NEW APPLICATIONS AND EXPANDING MARKETS FOR

SULPHUR POLYMER CEMENT CONCRETE

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ABSTRACT

There is growing interest in materials of construction which can reduce the rising costs of maintenance and improve productivity. The Sulphur Institute, in cooperation with the Bureau of Mines and a small group of dedicated Construction Contractors, has encouraged research and development activities to devise new and advanced sulphur construction materials. Sulphur polymer cement concrete (SC) is used in hostile chemical environments where corrosion due to acid and/or salt exposure results in failure of conventional materials such as portland cement concrete. SC is also finding valuable uses in other applications.

SC is gaining recognition in the increasing market for corrosion resistant materials. Examples of construction and maintenance projects utilizing SC are described for chemical environments encountered during production of sulfuric acid, ammonium sulfate, phosphoric acid, potash, and other fertilizer materials and compared with performance of conventional construction materials. SC materials show no signs of deterioration due to acid and salt corrosion after approximately 9 years of industrial testing.

New and expanding applications for SC are also explored. In addition to the summary of industrial projects, newly developed mobile construction equipment, SC precast production and other new and innovative applications are presented.

INTRODUCTION

Corrosion of concrete structures is a serious international problem resulting in multi-billion dollar annual losses. Noticed deterioration of the global infrastructure has created growing interest in the availability and use of new and innovative construction materials. Corrosion in industrial plants leads to costly replacement of concrete structures, reduced productivity, and ultimately a loss of competitiveness. Fertilizer and chemical manufacturing plant structures are particularly susceptible to chemical attack because both the raw materials (sulphuric acid, hydrochloric acid, Nitric acid etc.) and the final products (ammonium sulphate, phosphoric acid, potassium chloride, etc.) are corrosive in nature.

The Sulphur Institute is encouraging further research and development in cooperation with various government agencies and the construction industry to develop new and advanced uses for sulphur polymer cement concrete (SC) in hostile chemical environments where conventional materials such as portland cement concrete (PCC) and acid brick fail. The major sources of corrosion-induced failure are mineral acid and salt solutions which not only destroy the PCC and acid brick installations, but also induce failure of steel reinforcement which may be present. The Institute is also encouraging evaluation of new and unique applications for SC where its rapid setting, high-strength properties are extremely beneficial. The use of chemically modified sulphur polymer cement combined with proper design considerations, materials quality control, and good construction practices have resulted in a number of successful SC installations.

This paper describes recent activities of various construction companies to development uses for SC in both corrosive construction and maintenance applications together with a program of industrial construction and testing in phosphate, ammonium sulphate, and potash fertilizer plants. In addition, several new cast-in-place and precast applications taking advantage of SC's unique properties are briefly presented. This paper also describes the relative growth in the number of SC contractors and SC production capacity through the 1980's.

MATERIAL CHARACTERISTICS

Using sulphur to make concrete is hardly a new concept; elemental sulphur was used as a bonding agent in ancient times. In the 1930's and through the 1970's research showed that combining elemental sulphur and aggregates would produce a high strength, acid resistant product; however, the durability of this type of material was very poor and most materials failed in less than one month, especially in moist environments and when subjected to thermal cycling. Many references to sulphur concrete found in literature that are dated prior to the mid - 1980's describe the inferior performance of these materials through the use of elemental or unmodified sulphur. Durability of present sulphur concrete materials described in this report have been improved by chemically modifying sulphur into a polymeric form.

The development of modern chemically-resistant sulphur polymer cement (SPC) and sulphur polymer cement concrete (SC) has taken place during the last decade. The key to this development came with the discovery of a novel technique to stabilize sulphur by preventing the allotropic transformation which previously led to premature failure (1). This discovery allowed development of a new class of chemically resistant materials, formulated from either quartz or limestone aggregates, as appropriate.

The characteristics of the new material are listed in Table 1. Properly designed and constructed SC materials have been found to be highly superior to conventional PCC-type materials when used in a variety of non-structural and structural cast-in-place and precast applications. The major chemical usage environments to date are listed in Table 2 along with reported performance results. Usage in pre-casting large components and structural applications has thus far been limited due to inherent linear shrinkage in the range of approximately 0.1 to 0.15 pct. However, reduced shrinkage characteristics are constantly improving as a result of new advances in SPC binders, the use of glass-fiber reinforcement, and improved construction techniques.

The effects of glass fiber reinforcement within the range of 0.1 to 0.5 wt pct of total mixture had a variety of effects on the properties of the SC. Physical properties such as density, linear thermal expansion, air voids, water absorption, workability, and mechanical properties including compressive, flexural, and tensile strength maintained superior levels. However, linear shrinkage, resistance to creep, and freeze-thaw durability showed significant improvement as a result of fiber additions. Results of the evaluation of these properties are shown graphically in Figures 1, 2, and 3 and are discussed further in other reports (2,3).

Another reason for the excellent durability of SC in many harsh environments is its low permeability. Figure 4 shows a comparison between treated and untreated PCC's and SC subjected to a salt water absorption test employing 15 wt pct sodium chloride solution. Data for PCC samples is taken from previous tests reported in the literature (4). None of the twenty-one types of PCC sealers studied performed as well as SC. Using the same test method, it was determined that SC absorbed approximately one-fifth the amount of water absorbed by the best sealed PCC and one-fiftieth the amount of water absorbed by untreated PCC.

CONSTRUCTION EQUIPMENT AND PLACING TECHNIQUES

Many different methods of manufacturing SC's and various types of equipment are currently being used to produce, transport, and place the materials. Generally, SC can be prepared in almost any mixer utilized for preparing PCC or asphalt cement concrete, provided that it has been modified to monitor and closely control the optimum temperature range (275-300°F) of the mixture. Essential to the preparation of SC is a means of drying and heating the aggregate to the desired temperature for mixing and maintaining the SC mixture within a relatively narrow temperature range during transport and placement.

A general process flow diagram for one method of preparing SC is shown in Figure 5. Divided bins are used to proportion coarse and fine aggregates into a fuel-oil, propane-, or gas-heated rotary kiln. The kiln discharges a weighed batch of heated aggregate into a heat-jacketed mixer followed by proper proportions of ambient temperature flaked SPC and mineral filler. The heated aggregates transfer heat to the mineral filler and melt the SPC producing a homogenous SC hot mix.

Heat-jacketed PCC transit mixers with capacities up to 12 cubic yards are used to mix, transport, and place SC. Figure 6 shows heated aggregates being discharged into an 8-cubic yard, heat-jacketed PCC transit mixer. The mixer is equipped with an on-board micro-processor which controls four propane infrared catalytic heaters used to maintain the SC within its optimum temperature range for placement. Flaked SPC and mineral filler at ambient temperature are then added to the hot aggregates in the transit mixer to produce a homogenous SC mixture. The heat-jacketed PCC transit mixer maintains the SC within a narrow temperature range for long periods of time, keeping the SC plastic during transport and workable until placement at the job-site. Newer SC transit mixers also have on-board capability to efficiently dry and heat the aggregates, thereby eliminating the need for a separate rotary kiln.

A new generation, self-contained machine has been designed and built that is capable of producing successive batches of SC at rates of up to ten cubic yards per hour. The portable machine, shown in Figure 7, weighs each mix component before entering the mixer for enhanced quality control. The batching system is fully automated, allowing its operator to preset the desired mixture composition for continuous batch duplication. Each subsequent batch of SC is produced in approximately one minute intervals.

Proper techniques are necessary when placing and finishing thermoplastic SC to achieve both high density and a satisfactory surface (5,6). The key factors for successful SC placement include proper preparation of the placement area, appropriate manpower, experienced supervision, an adequate supply of SC, and a rapid placement and finishing operation. The finished texture and skid resistance of screeded SC are suitable in most industrial applications. The slab surface is dense, washable, and provides good resistance to abrasion.

APPLICATIONS AND PERFORMANCE

In fertilizer and chemical manufacturing plants, the extensive presence of acid and salt solutions employed in normal production processes lead to corrosive attack of PCC floors, column supports, pump foundations, walls, storage areas, and loading facilities which, in many cases, require frequent replacement. Figure 8 shows the effects that several acid and brine solutions typically used in fertilizer production have on PCC and consequently the overlying acid bricks. Constant exposure to potash and potash salt solutions have caused severe damage to the floors, walls, and structural supports of the potash storage facility shown in the upper portion of this figure. The center portion of the figure shows severe damage to the floors, walls, foundations, and loading areas constantly exposed to sulphuric and phosphoric acid in a phosphate fertilizer facility. Even acid bricks and specialty concrete coatings could not prevent damage to the floor in the lower portion of the figure showing an area in an ammonium sulphate fertilizer facility constantly exposed to ammonium sulphate and sulphuric acid solutions. The use of SC in several manufacturing facilities is demonstrating a number of performance advantages, including savings of time, labor, materials, and maintenance.

SC is being used successfully in locations where acid and salt corrosion result in continuous and costly repairs of portland cement concrete and other conventional construction materials. By using SC in these harsh environments, the intervals between repair and replacement of floors, walls, pump bases, column foundations, and other areas has increased significantly. Benefits such as reduced maintenance, increased service-life and improved performance have led to increased productivity and reduced operating costs. In addition, working conditions are improved because PCC floors deteriorate in short periods of time making employee walk areas unsafe. The following case histories of SC installations in a variety of fertilizer plant applications exemplify these advantages. SC materials used to construct these examples were not reinforced with glass fibers.

One example is the use of SC to repair the foundation of an existing molten sulphur storage tank. Deterioration of the PCC foundation generally occurs because moisture permeates the PCC and corrodes the internal reinforcing steel. Since SC is impervious to moisture, this type of deterioration no longer can occur. Figure 9 shows the excellent condition of a SC storage tank foundation after 5 years of service. The SC foundation repair has performed well and shows no signs of deterioration. These results are quite pleasing to management and no further repairs are anticipated for the remaining life of this tank foundation.

A potash manufacturer recently reported the performance advantages of SC in this harsh environment. Figure 10 shows the structural piers used for support of a potash storage building. The upper portion of this figure shows the SC structural pier immediately after placement. Notice the badly deteriorated wall of the building behind the SC pier and the failed PCC pier in the foreground which was replaced shortly after this photograph was taken. The center portion of the figure shows the same SC pier after nearly 7 years of maintenance-free service. The bottom portion of Figure 10 shows the second replacement PCC pier (same location as the PCC pier shown on the right side of the upper photograph) which is severely damaged after only 2 1/2 years of service. As a result of this improved performance, SC piers are planned for future replacement of the PCC piers at this facility.

Extended life and improved performance of SC is also being experienced in sulphuric acid and ammonium sulphate environments at fertilizer production facilities. Figure 11 shows SC pump foundations and SC column protection in a sulphuric acid/ammonium sulphate environment after nearly 6 years of service. During this period, minimum maintenance was required for expansion joint materials which occasionally required replacement. Additional areas where corrosion has destroyed PCC are currently being replaced with SC.

Phosphate fertilizer manufacturers are now taking advantage of the beneficial use of SC to reduce maintenance and improve materials performance in process areas of their plants. Figure 12 shows an SC floor, SC pump foundation/acid sump combination, SC column protection, and an SC wall after nearly 1 year of service in a sulphuric acid/phosphoric acid environment. The use of SC in these and similar applications has been very encouraging and is expected to provide many years of extended life and superior performance with minimum maintenance.

NEW MARKETS AND POTENTIAL GROWTH

SC is becoming recognized around the world and is now available through construction contractors in many geographic areas. Until recently, SC installations were limited in both size and type; however, current projects include everything from underwater pipe coatings and sewer pipes to building foundations and floors, acid storage tanks and even overhead walkways. Investigations being conducted by several government agencies and private laboratories are confirming the valuable properties of SC and are evaluating other applications such as hazardous materials containment, structural members, road repairs and other construction needs. These studies, combined with the high rate of success in previous projects, will increase the markets and uses for SC in the future.

The Sulphur Institute works cooperatively with the U.S. Bureau of Mines (USBM), contractors and engineering organizations such as the American Concrete Institute (ACI), the American Society for Testing of Materials (ASTM) and the American Society of Civil Engineers (ASCE) to develop new applications for SC. Research and development activities conducted through these cooperative efforts are published as new information becomes available. Other publications such as TSI's, "Design and Construction Manual for Corrosion - Resistant Sulphur Concrete," the ACI, "Guide for the Use of Sulphur Concrete in Construction," and the ASCE report entitled, "Sulphur Polymer Concrete for Special-Purpose Applications," provide current information about SC and have received wide distribution. Materials requirements, construction procedures and test methods are currently being developed by ASTM for preparing SC.

The list of companies producing SPC and SC materials has grown steadily during the last several years. In the 1970's, only a few organizations were interested in producing or placing SC materials and there were no commercial contractors engaged in production or placement of SC for large-scale projects. Following the 1986 International Symposium and Workshop on Sulphur Concrete -A New Construction Material, organized by The Sulphur Institute, interest in the applications and the potential market for this material has stimulated its growth. Significant investments were made in SPC production facilities and SC construction equipment (previously described) by several interested companies.

Based on the type and availability of construction equipment, the capacity for producing SC in 1980 was less than 3,000 cubic yards; in 1985, the capacity had increased slightly to approximately 12,000 cubic yards; and, the capacity in 1990 has increased to approximately 60,000 cubic yards. Continuation of this growth depends on the continuing successful performance of SC materials in large-scale, commercial installations. It also depends on acceptance of SC materials in both new construction and maintenance reconstruction as a replacement for portland cement concrete in acid and salt corrosion areas. There are also new applications for SC which offer potential for growth, in both its acceptance and use.

Four new uses for SC currently being evaluated are: 1- the construction of impervious containment areas needed to comply with environmental requirements; 2- use of sulphur polymer cement and SC for encapsulation of toxic wastes; 3- underwater joint protection of steel pipe; and, 4-

manufacture of sewer systems including sewer pipe. Figures 13 and 14 are examples of these new applications for SC in large commercial installations. Other new uses taking advantage of SC's rapid setting and high strength properties are also being investigated. For example, figure 15 shows SC being used for road repairs.

The Department of Energy (DOE) is evaluating the use of SC to dispose of both low-level radioactive wastes (LLW) and mixed waste ash residues. Work is currently being performed at Brookhaven National Laboratory (BNL) to evaluate the possible use of SC for encapsulation of DOE mixed wastes including incinerator ash. Monolithic waste forms containing as much as 55 wt% incinerator fly ash from Idaho National Engineering Laboratory (INEL) have been formulated with modified sulfur cement, whereas maximum loading for this waste in hydraulic cement is 16 wt%. Compressive strength of these waste forms exceeded 27.6 MPa (4000 psi) (8). Encapsulation of INEL fly ash (at waste loadings up to 43 wt-%) in modified sulfur cement with a small quantity of sodium sulfide added to enhance retention of soluble metal salts has shown promising results for compressive strength, water immersion, freeze-thaw resistance, and leachability (9).

ECONOMICS: REDUCED LIFE-CYCLE COSTS

SC costs slightly more to install than ordinary portland cement concrete, but is very competitive with other specialty concrete systems. Based on its extended performance in harsh environments, SC is now the lower cost, time-saving alternative to portland cement concrete. Direct comparison of SC versus other specialty concretes or composite systems show that SC generally costs less than toppings such as acid bricks, specialty coatings and several types of polymer concretes. In addition to direct costs for materials, properly designed and constructed SC installations are providing increased benefit-to-cost ratios in a variety of installations.

The projects summarized within this paper demonstrate the performance advantages of SC. In addition to the test specimen location, several large projects constructed in areas constantly exposed to sulphuric acid have remained in service with little or no maintenance for more than six years. When compared to the expected replacement intervals and the constantly increasing costs of alternatives, the initial higher investment in SC can usually be balanced against operating savings within three years after its installation. Several specific installations were compared and serve as examples of the benefits made available by using SC.

On one recent project, SC cost 30 percent less than acid bricks over portland cement concrete because of both time and materials savings (6). To complete a floor installation at a plant in Carthage, Tennessee, SC was chosen in place of the traditional acid bricks over portland cement concrete and not only cost less to install but also reduced the construction period from 7 weeks to 4 weeks thereby minimizing lost production and inconvenience to employees. In many circumstances, SC can offer substantial savings in life-cycle costs by increasing the period of performance, reducing maintenance, improving working conditions and decreasing lost production time. As more SC contractors become available and better SC design, preparation and placement techniques are learned, it is expected that these economic advantages will improve.

SUMMARY

SPC and SC materials have been developed and are being utilized to reduce the corrosive effects of hostile acid and saline chemical environments in a variety of industrial applications including fertilizer and chemical plant construction and maintenance. SC materials also exhibit excellent mechanical properties and are extremely resistant to a wide variety of mineral acid and salt solutions.

SC is a corrosion-resistant material that achieves 80 pct of its ultimate strength in less than 4 hours. It is superior to PCC in many mechanical properties, when using similar aggregates, and does not require specialized personnel or expensive equipment for installation. SC may be tailored to most applications by using a variety of mineral fillers and different levels of fiber reinforcement.

SC materials continue to demonstrate superior performance in many harsh environments through approximately 9 years of exposure to conditions which destroy PCC in less than 3 years.

SC materials are now being installed in many new and existing plants to reduce maintenance costs. SC materials are also being evaluated in a variety of new applications. The use of SC materials should continue to expand based on its performance advantages.

SC is becoming a cost-effective alternative for us in harsh acid and saline environments where high strength, and a rapid return-to-service are required. SC continues to demonstrate its superior characteristics in a variety of applications.

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ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to the USBM, Brookhaven National Laboratory, members of ACI Subcommittee 548-D on SC, ASTM Committee C-3 on Non-Metallic Corrosion Resistant Materials, and SC construction contractors for providing current information used to prepare this report.

Table 1. - Sulphur polymer cement concrete

Typical Mix Design

(by weight)

Coarse Aggregate	38 pct
Fine Aggregate	38 pct
Mineral Filler	8 pct
Sulphur Polymer Cement[1]	16 pct

Physical and Mechanical Properties

Compressive Strength (ASTM C 39), psi	4000-9000
Tensile Strength (ASTM C 496), psi	750-1100
Flexural Strength (ASTM C 78), psi	600-1600
Density (ASTM C 642), lb/cf	145-155
Coef. of Thermal Expansion, per °C (max)	$13-15 \times 10^{-6}$
Absorption (ASTM C 642), percent (max)	0.10
Air Voids (ASTM C 642), percent	4-8
Modulus of Elasticity, psi	$3-6 \times 10^{6}$
Impact Strength Compressive, ft-lbs	100
Freeze-Thaw Durability (ASTM C 666) modules retention after 300 cycles, percent (min)	60-90
Service Temperature	<190°F
Thermal Conductivity	0.215 BTU/hr ft °F

[1]The sulphur polymer cement is composed of 95 pct sulphur and 5 pct plasticizer. The plasticizer is composed of a 50/50 blend of dicyclopentadiene and oligomers of cyclopentadiene.
Source: USBM

Table 2. - Industrial usage of sulphur concrete materials

Environment	Performance[1]
Sulphuric acid	Non-reactive
Copper sulphate-sulphuric acid	" "
Magnesium chloride	" "
Hydrochloric acid	" "
Nitric acid	" "
Zinc sulphate-sulphuric acid	" "
Nickel sulphate	" "
Vanadium sulphate-sulphuric acid	" "
Uranium sulphate-sulphuric acid	" "
Potash brines	" "
Manganese oxide-sulphuric acid	" "
Hydrochloric acid-nitric acid	" "
Mixed nitric-citric acid	" "
Ferric chloride-sodium chloride-hydrochloric acid	" "
Boric acid	" "
Citric acid	" "
Acidic and biochemical	" "
Sodium chlorate-hydrochlorite	Attacked by solution at 50 to 60°C
Ferric-chlorate ion	Non-reactive
Sewage	" "
Hydrofluoric acid	Non-reactive with graphite aggregate
Glyoxal-acetic acid formaldehyde	Non-reactive
Chromic acid	Deteriorated at 80°C and 90% concentration - marginal at lower temperature and concentration

[1]Test results show no sign of corrosion or deterioration for test period of 6 to 9 years.
Source: USBM

FIGURE CAPTIONS

FIGURE 1. - Influence of glass fiber reinforcement and cement level on linear shrinkage of SC (USBM).

Figure 2. - Influence of glass fiber reinforcement on SC freeze-thaw durability (USBM).

FIGURE 3. - Absorption of sealed and unsealed PCC and unsealed SC (USBM).

FIGURE 4. - Compressive creep of PCC and SC under sustained loading (USBM).

FIGURE 5. - Typical SC process flow diagram.

FIGURE 6. - Dried and heated aggregates being discharged into a heat-jacketed, temperature controlled transit mixer.

FIGURE 7. - Self-contained SC mobile production plant.

FIGURE 8. - Rapid and severe corrosion damage of conventional construction materials in potash (top), phosphate (center) and ammonium sulphate (bottom) fertilizer plant areas exposed to both acid and salt solutions.

FIGURE 9. - Foundation of a molten sulphur storage tank protected with SC.

FIGURE 10. - SC structural pier (upper left) in excellent condition after 7 years of exposure to potash (lower left) compared to the second replacement of adjacent PCC structural pier (lower right) severely damaged after only 2 1/2 years.

FIGURE 11. - SC pump base and column protection after nearly 6 years of exposure to ammonium sulphate and sulphuric acid solutions.

FIGURE 12. - SC floor, wall, column protection and pump foundation/ acid sump combination exposed to sulphuric and phosphoric acid in a phosphate fertilizer production facility.

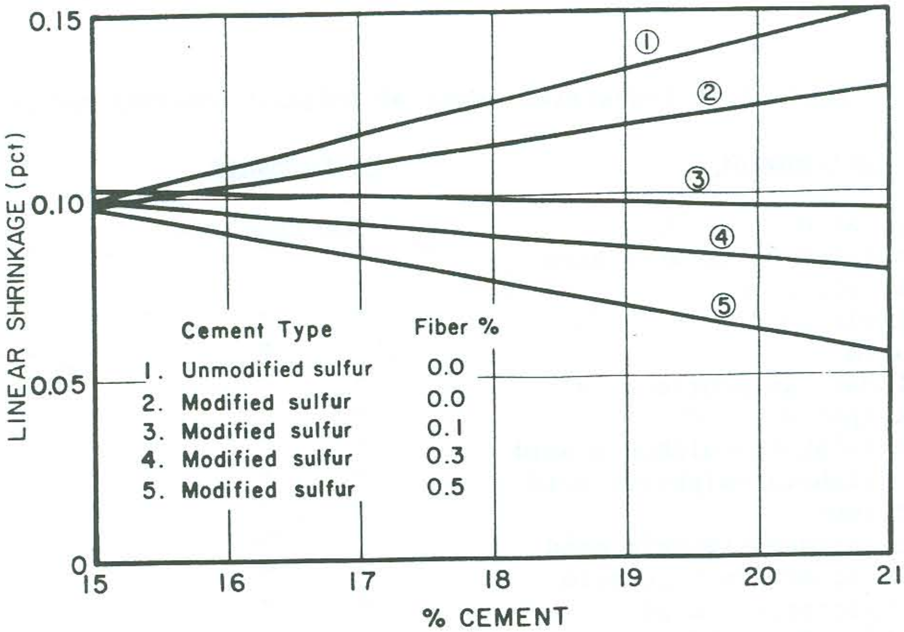
FIGURE 13. - SC foundations and storage tanks for ferrosulphate solutions used to precipitate phosphates at a sewage treatment facility and SC pipes used for sewer systems.

FIGURE 14. - SC is an excellent choice for liquid containment (top) and the only material to obtain sufficient strength within 3 to 5 minutes for use in protecting offshore pipeline joints (bottom).

FIGURE 15. - SC can be used to complete road repairs overnight to reduce public inconvenience.

High

Low



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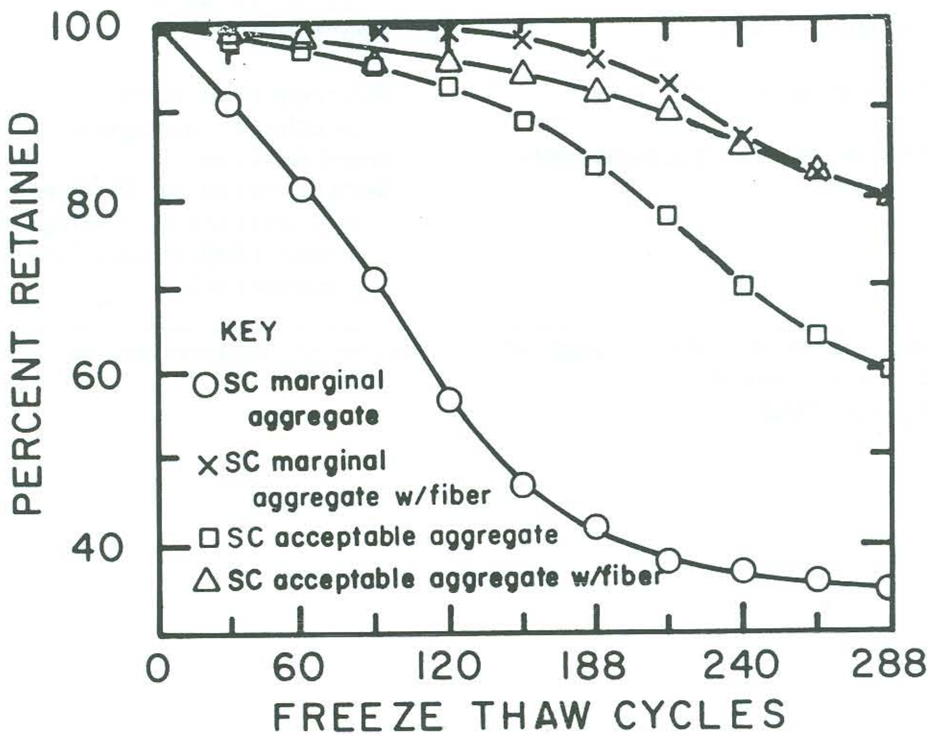


Figure 2. - Influence of glass fiber reinforcement on SC freeze-thaw durability.

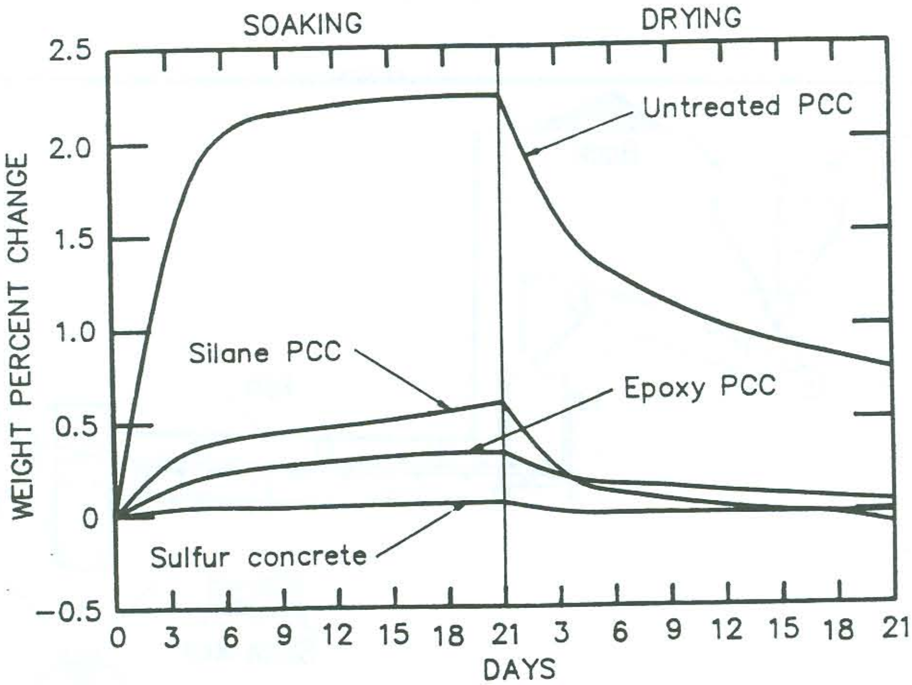


FIGURE 3. - Absorption of sealed and unsealed PCC and unsealed SC.

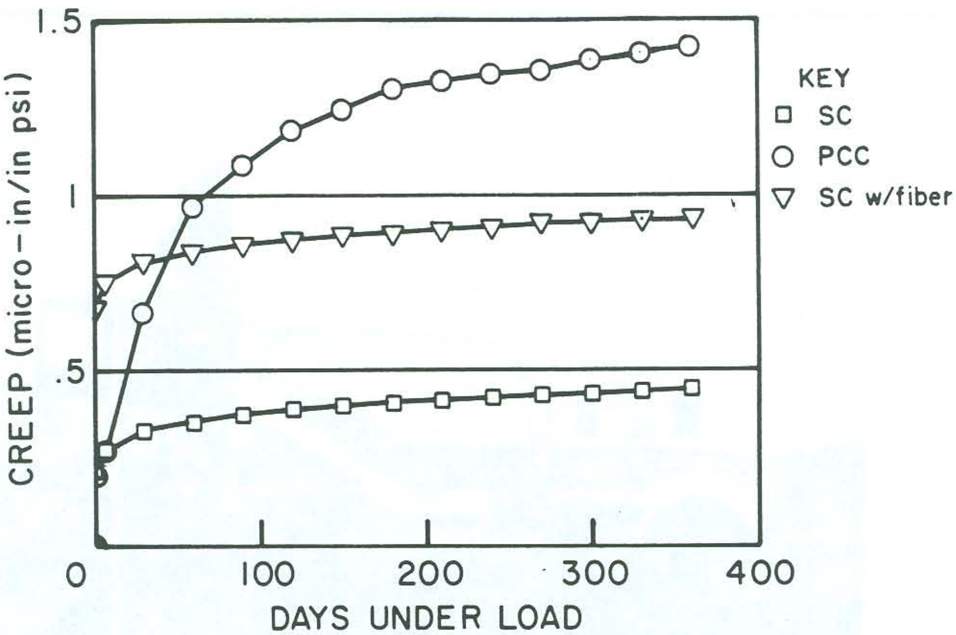
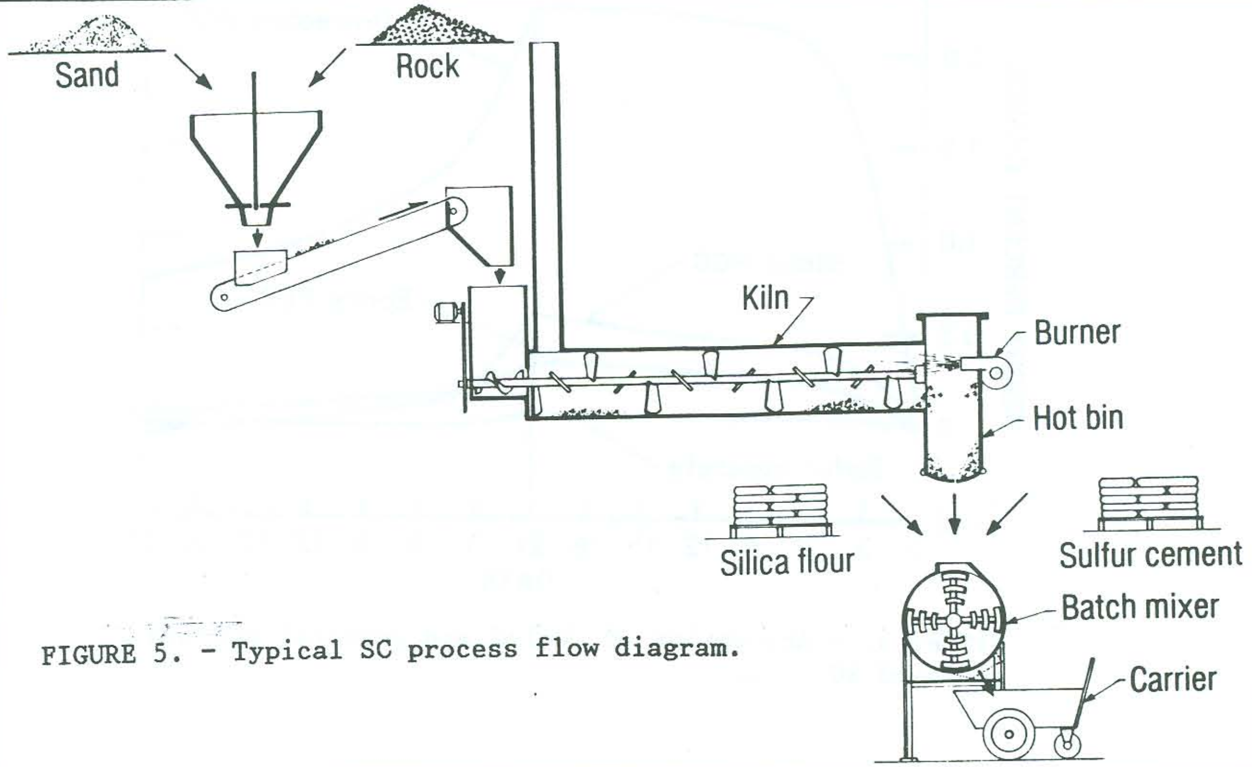


FIGURE 4. - Compressive creep of PCC and SC under sustained loading.



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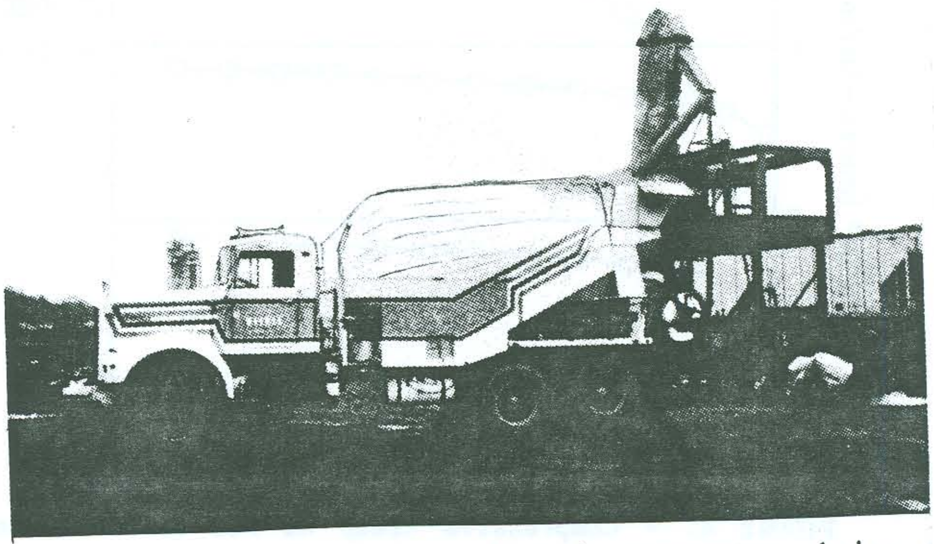

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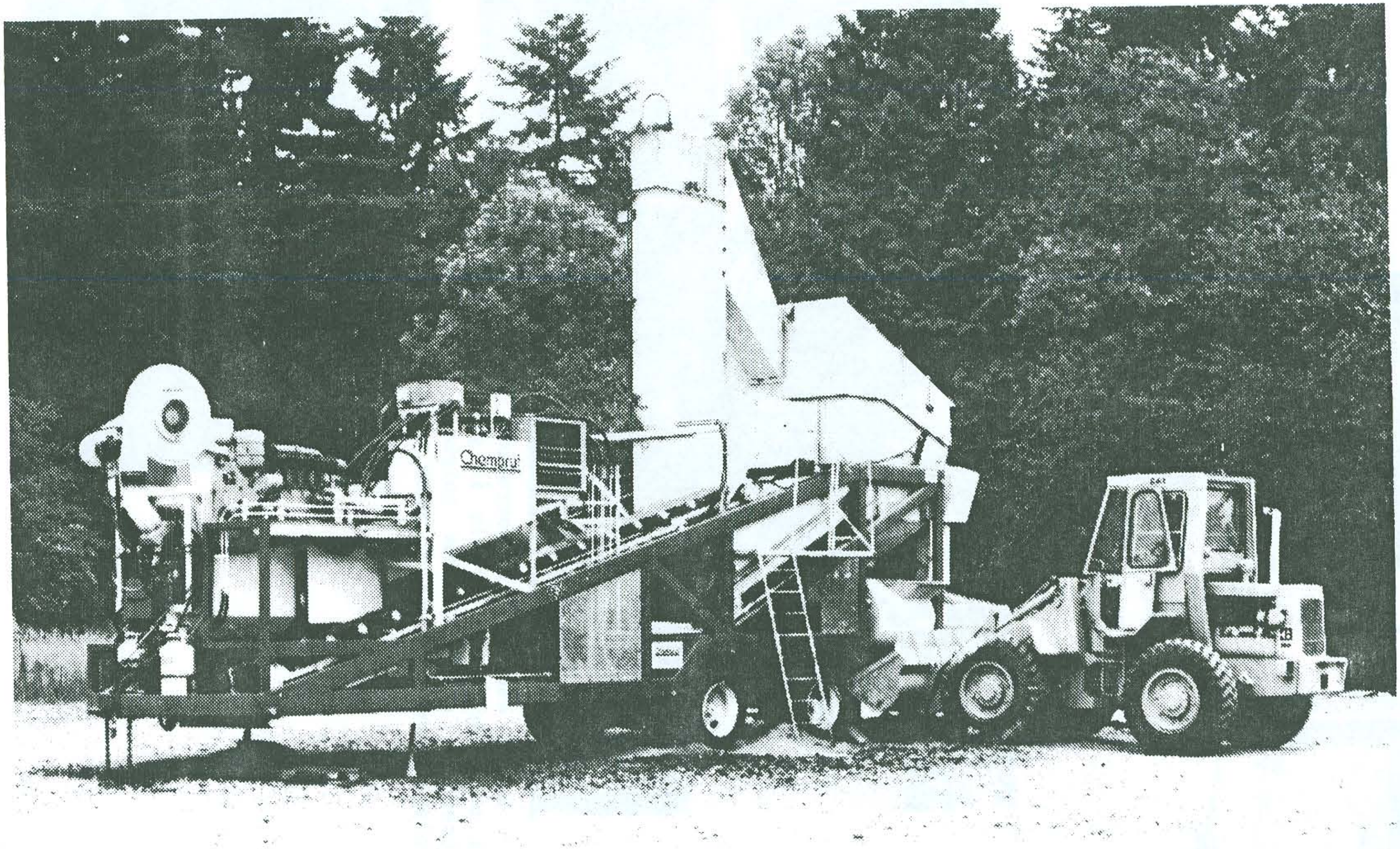
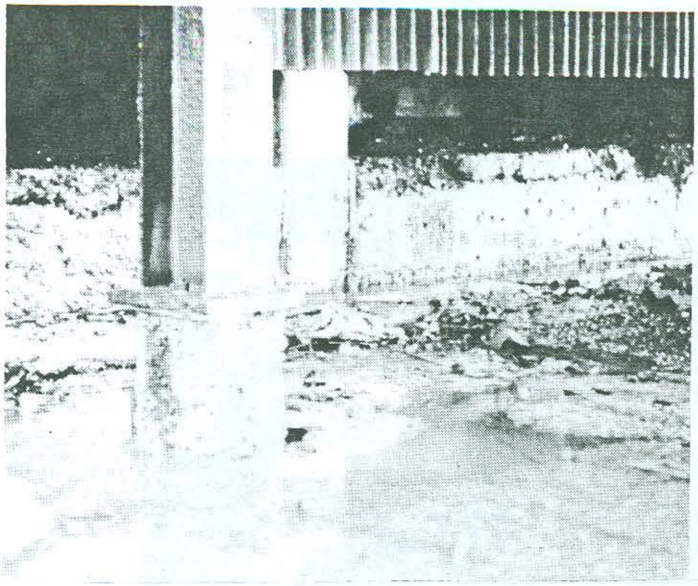


FIGURE 7. - Self-contained SC mobile production plant.



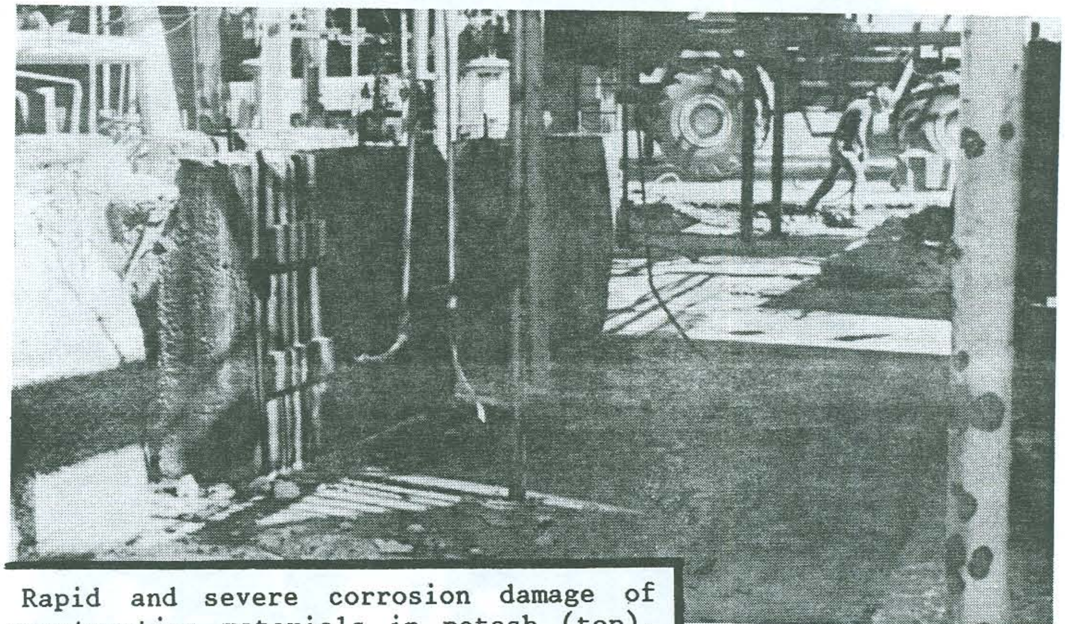


FIGURE 8. - Rapid and severe corrosion damage of conventional construction materials in potash (top), phosphate (center) and ammonium sulphate (bottom) fertilizer plant areas exposed to both acid and salt solutions.

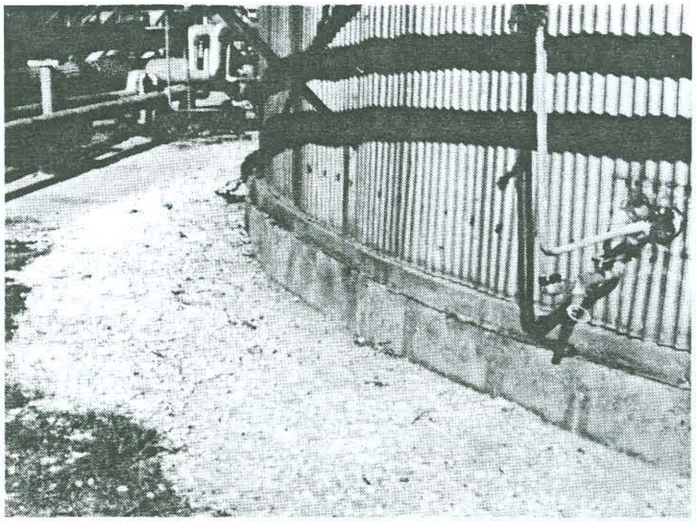
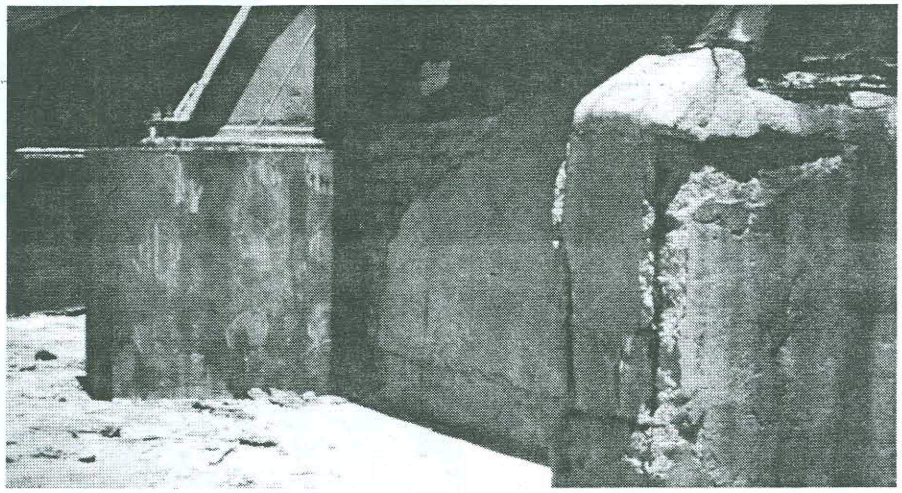


FIGURE 9. - Foundation of a molten sulphur storage tank protected with SC.



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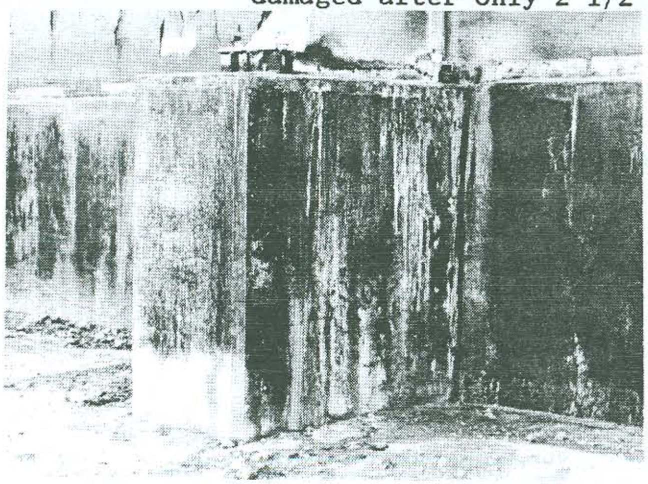

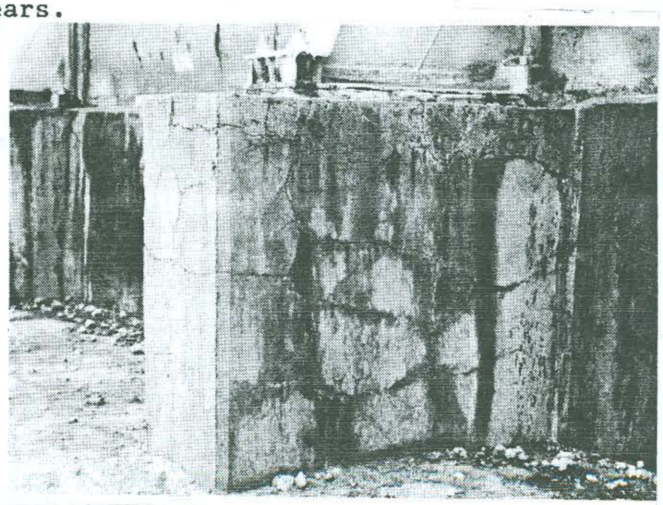

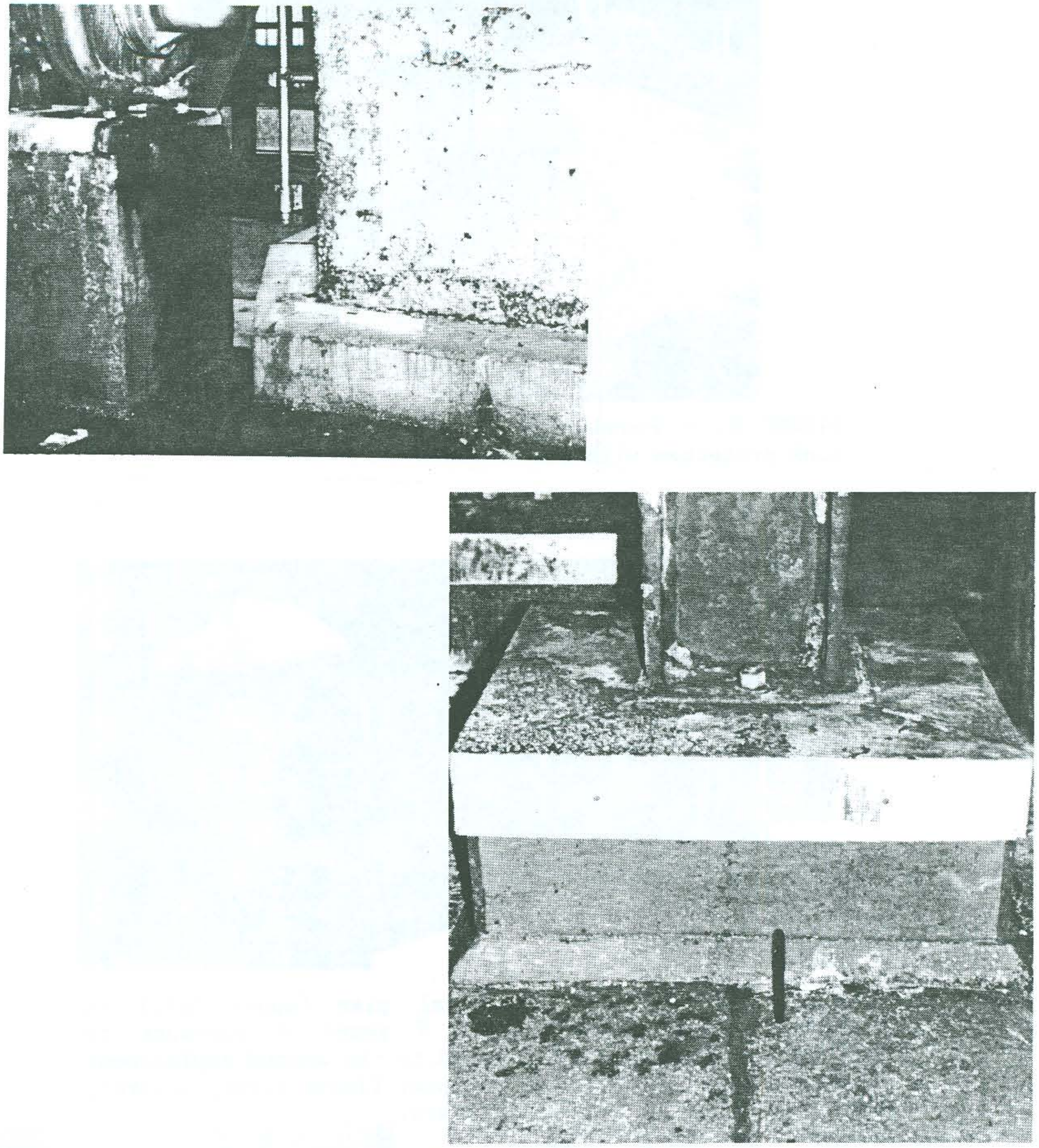

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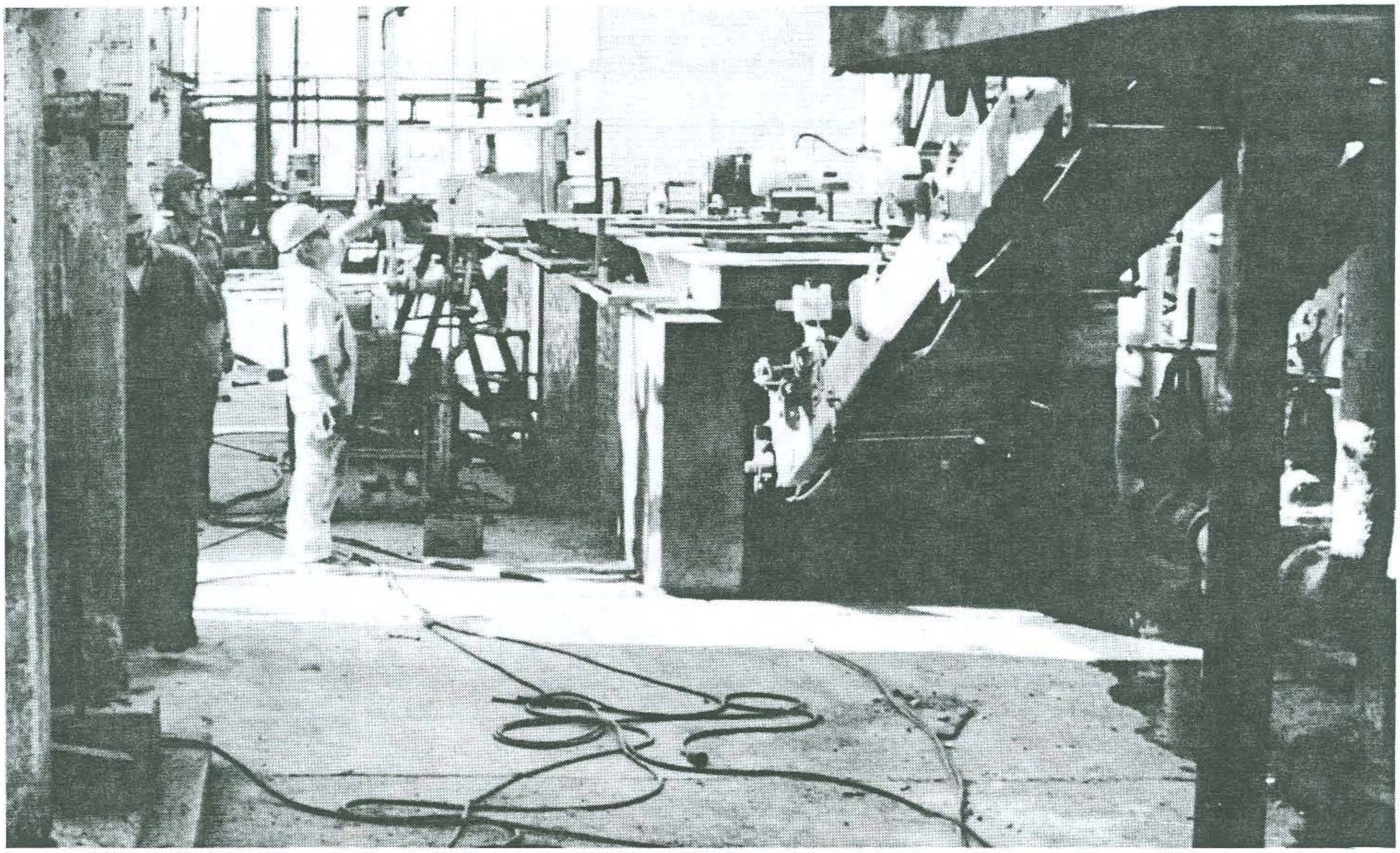
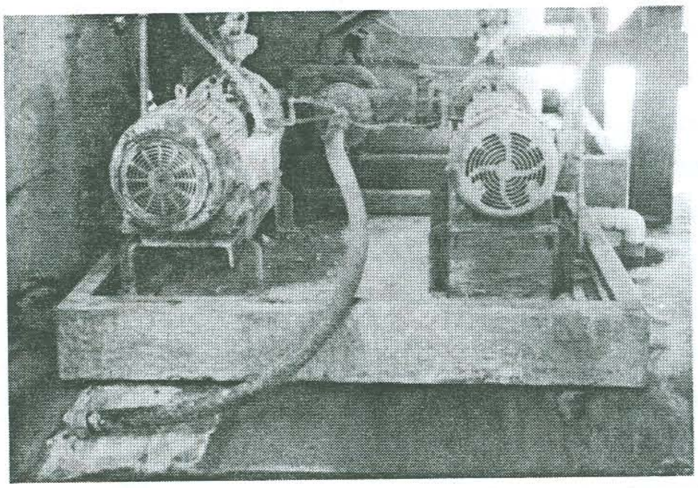


FIGURE 12. - SC floor, wall, column protection and pump foundation/ acid sump combination exposed to sulphuric and phosphoric acid in a phosphate fertilizer production facility.



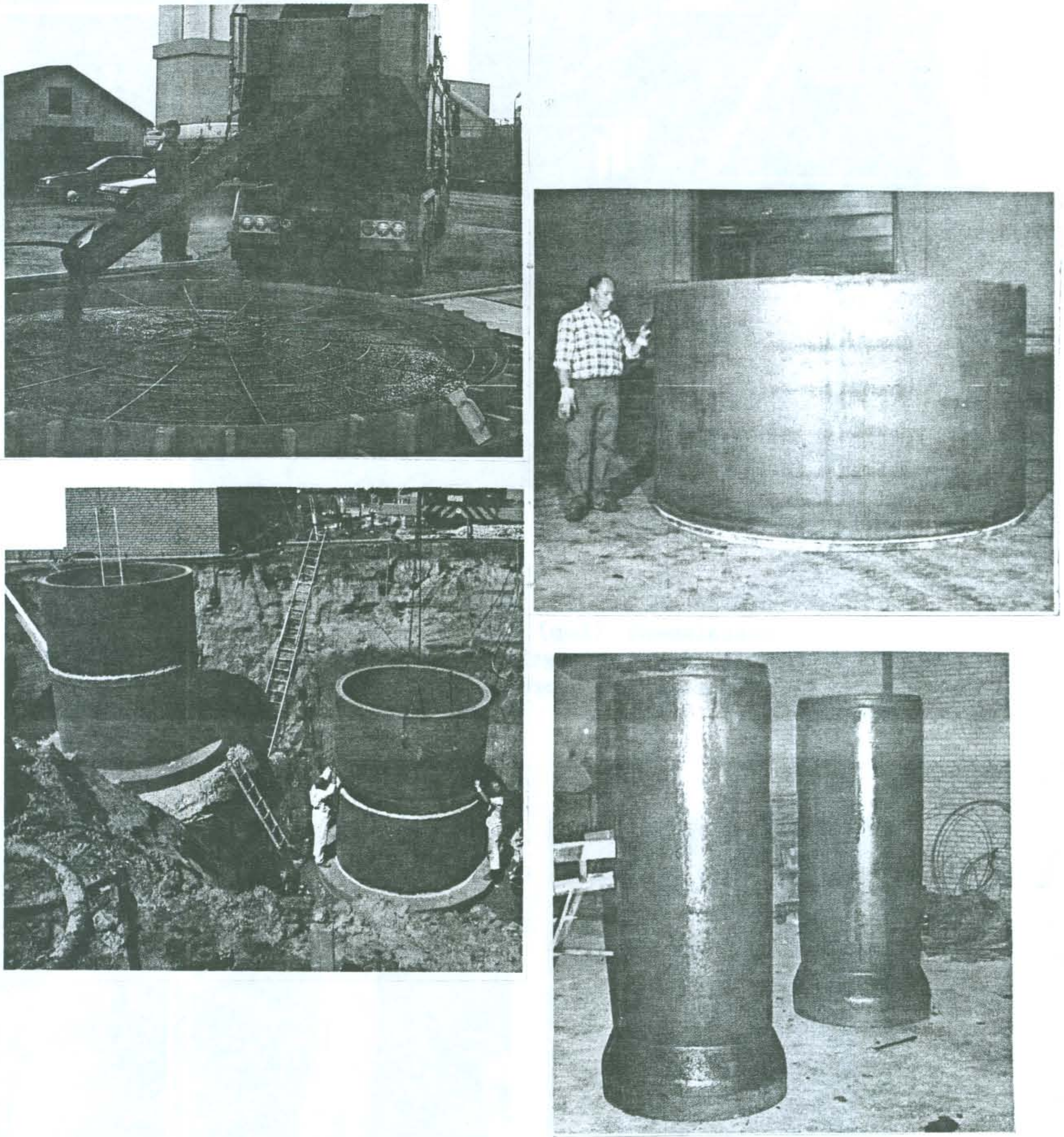


FIGURE 13 - SC foundations and storage tanks for ferrosulphate solutions used to precipitate phosphates at a sewage treatment facility and SC pipes used for sewer systems.

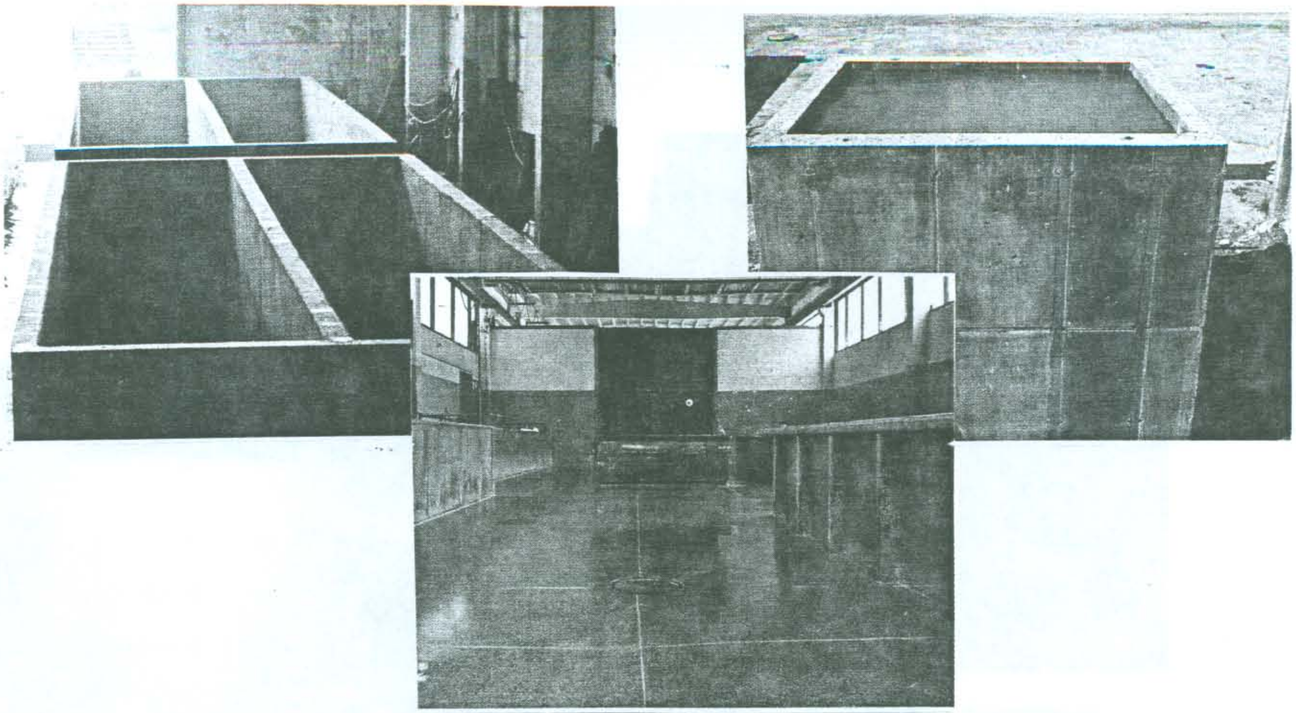
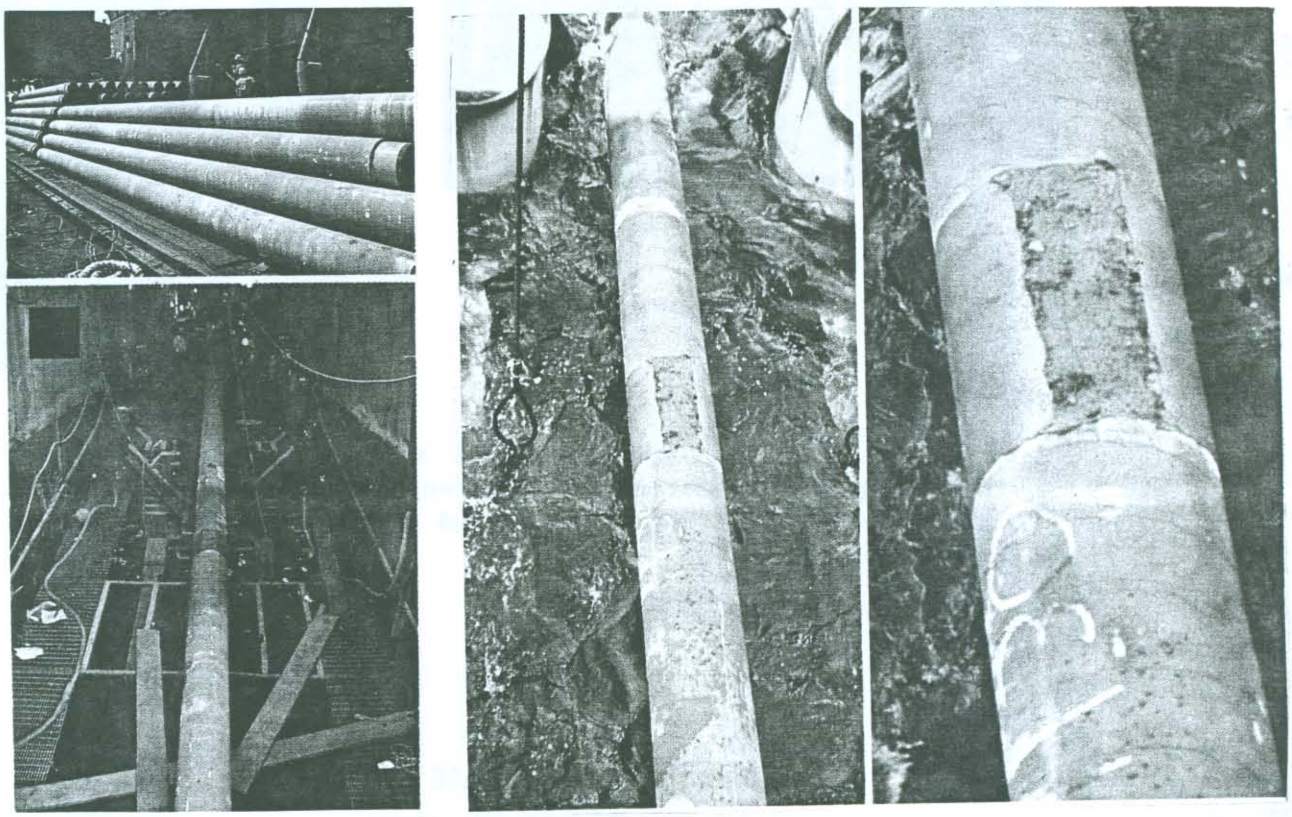


FIGURE 14 - SC is an excellent choice for liquid containment (top) and the only material to obtain sufficient strength within 3 to 5 minutes for use in protecting offshore pipeline joints (bottom).



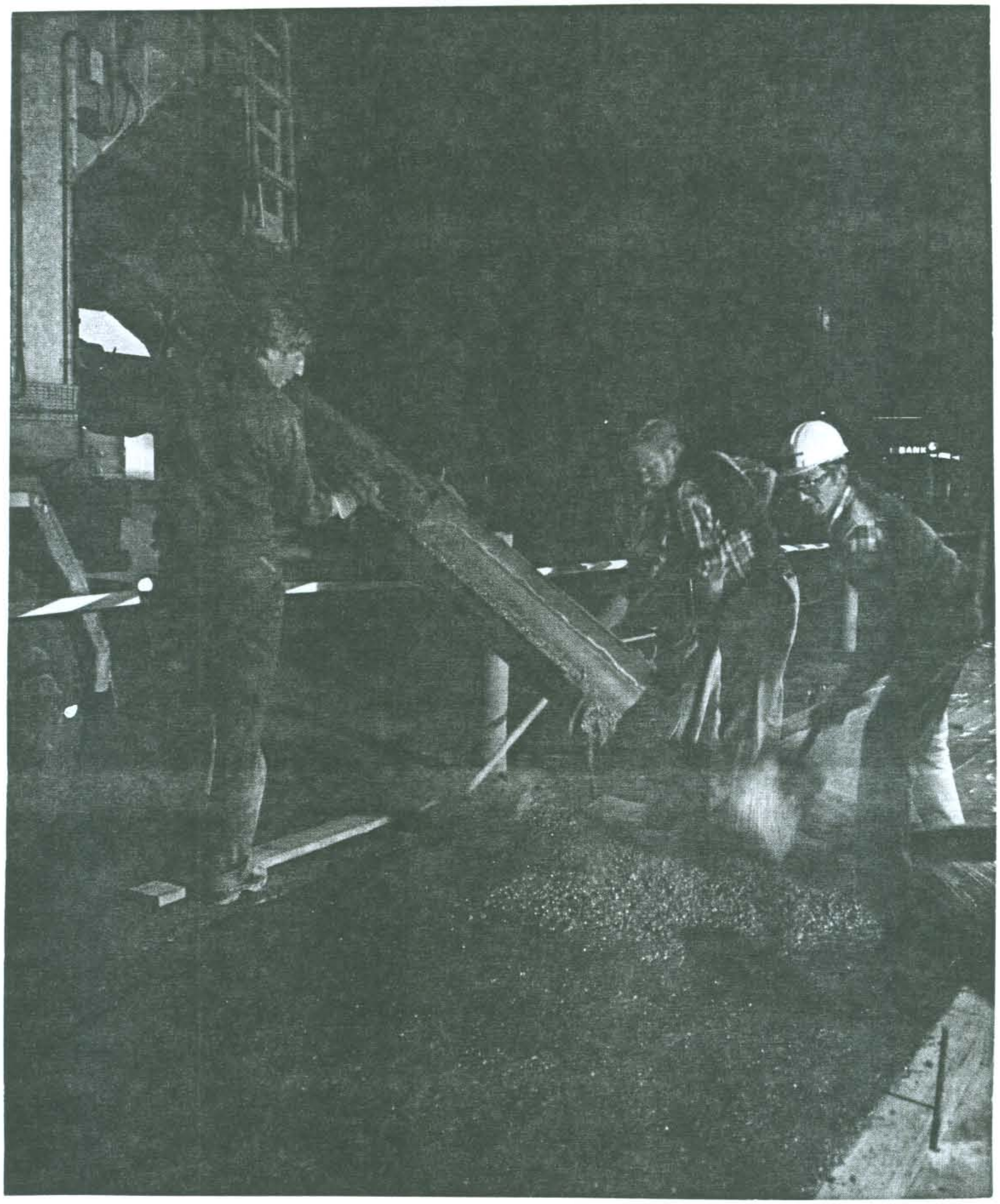


FIGURE 15 - SC can be used to complete road repairs overnight to reduce public inconvenience.