

Guide for Mixing and Placing Sulfur Concrete in Construction

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Sulfur concrete construction materials are now used in many specialized applications throughout industry and transportation. They are currently used primarily in areas where conventional materials like portland cement concrete (PCC) fail such as acidic and saline chemical environments. These new construction materials are thermoplastic and achieve compressive strength in excess of 9000 psi within one day of casting. The materials are impervious to moisture permeation and extremely resistant to attack by mineral acids and salts. This guide includes information on historical background as well as a user's guide to sulfur concrete construction.

ACI Committee Reports, Guides, Standard Practices, and Commentaries are intended for guidance in designing, planning, executing, or inspecting construction and in preparing specifications. References to these documents shall not be made in the Project Documents. If items found in these documents are desired to be a part of the Project Documents, they should be phrased in mandatory language and incorporated into the Project Documents.

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CHAPTER 1-HISTORICAL BACKGROUND

1.1-Introduction

Sulfur concrete is a relatively new material, and although similar in final appearance to portland cement concrete, its manufacture, handling, use, and testing are different. The purpose of this guide is to familiarize engineers, contractors, manufacturers, and users with sulfur concrete and its applications and to assist them in selecting proper materials, mixture proportions, and properties for optimum use of sulfur concrete.

Sulfur concrete is a thermoplastic material prepared by hot-mixing sulfur cements and mineral aggregates. Sulfur concrete solidifies and gains strength rapidly upon cooling. As with other concrete materials, such as portland cement concrete and asphaltic concrete, sulfur concrete is a generic term for a range of products that vary with aggregates, sulfur cements, and proportions used. By using sulfur cement binders and aggregates that are not attacked by many mineral acid and salt solutions, high-strength corrosion-resistant sulfur concrete can be produced for use in certain applications where other construction materials deteriorate rapidly. Sulfur concretes are generally not resistant to alkalis or oxidizers but exhibit excellent performance in many acidic and salt environments.

Early sulfur concrete products, prepared with unmodified sulfur as the binder, were plagued with durability problems. While materials with excellent mechanical strength properties were produced, in actual use they deteriorated and failed after a relatively short period of time. The development of modified sulfur cements, however, increased the durability of sulfur concrete and made its use as a construction material much more feasible.

When modified sulfur cement is used as the binding agent with appropriate aggregates, the resulting sulfur concrete has shown some unique properties:

- a) high strength and fatigue resistance;
- b) excellent corrosion resistance against most acids and salts; and
- c) extremely rapid set and strength gain.

One of sulfur concrete's greatest uses is for industrial floors that are exposed to highly corrosive substances.

1.2-Early research on sulfur

The utilization of sulfur as a molten bonding agent dates back to prehistoric times.¹ During the 17th century, sulfur was used to anchor metal in stone and similar practices are still being used in Latin America.²

The post World War I (1919) demand for sulfur led to the opening of the "Big Dome" sulfur deposit near Matagorda, Texas. This operation doubled the production of sulfur in the United States and resulted in a surplus.

Bacon and Davis in 1921 reported on the projected uses of sulfur in construction materials to utilize the surplus sulfur.³ They tested many suggested additives for modifying the properties of sulfur for specific uses and found almost all of them unsuitable. In their work, they found that a mixture of 60-percent sand and 40-percent sulfur produced an acid-resistant material with excellent strength.

Kobbe, in 1924, reported on the acid-resistant properties of materials prepared from sulfur and coke.⁴

Duecker, in 1934, found that the 60 percent sand and 40 percent sulfur product of Bacon and Davis increased in volume on thermal cycling with a loss in flexural strength.⁵ Duecker was able to retard both the tendency for volume increases and the resulting loss of strength on thermal cycling by modifying the sulfur with an olefin polysulfide. The use of additives to prepare more stable cements and products led to more industrial acceptance and more research and development on means of improving sulfur products for use as acid-resistant mortars and grouts.

McKinney, in 1940, outlined testing methods for sulfur materials that had been found satisfactory at the Mellon Institute.⁶ Many of these methods have been adopted and are found in ASTM specifications for chemical-resistant sulfur mortar.⁷

The developments that led to the ability to modify sulfur and produce a more durable product brought increased interest in research towards commercial activities. The research mainly has been divided into two categories: sulfur concrete and sulfur-infiltrated concrete. This report concentrates on the use of sulfur concrete because the latter has not as yet reached large-scale commercial usage.

1.3-Recent research on sulfur concrete

Major advances in the development of sulfur concrete have taken place in the last decade. Research was based on the premise that for sulfur concrete to be a viable construction material, its durability would have to be improved, improved sulfur cements would have to be developed, and better mixture designs would have to be developed for the production of uniform products on a routine basis.

In the late 1960s, Dale and Ludwig pioneered the work on sulfur-aggregate systems, producing mixes for well-graded aggregates to obtain optimum strength.^{8,9} This work was followed by the investigations of Crow and

Bates on the development of high-strength sulfur-basalt concretes.¹⁰ The United States Department of the Interior's Bureau of Mines and The Sulphur Institute (Washington, D.C.) launched a cooperative program in 1971 to investigate and develop new uses of sulfur.¹¹ At about the same time, the Canada Centre for Mineral and Energy Technology (CANMET), and the National Research Council (NRC) of Canada initiated a research program in the development of sulfur concrete.¹²⁻¹⁴ This was followed by work at the University of Calgary, Alberta.¹⁵

In 1973 the Sulfur Development Institute of Canada (SUDIC), jointly founded by the Canadian Federal Government, Alberta Provincial Government, and the Canadian sulfur producers, was established to develop new markets for the increasing Canadian sulfur stockpile. In 1978 CANMET and SUDIC sponsored an international conference on sulfur in construction.¹⁶ Also during this period a number of investigators including McBee and Sullivan, Malhotra, Vroom, Yuan, Loov et al., Gregor and Hackl, Diehl, Lee, and others published a number of papers and reports dealing with various aspects of sulfur and sulfur concrete.¹⁷⁻³⁰ All of these activities led to an increased awareness of the potential use of sulfur as a construction material.

While sulfur concrete materials could be prepared by hot-mixing unmodified sulfur and aggregate, durability of the resulting product was a problem. Unmodified sulfur concretes failed when exposed to repeated cycles of freezing and thawing, humid conditions, or immersion in water. Research was aimed at establishing reasons for failure of these sulfur concrete materials and determining means of preventing failures.

When unmodified sulfur and aggregate are hot-mixed, cast, and cooled to prepare sulfur concrete products, the sulfur binder, on cooling from the liquid state, first crystallizes as monoclinic sulfur (S_β) at 238 F (114 C) with a volume decrease of 7 percent. On further cooling to below 204 F (96 C), the S_β starts to transform to orthorhombic sulfur (S_α), which is the stable form of sulfur at ambient temperatures.³¹ This transformation is rapid, generally occurring in less than 24 hrs. As the S_α form is more dense than S_β , high stress is induced in the material by the solid sulfur shrinkage. Thus, the sulfur binder can become highly stressed and can fail prematurely. The expansion of mortar prisms made with sulfur sand is an example of the failure of a sulfur product through stress relief by thermal cycling; this was observed by Duecker.

It was necessary to develop an economical means of modifying the sulfur so that the sulfur concrete product would have good durability. While olefinic polysulfide additives had shown promise in these applications, their costs were deemed prohibitive for use in preparing sulfur concrete for large-scale construction uses.

In 1973, a process was developed by A.H. Vroom with assistance from the National Research Council of Canada and A. Ortega of McGill University, Montreal.¹⁴ This process involved modifying sulfur by reacting it with olefinic hydrocarbon polymers.^{29,30} It was also discovered

that a similar reaction would yield a sulfur soluble polymer concentrate. The resulting sulfur concrete was first produced for commercial use in Calgary, Alberta, in 1975.³²

Modification of sulfur by reaction with dicyclopentadiene (DCPD) has been investigated by many researchers, but its practical use in commercial applications has been limited because the reaction between sulfur and DCPD is exothermic and requires close control. Also, the DCPD modified sulfur cement is unstable when exposed to high temperatures (greater than 285 F [140 C]), such as when mixing with hot aggregates, and may react further to form an unstable sulfur product which reverts back from the S_β to the S_α form. McBee and Sullivan solved this problem through development of a process for preparing modified sulfur cement that is stable in the S_β form and is not temperature sensitive in the mixing temperature range for producing sulfur concrete.²⁰ This process utilizes the controlled reaction of cyclopentadiene (CPD).

Other researchers have reported methods for treating sulfur for use in sulfur concretes. They include: Leutner and Diehl³³ using DCPD; Gillott et al.³⁴ using crude oil and polyol additives; Schneider and Simic³⁵ using DCPD or a glycol; Woo³⁶ using phosphoric acid to improve freeze-thaw resistance; and Nimer and Campbell³⁷ using organosilane to improve water stability. In addition, Gregor and Hackl³⁸ have reported on laboratory design tests for DCPD modified sulfur concrete products; Bright et al.³⁹ on modified sulfur systems; and Bordoloi and Pierce⁴⁰ on stabilizing sulfur with DCPD.

Since 1976, commercial production and installation of corrosion-resistant sulfur concrete has been increasing continually.⁴¹⁻⁴⁷ The sulfur concrete materials are being either precast or installed directly in industrial plants where portland cement concrete materials fail from acid and salt corrosion. Typical installations are as floors, slabs on grade, overlays, curbs, walls, trench drains, sump pits, tanks, electrolytic cells, pump bases, column piers, foundations and pipes.⁴²

The descriptions in this report of sulfur concrete materials are based largely on published reports and experience gained during commercial installations.

1.4-Advantages and concerns with sulfur concrete

The main advantage of sulfur concrete is its use as a highly durable replacement for construction materials, especially portland cement concrete, in locations within industrial plants or other locations where acid and salt environments result in premature deterioration and failure of portland cement concrete.

There are several advantages in using sulfur concrete for construction in areas exposed to highly corrosive acids. While ultimate life or durability of sulfur concrete 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 several times the life of other construction materials now

being used in corrosive environments.²⁶ Other advantages of sulfur concrete are its fast setting time and rapid gain of high strength. Since it achieves most of its mechanical strength in less than a day, forms can be removed and the sulfur concrete placed in service without a long curing period.

Generally, sulfur concrete has the following useful characteristics:

1. Sulfur concrete's tensile, compressive, and flexural strengths²⁷ and fatigue life⁴⁸ are greater than those obtained with normal portland cement concrete. Fig. 1.4 illustrates compressive strength versus age for the two materials. Normal portland cement concrete is a material prepared with Type 1 cement (six sacks per cubic yard) and aggregates 0 to 1% in.⁴⁹

2. Sulfur concrete shows excellent resistance to attack by most acids and salts, some at very high concentrations.²⁶

3. Sulfur concrete sets very rapidly and achieves a minimum of 70 to 80 percent of ultimate compressive strength within 24 hr.²⁷

4. Sulfur concrete can be placed year-round, in below-freezing temperatures.

5. Sulfur concrete exhibits very low water permeability.²⁴

The handling, mixing, and use of sulfur concrete can be accomplished with proper concern for product safety.^{27,28,42,47} This is a general report and it does not purport to address all of the safety considerations associated with the use of sulfur concrete.

As with any other construction material, certain measures must be taken with sulfur concrete to insure safe handling in its preparation and use. Sulfur concrete should be produced within its recommended mixing temperature range of 260 to 300 F (127 to 141 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^{50,51} and should be observed when preparing and handling sulfur concrete.

If exposed to temperatures above the melting point of the sulfur cement, sulfur concrete will lose strength. Also, sulfur concrete must be used in applications consistent with its strength and thermoplastic properties.

CHAPTER 2—USER'S GUIDE TO SULFUR CONCRETE CONSTRUCTION

2.1—Modified sulfurs and aggregates

2.1.1 Modified sulfur cements—The need for using modified sulfur cements in sulfur concrete manufacture has been recognized since the 1930s. Sulfur cements are modified to improve the stability and durability and reduce the expansion-contraction of sulfur concrete during thermal cycling.

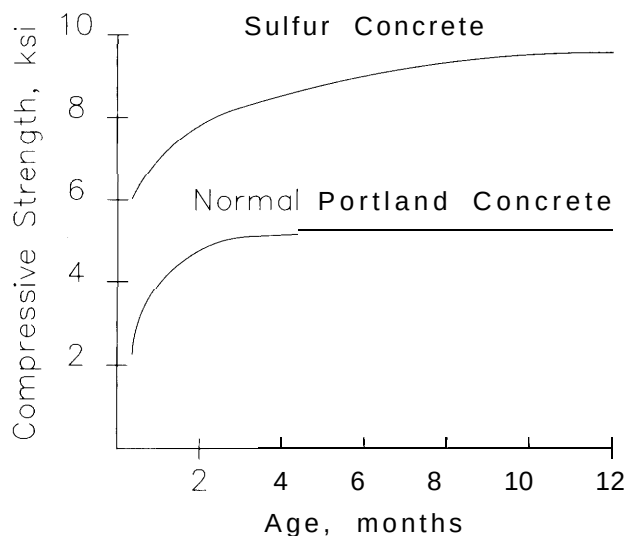


Fig. 1.4—Compressive strength versus age for sulfur concrete and normal portland cement concrete

There are several methods that can be used to produce modified sulfur cements. Two methods are currently used in North America to produce sulfur cements that are marketed under different trade names.

Method 1 is based on the polymeric reaction product of sulfur with a modifier containing equal parts of cyclopentadiene oligomer and dicyclopentadiene.²² The composition and properties of Method 1 modified sulfur cement are as follows:⁵²

Sulfur, percent by weight	95.0 ± 1.0
Carbon, percent by weight	5.0 ± .5
Hydrogen, percent by weight	.5 ± .05
Specific gravity at 77 F (25 C)	1.90 ± .02
Viscosity, centipoises at 275 F (135 C)	25 to 100

Method 2 utilizes a modified sulfur concentrate prepared by combining sulfur with olefinic hydrocarbon polymers such as Escopol.³⁰ This concentrate is then mixed with locally available pure sulfur in the ratio of 10 parts of sulfur to 1 part of concentrate, by weight. The concrete used with Method 2 modified sulfur has the following approximate composition:

Sulfur, percent by weight	80
Carbon, percent by weight	18
Hydrogen, percent by weight	2

Both methods of modifying sulfur give extremely long shelf life in the solid state. If stored in the molten state, both modifiers may continue to react and produce inferior concretes. The users should follow the recommendations of the material supplier for the time limits that the modified sulfur can be held in the liquid state.

Testing methods for modified sulfur cement are:

1. Sulfur and carbon are determined by combustion of