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# Industrial Evaluation of Sulfur Concrete in Corrosive Environments

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

UNITED STATES DEPARTMENT OF THE INTERIOR

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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

| | |
|---|---|
| ° C | degree Celsius |
| Cp | centipoise |
| ° F | degree Fahrenheit |
| ft | foot |
| ft-lb | foot-pound |
| gal | gallon |
| hr | hour |
| in | inch |
| lb | pound |
| $\mu$in/in·° C$^{-1}$ | microinch per inch per degree Celsius |
| min | minute |
| pct | percent |
| psi | pound per square inch |
| qt | quart |
| wt pct | weight percent |
| yd | yard |
| yr | year |

# INDUSTRIAL EVALUATION OF SULFUR CONCRETE IN CORROSIVE ENVIRONMENTS

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

## ABSTRACT

Over the past several years the Bureau of Mines has developed a sulfur concrete (SC) technology in which chemically modified sulfur is mixed with suitable mineral aggregates to produce construction materials that are resistant to corrosion by acids and salts. Modified SC materials have been tested in actual operating conditions in 50 corrosive process environments at 40 commercial plants. SC components ranging from small test coupons to 4-ton acid sump tanks were fabricated and installed at plant locations where chemical corrosion was destroying conventional concrete materials. Through cooperative agreements with several companies, floors, retaining walls, and foundations were cast in place using SC materials, then monitored for resistance to corrosion and retention of strength properties.

After 4 years of testing 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 portland cement concrete (PCC), occurred when sulfur concrete was exposed to strong alkali, hot chromic acid, and copper slimes solutions. Although long-term aging characteristics of SC materials are still being determined, already these materials are finding widespread use in metallurgical, chemical, and fertilizer processing plants.

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# INTRODUCTION

Sulfur, one of the most abundant elements, ranks 13th in amount in the earth's crust and occurs in both elemental and combined states; the United States is the world's leading producer of sulfur. In the past, the major source of sulfur has been native sulfur, but the supply picture is changing. Increasing amounts are being produced from secondary sources, such as recovery from sour gas, refining of high-sulfur crude oil, processing of metal sulfides ores, and recovery from coal.

In 1972, the Bureau of Mines instituted a research program to investigate new uses for sulfur and to take advantage of a forecasted surplus of the material predicted for the late 1980's based on increased recovery of secondary sulfur (10).[4] The objective was to formulate construction materials utilizing sulfur to replace energy-intensive materials, such as asphalt and cement. A portion of the program entailed the evaluation of specialized sulfur concretes (SC) in which modified sulfur cement replaces portland cement as the aggregate binder. These concretes were developed to resist acid and salt corrosion in applications where portland cement concretes (PCC) fail.

Metallurgical, chemical, and fertilizer industries in the United States sustain multimillion-dollar losses annually because of corrosive chemical attack on plant structures. The majority of the damage results from continual attack of acid and salt solutions on reinforced portland cement concrete. The losses decrease productivity; waste considerable quantities of steel, cement, and mineral aggregates; and require extensive labor for maintenance and repair.

In metallurgical plants employing acid electrolytes and leaching solutions, corrosive attack on PCC floors, support columns, and pump foundations may be severe, as illustrated in figure 1. In many cases replacement is necessary after very short periods of time. Chemical plants producing products such as potash and sodium salts sustain severe damage to floors, walls, and support columns from constant exposure to salts and salt solutions, as shown in figure 2. Catch basins under acid storage tanks, foundations for acid pumps, acid dock loading facilities, and acid sumps are also severely damaged on exposure to acid solutions and must be replaced periodically. Development of construction materials to withstand this type of corrosion would result in savings of time, labor, materials, and equipment necessary to maintain and replace deteriorated construction materials.

Sulfur concretes can be described as thermoplastic materials prepared by hot-mixing sulfur and aggregate materials. On solidification at ambient temperatures, a concrete product is formed with sulfur binding together the aggregate. While concrete products of good initial mechanical strengths could be prepared by this procedure, their durability and life in commercial applications have not proven satisfactory. Previous Bureau of Mines research toward the development of specialized sulfur materials was aimed at solving the durability problems associated with unmodified SC materials (2-3, 8-9). New modified sulfur cements were developed for use in preparing corrosion-resistant SC materials with improved durabilities (1, 6-7). Bench-scale testing of the materials showed their resistance to corrosion in most acid and salt environments.

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

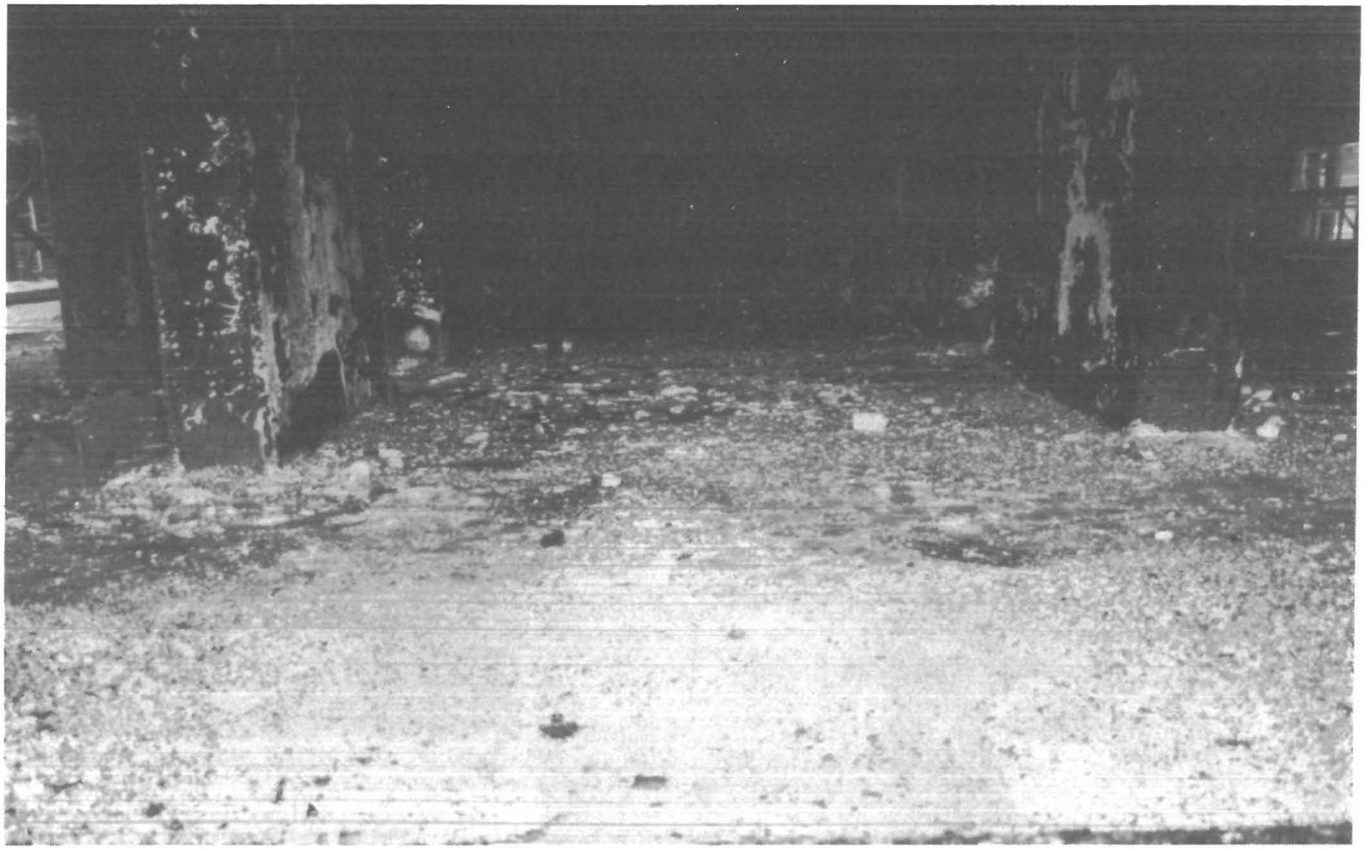

FIGURE 1. - Corrosion of portland cement concrete by acid electrolytes in an electrolytic zinc plant.

This report presents the current state-of-the-art of the modified SC and results of an industrial testing program to evaluate the performance of corrosion-resistant SC materials under operating conditions in 40 commercial plants. Precast SC components ranging from small test coupons to large 4-ton acid sump tanks and cast-in-place floors, retaining walls, and foundations were installed in areas of industrial plants where corrosive environments and solutions were destroying normal construction materials. The materials have been characterized by their ability to withstand corrosion in acid and salt environmental conditions and retain their strength properties. Materials described are "rigid" type concretes formulated with modified sulfur cement containing 5 pct chemical modifiers and dense-graded mineral aggregates.

## ACKNOWLEDGMENT

The assistance of The Sulphur Institute in arranging for the industrial evaluation of the corrosion-resistant modified SC and the cooperation of 30 industrial companies in testing SC under actual operating conditions in 40 of their plants is gratefully acknowledged.

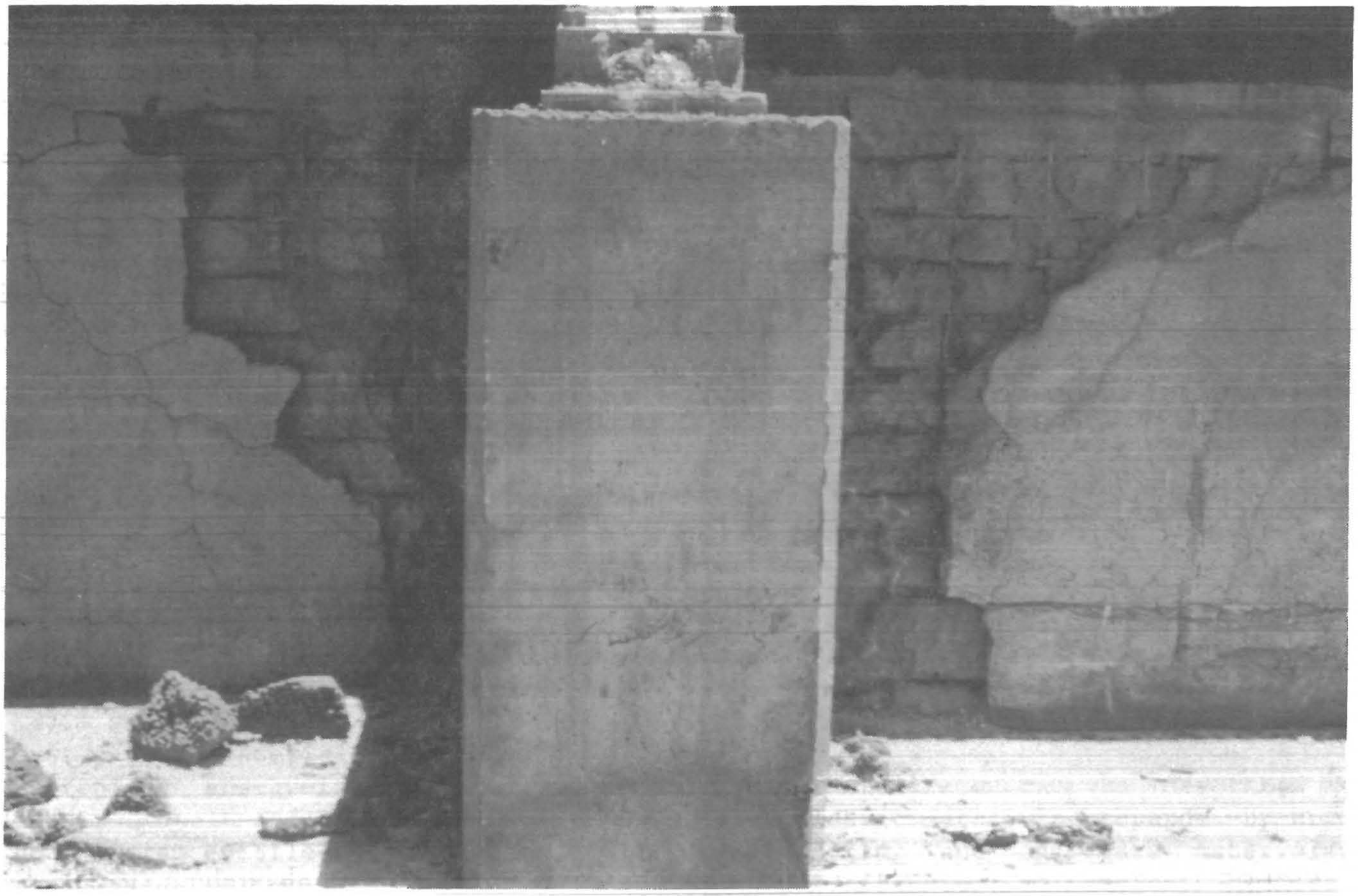

FIGURE 2. - A sulfur concrete support pier used to replace a deteriorated portland cement concrete pier in a potash storage facility. Disintegration of the tilt-up portland cement concrete wall is evident behind the pier.

## DESCRIPTION OF MODIFIED SULFUR CONCRETE

### MODIFIED SULFUR CEMENT

Preparation of corrosion-resistant SC became feasible with the development of modified sulfur cements that overcame the durability problems encountered with unmodified sulfur cement and the temperature susceptibility problems of dicyclopentadiene-modified sulfur cements. Modified sulfur cements for rigid-type sulfur concretes are prepared by reacting sulfur and 5 wt pct of a mixture of 50 wt pct dicyclopentadiene and 50 wt pct cyclopentadiene oligomers in a closed reactor for 6 to 12 hr at 145° C (6). The sulfur in the resultant cement is stabilized in the monoclinic form and may be used in the liquid state or solidified and flaked for later use. A typical analysis showing some of the properties of the modified sulfur cement is as follows:

| | |
|---|---|
| Sulfur....................pct.. | 94.80 |
| Carbon....................pct.. | 4.40 |
| Hydrogen..................pct.. | 0.45 |
| Specific gravity.............. | 1.90 |
| Viscosity at 135° C.......cp.. | 50 |
| Thermal expansion coefficient.......in/in ° C.. | $59 \times 10^{-6}$ |

Unmodified sulfur on cooling from the liquid state crystallizes in the monoclinic ($S\beta$) crystalline form and, on cooling below 95.5° C, goes through an allotropic transformation into the orthorhombic ($S\alpha$) crystalline form, which is more dense, occupies less volume, and results in a highly stressed material. Any process that will stress-relieve the material, such as thermal cycling, will result in disintegration of the concrete. The modified sulfur cement does not go through the rapid allotropic transformation. The resultant SC prepared is not highly stressed and is more durable. The modified sulfur cement and concrete formulations are patented (4-5), and the U.S. Department of Commerce is administering patent rights to the materials. Chemical Enterprises of Houston, TX, is presently producing and marketing the cement.

## MODIFIED SULFUR CONCRETE

Modified sulfur concrete is prepared by hot-mixing the cement and aggregate in a temperature range of 125° to 150° C. The resultant product is cast into the desired shape and on cooling to ambient temperature forms the SC. The process is thermosetting and reversible, and the SC products can be recycled.

Good-quality aggregates are required for corrosion-resistant SC. Aggregates must be clean, sound, and free of swelling clays, must exhibit low absorption (less than 1 pct), and after drying must contain <0.25 pct water. Aggregates that are insoluble in acids, such as quartz, are used for preparing acid-resistant SC. If corrosion is from salts alone, acid-insoluble or limestone aggregates may be used. Crushed aggregate materials are preferable to rounded gravels, because the sulfur binder bonds better to rough surfaces than to the polished surfaces of the rounded gravels. Cement requirements for preparing SC are minimized by dense-grading the aggregate. A gradation chart used in preparing dense-graded aggregate mixtures for SC is shown in figure 3. Typical properties of SC prepared with dense-graded aggregates are given in table 1. When larger, maximum size aggregate is used, the binder requirement for SC is decreased, while

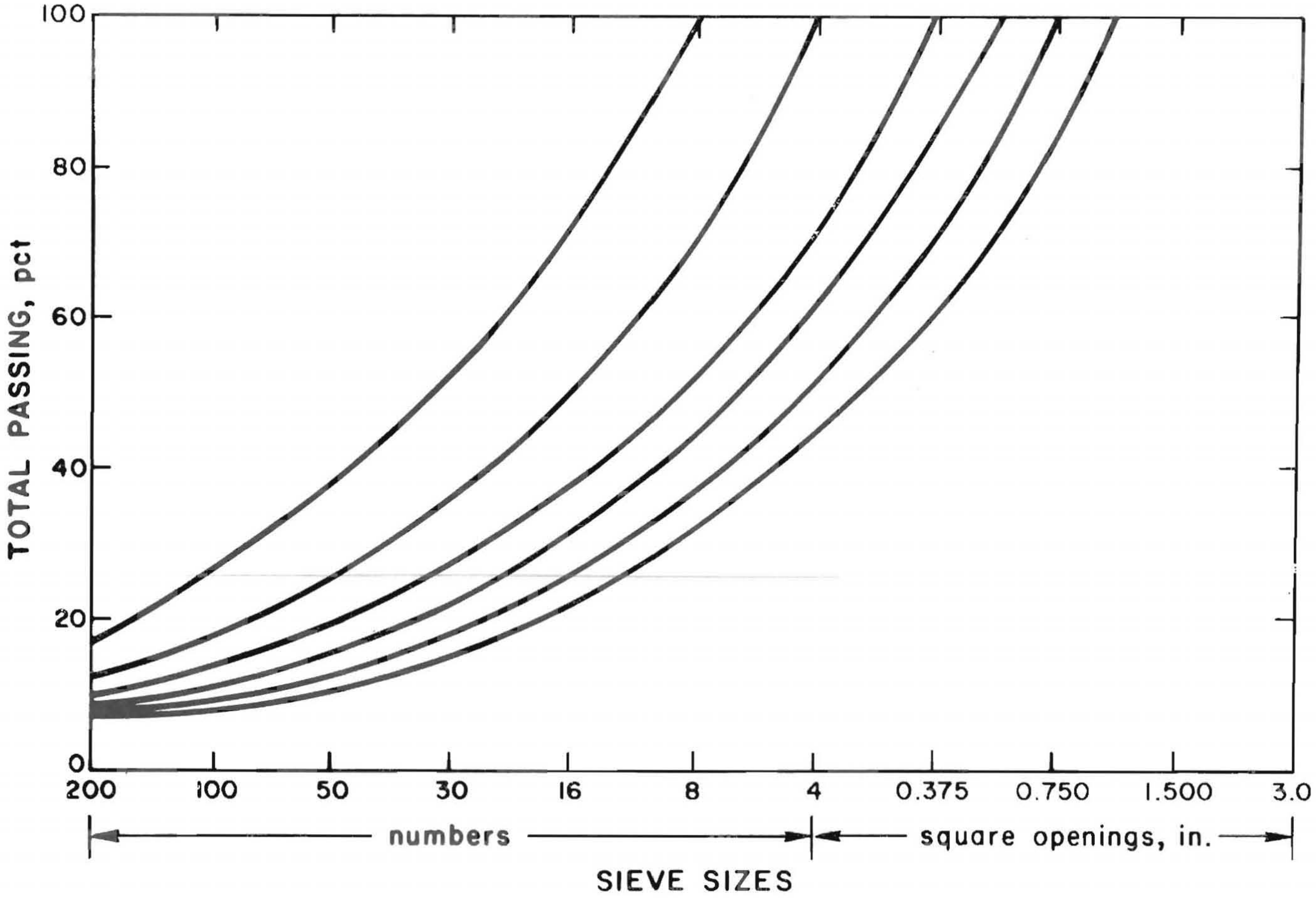

FIGURE 3. - Aggregate gradation chart.

the mechanical strength values remain essentially the same. Mixture designs for determining the proportions of aggregate and binder should be developed for each source and gradation of aggregate material.

TABLE 1. - Properties of typical dense-graded, 1-day-old sulfur concretes

| | Range |
|---|---|
| Strength, psi: | |
| Compressive | 7,000-9,000 |
| Splitting tensile | 1,000-1,100 |
| Flexural | 1,350-1,700 |
| Coefficient of thermal expansion...$\mu$in/in·° $C^{-1}$ | 14.0-14.7 |
| Moisture absorption...pct | 0.01-0.10 |
| Air void content...pct | 3.0-7.0 |
| Modulus of elasticity $10^6$ psi | 3.0-4.0 |
| Specific gravity | 2.40-2.50 |
| Impact strength, ft-lb: | |
| Compressive | 100-110 |
| Flexural | 0.3-0.5 |
| Composition,[1] pct: | |
| Aggregate, dense-graded | 82-88 |
| Sulfur cement | 12-18 |

[1] Composition varies according to type and maximum size of aggregate used.

Modified SC's attain about 80 pct of their mechanical strength in 1 day and full strength in approximately 6 months. The values reported in table 1 are for materials 1 day old. Sulfur concrete attains sufficient strength on cooling to ambient temperature to permit immediate use of the material.

## PREPARATION AND INSTALLATION OF SULFUR CONCRETE

Sulfur concrete is prepared by hot-mixing modified sulfur cement and aggregate. Any type of mixer can be used that will provide a homogenous mixture of the two components and maintain the mixture at the desired temperature. Preparation of SC materials for industrial evaluation has been done in equipment ranging from 2-qt, bench-scale-type bread mixers to 8-yd, ready-mix concrete mixers and hot-mix asphalt plants. Examples of types of equipment used are shown in figures 4-7 (bench-scale mixer, small-scale plant, commercial plant, and ready-mix truck, respectively.) Installation of the test units in corrosive industrial areas is illustrated by figures 8-13. Mechanical strength test cylinders and bars similar to those shown in figure 8 were supplied for direct insertion into electrolytes and corrosive solutions of commercial plants. Figure 9 shows the installation of a SC support unit for a chlorine gas pump equipped with concentrated sulfuric acid seals. Sump units, similar to the one shown in figure 10, for containing corrosive solutions were installed. Testing of slab units in corrosive environments was accomplished by insertion of the units into a concrete floor; PCC control units were also installed (fig. 11). Installation of entire floors was accomplished by manufacturing and casting the SC in place and is illustrated in figures 12 and 13.

Sulfur concrete is poured hot and must be cast and finished before it starts to solidify. Under normal conditions, approximately 30 min are available for pouring, compacting, and finishing the concrete. Insulated hoppers can be used to transport SC from the mixer to the casting areas. Concrete probe vibrators have been used to compact SC in large casting such as sumps. Vibratory wooden screeds are used to compact and level the poured SC in floor sections. Final finishing may be done with wooden or metal floats or trowels. Expansion joints should be left in SC and the joints sealed with an acid-resistant elastomer sealer to prevent acid or moisture penetration to the base material. Several commercial contracting firms have licensed the technology and are installing SC.

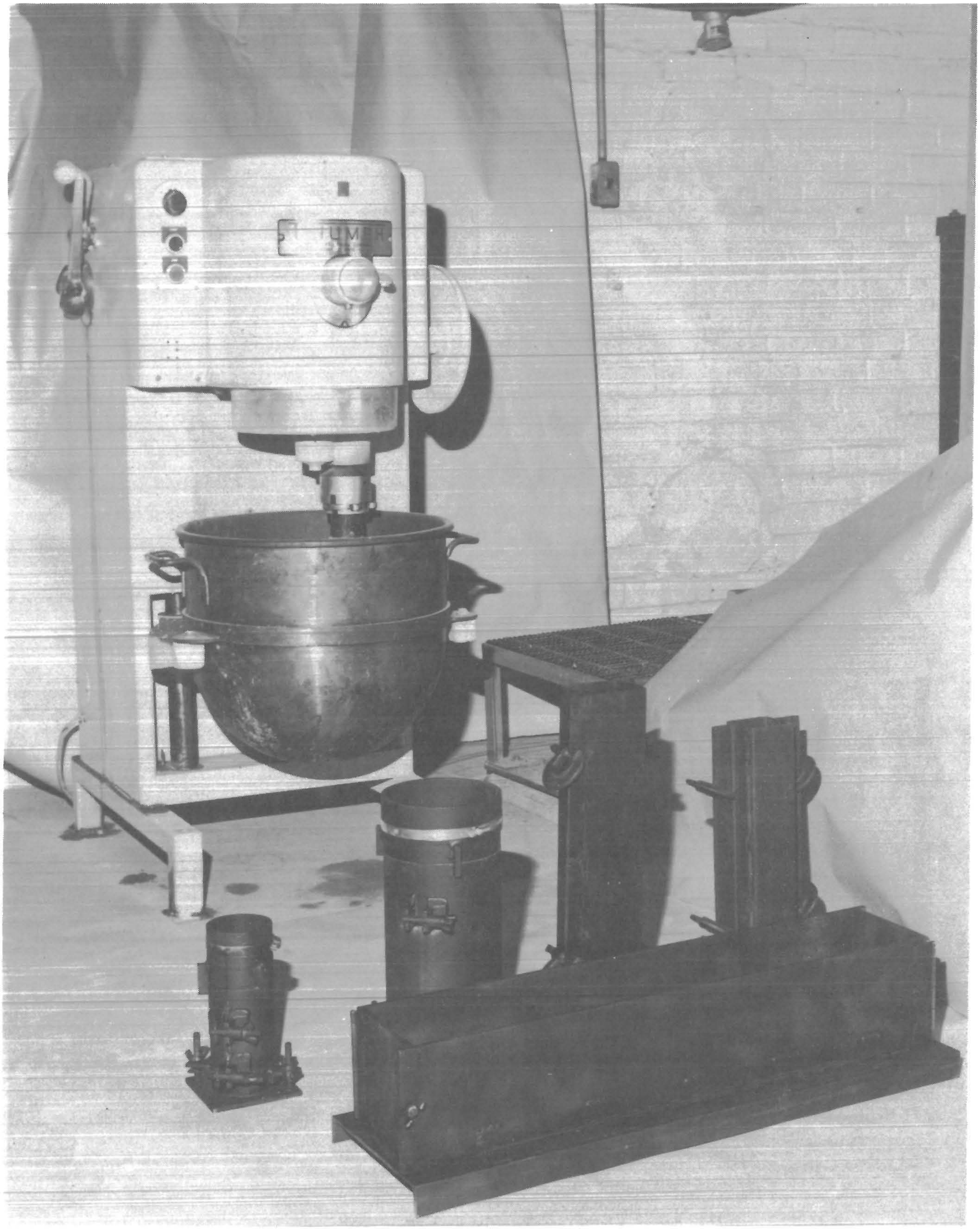

FIGURE 4. - Bench-scale mixer for sulfur concrete.

FIGURE 5. - Small-scale production unit for sulfur concrete.

FIGURE 6. - Commercial unit for production of sulfur concrete.

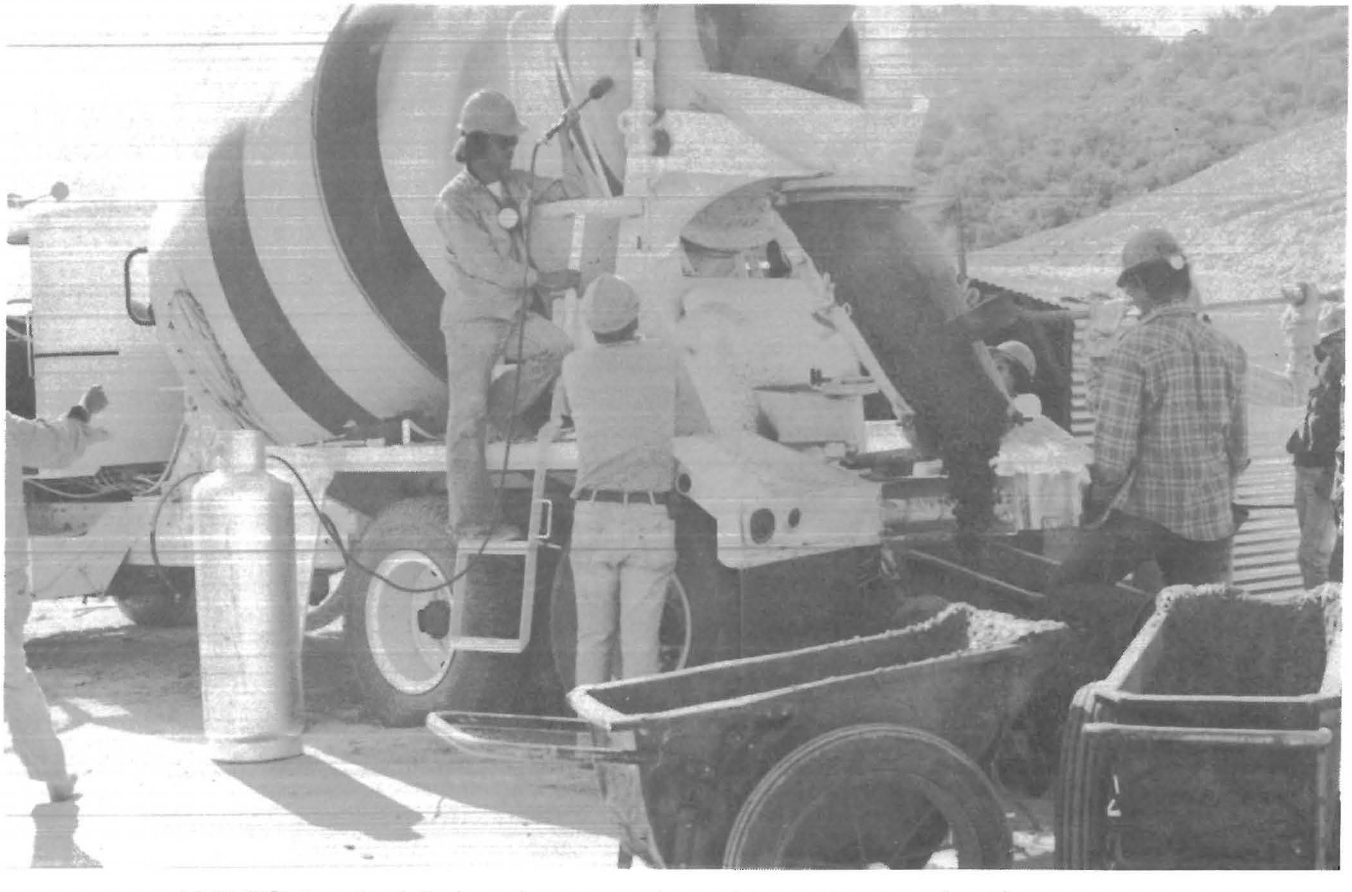

FIGURE 7. - Modified ready-mix truck used in production of sulfur concrete.

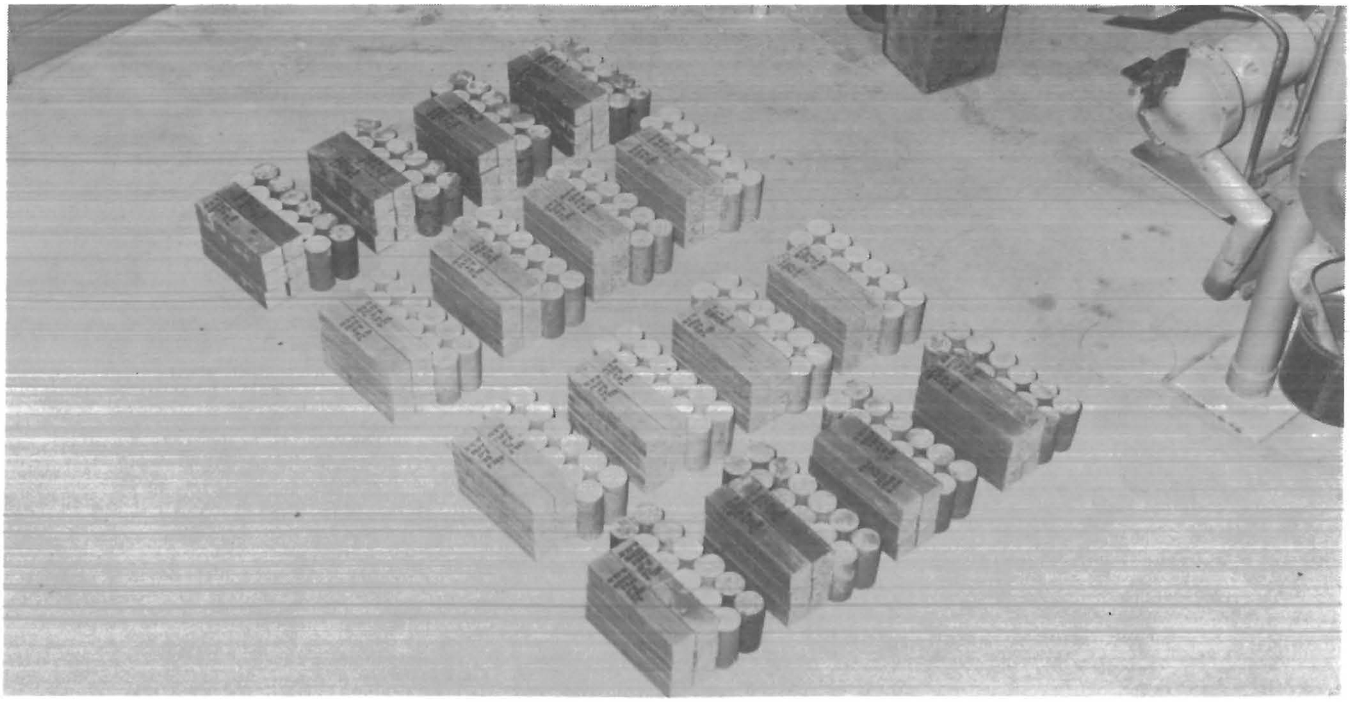

FIGURE 8. - Test cylinders and bars for corrosion testing.

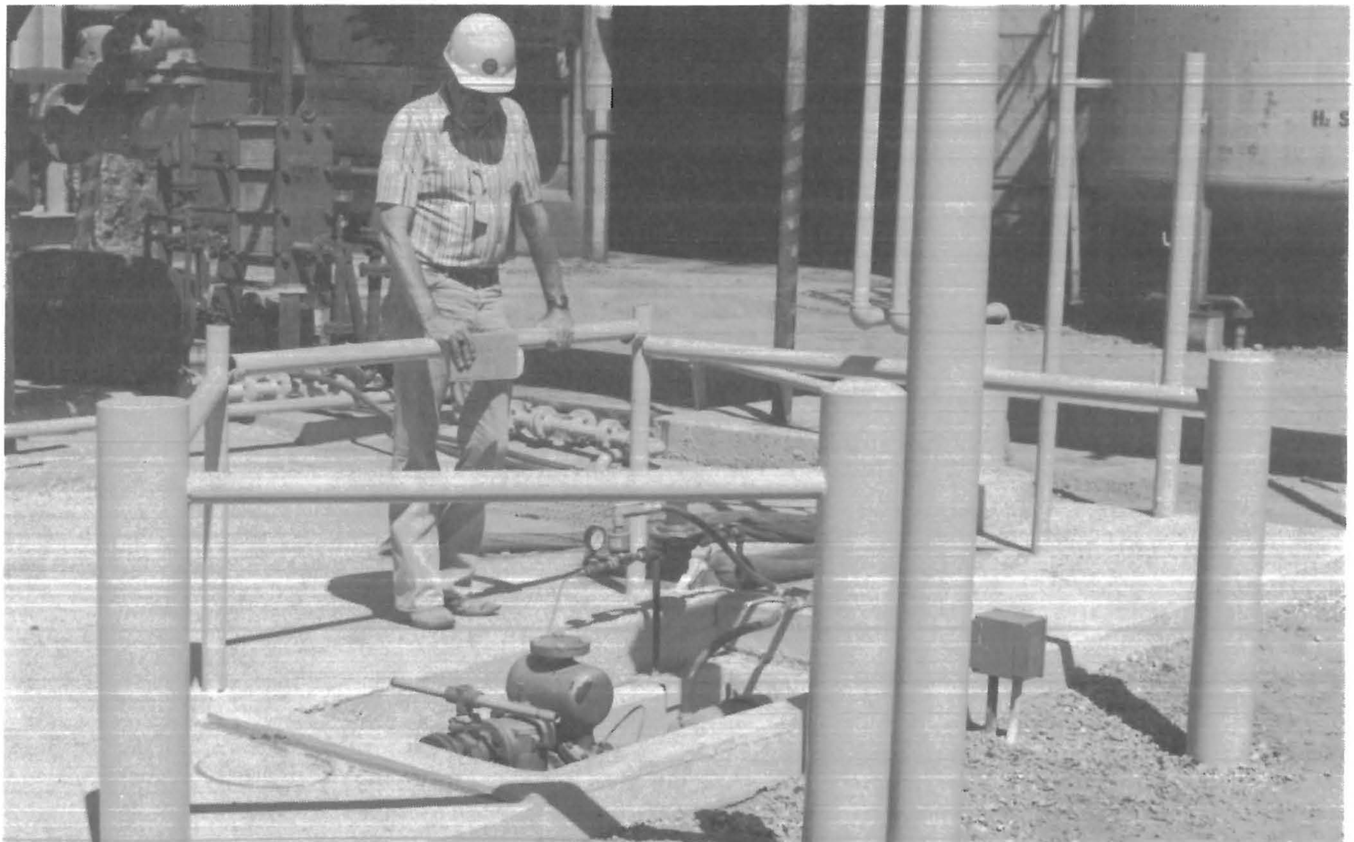

FIGURE 9. - Sulfur concrete pump support unit installed with a chlorine gas pump.

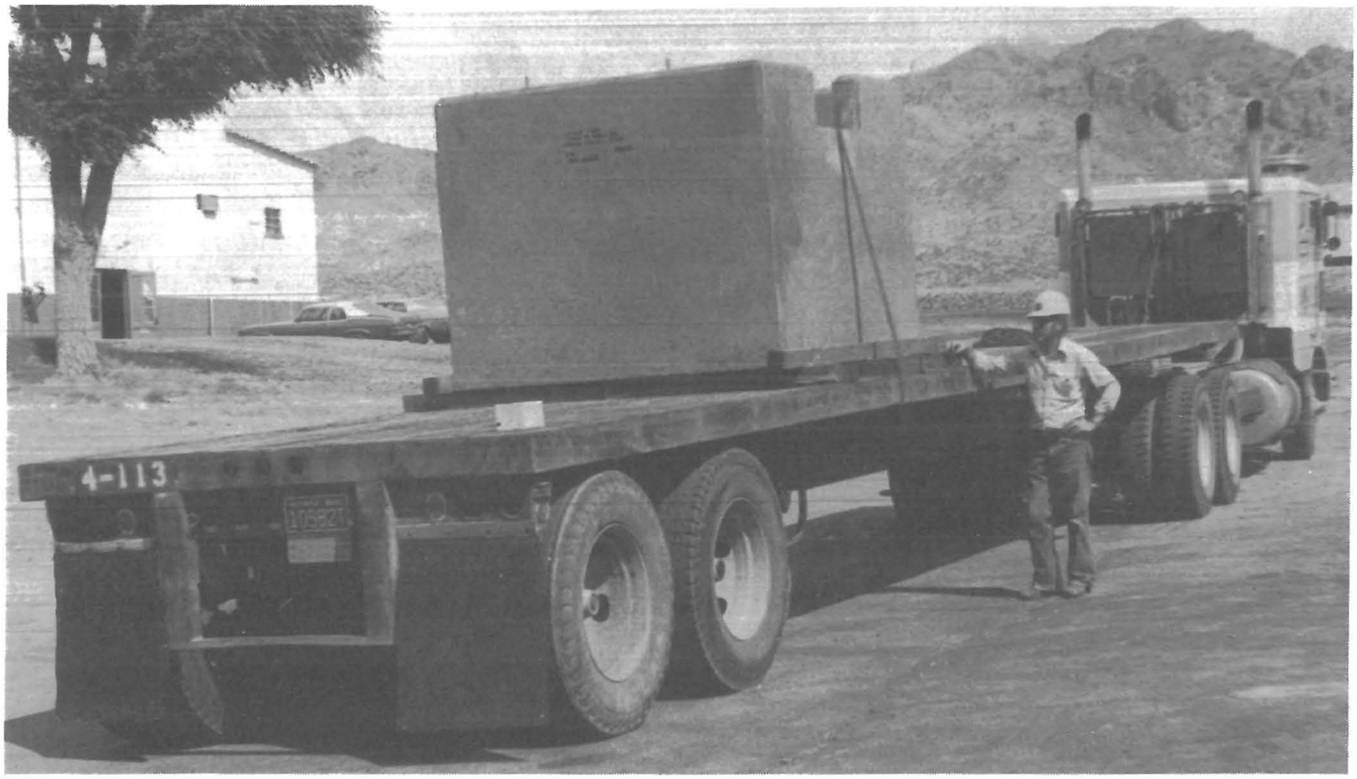

FIGURE 10. - Sulfur concrete sump unit for use in containing waste acidic solutions.

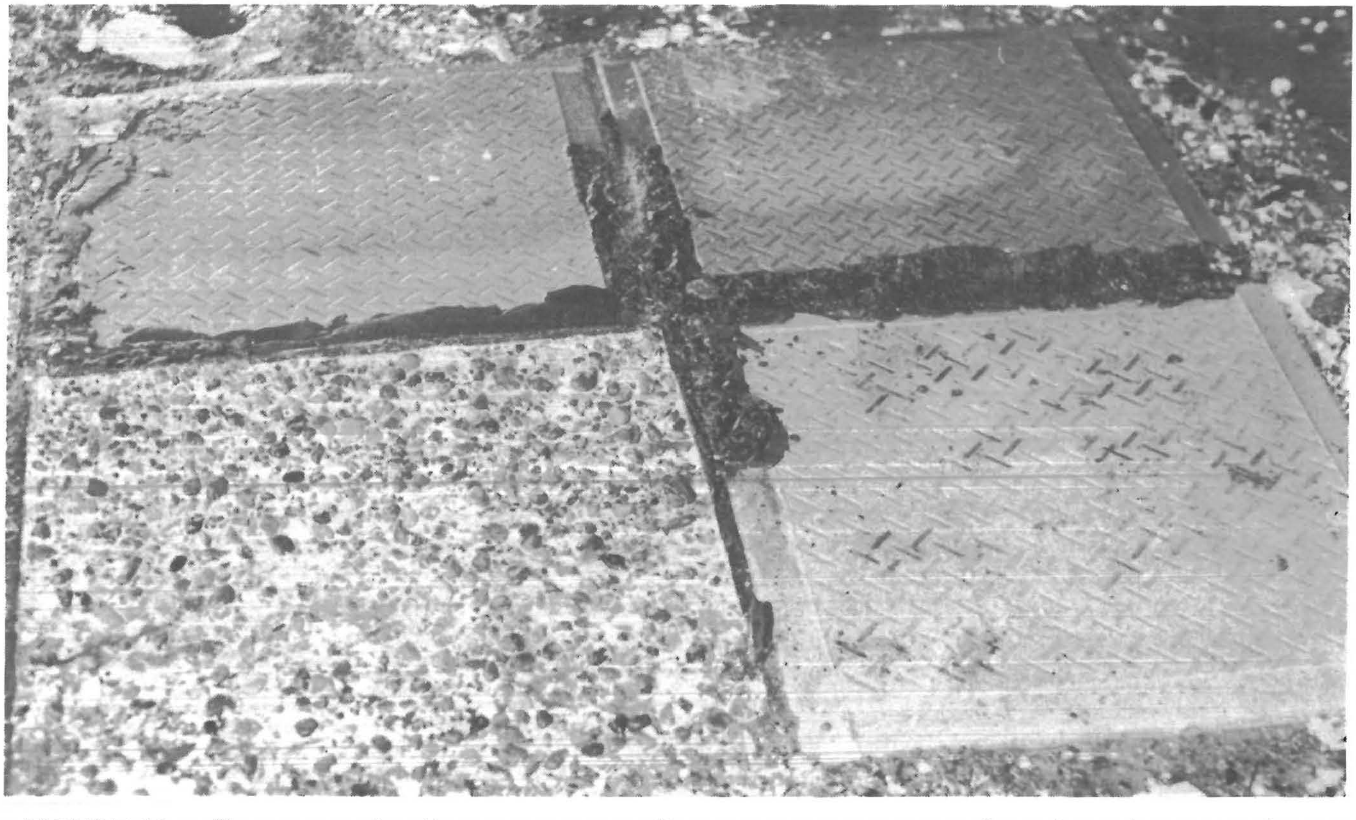

FIGURE 11. - Test units of sulfur concrete installed in a corrosive area of an electrolyte zinc plant.

FIGURE 12. - Installing sulfur concrete floor in an electrolytic copper plant.

FIGURE 13. - Finished sulfur concrete floor.

## EVALUATION OF MODIFIED SULFUR CONCRETE USE IN INDUSTRIAL PLANTS

Beginning in 1977, a cooperative industrial test program was initiated in conjunction with The Sulphur Institute to test SC in industrial corrosive environments. The major objectives of the program were to establish the feasibility of using the concrete in large-scale applications and to determine the ultimate longevity of the material under actual operating conditions in problem environments. Initially, precast components such as tiles, slabs, tanks, and pump foundations were cast at the Bureau's Boulder City Engineering Laboratory and subsequently transported and placed in industrial plants. When larger scale prototype equipment was developed for concrete production, larger scale projects were conducted onsite. A summary of the tests is listed in table 2. The results obtained on exposure to different chemical environments are listed in table 3.

TABLE 2. - Industrial test summary

| | |
|---|---|
| Precast tests: | |
| 1,000-gal sump tank | 3 |
| 400-gal basin | 2 |
| 4- by 4-ft by 4-in slab | 8 |
| 3- by 3-ft by 3-in slab | 17 |
| 2- by 2-ft by 3-in slab | 45 |
| 8- by 8-ft by 4-in foundation unit | 2 |
| 4- by 4- by 6-ft weir tank | 3 |
| 2- by 4-ft pump foundation | 2 |
| Tile loading dock | 1 |
| Tile drain ditch | 1 |
| Mechanical test specimens | 181 |
| In situ tests: | |
| 37,000-$ft^2$ floor | 4 |
| Pump foundations | 6 |
| Sumps | 3 |
| Acid loading dock | 1 |

The major industrial corrosion problems are created by mineral acids or mineral acid-containing metallic ion species. In these areas, many replicate tests were included. Test components included materials fabricated with and without the use of reinforcing steel. Fifty test environments are involved in cooperation with 40 industrial companies. The plants include 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 the potential of the material for use in many corrosive environments where other materials fail. The major areas where use of SC shows the most promise are those 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, specialized-type SC using dense graphite aggregate and modified sulfur cement is required.

Results show that SC materials performed well in the majority of corrosive atmospheres. Deterioration of SC material was observed in hot chromic acid solutions, sodium hydroxide solutions of more than 10-pct concentration, sodium chlorate-hypochlorite, copper slimes, and hot organic solvent solutions. Failures also resulted from use in areas where the material was exposed to temperatures in excess of 110° C (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 in copper electrolytic solutions. These units have shown no evidence of corrosion or deterioration after 7 yr of service. Since SC is a relatively new material, additional long-term testing will be necessary to fully establish its service life.

TABLE 3. - Industrial testing results of sulfur concrete materials

| Environment | Number of different environments | Status as of June 1, 1982[1] |
|---|---|---|
| Sulfuric acid.................... | 12 | 3, 2, 1. |
| Copper sulfate-sulfuric acid.... | 5 | 1. |
| Magnesium chloride.............. | 4 | 2. |
| 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 | 2. |
| Vanadium sulfate-sulfuric acid.. | 2 | 3. |
| Uranium sulfate-sulfuric acid... | 2 | 3. |
| 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 | 2. |
| 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° to 60° C. |
| Ferric-chlorate ion............. | 1 | 2. |
| Sewage.......................... | 1 | 3. |
| Hydrofluoric acid............... | 1 | 3, only graphite aggregate SC held up. |
| Glyoxal-acetic acid-formaldehyde | 1 | 3. |
| Chromic acid.................... | 1 | Deteriorated at 82° C and 90 pct concentration; marginal at lower temperature and concentration. |

[1] Test results showed no sign of corrosion or deterioration for (1) >3 yr, (2) 1-3 yr, and (3) <1 yr's exposure.

## SUMMARY AND CONCLUSIONS

The use of SC as a corrosion-resistant construction material has been demonstrated. The materials exhibit excellent mechanical properties when compared with those of PCC and show no signs of strength loss or degradation in more than 4 yr of industrial testing in 50 process environments. Minor degradation has occurred in sodium hydroxide, hot chromic acid, and copper slimes solutions. Industrial testing is continuing to establish durability and longevity of SC materials. Sulfur concrete should find widespread application in metallurgical, chemical, and fertilizer operations as replacement for materials that fail in acid and salt environments.

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