SULFUR POLYMER CEMENT CONCRETE

By

William C. McBee
Technical Consultant
30356 Butte Creek Road
Lebanon, Oregon 97355

and

Harold H. Weber, P.E.
The Sulphur Institute
1725 K Street, N.W.
Washington, D.C. 20006

ABSTRACT

Sulfur based composite materials formulated using sulfur polymer cement (SPC) and mineral aggregates are described and compared with conventional portland cement based materials.

Materials characteristics presented include mechanical strength, chemical resistance, impact resistance, moisture permeation, and linear shrinkage during placement and curing.

Examples of preparation and placement of sulfur polymer cement concrete (SC) are described using commercial scale equipment. SC application presented are focused into hostile chemical environments where severe portland cement concrete (PCC) failure has occurred.

INTRODUCTION

Corrosion of PCC structures is a serious national problem and results in multi-billion dollar losses annually for industries in the United States. This degradation due to continual attack of acid and salt solutions on reinforced PCC structures results in extreme structural damage.

Special purpose SC materials have recently been developed by the U.S. Bureau of Mines for use in hostile chemical environments to resist mineral acid and salt attack without the need for protective coatings or sealants. Materials developed utilize a SPC and include composites formulated both with and without glass fiver reinforcement providing a durable high strength, impermeable corrosion resistant concrete. As a result of this research sulfur concrete technology has moved from the laboratory into commercial application through world wide licensing of the government developed technology.

This paper describes research related to the development of SC for use in both structural and non-structural corrosive construction and maintenance applications together with the development of commercial-scale equipment including the development of the recently announced technology and equipment for manufacturing corrosion resistant concrete pipe.

Sulfur Polymer Cement (SPC)

Development of stable SPCs is the key to the success of SCs. The use of sulfur as a construction material was proposed as early as World War I, when an acid-resistant mortar of 40 pct sulfur binder mixed with 60 pct sand was used. However, thermal cycling of these mortars caused loss of mechanical strength, leading to cracking and failure. This loss of strength is attributed to the allotropic transformation that sulfur undergoes as it solidifies and ages. As it cools below 204° F (95.5° C), solid sulfur slowly transforms from the monoclinic (S_β) to the orthorhombic (S_α) form. The S_α form has a higher density; therefore, the solid state S_β-to S_α transformation is accompanied by a 6-pct volume reduction and high residual stresses in the finished product. Any process that tends to stress-relieve the product, such as thermal cycling, may result in disintegration (1).

Bureau of Mines research was targeted at overcoming this problem of disintegration. A sulfur modifier system consisting of a mixture of dicyclopentadiene (DCPC) and oligomers of cyclopentadiene (CPD) currently is being used commercially to produce durable SPCs (2). The oligomers are obtained from the production of DCPC resins, such as steam sparge oils. The major oligomer components are approximately 5 wt pct CPD, 10 wt pct dimer, 10 wt pct trimer, 20 wt pct tetramer, 45 wt pct pentamer, and 10 wt pct higher polymer. A 5-wt-pct mixed modifier content in the SPC was used for producing the rigid types of SC.

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

The cements are prepared in the temperature range of 280 to 300° F (139 to 149° C) at ambient pressure in a sealed, jacketed reactor. Normal reaction times are 4 to 6 hours, after which the molten cement can be used directly or allowed to solidify for future use.

Linear thermal expansion values as a function of temperature are shown in Figure 3 for plastics and elemental sulfur. Sulfur (A) goes through an S_α-to-S_β transformation with a rapid increase in volume. Cement (B) prepared using a 50-50 mixture of DCPC and oligomer, referred to as SPC, was heated to its softening point, but did not go through a S_α-to-S_β transition. For unmodified sulfur, a 13-vol-pct contraction occurs on solidification of the liquid and through the S_α-to-S_β transformation. The SPC does not go through the S_β-S_α 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.

Composition and properties were determined for SPC prepared by reacting sulfur with SPC and oligomer at 293° F (145° C) for 6 hours. Typical analysis and properties are shown in Table 1.

Sulfur Polymer Concrete (SC)

SC is a thermoplastic construction material produced by mixing the SPC with mineral aggregate at 280° F (138° C). The SPC replaces portland cement and water as the binder, producing, upon cooling, a high-strength concrete material. Table 2 shows a comparison of the physical and mechanical characteristics of SC and regular PCC. The American Concrete Institute has published a guide for mixing and placing SC (3).

Since there is no alkaline binder in the mix, SC is a highly acid-resistant structural material, suitable for either cast-in-place or precast construction of floors, walls, sump basins, trenches, pump basins, and other items (4). Because of SC's thermoplastic characteristics, the material's high mechanical strength properties are achieved rapidly upon solidification. The material achieves over 80% of its ultimate strength in a few hours, and full strength is achieved in approximately 30 days. In addition to the rapid strength gain, SC can be poured in below-freezing temperature and can be readily recycled by remelting and recasting without loss of mechanical properties.

The thermoplastic nature of SC, however, results in a maximum operating temperature of 190° F (88° C). The material will melt if exposed to prolonged temperature above the melting point of SPC, 248° F (120° C), thus losing structural integrity. SC's poor thermal conductivity will prevent destruction on short exposure to elevated temperatures. The material will burn if exposed to open flame, but the concrete does not contain sufficient sulfur to support combustion.

Mixture Design Considerations

SC mixtures are designed to achieve maximum strength and density, low void levels, and very low moisture absorption. While the materials exhibit mechanical properties comparable to those of PCC, moist of the mixture design considerations are similar to those of hot-mix asphalt concrete.

Good-quality aggregates are required for corrosion resistant SC. Aggregates must be clean, high strength, and free of swelling clays, and must exhibit low moisture absorption (less than 1%). Aggregates, such as quartz, that are insoluble in acids are used for preparing acid-resistant SC. If corrosion is from salt alone, limestone aggregates may be used. SPC requirements are minimized by dense-grading the aggregate.

Industrial Application of Sulfur Concrete

The Bureau of Mines, in conjunction with The Sulphur Institute, conducted a cooperative industrial testing program to test SC in industrial corrosive environments. Initially, precast components such as tiles, slabs, tanks, and pump foundations were cast and subsequently transported and placed in industrial plants. In subsequent tests, construction of floors and tank sections was accomplished directly at plant locations. Mechanical strength test specimens were also placed on site to test material properties after being subjected to the particular corrosive environment. Experiments using 50 test environments were conducted in cooperation with 40 industrial companies. A summary of industrial performance testing of SC structures has been reported previously (5). The results have shown the suitability of SC in many corrosive environments listed in Table 3.

The most promising uses are those where the material is exposed to corrosive electrolytes and mineral acid and salts solutions that can cause major damage to cells, floors, foundations and equipment.

The durability and performance life of AC is being established. The oldest corrosion-resistant SC materials being evaluated are components exposed to sulfuric acid solutions and copper electrolytic solutions. These units show no evidence of corrosion or deterioration after nine years of service. Since Sc is a relatively new materials, longer periods of testing will be necessary to fully establish its ultimate service life.

Production and Installation

This portion of the paper summarizes the development of commercial-scale equipment used to produce and transport SC and discusses some of the specialized techniques and construction practices used to successfully place and finish SC. Finished SC looks like PCC; however, preparation is similar to that of asphalt concrete materials. SC is proportioned, mixed, placed and finished at a temperature of approximately 280° F (138° C). Several critical points should be emphasized in the production of SC (6). Water or moisture must be eliminated during the mixing of SC, and it is essential that SC be placed on a dry base. If precautions are not taken, steam liberated by the action of hot SC and moisture in the Base will form tiny vents through the SC, making it porous. Enough SC should be prepared to complete the entire placement area in one pour and eliminate the potential for cold joints or an irregular surface. In precast work, forms and rebar should be preheated to preclude damage from flash setting of hot SC on cold surfaces and to eliminate moisture.

Equipment

Many different methods of manufacturing SCs and various types of equipment are currently available for producing, transporting, and placing SC. In general, mixing of SC can be accomplished in almost any type of mixer utilized for preparing PCC or asphalt concrete that has been modified to control the temperature of the mixture. Essential to the preparation of SC is a means of drying and heating the aggregate to the desired temperature for mixing. Some of the equipment that has been successfully used to prepare SC is described in the following paragraphs.

A unit capable of preparing 500-pound batches of SC was used to prepare early research test samples. A propane-heated kiln was used to heat the aggregate and feed it into an electrically heated mortar mixer. The SPC and mineral filler were added manually to the hot aggregate in the mixer. Larger scale units, having a SC capacity of 12 to 30 tons per hour, are now used for commercial production of SC. These types of plants use divided bins for proportioning the coarse and fine aggregates into fuel-oil, propane, or gas heated rotary kiln. The kiln discharges a weighed batch of heated aggregate into a heat-jacketed mixer. Flaked SPC and mineral filler are then added through a hopper which discharges directly into the mixer, where the aggregate melts the SPC and produces a homogeneous SC.

Heat-jacketed concrete transit mixers with capacities up to 12 cubic yards (9.2 cubic meters), are also used to produce and transport SC. Figure 4 shows an 8 cubic yard (6.1 cubic meters) transit mixer equipped with an on-board micro-processor which controls four propane infrared catalytic heaters used to maintain the SC in the optimum temperature range for placement. Coarse and fine aggregates may be heated in these mobile units, or in the rotary kiln plants described earlier. Solid SPC and mineral filler are then added to the hot aggregates in the mobile unit where thorough mixing takes place. One advantage of the heated mixer truck is that the SC can be maintained in a given temperature range, and unlike PCC, can be premixed and transported for long periods of time, yet remain plastic and workable until placement.

A new generation self-contained machine has been designed and built capable of mixing, in succession, a series of batches of SC at a production rate of up to ten cubic yards per hour (7.6 cubic meters per hour). For improved quality, the machine shown in Figure 5 weighs the aggregate components after heating, thus compensating for any resulting moisture loss. The batching system is fully automated, allowing the operator to preset desired mix designs and press a single button each time that a batch is to be duplicated.

Aggregate is loaded into two bins, one for fine and the other for coarse, and the two sizes are proportioned by adjustable gates and transported by a conveyor belt into a drum dryer. The heated aggregate is then transported by a bucket elevator to a holding hopper. From that hopper it is gravity-fed into the weight batcher, along with the other ingredients of the mix. The fine materials and SPC are added into the same weight batcher by screw conveyors, and following completion of the batching, all components are gravity-fed into the mixer. A separate compartment in the weight batcher, which is thermally insulated from the remainder of the batch ingredients, is reserved for the SPC so that it remains in a solid state until it contacts the aggregate in the mixer. After one minute of mixing, the batch is discharged for transport to the point of placement.

The types of mixers described have performed satisfactorily in preparing homogeneous mixtures of SC. Successful mixing of the concrete is indicated by a fluid mixture of completely coated aggregate without any segregation of fine materials. Complete mixing of SC components can usually be accomplished in relatively short periods of time, generally less than two minutes. Total mixing times for SC are generally not critical. SC does not set up until it has cooled. Depending on the type of mixer, mixing times of one minute to two hour per batch have been used.

Construction Techniques

Vibratory probes and screeds may be used for consolidating and finishing the SC in the forms or molds. Shovels and rakes may also be used in moving and leveling the SC. Leveling, consolidating, and finishing the SC should be done as rapidly as possible to prevent crusting over of solidified material.

Either wood or metal forms are used. Form-release agents should be used on wall pours but are not necessary on slab forms. When forming large surface areas (i.e., walls) with reusable metal forms, the forms should be preheated before poring to eliminate any moisture and to prevent flash solidification of a skin of sulfur cement when it contacts a cold form. Wall construction should be given some special considerations. The use of insulation on the outside of wall forms to retain heat during placement of SC should be considered. Use of successive lifts in wall construction will minimize shrinkage, resulting in a monolithic section.

Sc can be reinforced with Grade 60 reinforcing steel (SPC does not react with steel), epoxy-coated reinforcing steel, or synthetic fibers. Glass fibers may also be added to control shrinkage cracks and improve the ductility and impact resistance of SC.

Proper preparations for placing SC on either a subbase or existing PCC surfaces are very important. The most important requirements for subbase are compaction, grade, and dryness. A thin layer of sand may be used to adjust the well-compacted subbase to final grade. Whenever moisture is present, a suitable vapor barrier must be used to prevent formation of steam while placing the not-mixed SC. Existing PCC surfaces should also be properly prepared prior to placing SC. All deteriorated areas should be removed to render a sound surface, free of all loose materials and other debris. A vapor barrier or other flexible membrane is generally applied to seal this surface and prevent any absorbed moisture from reaching the SC. The flexible membrane provides an adhesive bond between the SC and the existing PCC surface and also additional protection against future chemical attack of the substrate.

Proper techniques must be employed when placing and finishing thermoplastic SC to achieve high density and a satisfactory surface. The key factors for successful SC placement include appropriate manpower, experienced supervision, an adequate supply of SC to readily fill the placement area, and a rapid placement and finishing operation.

SC can be placed on grades of nearly 8 pct without excessive flowing of the hot material to the low side. In general, mixes used on grades are designed for lower binder content and increased stiffness, by using silica flour rather than fly ash, or by adding fiber reinforcement to the SC.

As the placement section is filled with SC, it should be struck off with a simple screed. A vibrating screed is effective in obtaining a relatively smooth and sealed finish. For a properly designed SC mix, probe-type vibrators are seldom required. Strike-off and finishing should be completed in the shortest possible time for best results.

Quality metal or wood floats are generally used for finishing. One pass over the slab while it is still molten, to smooth and seal the surface, is all that is required. Continued work on the surface after it starts to crust will tear this crust and destroy the finish. If this should happen, any heat source can be used to quickly remelt that area so that it can be refinished. Hand tools should be kept in contact with the molten SC, when not in use, to maintain tool temperature and prevent SC buildup.

The finished texture and skid resistance of screeded SC are suitable in most industrial application. The slab surface is dense, washes down easily, and provided good abrasion resistance.

Joints are formed to control cracking, terminate pours, and allow for thermal expansion and contraction. Location of joints should be evaluated on a job-to-job basis with consideration given to the sequencing of pouring. Normally, the width of section is limited to 8 to 12 ft (2.2 to 3.7 m) because of shrinkage considerations.

Typically, control joints should be constructed at a distance in feet of not more than three times the slab thickness in inches. Control joints are usually 1/4 in (6.4 mm) to 3/8 in (9.5 mm) wide and extend 20 to 25% into the slab. If the control joint if formed at the termination of a pour, the incorporation of a key way is beneficial, but not normally necessary.

Expansion joints are constructed to relieve thermal stresses and to separate slabs from vertical surfaces of structural members. Maximum spacing of expansion joints is determined following the same guidelines as for PCC.

A flexible joint sealant compatible with the installation environmental conditions (i.e., chemically resistant) should be applied to all joints, extending the full length of the joint with a depth no greater than the width. A bond breaker should be provided below the joint sealant. A preformed back rod made of closed-cell polyethylene foam is often used as a bond breaker and will also keep the uncured sealant from seeping through the joint.

The handling, mixing, and use of SC should be accomplished with proper concern for product safety (7). This report does not purport to address all of the safety considerations associated with the use of SC. As with any other construction material, certain measures must be taken with SC to ensure safe handling in its preparation and use. SC is produced within the recommended mixing temperature range of 260 to 280° F (127 to 138° C) to minimize emissions. Adequate ventilation during construction operations and normal precautions for handling hot fluid materials (proper protective clothing, eye protection, gloves, and hard hats) should be observed. Practices for safe handling of both solid and liquid sulfur have been established by the National Safety Council and should be followed when preparing and handling SC.

Commercial installations, especially in the metallurgical and chemical industries, are increasing in scope and complexity. The largest, single installation to date consume approximately 800 cubic yard (610 cubic meters) of SC, which was placed in floors, acid sumps, footers, and walls. The entire SC portion of this project was completed in less than six weeks using the machine shown in Figure 5. Production rated of approximately 50 cubic yards (38.3 cubic meters) per day kept two work crews busy placing and finishing SC in nearly 80,000 square feet (7440 square meters) of floors. Figure 6 illustrates placing and finishing of SC. The use of SC in previously constructed, similar installations has provided exceptional performance. For example, the floor of a copper electrowinning facility, after five years, shows no evidence of deterioration in a sulfuric acid environment; PCC, under these same conditions, would have required complete replacement at least once. Maintenance on Sc has been limited to minor corner crack repairs (using SC) at joint intersections and the occasional replacement of deteriorated sealers.

SUMMARY

A sulfur polymer cement has been developed in which sulfur is reacted with SPC and oligomers of CPD to form a stable cement product. Technology has been developed to prepare stable SC for use as a chemically resistant construction material. SCs have been produced with excellent resistance to damage by most mineral acid and salt environments and with good mechanical strength properties. SC technology has been demonstrated on a commercial scale both in the manufacture of the sulfur polymer cement and in its utilization in producing SC construction materials.

There are still developments and improvements that can be achieved to enhance the techniques of manufacturing and placing SC. During the past few years, there have been significant developments to this end, and continued examples of the superior performance characteristics made possible by using SC will stimulate further advances in this technology. Continued cooperation between government, and industry, including contractors, is essential in further research targeted at effective use of sulfur in construction materials.

REFERENCES

1. McBee, W. C. and T. A. Sullivan. Development of Specialized Sulfur Concretes. Bureau of Mines RI 8346, 1979, 21 pp.

2. McBee, W. C. and T. A. Sullivan. Concrete Formulations Comprising Polymeric Reaction Products of Sulfur/Cyclopentadiene, Oligomer/Dicyclopentadiene. U.S. Patent 4,348,313, Sept. 7, 1982.

3. ACI Committee 548, Guide for Mixing and Placing Sulfur Concrete in Construction. ACI 548, 2R-88. ACI Materials Journal, July-August, 1988, 12 pp.

4. McBee, W. C., T. A. Sullivan, and B. W. Jong. Corrosion Resistant Sulfur Concretes. Bureau of Mines RI 7858, 1983, 28 pp.

5. McBee, W. C., T. A. Sullivan, and B. W. Jong. Industrial Evaluation of Sulfur Concrete in Corrosive Environments. Bureau of Mines RI 8786, 1983, 15 pp.

6. Sullivan, T. A. Corrosion-Resistant Sulphur Concrete--Design Manual. The Sulphur Institute, 1986, 44 pp.

7. McBee W. C., T. A. Sullivan, and H. L. Fike. Sulfur Construction Materials. Bureau of Mines Bulletin 678, 1985, 31 pp.

Table 1. Composition and properties of SPC

		Value
Sulfur	pct	95±1
Carbon	pct	4.5±0.2
Hydrogen	pct	0.5±0.05
Viscosity at 135° C	cp	50±25
Specific gravity		1.90±0.02

Table 2. Properties of typical sulfur concrete and portland cement concrete

	Sulfur concrete[1]	Regular PCC[2]
Strength, psi:		
Compressive	7,000 - 10,000	3,500 - 5,000
Splitting tensile	1,000 - 1,500	500
Flexural	1,350 - 2,000	535
Coefficient of Thermal expansion (μin/in)/°C	14.0 - 14.7	12
Moisture absorption pct	0.0 - 0.10	0.30 - 3.0
Air void content pct	3.0 - 6.0	4.0
Elastic Modulus 10^6 psi	4.0	4.0
Specific gravity	2.4 - 2.5	2.5
Linear shrinkage pct	0.08 - 0.12	0..6 - 0.10
Impact strength, ft lb:		
Compressive	100 - 119	81
Flexural	0.3 - 0.5	0.2
Mix proportions, wt pct:		
SPC	14 - 18	0
Water	0	6 - 9
Mineral filler	6 - 9	0
Portland cement	0	12 - 18
Sand	38 - 42	30
Coarse aggregate	33 - 37	45

[1]Properties obtained at age of 1 day.
[2]Properties obtained at age of 28 days.

Table 3. Industrial testing results of sulfur concrete materials

Environment	Performance[2]
Sulfuric acid	[1]NR
Copper sulfate-sulfuric acid	NR
Magnesium chloride	NR
Hydrochloric acid	NR
Nitric acid	NR
Zinc sulfate-sulfuric acid	NR
Copper slimes	attacked by organics used in processing
Nickel sulfate	NR
Vanadium sulfate-sulfuric acid	NR
Uranium sulfate-sulfuric acid	NR
Potash brines	NR
Manganese oxide-sulfuric acid	NR
Hydrochloric acid-nitric acid	NR
Mixed nitric-citric acid	NR
Ferric chloride-sodium Chloride-hydrochloric acid	NR
Boric acid	NR
Sodium hydroxide	attacked by >10 pct NaOH
Citric Acid	NR
Acidic and biochemical	NR
Sodium chlorate-hypochlorite	attacked by solution at 50 to 60° C
Ferric-chlorate ion	NR
Sewage	NR
Hydrofluoric acid	NR-with graphite aggregate
Glyoxal-acetic acid formaldehyde	NR
Chromic acid	Deteriorated at 80° C and 90 pct concentration, marginal at lower temperature and concentration.

[1]NR - Non-reactive.
[2]Test results show no sign of corrosion or deterioration for test period of 6 to 9 years.

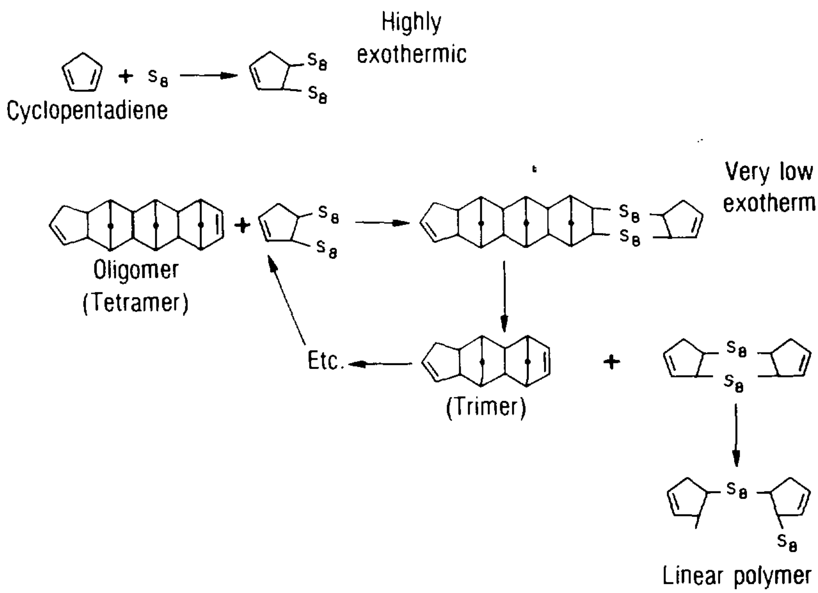

Figure 1. Generalized reaction for sulfur cement production employing mixed modifier

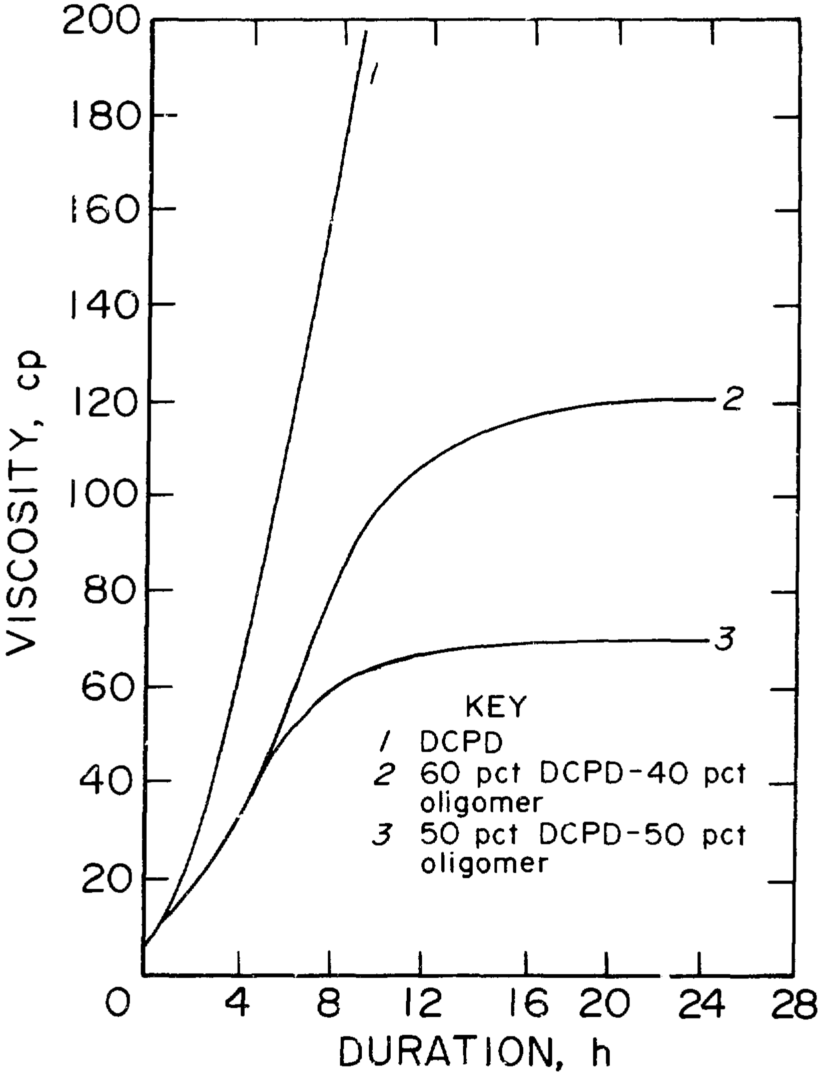

Figure 2. Viscosity of modified sulfur cements versus time at reaction temperature of 140° C

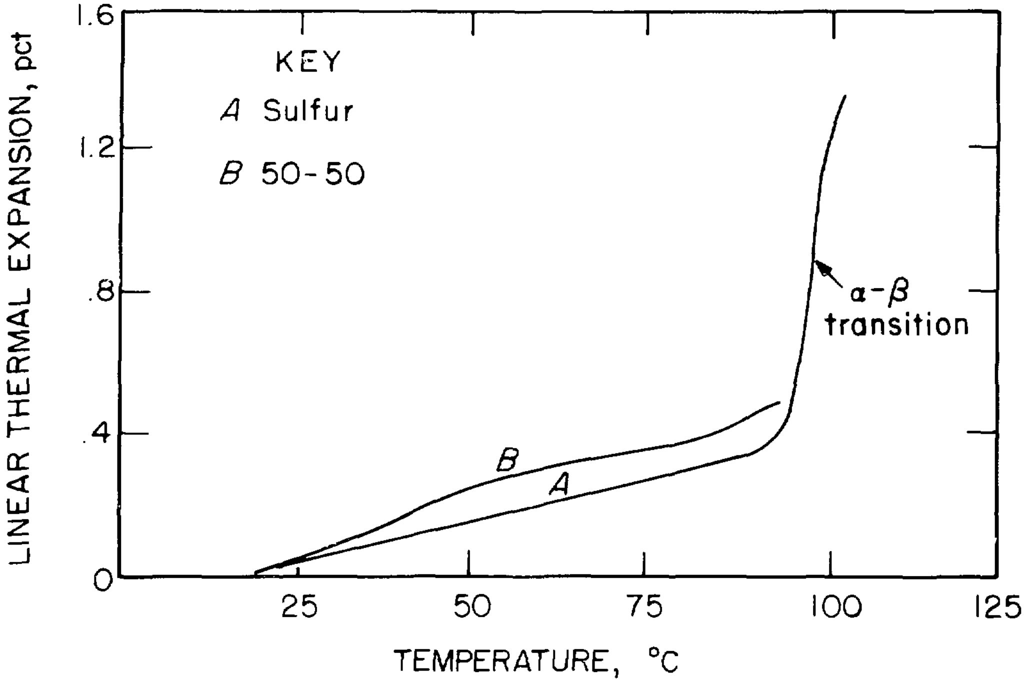

Figure 3. Linear thermal-expansion data for sulfur and sulfur concrete

Figure 4. Heat-jacketed concrete transit mixer

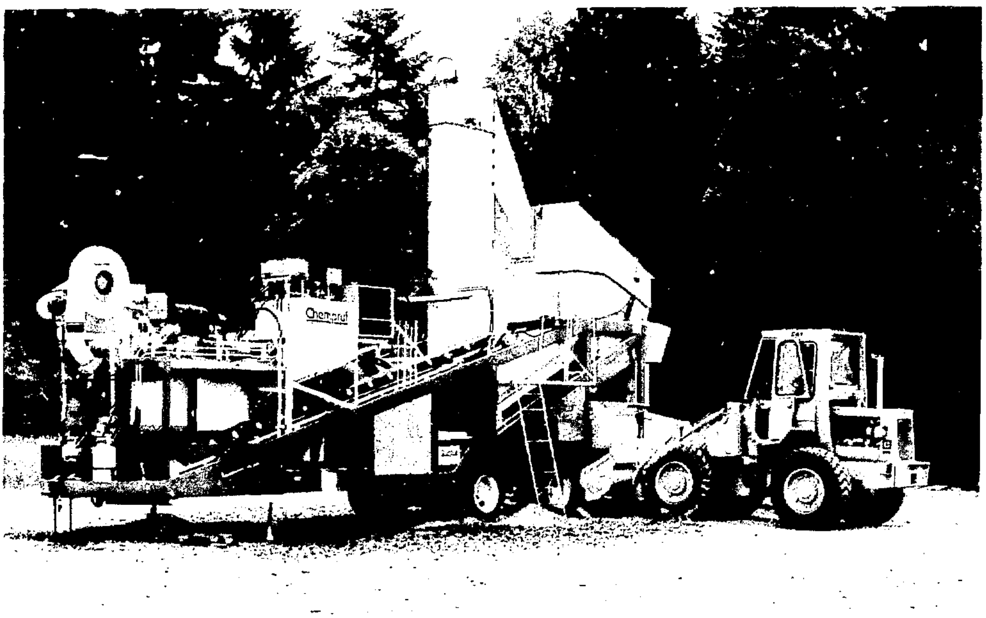

Figure 5. Self-contained SC mobile production unit

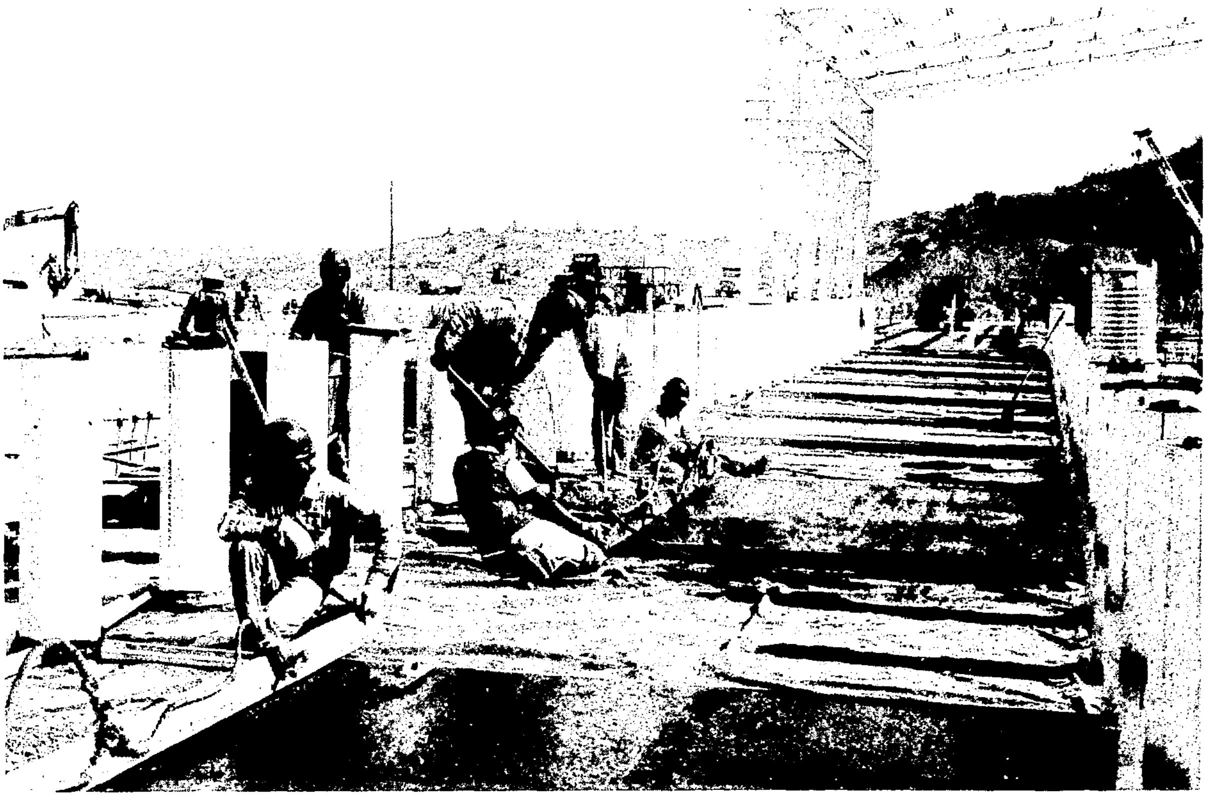

Figure 6. Placing and finishing SC