sensitivity can be made with a combined DCPD-oligomer modifier content of less than 30 pct. Above 30 pct modifier, greater thermal sensitivity is observed, which could probably be overcome by shifting to a mixture of 15 pct DCPD and 85 pct oligomer.

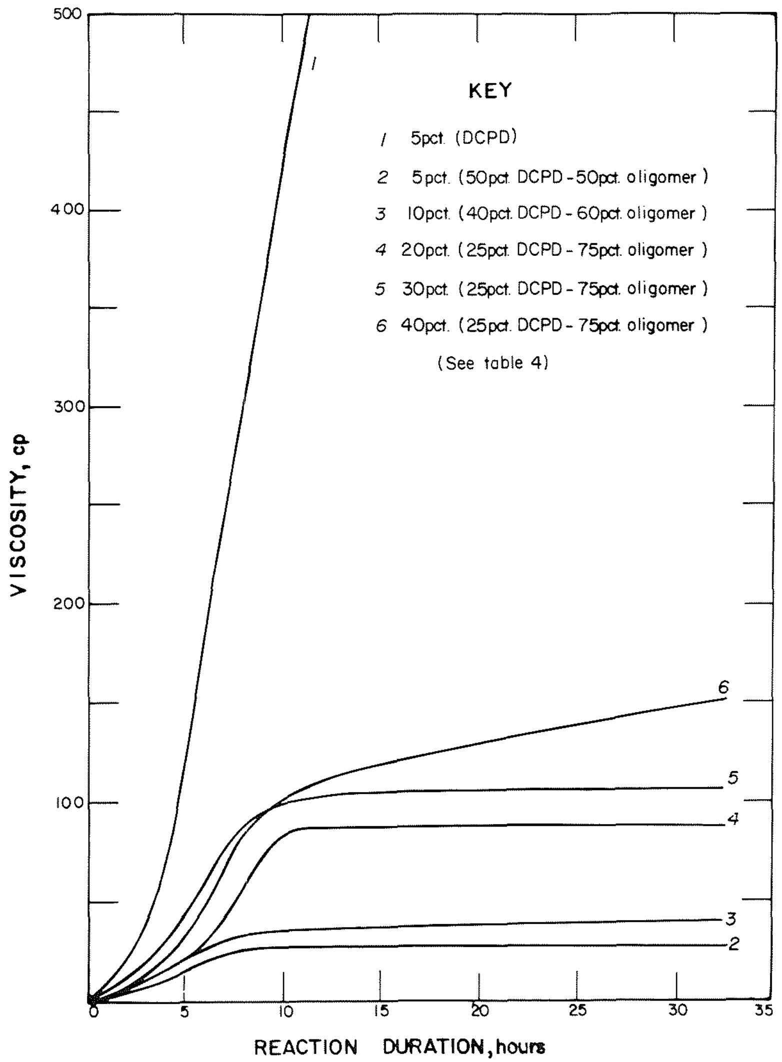


FIGURE 2. - Thermal stability profiles for modified-sulfur cements.

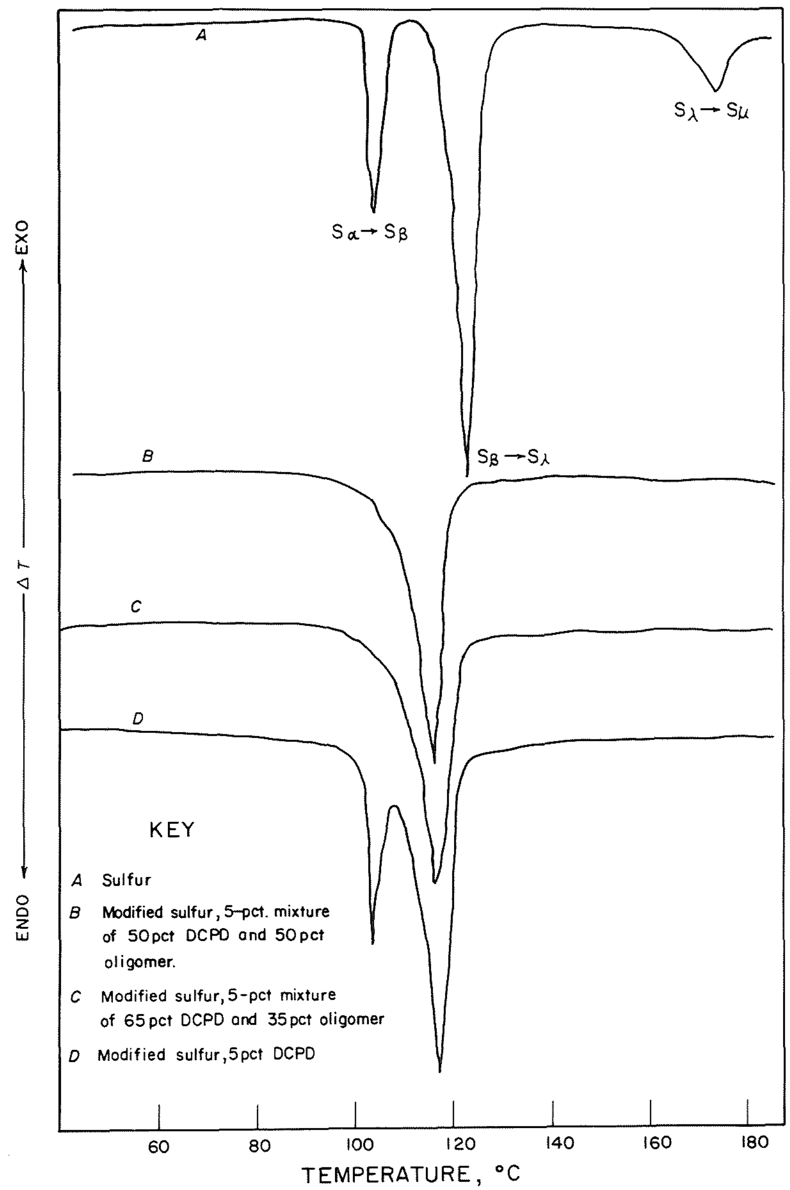


FIGURE 3. - DSC thermograms of sulfur and modified-sulfur cements.

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. Results indicate there was transformation to orthorhombic sulfur (S_α) in DCPD-modified sulfur upon aging, while the sulfur cements with DCPD-oligomer modifiers remained essentially in the monoclinic form (S_β). Thus, DCPD-oligomer modifiers are more effective than DCPD modifiers in retarding unreacted sulfur transformation from S_β to S_α. Durability of sulfur concretes will be enhanced by eliminating internal stressing of the sulfur caused by the phase transformation.

The more flexible materials developed at modifier concentrations above 10 pct were further characterized using standard ASTM techniques developed for road-paving asphalts. Data for these tests are listed in table 5. These cements exhibit viscoelastic properties similar to those of asphaltic cement. These properties indicate a potential use for the cements in mechanically compacted concretes.

TABLE 5. - Typical properties of modified-sulfur cements and asphalt cement

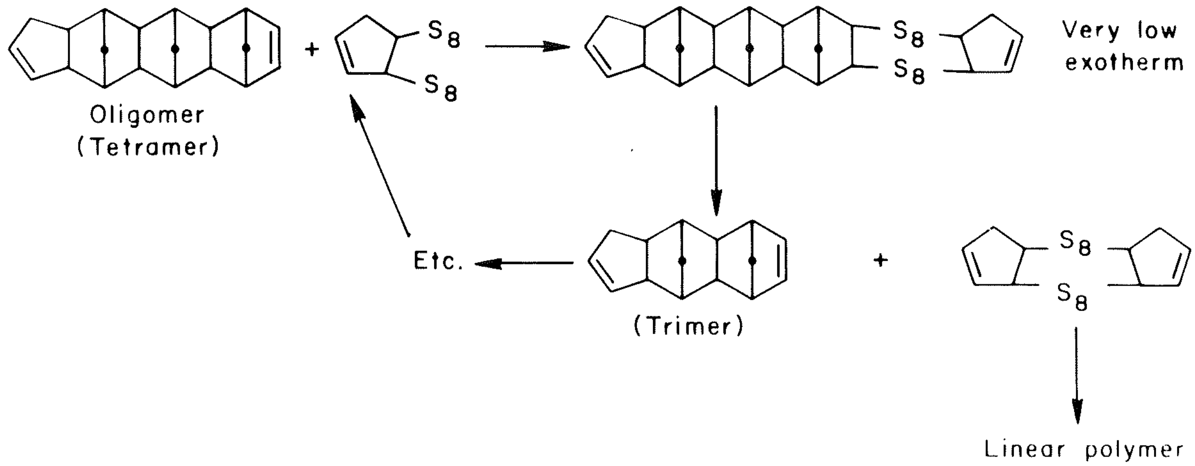
Materials	Viscosity at 135° C, cp	Softening point, ° C	Penetration, 0.01 mm	Specific gravity
90 pct sulfur, 10 pct modifiers[1]..........	105	106	0	1.820
80 pct sulfur, 20 pct modifiers[1]..........	149	105	5	1.740
70 pct sulfur, 30 pct modifiers[1]..........	169	94	16	1.613
60 pct sulfur, 40 pct modifiers[1]..........	176	55	245	1.485
Asphalt cement (AR 4000 grade)............	252	49	41	1.020

[1]Prepared by reacting sulfur with modifiers containing 25 pct DCPD and 75 pct oligomer.

Discussion

The reaction between the polysulfide and the oligomer exhibits little exothermicity, as illustrated by the thermal stability profiles, because the oligomer breaks down very slowly to the final DCPD state. This is why the reaction is only slightly exothermic and why the oligomer is used to moderate the polymerization reaction of sulfur with CPD.

The reaction between sulfur and a combination of DCPD and oligomer is conducted at a temperature and for a time sufficient to complete the reaction, normally 120° to 150° C and 4 to 24 hours. Depending on the type of sulfur cement desired, the amounts of DCPD relative to oligomer in the reaction mixture may range from 80 pct DCPD and 20 pct oligomer to 0 pct DCPD and 100 pct oligomer. Conventionally, sulfur content of the mixtures ranges from 55 to 98 pct. The reaction between the DCPD and sulfur can be smoothly modulated at any modifier concentration through variation of the amount of oligomer in the mixture. The reaction between oligomer and the polysulfide product of reaction 1 may be illustrated as follows.



(3)

Compositions of modified-sulfur cements are tailored for their specific end uses. The following examples typify cements developed for various types of sulfur products.

Product type	Composition, pct		Modified-sulfur cement composition, pct	
	Aggregate	Modified-sulfur cement	Modifiers	Proportion, DCPD to oligomer
Sulfur concretes (rigid).............	75-90	10- 25	5-10	65/35, 50/50
Sulfur concrete (flexible paving)...	85-94	6- 15	10-40	50/50 to 20/80
Sulfur coatings......	[1]2-20	80- 98	3-10	65/35, 50/50
Sulfur grouts........	[2]0-40	60-100	5-40	65/35 to 0/100

[1]Mica or fiberglass.
[2]Sand plus fibers.

Modified-sulfur cements may be formulated with a wide range of properties that make them adaptable to producing sulfur products ranging from rigid sulfur concretes to flexible viscoelastic paving and grout materials.

COMMERCIAL-SCALE PRODUCTION OF MODIFIED-SULFUR CEMENT FOR USE IN SULFUR CONCRETE

Production of 300 tons of modified-sulfur cement was accomplished as a joint project between the Bureau of Mines, The Sulphur Institute, and Chemical Enterprises, Inc., using technology developed by the Bureau of Mines. The chemical modification of liquid sulfur (140° C) was performed by reacting sulfur with a 5 pct mixture of DCPD and an oligomer of DCPD. Chemical Enterprises' plant in Odessa, Tex., was used to prepare the material. The objectives of the test were

1. To determine the changes required to scale up modified-sulfur production technology from 500-lb laboratory reactor batches to 9-ton commercial

reactor batches. To determine if variables in the chemical modification of sulfur on a large scale (such as addition rates, reaction times, and reaction temperatures) differ significantly from those in the laboratory studies.

2. To prepare sufficient amounts of homogenous modified sulfur for use as a binder in the preparation of sulfur concrete materials of suitable size for installation and evaluation under corrosive environments in commercial usage.

3. To evaluate various commercial sources and grades of modifying chemicals.

4. To investigate the feasibility of continuous production of modified sulfur.

Materials used in the scaleup test included commercial-grade pure sulfur (99.5 pct), three sources of DCPD, and two sources of the oligomer. Table 6 lists the chemical modifier designations.

TABLE 6. - Designations of chemical modifiers for sulfur cements

Designation	Grade[1]
A......................	Commercial 80 pct DCPD.
B......................	Commercial 77 pct DCPD.
C......................	Pure 97 pct DCPD.
D......................	Commercial oligomer.
E......................	Do.

[1]Manufacturer's designation.

Laboratory Reaction Tests

Initial reaction tests using commercially available materials were made in the Bureau of Mines 500-lb laboratory reactor, shown in figure 1. In these tests, the monitored parameters were the reaction temperature and viscosity with time. In separate tests, 5 pct (25-lb) of modifier mixture (table 7) was charged into liquid sulfur stabilized at 140° C in the reactor. In all tests, the temperature dropped about 10° C with the addition of the modifier charge, then rose quickly to 142° to 148° C before stabilizing at 140° C for the duration of the test. Viscosity data for tests with eight different modifier mixtures are shown in figure 4.

TABLE 7. - Chemical modifiers used in laboratory tests

Test[1]	Modifier composition,[2] pct		Test[1]	Modifier composition,[2] pct	
	DCPD	Oligomer		DCPD	Oligomer
1.........	65 C	35 D	5.........	65 A	35 E
2.........	65 C	35 E	6.........	50 A	50 D
3.........	50 C	50 E	7.........	58 C	42 D
4.........	65 A	35 D	8.........	58 C	42 E

[1]Corresponds to curve numbers on figure 4.
[2]A-E refer to designations in table 6.

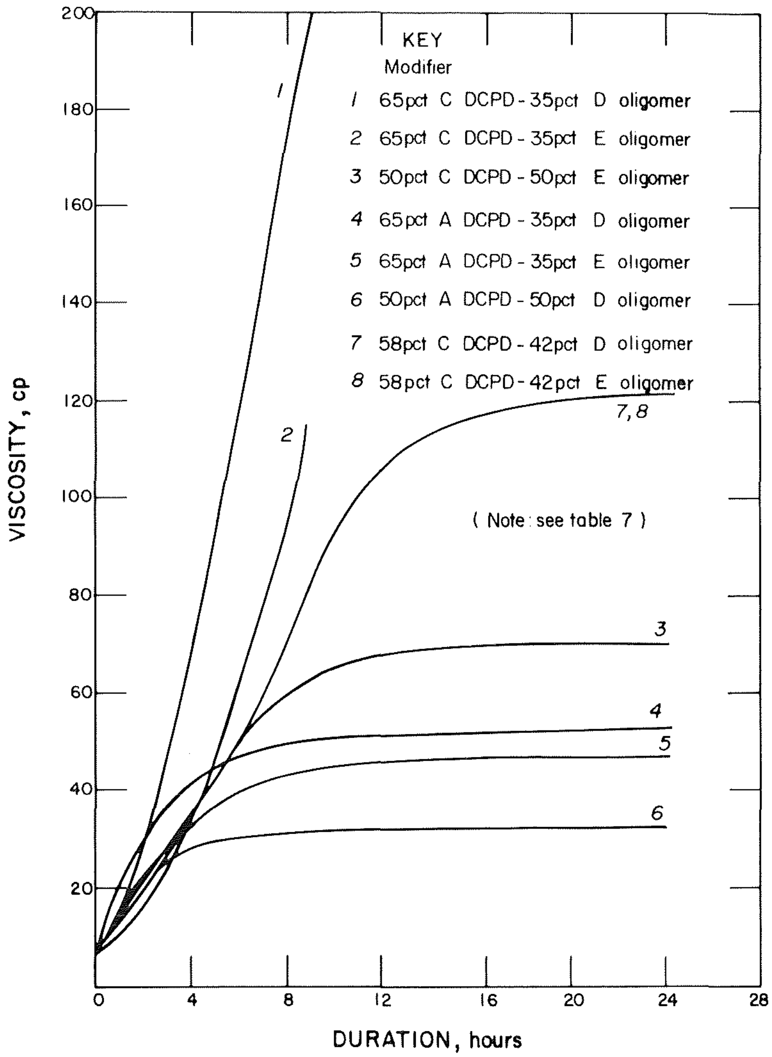


FIGURE 4. - Viscosity of modified-sulfur cements versus time at a reaction temperature of 140° C.

Reactions were performed over a 24-hour period, except for two tests where it was necessary to remove the material earlier because of rapid viscosity increases. Tests with mixtures 1 and 2 continued to react vigorously after 8 hours, and the materials were removed to prevent their setting up in the reactor. Tests with the remaining mixtures produced essentially complete reactions in 4 to 6 hours, as indicated by viscosity measurements.

These tests indicated that using a mixture of 65 pct commercial-grade DCPD with 35 pct commercial-grade oligomer resulted in a controllable reaction at 140° C that was essentially complete after 4 to 6 hours. Also, by lowering the amount of DCPD to 50 pct in the mixture when using the pure-grade DCPD (C) and increasing the oligomer (E) to 50 pct (mixture type 3), the reaction at 140° C was controllable.

The results indicated the feasibility of scaling up the reaction process from 500 to 18,000 lb, and arrangements were made with Chemical Enterprises, Inc. to conduct the commercial-scale tests at their Odessa, Tex., plant.

Modified-Sulfur Cement Production

The Chemical Enterprises, Inc. reactor system consisted of two steam-heated reactor units, each with a capacity of 9 tons of molten sulfur. One reactor was located above the other, with the upper one discharging into the lower. Both units were equipped with stirrers to agitate the molten sulfur. For these tests, 17,100 lb of sulfur at 140° C were pumped from a storage tank into the top reactor, and 900 lb of the chemical modifier mixtures were injected under the surface of the sulfur in the vicinity of the apex formed in stirring. Preparation of the 5-pct chemically modified-sulfur cement was accomplished using the following batch sizes to produce 35- and 50-pct oligomer mixtures.

	Mixture 1 (65-35) DCPD-Oligomer		Mixture 2 (50-50) DCPD-Oligomer	
	Lb	Pct	Lb	Pct
Sulfur......	17,100	95	17,100	95
DCPD........	585	3.2	450	2.5
Oligomer....	315	1.8	450	2.5

The reactor was sealed to prevent loss of the modifiers to the atmosphere. Approximately 15 minutes were required to add the modifiers to the sulfur in the top reactor. In general, a 2-hour total retention time was sufficient in the top reactor to get a good mixture of the sulfur and modifiers. Reactants were then discharged into the bottom reactor where approximately 2 hours additional stirring was necessary to complete the reaction. The stabilized temperature in both reactors was held at 140° ±5° C.

Upon completion of reaction, the modified sulfur was pumped from the bottom reactor to a storage tank which fed the product onto dual Sandvick[5] belt flaking machines. The material solidified on the water-cooled belt into a 1/16-inch sheet that came off the end of the belt and was chopped and screened into 1/8-inch-diameter flakes. Fines from the screening operation were recycled to the lower reactor. Flaked materials were elevated into a storage bin from which they flowed into a commercial bagging machine and were packed into 50-lb bags. The production rate was dependent on the rate the dual flaking units could solidify the material; about 5 hours were required to flake a 9-ton batch. A total retention time in the two reactors of 4 hours was sufficient to complete the reaction.

The first 9-ton batch of material produced required a longer reaction time to reach completion, because reacted material was not available to seed the batch. Thereafter, approximately 500 lb of reacted material was left in the bottom reactor to catalyze the reaction of the next batch. In addition, recycled fines from the flaking operation served as a catalyst seeding material.

Figures 5 through 7 illustrate the equipment used commercially to produce the modified sulfur. While a dual-reactor system was used in the test because of the plant layout, a single reactor could be used with a 4-hour reaction time.

[5]Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

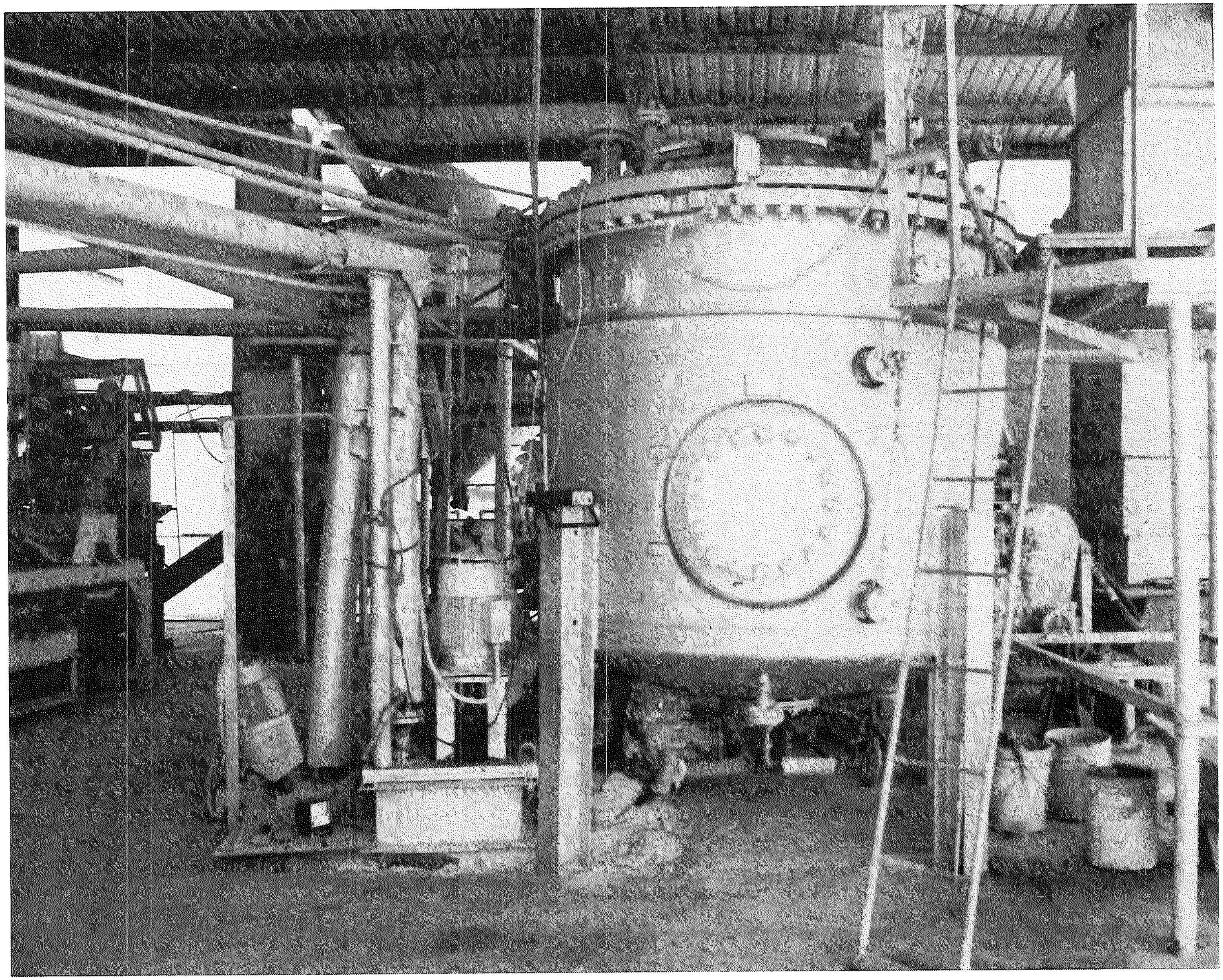


FIGURE 5. - Upper reactor.

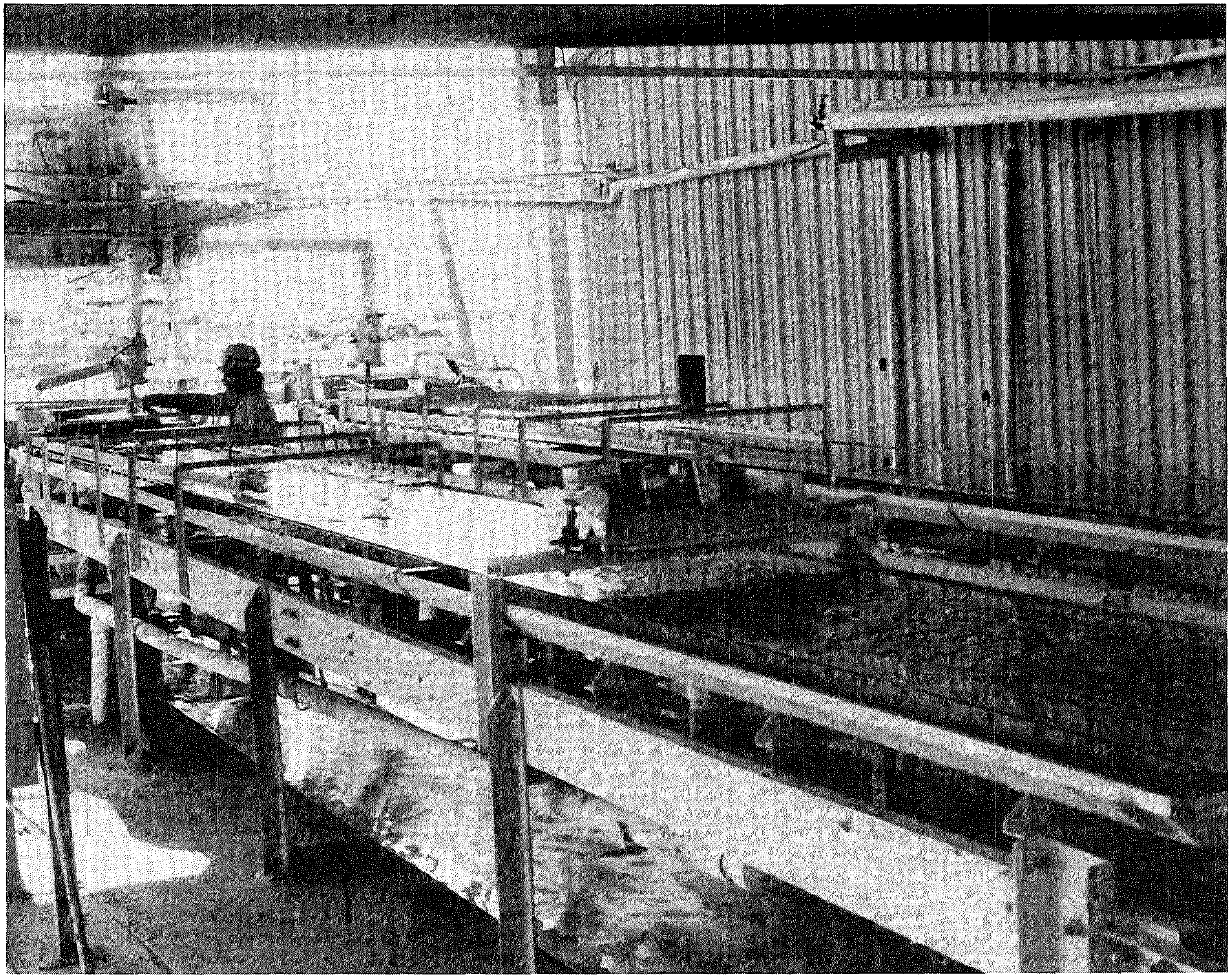


FIGURE 6. - Cooling and solidification of the modified sulfur on the stainless steel belts.

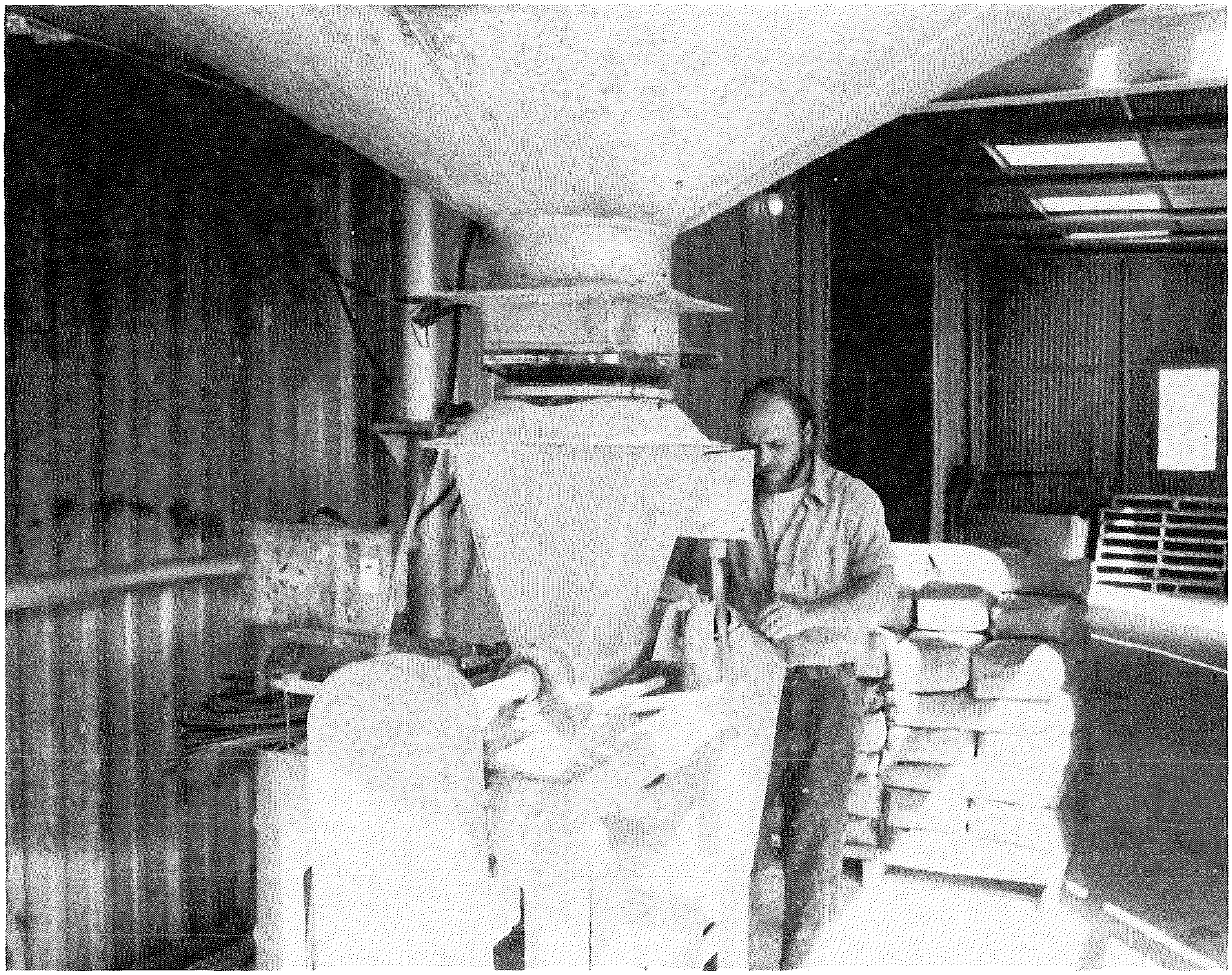


FIGURE 7. - Bagging the modified-sulfur cement product.

The initial 10 batches of modified sulfur were made to determine operating conditions in the large-scale plant with five variations in the modifier feed materials indicated in table 8. The remaining 24 batches were made on a production basis using the described operating conditions. Material from each batch was tested for viscosity; the averaged results are also given in table 8.

TABLE 8. - Chemical modifiers used in production tests

Modifier composition,[1] pct		Batches	Average viscosity at 135° C, cp	Production, tons
DCPD	Oligomer			
50 C	50 D	1	27	9
65 A	35 D	3	27	27
50 A	50 D	1	28	9
65 B	35 E	13	41	117
50 C	50 E	16	25	144

[1]A-E refer to designations in table 6.

USES OF MODIFIED-SULFUR CEMENTS

Sulfur Concretes

Modified-sulfur cements prepared by reacting sulfur with 5 pct mixed modifiers are used as the binder in preparing thermosetting sulfur concretes. Sulfur concretes can be prepared with mechanical properties equal to or greater than those of portland cement concretes using the same aggregate. If the sulfur concretes are made using acid and salt-resistant aggregates such as quartz and basalt, the sulfur concrete materials produced will resist corrosive attack by acid and salt solutions. Higher strength (9,000-psi compressive strength) concretes can be prepared using modified-sulfur cements and limestone aggregates. Sulfur concretes made with limestone aggregate are more resistant to acid corrosion than portland cement concrete made with the same aggregate. However, these sulfur concretes are extremely resistant to corrosion by salt solutions. Table 9 lists the properties of several types of sulfur concrete materials prepared with modified-sulfur cements.

TABLE 9. - Properties of typical sulfur concretes

Aggregate		Sulfur cement,	Strength, psi		
Type	Pct	pct	Compressive	Tensile	Flexural
Quartz, open-graded....	77	[1]23	5,030	730	1,130
Limestone, open-graded.	79	[1]21	9,100	1,050	1,480
Quartz, dense-graded...	84	[1]16	6,970	1,090	1,510
Do..................	84	[2]16	7,720	1,040	1,440
Limestone, dense-graded	84	[2]16	8,800	1,090	1,100

[1]Sulfur modified by reaction with 5-pct mixture of 65 pct DCPD-35 pct oligomer.

[2]Sulfur modified by reaction with 5-pct mixture of 50 pct DCPD-50 pct oligomer.

Sulfur concrete materials are normally prepared by mixing modified-sulfur cement and hot aggregate, so the resultant sulfur concrete is produced in the 130° to 150° C range. Modified-sulfur cement may be added in either the solid flake form or as a liquid cement. A laboratory-size sulfur concrete mixing unit, shown in figure 8, was developed to prepare 500-lb batches of sulfur concrete. The aggregate charge is heated in the propane-fired kiln and discharged into a heated mortar-mixer. If solid sulfur is used, the aggregate must be heated to about 175° C. If liquid sulfur is used, the aggregate is heated to only 150° C. The components are mixed for 1 to 2 minutes and then cast into the shapes or forms desired. This unit has been used to prepare sulfur concrete for casting components weighing up to 8 tons.

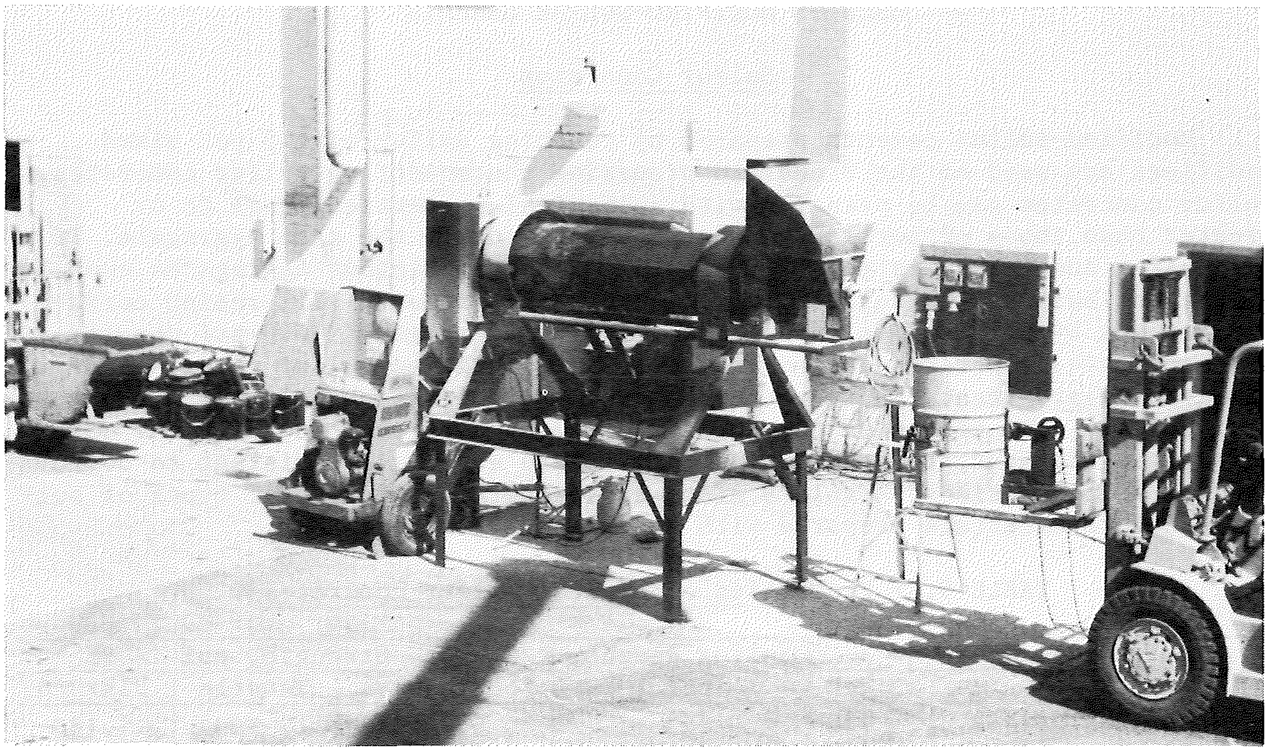


FIGURE 8. - Laboratory-scale production unit for sulfur concrete.

Laboratory corrosion studies in progress on sulfur concretes prepared with quartz aggregates have shown no attack or loss in mechanical properties after 1 year of immersion in water, 10, 20, 60, and 98 pct H_2SO_4 solutions. Sulfur concrete materials are also being tested in cooperation with a number of chemical and metallurgical companies to determine the durability and corrosion resistance of sulfur concretes when used under actual plant operating conditions. Test specimens in the form of slabs, bars, tiles, cylinders, and tanks have been under continuing evaluation in highly corrosive acid and salt environments in 14 commercial plants for periods of up to 3 years. None of the tests have shown any signs of corrosion or loss of strength in these components. Figure 9 shows four 4-foot-square test slabs installed in a highly corrosive area of a potash plant. A 1,000-gallon acid sump tank, shown in figure 10, is in service in an electrolytic zinc refinery where H_2SO_4 concentrations of up to 18 pct flow into the tank. Figure 11 shows four sulfur concrete slabs (with four portland cement concrete control slabs) installed in a floor area below a battery of electrolytic zinc cells. After 8 months in service, the control slabs were severely attacked, but there was no attack on the sulfur concrete slabs.

The ability of sulfur concrete materials to withstand acid and salt corrosion has aroused considerable industrial interest in these materials. Cooperative programs between the Bureau of Mines, industry, and The Sulphur Institute are currently underway to evaluate the use of corrosion-resistant, sulfur concrete materials in both precast and poured-in-place industrial applications. Results of these field testing programs will be made available upon their completion.

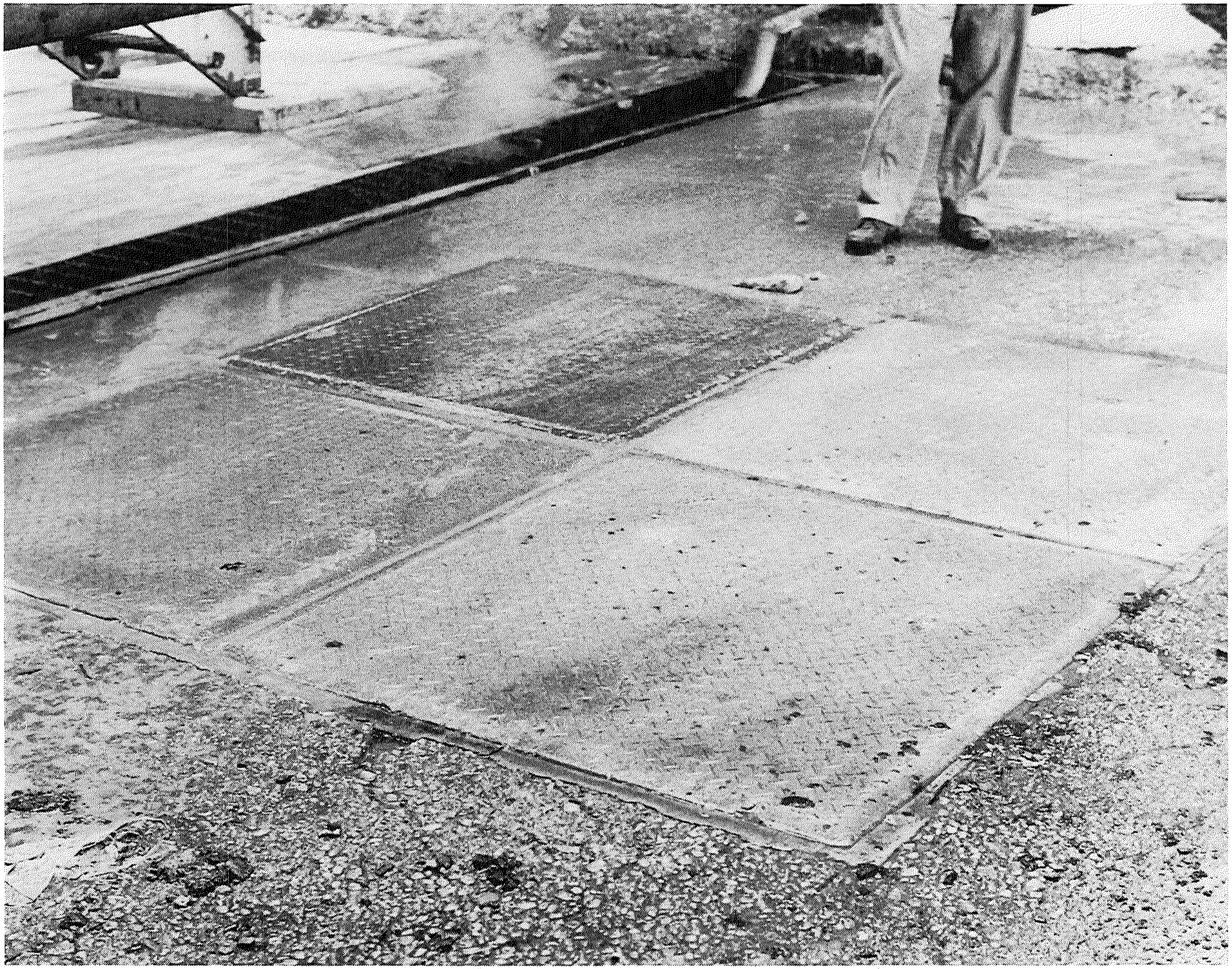


FIGURE 9. - Sulfur concrete test slabs in a highly corrosive area of a potash processing plant.

FIGURE 10. - Sulfur concrete sump tank.

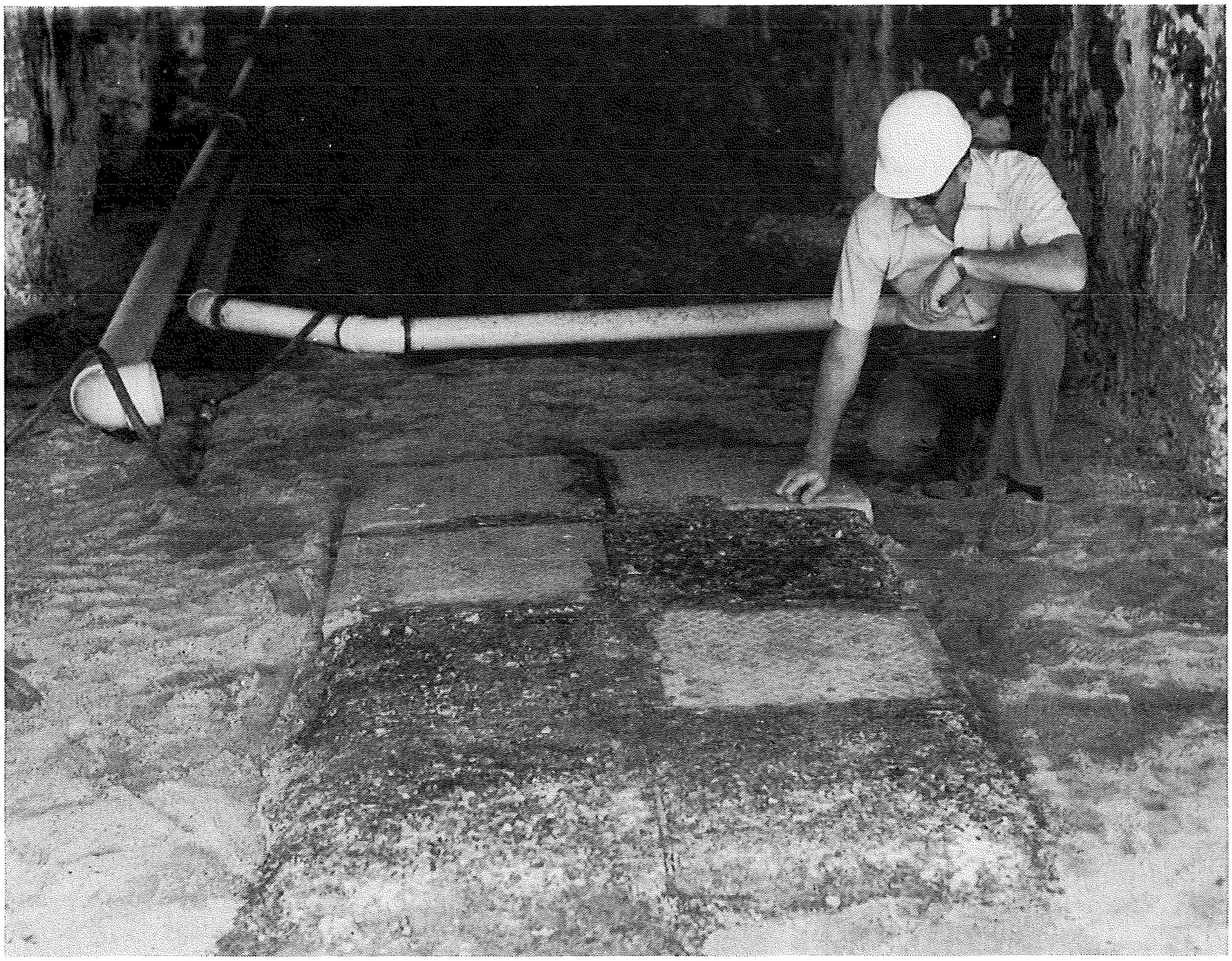


FIGURE 11. - Sulfur concrete test slabs installed with portland cement control slabs in an electrolytic zinc refinery.

Flexible Sulfur Concrete

Modified-sulfur cements containing 10 to 40 pct of DCPD-oligomer mixtures were used as the binder with graded aggregates to prepare paving materials having flexibility properties similar to those of asphaltic concrete. These materials are prepared by hot-mixing the sulfur binder and aggregate in a suitable mixer at 130° to 150° C. The mixture is then compacted mechanically by rolling or use of vibratory plate-type compactors. When dense-graded aggregates are combined with the sulfur cements in this manner, paving materials can be mixed and laid with conventional asphaltic concrete equipment. If quartz aggregate is used, the material will be resistant to acid and salt solutions.

Flexible sulfur concrete materials have many potential uses, including the lining of leach and settling ponds with an impervious coating to contain corrosive and hazardous materials, paving of plant floors to prevent acid and salt corrosion, paving of roads, paving of pads for heap leaching of ore and tailings, and paving of noncorrosive bridge decking.

Characterization of these materials is currently underway. Table 10 shows typical properties of selected sulfur flexible paving materials that were developed using the modified-sulfur cement binders and a dense-graded quartz aggregate.

TABLE 10. - Properties of selected flexible sulfur concrete materials and asphaltic concrete

Modifier, pct	Aggregate, pct	Binder, pct	Marshall		Air voids, pct	Specific gravity
			Stability, lb	Flow, 0.01 mm		
20........	89.0	11.0	23,400	11	2.9	2.4628
30........	90.5	9.5	3,430	9	3.2	2.3950
40........	89.0	11.0	3,860	15	4.4	2.3152
AR4000[1]...	94.0	6.0	3,660	10	2.1	2.3544

[1]Asphalt cement--AR4000 grade.

The properties, as shown, are similar to those prepared using different grades of asphalt cements. To date, results obtained indicate that the materials are stable, are not affected by exposure to corrosive acid or salt environments, and can be used with conventional asphaltic concrete mixing and paving equipment. Durability and corrosion tests are in progress.

Sulfur Coating Materials

Sulfur coating materials were developed using the modified-sulfur cements with fiber and filler materials. Materials were used to spray-coat portland concrete sumps and drainage ditches to protect them from the corrosive action of waste acid and salt solutions. A typical spray coating consisted of 80 pct modified-sulfur cement (sulfur reacted with 5 pct modifiers), 15 pct mica, and 5 pct 1/4-inch glass fibers. Sulfur spray coating of a nitric acid waste sump is illustrated in figure 12. Other spray coating materials have been developed for stabilizing waste materials such as tailings from mineral processing plants. While such coatings protect the materials coated, as long as the coating is sound, they become vulnerable to failure when chipped or cracked.

Sulfur Grout Materials

Various types of sulfur grouting materials can be prepared from the modified-sulfur cements. For example, a rigid-type grouting material can be prepared using a modified-sulfur cement similar to those used for sulfur concrete. A typical composition would be 45 pct modified-sulfur cement (sulfur reacted with 5 pct modifiers) mixed with 45 pct No. 47 sand, and 5 pct each of silica flour and 1/4-inch glass fibers. This grout was used to install the four sulfur concrete test slabs in the concrete floor of a potash plant shown in figure 9.

Thermoelastic grouts can be prepared using higher amounts of modified-sulfur cements. A pourable sulfur grout using 50 pct modified-sulfur cement

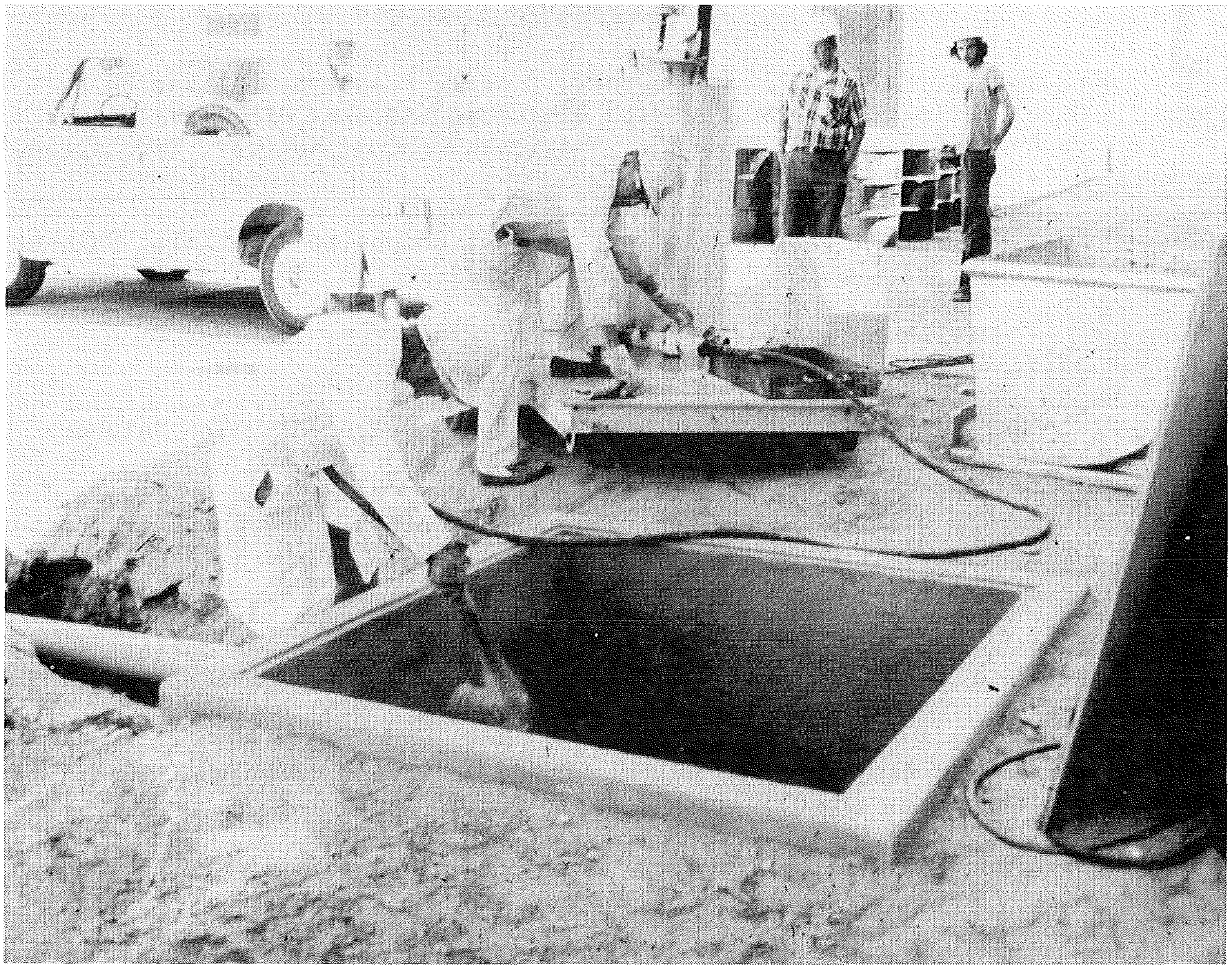


FIGURE 12. - Spray coating an acid sump with a sulfur coating material.

(sulfur reacted with 40 pct modifier) with 40 pct No. 47 sand, 5 pct silica flour, and 5 pct 1/4-inch glass fiber was used to install sulfur concrete slabs in the floor of an alumina pilot plant. This grout is flexible enough to resist cracking from the temperature cycling that occurs.

CONCLUSIONS

Newly developed modified-sulfur cements have properties suitable for use as the binder in preparing a variety of concrete, flexible paving, coating, and grouting materials. In preparing these cements, the highly exothermic reaction of sulfur with DCPD can be modulated by adding 3 to 40 pct of different CPD oligomers. The new cements do not exhibit the normal sulfur phase transformation and remain essentially in the monoclinic crystalline form.

Commercial production of sulfur cement with 5 pct modifiers was successfully demonstrated in a 9-ton reactor. Sulfur cement with 20 to 40 pct modifiers was prepared in 1,000-lb batches for use in flexible sulfur concrete demonstration tests.

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