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CONCRETE-POLYMER MATERIALS

FIFTH TOPICAL REPORT

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CONCRETE-POLYMER MATERIALS

FIFTH TOPICAL REPORT

1. SUMMARY

This report covers work performed from July 1, 1971, to June 30, 1972.

The development program for concrete-polymer materials covers three distinct types of material: polymer-impregnated concrete (PIC), polymer-concrete (PC), and polymer-cement concrete (PCC).

Concrete-polymer materials offer potential advantages of high strength and improved durability, as compared with conventional concrete. Because consistently good results were obtained with PIC in early tests, the main efforts in the program have been directed toward its development. Investigations are continuing with PC and PCC because these materials have many potential applications.

Progress in the development of PC as a practical construction material has continued with the development of an economical fabrication process. The new process uses conventional concrete mixing and placing equipment and produces a product which, on the basis of initial tests, has about the same polymer content and compressive strength as standard PIC. The product may be polymerized at room temperature by promoter-catalyst methods. PC should be more economical to produce than PIC since it does not require special process equipment and it can be field-installed using the techniques used for conventional concrete. Studies were continued on increasing the compressive strength of PC through the use of silane coupling agents. An investigation was started to determine whether the plasticity of PC could be increased by copolymerizing methyl methacrylate (MMA) and butyl acrylate.

Investigation of PCC continued on a limited basis with a preliminary study of furfuryl alcohol PCC. Studies to date have shown strength improvements with furfuryl alcohol similar to those found previously with epoxy resins.¹⁴ However, large amounts of epoxy resins were required to increase compressive strengths. Furfuryl alcohol appears promising since it can be polymerized in

an alkaline environment, does not appear to interfere with the hydration of portland cement, and is much lower in cost than epoxy resins. Increases in compressive strength of up to 24% were obtained with relatively small amounts of furfuryl alcohol.

Monomer survey experiments continued with an evaluation of diallyl isophthalate (DAIP), a mixture of 50 wt % MMA and 50 wt % ethylene glycol dimethacrylate (EGDM), and a mixture of 70 wt % MMA and 30 wt % trimethylolpropane trimethacrylate (TMPTMA) for high-temperature applications in desalting plants. Based on short-term exposure tests to brine and vapor at 143° and 177°C, the MMA-TMPTMA system was selected for further testing.

Several plasticizers were tested as additives for monomer systems to increase the flexibility or plasticity of PIC. Stress-strain curves showed that using 35 wt % butyl acrylate - 65 wt % MMA produced the most pronounced effect in PIC. However, it appears that the concrete itself has an overriding effect and that for a wider change in mechanical properties, energy-absorbing materials should be incorporated into the concrete.

The basic procedure for fully impregnating precast concrete, described in detail in the First and Second Topical Reports,^{1,2} consists of oven-drying the concrete, evacuating the dried sample, soaking it in monomer, wrapping the specimen, and polymerizing it by radiation or chemical initiators. Work is in progress to evaluate process variables and to improve specimen preparation techniques. These studies include the determination of the effects of concrete composition, method of curing, monomer-filling techniques, the use of different catalysts and polymerization techniques, and the development of methods for reducing monomer evaporation and drainage losses and elimination of specimen wrapping.

Studies were continued on the effects of composition of the concrete and concrete curing conditions on compressive strength and polymer loading of PIC. Compressive strengths of PIC specimens ranged from about 17,000 psi for PIC made with

a poor-quality high-porosity limestone aggregate to 32,400 psi for a high-strength, high-pressure steam-cured specimen; this is the highest compressive strength obtained to date. These tests indicate that good-quality PIC can be produced from concrete containing very-poor-quality aggregates. The primary factors in producing good-quality high-strength PIC appear to be achievement of a high degree of impregnation and complete polymerization. For production of very-high-strength PIC, a high-strength concrete mix with high-pressure steam curing is advantageous.

Experiments are in progress to determine the vacuum time, soaking time, and pressure requirements for full impregnation of various types of concrete. Impregnation rates depend on the porosity of the portland cement matrix and to a certain extent on the porosity of the aggregate. For impregnation of standard-weight, high-pressure steam-cured concrete specimens up to 12 in. thick, the recommended process consists of oven-drying the specimens to constant weight, evacuation at 30 in. Hg for 30 min, soaking in monomer for 60 min at 10 psig, and polymerization under water by radiation or thermal-catalytic methods.

Partial impregnation and coating techniques were developed for protective treatment of concrete linings in desalting plants. The concrete liner of a flash distillation chamber and various sections of mortar-lined steel pipe were treated and are being field-tested at the OSW Water Desalting Facility in Freeport, Texas. Two monomer systems were used: 60 wt % styrene - 40 wt % TMPTMA followed by a seal coat of 53 wt % polyester - 28 wt % styrene - 19 wt % TMPTMA; and 70 wt % MMA - 30 wt % TMPTMA followed by a seal coat prepared by dissolving 20% MMA prepolymer and a small amount of paraffin wax in some of this mixture. Polymerization of both systems was accomplished at ambient temperatures by promoter-catalyst methods. Preliminary inspection after 6 weeks of normal operation indicated no deterioration in the treated areas.

Studies of polymerization techniques have included experiments to remove the inhibitor in a monomer by radiation and then thermally polymerize the uninhibited and uncatalyzed monomer. A process flow sheet was developed for impregnating concrete and other porous materials and polymerizing by the thermal method. Other polymerization techniques studied were promoter-catalyst methods for ambient-temperature polymeriza-

tion, polymerization of impregnated specimens immersed in water to reduce monomer drainage and evaporation, and thermal-catalytic polymerization of specimens in the impregnation tank with use of steam heat.

The testing program on PIC for ambient-temperature applications is continuing. Structural properties of MMA, styrene, acrylonitrile, MMA - 10 wt % TMPTMA, chlorostyrene-impregnated concrete, and MMA-impregnated concrete polymerized under water, are given in previous topical reports.¹⁻⁴ Results for 10 wt % polyester - 90 wt % styrene-impregnated concrete are given in this report. The polyester and styrene specimens were polymerized by radiation and had an average compressive strength of 20,500 psi, modulus of elasticity of 6.5×10^6 psi, direct tensile strength of 1530 psi, and modulus of rupture of 3300 psi.

Structural properties tests during the year included direct tension tests at -12°C and 20°C , single- and double-shear tests, continuation of long-term creep tests under several compressive and tensile loadings, flexural strength tests of beams impregnated from one and two sides, and flexure and shear tests of steel-reinforced PIC beams. Preliminary design values were obtained for tensile strength at -12°C and 20°C of MMA and of 10 wt % polyester - 90 wt % styrene PIC. Shear tests indicated that single-shear or double-shear test methods have little effect on results with PIC. The shear strength of MMA-impregnated concrete is ≈ 3700 psi, two to three times greater than that of unimpregnated concrete.

Durability tests include resistance to freezing and thawing, acids, sulfates, sodium hydroxide, and weathering. Freeze-thaw tests of PIC show all specimens to have greatly improved durability when compared with unimpregnated concrete. An MMA-impregnated and radiation-polymerized specimen that has been in test for the longest time has shown only 0.5% weight loss after 12,010 cycles, an improvement of $>1523\%$ over unimpregnated concrete. Unimpregnated concrete generally fails the test at about 740 cycles with a 25% weight loss. PIC specimens still under test include MMA - 10 wt % TMPTMA with no weight loss at 9450 cycles, acrylonitrile with 11% weight loss at 8910 cycles, MMA radiation-polymerized under water with 2% weight loss at 2780 cycles, and 10 wt % polyester - 90 wt % styrene with 1 % weight loss at 1530 cycles. Testing has been concluded on MMA, styrene, chlorostyrene, and the bulk of the

MMA - 10 wt % TMPTMA and acrylonitrile specimens.

In the accelerated sulfate attack test, PIC specimens have shown moderately to greatly improved resistance as compared with unimpregnated concrete. MMA-impregnated concrete has been under test longer than other CP test series specimens and has shown from 0.016 to 0.032% expansion after 1436 cycles. Unimpregnated concrete failed the test at 480 cycles with 0.5% expansion.

Unimpregnated concrete and MMA, 10 wt % polyester - 90 wt % styrene, and 60 wt % styrene - 40 wt % TMPTMA PIC specimens were continuously exposed to a 5% solution of sodium hydroxide for >1 year. All specimens showed no loss in weight and no visible signs of deterioration. After removal from test, specimens had compressive strengths ranging from 16,000 to 19,000 psi for PIC specimens and 6500 psi for unimpregnated concrete.

Acid-resistance tests were conducted with PIC specimens immersed in 15% HCl and 5% H₂SO₄. Weight losses from exposure to 15% HCl ranged from 10 to 12% for MMA specimens after 1395 days of exposure to about 12% for chlorostyrene specimens after 882 days. Unimpregnated concrete specimens failed with 25% weight loss after 105 days. In the 5% H₂SO₄ test, which is still in progress, 10 wt % polyester - 90 wt % styrene and MMA specimens polymerized under water show a weight loss of about 17% after 252 days. Unimpregnated concrete failed the test with a 32% weight loss after 210 days. Sewer pipe impregnated with MMA and coated with polyester-styrene has shown no attack after exposure for 150 days to 5% H₂SO₄.

Flammability tests patterned after ASTM D 635-68, Flammability of Self-Supporting Plastics, were performed on PIC and PC specimens and on the polymers themselves. Most of the polymers support combustion according to this test, but when incorporated in PIC or PC, the composite materials are either self-extinguishing or do not burn at all.

Development of partially impregnated concrete as a less costly alternative to fully impregnated concrete continued during the year. Durability tests (freeze-thaw, sulfate attack, and resistance to acid) show generally beneficial but somewhat erratic improvement in durability as compared with unimpregnated concrete. A new series of tests was started to evaluate partially impregnated con-

crete prepared from a concrete mix with a high entrained air content, and high-pressure steam-cured concrete.

Development of PIC for desalting plant applications continued with testing of 60 wt % styrene - 40 wt % TMPTMA and 70 wt % MMA - 30 wt % TMPTMA impregnated concrete for compressive strength, tensile strength, flexural strength, shear strength, thermal properties, creep deformation, and long-term exposure to distilled water, brine, vapor, and the brine-vapor interface. Tests were conducted at temperatures ranging from -23° to 177°C.

Preliminary design values have been calculated for compressive strength, Poisson's ratio, and modulus of elasticity for 70 wt % MMA - 30 wt % TMPTMA and 60 wt % styrene - 40 wt % TMPTMA impregnated concrete at various temperatures. The values were obtained from compressive strength tests and are for short-term exposures at the various temperatures. A trend toward lower values with increasing temperature was observed. The lowest values for compressive strength, found at 143°C, are 13,700 psi for the styrene - TMPTMA and 12,000 psi for the MMA - TMPTMA impregnated concrete.

OSW-type concrete impregnated with 60 wt % styrene - 40 wt % TMPTMA has been exposed for 2 years to brine at 121° and 143°C. CP-type concrete impregnated with the same monomer system has been exposed for 1 year to brine, vapor, and the brine-vapor interface at 121° and 143°C. The PIC specimens show a trend toward lower compressive strengths with increases in exposure time and temperature. Compressive strengths ranged from 16,200 psi for specimens exposed for 215 days in 121°C brine to 10,300 psi for specimens exposed for 2 years in 143°C brine. The specimens also show minor increases in weight, due to moisture absorption, and a small progressive expansion with increase in exposure time and temperature. Specimens of 70 wt % MMA - 30 wt % TMPTMA impregnated concrete are being tested, but results are not yet available. In pressure vessel tests of PIC specimens exposed to brine and distilled water, 70 wt % MMA - 30 wt % TMPTMA PIC specimens were observed to undergo failure after 270 days of exposure at 143°C and 83 days at 177°C. Analysis of these results will determine whether continued testing of this system is desirable.

In the area of fundamental studies, composite materials theory was used to calculate the modulus

of elasticity of concrete-polymer materials, porosimetry studies of high-pressure steam-cured cement paste were made, and the stability of 60 wt % styrene - 40 wt % TMPTMA polymer exposed to brine at high temperatures was determined. The high modulus of elasticity of PIC appears to result from the stiffening produced by incorporation of a rigid polymer into the pores of the cement paste.

High-pressure mercury porosimetry studies showed that cement paste with a high water-to-cement ratio has a group of large pores that are not present in cement paste with a low water-to-cement ratio. Studies were also conducted to determine whether steam-cured and water-cured polymer-impregnated cement pastes undergo changes in porosity when exposed to a high-pressure steam environment. Results indicate that steam-cured cement is more stable than water-cured cement in a high-pressure steam environment, and that polymer impregnation does not completely seal either water-cured or steam-cured cement.

The studies of 60 wt % styrene - 40 wt % TMPTMA indicate that this polymer is stable in sealed exposure to brine, air, $\text{Ca}(\text{OH})_2$ slurry, and distilled water at 150°C . In preliminary studies of 70 wt % MMA - 30 wt % TMPTMA PIC, several specimens have failed in exposure to hot brine. Differential thermal analysis has revealed changes in the MMA-TMPTMA polymer after exposure to hot brine, which indicates that the failure of PIC is due to degradation of the polymer rather than of the concrete.

Fundamental studies were conducted of the reaction between MMA and $\text{Ca}(\text{OH})_2$. One study indicated that MMA reacts with $\text{Ca}(\text{OH})_2$ during thermal polymerization. The other showed that MMA reacts rapidly with $\text{Ca}(\text{OH})_2$ in the presence of water to form calcium methacrylate and methyl alcohol. The significance of these findings is not understood.

In the search for nondestructive test methods for quality control of PIC, the acoustic impact and the dielectric methods were investigated. The acoustic method appeared more suitable for measuring resonant frequency than dampening of transmitted signals. Further work on dielectric and electrical resistivity measurements indicated that the dielectric method was not feasible for PIC.

The use of PIC as a construction material is under investigation in such diverse areas of applica-

tion as desalting plants, concrete pipe, bridge decks, piling, housing construction, marine applications, and tunnel lining and support systems.

PIC drain tile has been under test for 3 years in the laboratory and in the field at the Westlands Experimental Drainage Plot, Tranquillity, California. This area has a high concentration of sulfates in the soil. A field inspection last year revealed no indication of sulfur attack; further inspection is planned.

In a cooperative program with the American Concrete Pipe Association, 3-ft-i.d. $\times$ 6-ft-long lengths of concrete pipe are being impregnated and polymerized at the USBR and BNL. Steel-fiber-reinforced concrete pipe has also been included in the program. The PIC pipes will be tested at the USBR next year. The testing program includes three-edge bearing and hydrostatic pressure tests and tests for resistance to attack by sulfate and sulfuric acid. The performance of the unreinforced PIC pipe will be compared with that of conventional steel-reinforced precast concrete pipe. The goal of the program is to provide design information, determine service requirements and manufacturing techniques, and make an evaluation of economic benefits.

Field tests of PIC sewer pipe are in progress in the San Diego sewage system in a cooperative program with the city of San Diego. In laboratory tests, PIC pipe specimens treated with a polyester-styrene seal coat and exposed to 5% sulfuric acid show no deterioration. PIC pipe installed in the San Diego sewage system is scheduled for inspection after 18 months in service.

A low-cost high-strength PIC tunnel lining and support system is under development. A full-scale laboratory test was conducted on an 8-ft-i.d. tunnel test chamber. Tunnel liner segments of PIC and unimpregnated concrete were assembled in the test chamber, backfilled with concrete, and loaded until failure. Single segments were also tested for arch deflection and failure and analysis of the joint. The tests showed that 2-in.-thick PIC segments with 3.5 in. of concrete backfill can support 60% more load than a similar system composed of unimpregnated concrete segments. Further full-scale tests are planned for next year.

The Federal Highway Administration is interested in the potential of concrete-polymer materials for use in a number of highway applications. These include bridge decks, pilings, and culverts. Programs have started on design of a precast, pre-

stressed PIC bridge-deck system, repair of deteriorated bridge decks, and treatment of new concrete bridge decks to improve durability.

2. INTRODUCTION

2.1 BACKGROUND AND PROGRAM DESCRIPTION

The Concrete-Polymer Materials Program was initiated in 1967 by the Division of Applied Technology, Isotopes Development Section (formerly the Division of Isotopes Development), of the U.S. Atomic Energy Commission (AEC) as a cooperative research and development program between the Department of Applied Science at Brookhaven National Laboratory (BNL) and the U.S. Department of the Interior's Bureau of Reclamation (USBR). Because of its interest in the potential application of concrete-polymer materials for the construction of vessels for water desalination plants, the Office of Saline Water (OSW) also contributed to the support of the program the same year. The OSW has a direct interest in improving the properties of concrete so that it can be effectively used as an economical material of construction in, for example, multistage distillation units in water desalting plants. The main characteristics required are resistance to chemical attack by hot brine and distilled water, and high strength. The Materials Technology Division of the OSW has provided major funding support for a portion of the Concrete-Polymer Program and has contributed to the planning and development of the program. This function is now being performed by the Materials Research Division of the OSW.

Four topical reports have been published on the work performed to date. The first,¹ issued in January 1969, covered the results to the end of June 1968. The second² extended coverage through June 1969. The third³ and fourth⁴ describe work through June 1970 and June 1971, respectively. On the basis of this work a patent on the thermal-catalytic process for the production of PIC has been issued.⁵ The current report deals with work performed through June 1972.

A number of other governmental agencies and industrial associations have become interested in specific applications of concrete-polymer materials. Cooperative programs have been initiated with these agencies, as described in Section 2.3.

The long-range objectives of the program are the investigation and development of concrete-polymer composite materials for use as improved

or new materials of construction. At least three distinct types of material have been under investigation: (1) polymer-cement concrete (PCC), a premixed material of water, portland cement, and aggregate to which monomer or resin is added during mixing and subsequently cured and polymerized in place; (2) polymer-concrete (PC), consisting of an aggregate mixed with a monomer or resin that is subsequently polymerized in place; and (3) polymer-impregnated concrete (PIC), which consists of a precast portland cement concrete impregnated with a monomer system that is subsequently polymerized *in situ*. A fourth type of material, a further development of PIC, could be added to the list. This is precast concrete that has been partially impregnated to a finite depth with a monomer that is subsequently polymerized *in situ*. For each of these main types of material, process variations can be exercised, with resultant variations in properties and characteristics.

The main, and most successful, effort in improving the structural and durability properties of a portland cement concrete has been with PIC. As a result, the reports issued to date deal mainly with the development of this material. The least success has been attained with PCC. Since PCC would have the greatest potential for field applications, attempts to improve it have been continued. For a premixed material, PC seems most promising. This relatively new material has interesting properties, but to bring it into actual application will require great effort.

The Concrete-Polymer Materials Program has been divided into the following major tasks: (1) evaluation and selection of monomers for incorporation in concrete-polymer composites; (2) development of process techniques for preparation of the composites; (3) testing and measurement of pertinent physical, mechanical, and chemical properties; (4) development of applications including the design, preparation, and testing of full-scale specimens; (5) development of preliminary cost estimates for concrete-polymer products; and (6) conducting fundamental studies of concrete-polymer composites to obtain a basic understanding of the nature of these materials.

In the cooperative program for PIC development, the USBR fabricates the concrete specimens and ships them to BNL for impregnation and polymerization. At BNL, polymerization is initiated by ⁶⁰Co γ radiation or by thermal-catalytic techniques. The PIC specimens are returned to the

USBR for measurement of structural and durability properties. In 1971 the USBR constructed and put in operation a facility for impregnation and for polymerization by the thermal-catalytic technique. BNL also prepares some concrete test specimens and performs preliminary structural and durability measurements. In the past year BNL has completed construction of a large-scale impregnation facility and placed it in operation. Both the USBR and BNL perform studies on PC materials. A low-level effort on PCC is being conducted at the USBR. A joint program plan is developed each year and at least two meetings are held annually for technical review of the programs in order to avoid duplication and to ensure augmentation and complementation of each laboratory's investigations.

2.2 SUMMARY OF PREVIOUS WORK

The principal findings in the four previous topical reports are summarized below.

The testing program is continuing on PIC for ambient-temperature applications. Structural properties of MMA, styrene, acrylonitrile, MMA - 10 wt % TMPTMA, and chlorostyrene-impregnated concrete have been measured. The properties of MMA-impregnated concrete radiation-polymerized under water have also been measured. Data from a test series impregnated with 10 wt % polyester - 90 wt % styrene are given in this report.

In general, all the composite systems showed significant improvements in strength and durability. The MMA and MMA-TMPTMA impregnated concretes have given the best results. High-pressure steam-cured samples impregnated with MMA in glass forms and radiation-polymerized had strengths up to 27,200 psi. The improvements in strength appear to be a function of polymer loading, and radiation polymerization gives slightly better strength properties than thermal-catalytic polymerization. Improvements in durability seem to be mainly a function of the polymer loading and the degree of success in sealing the surfaces of the concrete.

A number of preparation variables including concrete composition, method of curing, and duration of curing have been studied. Processing variables such as monomer-filling techniques, the use of different catalysts, and the development of methods for reducing monomer evaporation and drainage losses are also being investigated.

On the basis of limited data it appears that minor changes in concrete composition do not sig-

nificantly affect the compressive strength of PIC. This work has been expanded to include a wider range of mix variables and the results are given in this report.

Three methods of concrete curing, fog, low-pressure steam, and high-pressure steam, have been studied. The impregnation of high-pressure steam-cured concrete with MMA produced PIC specimens with the highest compressive strengths obtained in the Concrete-Polymer Program.

Radiation-induced polymerization under water appeared to be a practical method for reducing monomer evaporation and drainage losses from concrete. Test data indicated that underwater polymerization of MMA had no detrimental effects on properties. The use of heated water as a means of initiating the thermal-catalytic polymerization of MMA has also been tested in the laboratory and appears to be an alternative processing method.

Two monomer systems, 60 wt % styrene - 40 wt % TMPTMA and 90 wt % diallyl phthalate (DAP) - 10 wt % MMA, have been evaluated to determine the high-temperature structural properties and durability for applications such as would be encountered in desalting plants. Preliminary design values have been established for operating temperatures up to 143°C. Resistance of specimens to chemical attack by hot brine and distilled water at temperatures up to 177°C is being measured in autoclave screening experiments and recirculating loops. Data for exposures for up to 1 year were available. The rate of attack on the styrene-TMPTMA system by hot distilled water was very small. In brine, a trend to lower strengths with increased exposure time and temperature was indicated. Rapid deterioration of the DAP-MMA system was noted and as a result the tests were terminated. Six additional monomers were surveyed for OSW applications, and a system consisting of 70 wt % MMA - 30 wt % TMPTMA was selected for additional study. This work is discussed in the current report.

Investigations to develop reliable methods for quality control of concrete-polymer products were being continued. Although several promising methods have been explored, no simple, convenient, nondestructive technique that meets the unique requirements of concrete-polymer materials has been found.

Considerable progress has been made in the development of PC. Specimens produced by using

MMA containing a silane coupling agent for improved bonding had polymer loadings of 5 to 6% and compressive strengths of 16,000 psi compared with strengths of 11,000 psi for samples without silane. The monomer content of this material has been reduced to approximately that used in PIC.

To date little success has been obtained with PCC. Several monomer systems have been used to prepare samples; only epoxy resin showed limited promise of producing concrete with increased compressive strength. However, high concentrations of epoxy are required.

In this report, data are presented on the structural properties of PIC as well as on the longer-term mechanical properties, such as creep. Extensive data are given on durability properties, such as freeze-thaw, acid, and sulfate resistance, and data on resistance to chemical attack by brine and distilled water at temperatures up to 177°C are also presented.

Experiments to evaluate processing techniques for producing PIC have been continued and the results are summarized. Investigations on the incorporation of monomers in premixed concrete and the study of PC composites are described.

In addition, brief status reports on programs to evaluate the potential of PIC for use in pipes, tunnel supports, and bridge decks are presented.

2.3 COOPERATIVE PROGRAMS AND OTHER DEVELOPMENTS

Several government agencies have joined the Concrete-Polymer Program to investigate specific applications.

The Federal Highway Administration (FHWA) of the U.S. Department of Transportation is interested in the potential use of concrete-polymer materials for a number of highway applications, including improvement in the strength and durability of pavements, bridge decks, pilings, and culverts. Work has been performed at BNL on the use of structural lightweight and insulating lightweight concrete for breakaway lamp posts and sign posts. Three-dimensional finite-element structural analysis for design of bridge decks has also been performed. Design and construction of reinforced PIC bridge-deck panels have been initiated at the USBR in a cooperative program between the USBR, the FHWA, and the Prestressed Concrete Institute (PCI). Recently, studies were initiated by the FHWA on partial in-depth impregnation in the field of new concrete bridge decks (USBR) and

on the repair of deteriorated bridge decks (BNL). Several reports have been prepared on the FHWA work and the program is continuing.⁸⁻⁹

The Naval Civil Engineering Laboratory (NCEL), at Port Hueneme, California, has been interested in high-strength concrete with low water permeability for use in underwater applications. In cooperation with BNL exploratory tests on impregnated hulls have been conducted.¹⁰ More recently independent studies of partial impregnation have been conducted at NCEL.¹¹

The Construction Engineering Research Laboratory (CERL) of the Department of the Army, Champaign, Illinois, has shown interest in polymer-impregnated lightweight concrete for military housing applications.

The Bureau of Mines (USBM) of the U.S. Department of the Interior is interested in applying the technology developed in the concrete-polymer program to the strengthening of rock structures in mines for improving underground support and mine safety systems. The first annual report on the USBM work has been issued.¹² The program involves impregnation of coal-mine rock and development of a pumpable polymer rockbolt to replace conventional steel rockbolts.

A cooperative program with the city of San Diego to test polymer-impregnated sewer pipe is in progress. The effort involved development of techniques for impregnating 8-in.-diam sewer pipe conforming to ASTM Designation C-14 and the testing of 40 ft of impregnated sewer pipe in the San Diego sewer system.

A program at the USBR on the design and construction of PIC tunnel linings is part of an overall program conducted by the Department of the Interior on rapid tunneling techniques and testing of various linings. PIC tunnel linings give promise of providing a more competent and economical installation. Plans are being made to install a test section in a tunnel.

A cooperative program between the USBR, BNL, USAEC, and the American Concrete Pipe Association (ACPA) was established in 1970 to study polymer-impregnated sewer and culvert pipe. A number of 3-ft sections of 12- and 24-in.-diam pipe were impregnated and tested. The results of three-edge bearing and hydrostatic tests showed sufficient improvement in strength to warrant further investigation. As a result, twenty-eight 6-ft lengths of 36-in.-diam pipe made by two methods, the roller suspension and the packer head

process, have been impregnated and are being tested. The properties of unimpregnated steel-reinforced pipe will be compared with those of radiation- and thermal-catalytically polymerized unreinforced pipe. A detailed economic evaluation is planned at the end of these tests.

The Perlite Institute has become interested in the possibility of producing a structurally strong lightweight concrete by polymer impregnation of perlite cement.¹³

The work on concrete-polymer materials has stimulated worldwide interest in conducting studies and in developing applications of these materials. Reports of such work come from Japan, Italy, the Union of South Africa, Norway, Spain, France, Sweden, Great Britain, West Germany, and the Soviet Union.

In the past year the American Concrete Institute (ACI) has established Committee 548 to report on all phases of development of polymers in concrete. Symposia were held in November 1972 in Hollywood, Florida, and March 1973 in Atlantic City, and a seminar was held in Denver in April 1973. A state-of-the-art review is also being planned for publication by the ACI.

2.4 DATA BANK

The information for each specimen examined or tested as part of the Concrete-Polymer Materials Program will be made available through a data bank or data information system. Programming of the data bank of concrete-polymer materials was initiated last year. Upon completion, it will be possible to extract any one item, selected items, or all items of information pertaining to an individual specimen. This information can also be obtained for any group of specimens whose data are within some predetermined parameters. Thus, it will be possible to retrieve as much or as little information as desired. The data bank will be operational on the Control Data Corporation 3800 computer system and, after modification, other computer systems.

3. MONOMER AND COMPOSITE SURVEY EXPERIMENTS

The selection of monomers for use in the preparation of concrete-polymer materials depends primarily on the requirements of the proposed application. In general, monomers are selected for two operating conditions: ambient temperature ($<100^{\circ}\text{C}$), and temperatures $>100^{\circ}\text{C}$.

3.1 POLYMER-IMPREGNATED CONCRETE STUDIES

3.1.1 Monomer Selection for High-Temperature Applications. A series of screening tests for high-temperature polymer systems has been completed. The systems under study were diallyl isophthalate (DAIP), a mixture of 50 wt % MMA and 50 wt % ethylene glycol dimethacrylate (EDGM), and a mixture of 70 wt % MMA and 30 wt % trimethylolpropane trimethacrylate (TMP-TMA). The screening procedures and the thermal and mechanical properties for these systems were described in Ref. 4. The system that appeared most stable after short-term autoclave tests in brine and water vapor at 143° and 177°C was the mixture of MMA and TMPTMA. This system has since been subjected to additional testing in hot brine and distilled water (see Section 5.2.2.1).

A concentrated effort has been made to develop a low-temperature polymerization method for the 60 wt % styrene – 40 wt % TMPTMA system using promoter-catalyst systems. The thermal-catalytic and radiation-induced polymerization of the styrene-TMPTMA system has been studied previously with satisfactory results.²⁻⁴ The development of a promoter-catalyst system (see Section 4.5.2) extends the use of a high-temperature polymer to partial impregnations and coatings for field-type application. This has been demonstrated in a field application for the OSW (see Section 4.3.1).

A sealant that will resist high temperature has also been developed for increasing the durability of concrete. The formulation consists of an unsaturated polyester dissolved in a 60 wt % styrene – 40 wt % TMPTMA monomer mixture. The polyester concentration of the mixture can be varied to obtain the desired viscosity. Formulations containing as much as 65 wt % polyester that have been tested in accordance with screening procedures previously described⁴ have shown good thermal, mechanical, and durability properties. The ability of the material to cure rapidly at ambient temperature when 1 wt % benzoyl peroxide and 1 wt % dimethyl aniline are used makes it applicable for direct use as an impregnant for concrete or as a coating on an impregnated specimen. The application of this system in an OSW facility is discussed in Section 4.3.1.

3.1.2 Plasticizers. The compressive stress-strain properties of MMA-impregnated concrete indicate that the composite is a hard, brittle mate-

Figure 1. Compressive stress-strain curves for polymer-impregnated concrete. Curve *a*, MMA; curve *b*, 75 wt % MMA - 25 wt % dibutyl phthalate; curve *c*, 65 wt % MMA - 35 wt % butyl acrylate; curve *d*, unimpregnated concrete; curve *e*, butyl acrylate.

rial.³ The data show that the ultimate stress is only a few percent more than the yield stress. Normally polymethyl methacrylate (PMMA) in the glassy state yields at $\approx 25\%$ of the ultimate stress, but this effect is obscured in the composite, primarily because of the low polymer content and the inelastic properties of concrete.

Attempts have been made to reduce the brittleness of the composite by adding plasticizers to the monomer system. Polymer chains are bound to each other by Van der Waal forces. The strength of these bonds determines the rigidity or flexibility of the polymer. Plasticizer molecules mixed into the matrix tend to weaken the Van der Waal forces and thus produce a more flexible material.

Two types of plasticizer, external and internal, were investigated. The former do not react chemically with monomers; the latter react to form copolymers that have mechanical properties differing from those of the homopolymers. In these studies dibutyl phthalate was used as an external-type plasticizer. This material is used commercially in the manufacture of PMMA sheet. Butyl acrylate was used as an internal plasticizer. This monomer has a low glass temperature of -55°C and can be homopolymerized or readily copolymerized with MMA.

The compressive stress-strain curves for concrete and PIC are given in Figure 1. The composite con-

taining MMA (curve *a*) is an elastic material. The addition of up to 25 wt % dibutyl phthalate produced no detectable changes in the curve. With 25 wt % dibutyl phthalate (curve *b*) a decrease in yield stress was observed, but the stress-strain curve was otherwise similar to that for MMA alone.

The addition of butyl acrylate to MMA showed similar trends until a monomer mixture of 65 wt % MMA - 35 wt % butyl acrylate was used (curve *c*). This is an elastic material with a yield stress $\approx 35\%$ lower than that obtained with MMA. The differences in strain between the yield stress and the rupture stress for the two materials indicate that the mixture is more ductile than MMA alone.

Specimens were also prepared of concrete impregnated with butyl acrylate. Because of its low glass temperature this polymer is a rubbery material. The stress-strain behavior of butyl acrylate impregnated concrete (curve *e*) is similar to that of unimpregnated concrete (curve *d*).

In view of the overbearing effect of the concrete on the stress-strain properties of these composites, materials that can act as plasticizers for concrete should also be investigated. A combination of plasticized monomer and energy absorbers in the concrete, such as polymer and metal fibers, should produce composites with a wide range of mechanical properties.

3.2 POLYMER-CEMENT CONCRETE STUDIES

Investigators at Washington State University made a preliminary evaluation for the USBR of the feasibility of preparing PCC with furfuryl alcohol resins.¹⁴ The study was limited to a determination of the effects of various proportions of aniline hydrochloride catalyst and calcium chloride on the development of compressive strength. The system has been reported in the Soviet Union as producing increases in the tensile and compressive strengths of concrete as well as increases in resistance to frost and to corrosion by salt solutions.¹⁵

Test specimens were prepared from a mix containing 480 g cement, 1200 g graded Ottawa sand, and 240 g water. Portland cement, a shrinkage-compensating cement, and a blend of fly ash and portland cement in equal weight proportions were used. The additives were furfuryl alcohol, aniline hydrochloride, and calcium chloride. Cylindrical specimens 2 in. in diameter and 4 in. long were cast and cured in a moist atmosphere for periods of 7, 14, 28, or 45 days and then placed in a cold oven and heated to 110°C for 6 hr. Specimens

Figure 2. Compressive strength of furfuryl alcohol polymer-cement concrete after curing for 7, 28, and 45 days – first mix series.

Figure 3. Compressive strength of furfuryl alcohol polymer-cement concrete after curing for 7 and 14 days – second mix series.

Table 1

Polymer-Concrete
Effects of Silane Coupling Agent on Compressive Strength
Specimens, 3-in.-diam × 6-in.-long cylinders
Monomer, 60 wt % styrene – 40 wt % TMPTMA
Average polymer loading, 6.4 wt %

Specimen No.	Silane concentration, %	Test temperature, °C	Compressive strength, psi
206	1	21	12,500
208	1	21	12,100
209	1	121	9,520
228	1	121	9,880
231	1	143	8,670
232	1	143	8,840
234	0	21	6,420
238	0	21	6,200
235	0	121	5,260
240	0	121	4,670
242	0	143	3,650
246	0	143	4,090

Aggregate Size Distribution

Mesh size	Concentration, wt %
170-270	6.1
40- 60	10.2
20- 30	23.0
0.5-in. stone	60.7

Figure 4. Polymer-concrete specimens after contact with boiling benzene for 24 hr. Left, PC containing MMA; right, PC containing MMA and silane.

were then allowed to cool to room temperature and were tested for compressive strength.

The first series of tests (Figure 2) showed that mix combination No. 7, containing 5% furfuryl alcohol, 0.75% aniline hydrochloride, and 1% calcium chloride, developed a compressive strength of 6700 psi after 45 days of moist curing and appeared to have the best potential for further development. Mixes with furfuryl alcohol in amounts $>5\%$ produced lower compressive strengths.

A second series of specimens was prepared to improve on mix combination No. 7. The amount of furfuryl alcohol was held constant at 5%, but the amounts of aniline hydrochloride and calcium chloride were varied. These specimens were tested after 7 and 14 days of moist curing (see Figure 3). Mix combination No. 7 had a compressive strength of 6500 psi at 14 days, which is 24% higher than that of the control mix at the same age.

The furfuryl alcohol PCC looks promising in view of the strengths developed and the relatively small amounts of chemicals required. Furfuryl alcohol apparently does not retard cement hydration and can be polymerized in an alkaline environment. The materials are easily incorporated in a cement mix with use of conventional equipment. In future investigations durability will be evaluated, and attempts will be made to increase the curing rate by using other catalysts and to further improve strength properties.

3.3 POLYMER-CONCRETE STUDIES

The effects of sand size and distribution on the monomer loading and compressive strength of PC composites have been given in previous reports.^{3,4} The data indicate that when fairly uniform sand sizes are used, ≈ 20 wt % of monomer is required to fill the void volume, regardless of the sand particle size. It was also indicated that sand graded to specific sizes and proportions resulted in a lower void volume and consequently in lower monomer loadings (≈ 6 wt %). With MMA as the monomer, compressive strengths of $\approx 11,500$ psi were obtained, regardless of sand size or sand size proportions.

The effects of the addition of silane coupling agents on the compressive strength of PC were also discussed in previous reports.^{3,4}

During the current report period PC materials have been produced with use of a monomer mixture consisting of 60 wt % styrene - 40 wt % TMPTMA. Compressive strength data at 21°, 121°, and 143°C are given in Table 1. The effect of adding a coupling agent, γ -methacryloxypropyltrimethoxysilane, on the strength at each temperature is also shown. The silane coupling agent was added to the monomer system prior to forming the composite. At 21°C, the specimens containing silane had an average compressive strength of 12,300 psi, compared with 6310 psi for specimens

Figure 5. Compressive stress-strain curves for polymer-concrete. Curve *a*, MMA; curve *b*, 95 wt % MMA - 5 wt % butyl acrylate; curve *c*, 80 wt % MMA - 20 wt % butyl acrylate.

without silane. This strength ratio (≈ 2.1) was maintained at all test temperatures. At 143°C the specimens containing silane had an average compressive strength of 8750 psi. As shown here and in previous reports, the increase in strength obtained by using silane coupling agents at concentrations as low as 1% has been significant.

The role of the silane coupling agent is to form a covalent bond between the silica and the polymer. The effectiveness of this reaction was confirmed by solvent extraction methods. PC specimens containing MMA with and without γ -methacryloxypropyltrimethoxysilane were exposed to boiling benzene for 24 hr. The PMMA in the composite containing no silane completely dissolved in benzene. The polymer in the composite containing silane did not dissolve, and the sample retained its original configuration, as shown in Figure 4.

A control experiment was performed in which mixtures of MMA and silane were polymerized under the same conditions as the PC specimens. These polymers dissolved when subjected to the benzene extraction test. This indicates that the significant improvement in the chemical and mechanical properties of the PC composite containing silane is a result of the formation of a covalent bond between the polymer and the silica.

PC formed with MMA is a brittle material (see Figure 5). Its brittleness has been greatly reduced by the addition of a comonomer, butyl acrylate. This monomer readily reacts with MMA to form a

copolymer with mechanical properties different from those of each homopolymer. Figure 5 indicates that addition of 5 wt % butyl acrylate has little effect on the stress-strain properties of the composite (curve *b*). However, when 20 wt % is added, the properties are significantly affected. The stress-strain curve identified as *c* in Figure 5 shows a more ductile material with probably a higher impact strength than that of MMA (curve *a*).

Compared with PIC, the plasticizing effects are more pronounced for PC. In the latter, the polymer is the only binder, and thus the thermal and mechanical properties of the composite reflect those of the polymer. It is therefore important that monomer formulations be further investigated so that highly desirable properties such as plasticity can be incorporated in PC composites.

4. PROCESS TECHNOLOGY DEVELOPMENT

4.1 CONCRETE COMPOSITION AND CURING

Studies were initiated in the previous year to investigate the effects of concrete-mix design variables and concrete curing conditions on the compressive strength and polymer loading of PIC.⁴ These studies have been broadened to include a wider range of differences in concrete composition. Specimens were fabricated of expanded shale aggregate, high-quality low-porosity limestone aggregate, low-quality high-porosity limestone aggregate, pit-run Clear Creek aggregate, and processed Clear Creek aggregate in mixes designed to produce high- and low-entrained-air and high- and low-strength concrete. These specimens were given 28-day fog and high-pressure steam cures. Another set of specimens was made with CP-type concrete and given 28-day fog, high-pressure steam, and low-pressure steam cures. Specimens were oven-dried at 110°C , impregnated with MMA, radiation-polymerized in water, and tested for strength and absorption (Table 2).

The average absorption of unimpregnated fog-cured concrete control specimens ranged from 6.2% for the high-strength specimens to 17.6% for the high-porosity limestone specimens, and in general reflected the differences in concrete composition. High-pressure steam-cured specimens in general had from 0.3 to 1.0% higher absorption than companion fog-cured specimens, but ranged from 3.3% greater absorption for expanded shale specimens to 6.2% less absorption for the high-porosity limestone specimens.

Polymer loadings were generally equal to or slightly greater than the water absorptions for the denser concrete mixes and significantly greater than the absorptions for the expanded shale and high-porosity limestone specimens. Polymer loadings were consistently higher in high-pressure steam-cured specimens than in fog-cured specimens, ranging from about 0.5 to 2.0% for the denser mixes to about 4% for the expanded shale specimens.

The absorption of polymer-impregnated specimens ranged from an average of 0.3% for the high-strength fog-cured specimens to 1.2% for high-porosity limestone, high-pressure steam-cured

specimens. High-pressure steam-cured specimens consistently had a slightly higher absorption than companion fog-cured specimens.

The compressive strengths of the PIC specimens were fairly high, ranging from about 17,000 psi for the high-porosity limestone specimens to 32,400 psi for a high-strength, high-pressure steam-cured specimen; this is the highest compressive strength yet obtained in the program. The compressive strengths of the high-pressure steam-cured specimens were 700 to 5200 psi higher than those for companion fog-cured specimens for the low-porosity limestone, expanded shale, low-strength, and

Table 2

Summary of the Effects of Concrete Composition and Curing Method on the Absorption, Polymer Loading, and Compressive and Tensile Strengths of Unimpregnated and MMA-impregnated Concrete

Concrete mix ^b	Unimpregnated concrete				MMA-impregnated concrete ^a				
	Concrete cure	Absorption, wt %	Compressive strength, psi	Direct tensile strength, psi	Absorption, wt %	Polymer loading, wt %	Compressive strength, psi	Polymer loading, wt %	Direct tensile strength, psi
Low-entrained air	Fog ^c	6.3	8,200	—	0.4	5.9	24,600	—	—
	HPS ^d	7.4	2,900	—	0.5	7.3	23,700	—	—
High-entrained air	Fog	8.0	1,800	—	0.5	9.9	24,200	—	—
	HPS	8.3	1,800	—	0.5	10.4	21,800	—	—
Low strength	Fog	6.5	5,900	—	0.3	7.4	24,800	—	—
	HPS	7.3	4,200	—	0.6	8.4	27,000	—	—
High strength	Fog	6.2	9,000	—	0.3	6.1	25,500	—	—
	HPS	5.8	8,400	—	0.3	7.2	30,700	—	—
Pit-run aggregate	Fog	10.0	5,100	—	0.3	10.2	21,800	—	—
	HPS	10.2	2,600	—	0.9	12.2	19,900	—	—
Low-porosity limestone aggregate	Fog	6.5	6,300	—	0.3	6.9	22,500	—	—
	HPS	7.8	2,600	—	0.6	8.5	23,200	—	—
High-porosity limestone aggregate	Fog	17.6	2,500	—	1.1	18.0	17,100	—	—
	HPS	11.5	2,300	—	1.2	20.3	17,100	—	—
Expanded shale aggregate	Fog	12.9	7,800	—	0.7	25.9	24,000	—	—
	HPS	16.2	5,200	—	0.9	30.3	26,200	—	—
CP concrete ^b	Fog	—	6,100	440	—	7.3	24,400	7.2	1,800
	HPS ^e	—	4,100	230	—	6.6	21,200	6.4	1,300
	LPS ^f	—	5,000	340	—	7.0	24,700	7.1	1,900

3 × 6-in. specimens oven-dried at 110°C prior to impregnation.

Radiation-induced polymerization in water.

^aMMA = methyl methacrylate.

^bValues are averages of three specimens, except that those for CP concrete are averages of 10 specimens.

^cFog = 28-day fog cure.

^dHPS = high-pressure steam cure.

^eHPS = nonstandard HPS cure: specimens steam-cured after 24-hr fog cure.

^fLPS = low-pressure steam cure.

high-strength mixes. Compressive strengths of high-pressure steam-cured specimens were from 900 to 2400 psi lower than those for companion fog-cured specimens for the low-entrained-air, pit-run aggregate, and high-air specimens. For the PIC CP-mix specimens in the curing-method test series, low-pressure steam-cured specimens had about the same compressive strength as fog-cured specimens, 24,690 and 24,430 psi, respectively. The high-pressure steam-cured specimens were not given the standard treatment and were high-pressure steam-cured after a 24-hr fog cure; these specimens had a compressive strength of 21,240 psi. The improvement in strength due to polymer impregnation ranged from 2.8 to 13.4 times that of companion unimpregnated concrete.

It is of interest to note that good-quality PIC could be produced with concrete containing two poor-quality aggregates. The pit-run aggregate had not been washed or graded. The high-porosity limestone (marl) is a soft, highly absorptive, poor-quality rock with a high clay content that weakens in water and is abraded during concrete mixing. These two aggregates are of much poorer quality than those normally used for concrete, yet the compressive strengths after polymer impregnation were in the range of 17,000 psi for the high-porosity limestone and 20,000 psi for the pit-run aggregate. The relatively high compressive strengths apparently are due to a high polymer loading.

In producing good-quality PIC, the strength and quality of the concrete prior to impregnation do not appear to be as important as achieving a high degree of impregnation and complete polymerization. However, the porosity of concrete will affect the costs of producing PIC, since high-porosity concrete will require more monomer for full impregnation. At this point in the program it seems that good-quality PIC can be made from concretes of widely varying composition. The entrained-air content primarily affects the polymer loading and has little effect on compressive strength. For very-high-strength PIC, the high-strength mix and high-pressure steam curing are definitely advantageous. Use of a very-high-quality aggregate would also contribute to increasing compressive strength.

4.2 FULL IMPREGNATION TECHNIQUES

The process conditions required to fully impregnate various types of concrete are being determined. In the current work the effects of degree of

vacuum, soaking time, and pressure are being studied. Methods to reduce monomer evaporation and drainage losses during polymerization are also being evaluated. These studies are summarized below.

The effects of vacuum, pressure, and soaking time on the impregnation rate of 3-in.-diam $\times$ 6-in.-long concrete specimens were studied. Test specimens of CP concrete and three of its variations, all high-pressure steam-cured (HPS), were compared. The mix variations were (1) high air content (10%), (2) structural lightweight (expanded shale aggregate), and (3) low strength (low cement factor). The specimens were oven-dried at 110°C, impregnated with MMA, dipped in a prepolymer solution of PMMA, wrapped in foil, and radiation-polymerized under water. Encapsulation methods were also evaluated; in these studies, the impregnation and polymerization conditions differed. This work will be discussed later in this section.

The impregnation rates were measured with and without prior vacuum treatment and at two levels of soak pressure, 10 and 100 psig. The effect of vacuum treatment was determined by comparing results from fully evacuated samples (held at 30 in. Hg for 15 min) with those from partially evacuated (equilibrated at $\approx$ 15 in. Hg) samples and samples that were not evacuated.

Impregnation-rate measurements for CP concrete under various impregnation conditions are given in Figure 6. Without prior vacuum treatment and with use of 100 psig pressure, the monomer loading approached equilibrium (polymer loading, 6.2 wt%) after about 10 min. At 10 psig, equilibrium had not been achieved after 1000 min. The data also indicate that holding a sample at 30 in. Hg vacuum for 15 min and then soaking at 10 psig for $\approx$ 30 min was adequate to reach saturation. At 100 psig, saturation was achieved in considerably less time ($\approx$ 9 min). Partial evacuation of samples to 15 in. Hg followed by pressurization to 10 and 100 psig gave intermediate filling rates and monomer loadings. Compressive strength measurements of the polymerized samples indicated that strength was related to monomer loading, i.e., 27,200 psi at 7.6 wt % to 19,150 psi at 5.6 wt %.

Impregnation-rate measurements for concrete containing structural-lightweight (expanded-shale) aggregate are given in Figure 7. The saturation level for this material was considerably higher ($\approx$ 28 wt %) than that for CP concrete because of

its higher porosity. The effect of 30 in. Hg vacuum treatment on the filling rate and saturation time was consistent with that observed for CP concrete. At 100 psig and 10 psig, saturation at a monomer loading of $\approx 28\%$ was achieved after ≈ 20 and ≈ 200 min, respectively. Without vacuum treatment, saturation had not been achieved after 1000 min. The saturation times measured for this material were greater than for CP concrete. Partial

evacuation (15 in. Hg), followed by soaking at 100 psig, was as effective as full vacuum treatment. The highest compressive strength measured on any sample in this entire investigation (30,775 psi) was obtained from one of the polymer-impregnated shale-concrete specimens. Compressive strength measurements made on these specimens were generally in agreement with monomer loading, but were not as consistent as the results for CP concrete.

Impregnation-rate measurements for the high water-to-cement ratio (0.6) specimens are given in

Figure 6. Impregnation-rate curves and compressive strength measurements for high-pressure steam-cured CP-type concrete. Specimens (3-in.-diam $\times$ 6-in.-long) were oven-dried at 110°C , impregnated with MMA, and radiation-polymerized under water.

Figure 8. Impregnation-rate curves and compressive strength measurements for high-pressure steam-cured concrete having a water-to-cement ratio of 0.6. Specimen size and treatment as in Figure 6.

Figure 7. Impregnation-rate curves and compressive strength measurements for high-pressure steam-cured concrete containing expanded shale aggregate. Specimen size and treatment as in Figure 6.

Figure 9. Impregnation-rate curves and compressive strength measurements for high-pressure steam-cured concrete having a high air content ($\approx 10\%$). Specimen size and treatment as in Figure 6.

Figure 8. The trends obtained are similar to those obtained with CP concrete. However, the saturation levels achieved are higher, probably because of the higher porosity. An average compressive strength of 26,790 psi was measured for fully evacuated specimens.

Impregnation-rate measurements for the high-air-content ($\approx 10\%$) specimens are given in Figure 9. The results are similar to those discussed above, namely, the monomer loadings at saturation are

Figure 10. Comparison of impregnation rates and compressive strength measurements for CP-type concrete, concrete containing expanded shale aggregate, concrete with a high water-to-cement ratio, and concrete having a high air content. Specimens (3-in.-diam $\times$ 6-in.-long) were oven-dried at 110°C , evacuated to 30 in. Hg for 15 min, soaked in MMA at 10 psig, and radiation-polymerized under water.

Figure 11. Effect of monomer viscosity on the impregnation rate and final compressive strength of concrete containing expanded shale aggregate. Specimens (3-in.-diam $\times$ 6-in.-long) were oven-dried at 110°C , evacuated to 30 in. Hg for 15 min, soaked in MMA and solutions of PMMA at 10 psig, and radiation-polymerized under water.

higher but the strengths are generally lower than for CP concrete and concrete with a high water-to-cement ratio. After polymerization, an average compressive strength of 23,100 psi was measured for the fully evacuated specimens. Unevacuated samples soaked at pressures of 10 and 100 psig had strengths of 14,300 and 18,030 psi, respectively.

The initial impregnation rate of the high-air-content concrete is significantly higher than that of any of the other concretes tested, as shown in Figure 10. The data given are for specimens under identical impregnation and polymerization conditions, 30 in. Hg vacuum, and 10 psig soak pressure. The curves are normalized for the different

Figure 12. Effect of monomer viscosity on the impregnation rate and final compressive strength of concrete having a high water-to-cement ratio (0.6). Specimen size and treatment as in Figure 11.

Figure 13. Effect of monomer viscosity on the impregnation rate and final compressive strength of concrete having a high air content ($\approx 10\%$). Specimen size and treatment as in Figure 11.

saturation levels, determined by comparing elapsed time with percent of maximum monomer loading. On the basis of these data, the impregnation rates seem to be directly related to the cement-phase porosity. For the shale aggregate, long impregnation times are required, probably because of the large number of pores.

The effect of monomer viscosity on the impregnation rates of three concrete mixes was measured (see Figures 11 to 13). Prepolymer solutions were prepared by dissolving PMMA in MMA until viscosities of ≈ 20 and ≈ 70 cP were measured. These data are compared with impregnation data using normal MMA (0.7 cP) with impregnation conditions of 30 in. Hg vacuum and soaking at 10 psig. Both specimens of concrete with a high water-to-cement ratio (see Figure 12) were fully impregnated with the higher viscosity monomer solutions in 1000 min, whereas the concretes with a high air content or shale aggregate were only partially filled in that time period. Compressive strength measurements reflect the lower monomer loadings achieved in each case.

Impregnation parameters such as vacuum, pressure, soaking time, and method of encapsulation were all found to affect the strength of PIC. The degree of evacuation of a concrete sample is one of the most important parameters. Complete saturation of concrete is accomplished only after prior evacuation to ≈ 30 in. Hg. Without prior evacuation, soak pressures of ≈ 100 psig are required in order to approach saturation in a short time (≈ 60 min).

The simplest type of impregnation process would consist of soaking unevacuated samples at atmospheric pressure. This would result in partially saturated specimens and therefore somewhat lower strengths. In general, overnight soaking of dried CP-type concrete in MMA will result in filling ≈ 70 to 80% of the voids that can be filled by prior evacuation. Compressive strengths of 15,000 to 17,000 psi would be anticipated.

Concrete composition has a significant effect on the monomer impregnation rate. Samples of concrete having high air and high water contents were saturated with monomer in shorter periods of time than CP-type concrete. Samples containing expanded shale aggregate were saturated with monomer in longer periods of time than CP-type concrete, probably because of the high porosity of the aggregate.

As part of an effort to develop methods for reducing monomer evaporation and drainage losses

during processing, encapsulation experiments were performed with each of the aforementioned types of concrete. All the specimens were impregnated with MMA and radiation polymerized. The studies covered (1) the effect of dryness of the concrete, (2) the effectiveness of aluminum foil wrapping, (3) irradiation in air or under water, (4) encapsulation in forms, (5) the effectiveness of prepolymer dip coating, and (6) the use of higher viscosity solutions. The observations were in general agreement with those in earlier reports.^{4,8} A specimen dried at 150°C, impregnated with MMA by the vacuum-soak method, dip-coated with a viscous prepolymer solution, wrapped in aluminum foil, and irradiated under water had the most uniform distribution of polymer and least evaporation from the surface. Samples immersed in water without being wrapped in aluminum foil exhibited slight surface evaporation, but final compressive strengths were not affected.

On the basis of this work, a processing cycle requiring the shortest time period was selected. It consisted of evacuating for 15 min and rapidly pressurizing for 15 min, after which the sample was removed and polymerized under water. Although the data indicated little difference between pressurizing to 10 or to 100 psig, the latter was selected. One sample of each type of concrete, with the exception of expanded shale concrete, was processed. The results, in agreement with previous trends, are listed below.

Concrete	Monomer loading, %	Compressive strength, psi
CP type	7.5	24,230
High air content	9.8	21,200
High w/c ratio	7.7	21,700

High-quality PIC can be made from concretes varying widely in composition. For best results, the use of standard-weight concretes containing low-porosity aggregate is recommended. With this type of concrete, HPS curing appears to be advantageous.

For HPS-cured, standard-weight concrete containing a low-porosity aggregate, the following processing cycle is recommended for sections up to ≈ 12 in. thick.

1. Oven-dry to constant weight at 150°C. Dryness should be achieved in ≈ 24 hr.
2. Evacuate at ≈ 30 in. Hg and maintain for ≈ 30 min.
3. Introduce monomer under vacuum and subsequently pressurize to ≈ 10 psig. Pressure-soak for ≈ 60 min.

4. Remove monomer.

5. Remove and place section under water or, for larger sections, backfill impregnator with water.

6. Polymerize monomer *in situ* with radiation, hot water, or steam. The method of polymerization should be based on a detailed process cost analysis for each specific product.

7. Remove water and clean section.

Data on larger sized sections are currently being obtained.

As described above, when attempts were made to impregnate concrete without the use of vacuum and pressure, full saturation could not be obtained.

Experiments are being conducted to impregnate concrete by using a condensation filling process, which would minimize or eliminate the need to evacuate prior to impregnation. Attempts have also been made to minimize the pressure requirements by using a porous concrete. The concrete has a high water-to-cement ratio ($w/c = 0.7$) and is steam-cured for several hours at a temperature slightly above 105°C . After curing, the hot specimen is immediately immersed in a bath containing monomer and catalyst. During quenching in the monomer, condensation of the residual water vapor in the voids produces a pressure differential and therefore a flow of monomer into the specimen.

The process can be adapted to thermal-catalytic polymerization by using a catalyzed monomer, or to radiation polymerization by using monomer without catalyst. Specimens containing monomer and catalyst can also be polymerized at room temperature in a radiation field. The presence of catalyst in the monomer greatly reduces the radiation dose required for polymerization.

Experiments were performed using a concrete with a water absorption of $\approx 11.5\%$. After condensation filling, the monomer loadings obtained were between 11 and 11.5%. This indicates that the amount of water remaining in the specimen after steam curing is very small. The soaking time required to obtain a fully impregnated specimen ranged between 3 and 5 hr. After polymerization, the compressive strengths of MMA and styrene-impregnated specimens were 22,000 and 16,000 psi, respectively.

4.3 PARTIAL IMPREGNATION AND COATING TECHNIQUES

Partially impregnated concrete is characterized by durability rather than high strength, and therefore requires less monomer than fully impregnated

concrete. The concrete is impregnated to controlled depths of penetration. The monomers should effectively seal the surface and penetrate far enough to avoid separation of the impregnated layer and premature failure. Viscous monomer systems are generally used because penetration depths are more easily controlled, voids in the penetrated portion remain filled, and monomer losses due to evaporation and drainage during the time between impregnation and complete polymerization are lower. However, for field applications such as the repair of concrete-lined vessels and bridge decks, low-viscosity monomers such as MMA, MMA-TMP-TMA, and styrene-TMTPMA are preferred since they penetrate concrete more readily than higher-viscosity monomers. These studies are summarized below.

4.3.1 BNL Studies. Laboratory techniques have been developed for controlling the depth of penetration of MMA and polyester-styrene in the following types of concrete: CP-type, CP-type containing $\approx 10\%$ entrained air, and structural lightweight containing expanded shale aggregate. Methods for the partial impregnation of CP-type concrete were described previously.⁴

Controlled and reproducible depths of penetration can be obtained with both of the monomer systems listed above. Based upon water absorption measurements made prior to impregnation, the amount of monomer required for any desired depth of penetration can be calculated. By monitoring the monomer liquid level during impregnation, the specimens can be removed when the desired amount of monomer has been absorbed.

Fifty-four 3-in.-diam. $\times$ 6-in.-long samples have been impregnated to nominal depths of $\frac{1}{4}$, $\frac{3}{8}$, and $\frac{1}{2}$ in. and are being tested for water absorption, freeze-thaw durability, and resistance to chemical attack by 5% H_2SO_4 . The results to date are discussed in Section 5.1.3.

Partial impregnation and coating techniques are being tested in a field experiment at the OSW Water Desalting Facility in Freeport, Texas. The field application required partially impregnating the concrete liner of a vertical tube evaporator (VTE) to a depth of $\approx \frac{1}{4}$ in. The VTE was fabricated of steel plate lined with ≈ 1 in. of lumnite concrete. A mixture of 60 wt % styrene - 40 wt % TMPTMA containing 1% benzoyl peroxide catalyst and 1% dimethyl aniline promoter was applied to the concrete surfaces with brushes and rollers, and a second coat was then applied. Because

of its low viscosity (2 cP), this monomer system was readily absorbed by the concrete. One percent concentrations of the promoter and catalyst were used, and a working time of 45 min was possible before gelation occurred.

After the partial impregnation, a seal coat of 53 wt % polyester, 28 wt % styrene, and 19 wt % TMPTMA was applied. The mixture, which had a viscosity of ≈ 400 cP, appeared to be effective in reducing evaporation of the impregnating monomer system; it also sealed cracks and other flaws in the concrete surface. Gelation of the sealant coat occurred in 15 min.

In addition to the VTE, mortar-lined steel pipes of 6, 8, and 10-in. diam were treated. Tees and ells were also treated. Partial impregnation and coating of short-length pipes, tees, and ells was accomplished with brushes. Longer-length pipes (up to 20 ft) were impregnated by using a long-handled swab, a 4-in.-thick piece of open-cell polyurethane foam cut to the diameter of the pipe (see Figure 14). The swab was saturated with monomer and then slowly pushed through the pipe. Several applications were required to obtain a $\frac{1}{4}$ -in. penetration. A seal coat was then applied in the same manner.

On visual inspection after 6 weeks of normal plant operation, the impregnated sections showed no signs of deterioration. Testing is continuing.

4.3.2 USBR Studies. A two-coat MMA-TMP-TMA-based monomer system was applied to one

of the multistage flash distillation chambers and to various sections of mortar-lined pipe at the OSW Demonstration Plant, Freeport, Texas. The first application was a low-viscosity monomer system designed to saturate the mortar-lined chamber to a depth of about $\frac{1}{4}$ in. A lightly promoted catalyst system was added to this monomer system to enable the monomer to soak into the mortar before polymerization began.

The second application, or top coat, consisted of a higher-viscosity monomer system that polymerizes rapidly at room temperature. This material acted as a sealant to prevent evaporative loss of the first monomer system and to provide surface protection to the mortar lining.

The low-viscosity monomer system was prepared by mixing 70 wt % MMA with 30 wt % TMPTMA. The estimated quantity needed was then measured into two equal parts, A and B. Two wt % benzoyl peroxide (BP) was then added to part A which was then dissolved in part B, which contained 0.25% of the promoter dimethyl-*p*-toluidine (DMT). The resulting catalyst-promoter concentration gave the mixture a pot life of about 15 to 25 min at 24°C.

The high-viscosity seal coat was prepared by dissolving Rohm and Haas Acryloid A-11 polymer in a 70 wt % MMA - 30 wt % TMPTMA monomer system at a concentration of 20% A-11 to 80% monomer. To accelerate the mixing process, the

Figure 14. Concrete-lined steel pipes being treated with polyester-styrene at the OSW Water Desalting Facility, Freeport, Texas.

monomer was heated to 60°C before the Acryloid powder was added. While the A-11 was being dissolved, paraffin wax (3 wt % of MMA) was added to the monomer-polymer system. After the A-11 and wax were completely dissolved in the monomer, the system was cooled and divided into two equal parts, A and B.

Just prior to application, BP (2 wt % of part A) was dissolved in part A, and DMT (4 wt % of part B) was dissolved in part B. The high viscosity of this system made the use of a high-shear mixer necessary.

Several techniques for applying the two monomer systems, including the use of two-part spray equipment, were available for use at the Freeport plant. For simplicity, however, both applications were made by paintbrush and roller. Parts A and B of the low-viscosity monomer system were mixed in a 1:1 ratio and applied to the mortar lining. Several applications were made to ensure complete saturation of the mortar surface. Immediately afterward, the seal coat was applied. The monomer system for this coat was formulated to polymerize very rapidly to prevent evaporative loss of the impregnating monomer system. In order to apply this short-pot-life system by brush and roller it was necessary to chill the components prior to use. The two parts were then mixed in a 1:1 ratio and quickly brushed onto the saturated mortar surfaces. Complete polymerization of the seal coat generally occurred in 2 to 4 min after mixing. Formulas for preparing both monomer systems are shown in Table 3.

Preliminary inspections of the treated areas after about 6 weeks of normal plant operation indicated no deterioration of the protective systems.

4.4 POLYMER-CONCRETE FABRICATION TECHNIQUES

During this report period the USBR has developed a method of preparing PC specimens that closely approach standard PIC in compressive strength and polymer content.

In initial work, a graded sand-aggregate mix closely approximating that of CP-type concrete was integrally mixed by hand with catalyzed MMA and polymerized at 70°C. The heat generated during polymerization of these specimens was quite high and as a result the samples developed relatively low compressive strengths, of the order of 8000 to 12,000 psi. Subsequent work on the method and incremental temperature control during polymerization resulted in more consistent specimens with compressive strengths of 11,000 to 12,000 psi. The addition of cross-linking and coupling agents,

Table 3
MMA-TMPTMA Monomer Systems
for Penetrating and Protective Coatings

	Weight in	
	Lb	g
Formulation for Impregnating Coat (8 lb $\approx$ 1 gal)		
(1) MMA (70 wt %)	5.60	2542.4
(2) TMPTMA (30 wt %)	2.40	1089.6
Divide into equal (4-lb) parts A and B just prior to use.		
(3) Benzoyl peroxide (2 wt % of part A) Add to part A.	0.08	36.3
(4) Dimethyl- <i>p</i> -toluidine (0.25 wt % of part B). Add to part B. ^a	0.01	4.5
Formulation for Seal Coat (8 lb $\approx$ 1 gal)		
(1) MMA (70 wt %)	4.48	2033.9
(2) TMPTMA (30 wt %)	1.92	871.7
(3) Acryloid A-11 polymer	1.60	726.4
(4) Paraffin wax (0.3 wt % of MMA)	0.01	6.1
Divide into equal parts A and B after cooling to $\approx$ 21°C just prior to use.		
(5) Benzoyl peroxide (2 wt % of part A) Add to part A.	0.08	36.3
(6) Dimethyl- <i>p</i> -toluidine (4 wt % of part B). Add to part B.	0.16	72.6

^aThis ratio of promoter will give an $\approx$ 24-min pot life at 23°C.

glass-fiber reinforcement, and a change to tert-butylazoisobutyronitrile catalyst improved the strength to 14,800 psi. As the test program advanced, hand mixing of individual 6 $\times$ 12-in. specimens became impractical, and a conventional 3/4-cu ft concrete mixer was used in accordance with the standard mixing and placing procedures for portland cement concrete.

Development of the method has continued until in its present form oven-dried Clear Creek aggregate is machine-mixed with the monomer system, placed in molds, and polymerized at room temperature by the promoter-catalyst technique. The specimens are prepared with 7 to 8% monomer by total weight of the wet mix. Depending on the maximum size of the aggregate and the amount of cross-linking agent in the monomer system, the specimens develop average compressive strengths varying from 18,400 to 20,000 psi. These mixes

Table 4

Formula for USBR Polymer-Concrete^a

Aggregate ^b		Monomer system	Weight, g
Sieve size	Weight, lb		
Pan	14.8	MMA	3457.0
100	5.6	TMPTMA	88.7
50	8.5	BP	35.5
30	8.8	DMA	17.7
16	5.3	Silane	17.7
8	5.3		
4% in.	19.2		
% to 4% in.	28.8		

MMA = methyl methacrylate.

TMPTMA = trimethanolpropane trimethacrylate.

BP = benzoyl peroxide.

DMA = dimethyl aniline.

Silane = γ -methacryloxypropyltrimethoxysilane.^aQuantity to prepare three 6-in.-diam $\times$ 12-in. cylinders.^bLocal Clear Creek sand and aggregate oven-dried at 163°C to constant weight.

have produced very consistent specimens with individual strengths that vary <2% from the mix average. The formula for a mix for three 6 $\times$ 12-in. cylinders is shown in Table 4.

Specimens prepared with this mix, using conventional concrete-mixing procedures and room-temperature polymerization, have been tested for compressive stress-strain, tensile splitting, unit weight and specific gravity, and water absorption (see Table 5.) Other specimens have been exposed to a 5% H₂SO₄ solution for two months without any apparent effect on their properties.

Initial tests have been performed in which PC was used to prepare three tunnel-lining segments. These segments were cast in the same molds as the PIC segments discussed in Section 8.2. Single-segment tests on one of the PC segments gave strength results comparable to those for PIC.

Some initial work has been done on styrene-based monomer systems polymerized at 60° to 70°C. As with the oven-cured MMA specimens, the compressive strengths have been relatively low (11,000 to 13,000 psi). A test series is under way to determine the behavior of styrene PC specimens polymerized at room temperature.

4.5 POLYMERIZATION TECHNIQUES

4.5.1 Radiation Process. In processes involving large quantities of catalyzed monomers, potentially

Table 5

Summary of Properties Tests on 6-in.-Diam $\times$ 12-in.-Long Polymer-Concrete Cylinders

Test	Temperature, °C	Result
Tensile splitting strength ^a	-26	1,510 psi
	21	1,430 psi
	88	1,370 psi
Compressive strength stress ^a	-26	24,600 psi
	21	19,600 psi
	49	15,800 psi ^b
	88	14,100 psi
Modulus of elasticity ^a	-26	6.11×10^6 psi
	21	5.28×10^6 psi
	88	4.44×10^6 psi
Poisson's ratio ^a	-26	0.24
	21	0.23
	88	0.22
Elastic limit stress ^a	-26	14,000 psi
	21	7,500 psi
	88	4,800 psi
Ultimate compressive strain	-26	5,360 $\mu\text{in./in.}$
	21	7,080 $\mu\text{in./in.}$ ^c
	88	>8,000 $\mu\text{in./in.}$
Unit weight ^a	-	149.1 lb/ft ³
Specific gravity ^a	-	2.40
Water absorption ^c	-	0.6%

^aAverage values for three specimens.^bValue for single specimen.^cAverage value for two specimens.

hazardous conditions can exist. One method of reducing this hazard is to eliminate reuse of excess monomer, but this may be uneconomical.

Experimental work was initiated to find a safer and more economical method of handling excess monomer from the concrete impregnation process. The method proposed was to first remove inhibitors from the bulk monomers by exposure to γ radiation, then impregnate the concrete with the radiation-conditioned monomer, and subsequently polymerize thermally in the absence of chemical initiators.

Initial experiments were to establish the principle of radiation conditioning followed by thermal polymerization in bulk. Test tube quantities (10 g) of various monomers containing inhibitors were irradiated and tested for polymer conversion. Polymerization occurs after the inhibitor has decomposed. The radiation doses required to remove the

Table 6
Thermal Polymerization of Radiation-Conditioned Monomers^a

Monomer	Inhibitor	Conc., ppm	Dose rate, 10 ⁵ rads/hr	Dose, 10 ⁵ rads	Conver- sion, %	Polymerization		Conver- sion, %
						T, °C	Time, hr	
MMA ^b	HQ ^c	30-40	1.65	4.95	1-3	80	48	100
MMA	HQ	30-40	—	—	—	80	48	—
MMA	HQ	30-40	1.65	4.95	1-3	85	24	100
MMA	HQ	30-40	1.65	4.95	1-3	90	<24	100
Styrene	t-BPC ^d	45-55	1.60	8.05	1-3	95	≈72	100
60% styrene - 40% TMPTMA ^e	t-BPC MEHQ ^f	30 80	1.60	4.80	1-3	95	30	100
60% styrene - 40% TMPTMA	t-BPC MEHQ	30 80						
60% styrene - 40% TMPTMA	t-BPC MEHQ	30 80	—	—	—	90	2	—
60% styrene - 40% TMPTMA	t-BPC MEHQ	30 80						
60% styrene - 40% TMPTMA	t-BPC MEHQ	30 80	3.00	2.75	1-3	90	4	100
60% styrene - 40% TMPTMA	t-BPC MEHQ	30 80						
60% styrene - 40% TMPTMA	t-BPC MEHQ	30 80	—	—	—	90	4	100
60% styrene - 40% TMPTMA	t-BPC MEHQ	30 80						
tert.-butyl styrene	t-BC ^g	10	1.60	5.06	1-3	95	48	100
tert.-butyl styrene	t-BC	10	3.00	5.25	1-3	90	13	<100
tert.-butyl styrene	t-BC	10	—	—	—	90	13	—
tert.-butyl styrene	t-BC	10	3.00	5.25	1-3	150	4	100
tert.-butyl styrene	t-BC	10	—	—	—	150	4	100

^aBulk polymerization; sample size, 10 g.

^bMMA, methyl methacrylate.

^cHQ, hydroquinone.

^dt-BPC, tert.-butyl pyrocatechol.

^eTMPTMA, trimethylolpropane trimethacrylate.

^fMEHQ, monomethyl ether of hydroquinone.

^gt-BC, tert.-butyl cathechol.

Table 7
Thermal Polymerization of Monomer-Impregnated Concrete Specimens

Sample No. ^a	Monomer system	Radiation dose, 10 ⁵ rads	Polymer loading, wt %	Thermal polymerization		Compressive strength, psi
				T, °C	Time, hr	
CP-5B-11C	MMA ^b	3.30	6.8	95	43	6,670 ^c
CP-5A-15C	MMA - 1% TMPTMA ^d	3.30	4.3	90	18	7,100 ^c
CP-5B-12C	MMA - 5% methacrylic acid	2.40	—	85, 145	20, 20	11,420 ^c
CP-5A-Y	Styrene	8.05	6.5	95	72	4,780
72.T1-10	Styrene	—	6.0	125, 200	24, 8	14,300 ^c
CP-R-8	Styrene	—	5.3	150, 200	24, 24	14,285
CP-5B-14E	Styrene - 1% TMPTMA	8.05	6.6	95	72	8,310 ^c
CP-5B-14C	60% styrene - 40% TMPTMA	3.20	8.1	95	48	21,400
CP-4B-14C	60% styrene - 40% TMPTMA	1.60	6.5	90- 95	6	15,850 ^c
CP-0-11A	60% styrene - 40% TMPTMA	—	6.6	90- 95	6	14,250 ^c
CP-HB-15C	60% styrene - 40% TMPTMA	—	7.0	90- 95	10	19,600
CP-2A-11B	90% styrene - 10% TMPTMA	—	5.4	90- 95	72	16,550 ^c
CP-R-41	80% styrene - 20% TMPTMA	—	6.0	90- 95	72	18,170
CP-4B-15E	70% styrene - 30% TMPTMA	—	6.2	90- 95	72	18,342
CP-5B-13F	tert.-butyl styrene	5.06	5.7	90, 150	20, 20	17,630
CP-4B-Y	tert.-butyl styrene	5.06	5.7	90, 150	20, 20	17,550
CP-4B-15B	tert.-butyl styrene	5.06	6.1	150	7.5	15,750 ^c
CP-4B-13F	tert.-butyl styrene	—	6.1	150	7.5	8,400 ^c

^aSpecimens, 3-in.-diam × 6-in.-long cylinders.

^bMethyl methacrylate.

^cNot fully polymerized; detected strong odor of monomer or found soft polymer.

^dTrimethylolpropane trimethacrylate.

Figure 15. Flow sheet of concrete-polymer materials plant for production of polymer-impregnated concrete by thermal polymerization of radiation-conditioned monomers.

inhibitor from various monomers are given in Table 6. The initial inhibitor concentrations shown in the table are as received from the manufacturer. The total dose requirements for destruction of inhibitor will vary with the type and concentration of inhibitor in each monomer. MMA containing 30 to 40 ppm hydroquinone required a total dose of $\approx 4.95 \times 10^5$ rads to overcome the inhibitor. After conditioning, monomer samples were exposed to temperatures of 80°, 85°, and 90°C. Polymerization at 90°C was completed in <24hr. At 80°C, ≈ 48 hr were required for complete polymerization. The rate of polymerization for MMA is highly temperature dependent. Data for styrene, styrene-TMPTMA and tert.-butyl styrene are also included in Table 6.

Following the initial bulk monomer studies, a series of tests was performed in which 3-in.-diam $\times$ 6-in.-long concrete specimens were impregnated with radiation-conditioned monomer and thermally polymerized. Complete polymerization was obtained with several monomer systems, and for those materials the strength values were comparable with those obtained for PIC produced by radiation or chemically initiated polymerization. The results of these experiments are given in Table 7.

As shown in Table 7, low strength values were obtained for several specimens that did not fully polymerize. This was particularly the case with MMA-impregnated specimens. Although the specimens were completely impregnated, the monomer at the center did not polymerize. This was observed in repeated experiments. Addition of 5% methacrylic acid to the MMA produced some improvement in strength, but complete polymerization was not achieved.

To minimize loss of monomer through evaporation at the temperatures required to give satisfactory polymerization at all times, the polymerization

was performed by subjecting the specimen to several temperatures (see Table 7). A low temperature was maintained until the gel point was reached. The temperature was then increased to complete the polymerization.

Figure 15 is a conceptual flow sheet for the production of PIC by the thermal polymerization of radiation-conditioned monomers. In this process, standard mixes of concrete are cast and cured in a concrete batch plant, then dried and placed in a closed vessel for impregnation. After evacuation the radiation-conditioned monomer is introduced and the concrete specimen is allowed to soak.

The inhibited monomer is delivered to the plant and placed in storage tanks. From these it is fed to a monomer makeup tank, where it is mixed with excess uninhibited monomer from the impregnator. The mixed recycled monomer is fed to a ⁶⁰Co γ irradiator for the time required to remove inhibitor. The monomer is then used for impregnation. After saturation, the concrete specimens are placed in ovens for polymerization.

The method of radiation conditioning followed by thermal polymerization is also applicable to the process for impregnating other porous materials and for PC composites.

4.5.2 Promoter-Catalyst Process. The thermal-catalytic and radiation polymerization techniques are normally used to produce PC and PIC composites. Currently promoter-catalyst systems are being investigated. The use of promoter-catalysts for effecting rapid polymerization at ambient temperature is particularly desirable in field-type applications, where it is impractical to use elevated temperature or radiation. A typical field application was described in Sections 4.3.1 and 4.3.2.

Promoters are chemical compounds that decompose catalysts to form free radicals, which in turn initiate the polymerization reaction. Depending

on the promoter-catalyst and monomer system used, polymerization can be initiated at temperatures well below 15°C. Increasing the temperature tends to accelerate the polymerization rate.

Several promoter-catalyst systems have been developed to initiate polymerization of the monomers currently being used to form concrete-polymer materials. These are listed in Table 8, together with data on monomer viscosity, promoter-catalyst concentrations, and the times for gel and complete polymerization at 22°C. For some systems, the gel and cure times can be changed by varying the concentrations of promoter-catalyst.

A monomer containing a promoter-catalyst system usually has a short gel time. This is a disadvantage in processing PIC, for which relatively long monomer soaking times are normally required. The short curing time at ambient temperature is an advantage, however, in surface-sealing applications such as on bridge decks or concrete-lined vessels (see Sections 4.3.1 and 4.3.2). It is also a convenient technique for producing PC.

Because of the nature of the reaction, the polymerization of monomer with promoter-catalysts starts immediately after both components have been added. The reaction is slow initially and accelerates with time. Figure 16 shows the increase in monomer viscosity with time at 20° and 32°C for MMA containing a promoter and a catalyst. At the higher temperature, polymerization occurs more rapidly, as indicated by viscosity changes. Although the monomer contains 35 ppm hydroquinone inhibitor, the onset of polymerization is immediate.

For some applications, such as surface impregnation of dense concrete, the increase in viscosity with time imposes limitations on the degree of penetration. Attempts have been made to decrease the polymerization rate by the use of additives or retarders. The results of these experiments are given in Figure 17. An increase in inhibitor concentration from 35 to 85 ppm did not appreciably extend the induction period and only slightly retarded the polymerization. The amount of inhibitor that can be added is limited, since its tendency to destroy the catalyst can result in incomplete polymerization.

The effect of adding incremental amounts of styrene monomer, which is not polymerized by the promoter-catalyst system, is also shown in Figure 17. The addition of styrene retarded the polymerization rate of MMA appreciably. The gel time was not appreciably affected by the addition of styrene in concentrations up to 5%; however, the curing time was significantly extended. Studies are being made in an attempt to predictably vary the polymerization rates of various monomer systems according to the promoter-catalysts used.

4.5.3 Thermal-Catalytic Process, Under Hot Water. Experiments have been conducted to determine the feasibility of using water to reduce monomer evaporation and drainage from concrete specimens during polymerization by radiation or thermal-catalytic techniques.

A detailed testing program is under way to determine the effects of the presence of water during the polymerization reaction on the structural and durability properties of the composite. The struc-

Table 8
Curing of Low-Viscosity Monomers

Monomer mixture	Viscosity, cP, at 25°C	Promoter, " . %	Initiator	Cure time, min	Gel time, min
60 wt % styrene – 40 wt % TMPTMA	2.0	0.5% <i>N,N</i> -dimethyl- <i>p</i> -toluidine + 0.5% dimethyl aniline	1.0% benzoyl peroxide	45	15
70 wt % MMA – 30 wt % TMPTMA	1.9	1.0% <i>N,N</i> -dimethyl- <i>p</i> -toluidine	1.0% benzoyl peroxide	10–15	5–10
MMA	0.5	0.5% <i>N,N</i> -dimethyl- <i>p</i> -toluidine + 0.5% dimethyl aniline	0.5% benzoyl peroxide + 0.5% AIBN ^a	≈60	≈20
90 wt % styrene – 10 wt % polyester	1.8	1.0% Advacat 30 ^b	1.0% methyl ethyl ketone peroxide		≈60

Temperature, 22°C.

^aAzobisisobutyronitrile.

^bCobalt(II) halide azinate.

tural properties of MMA-impregnated CP-type concrete polymerized by radiation while in direct contact with water (test series CP-8) were given in Ref. 4. Current data on durability testing are summarized in Section 5.1.1. In general, they indicate that underwater radiation-induced polymerization has no detrimental effects on the properties and may even produce benefits because of reductions in monomer loss. Similar effects have been observed

Figure 16. Change in viscosity of MMA during initial stages of polymerization by promoter-catalyst techniques. Catalysts, 1 wt % AIBN and 1 wt % benzoyl peroxide; promoters, 1 wt % dimethyl aniline and 1 wt % dimethyl toluidine.

Figure 17. Effects of additives on the change in viscosity of MMA at 32°C during initial stages of polymerization by promoter-catalyst techniques. Curve *a*, MMA containing 35 ppm hydroquinone; curve *b*, MMA containing 85 ppm hydroquinone; curve *c*, 99.5 wt % MMA - 0.5 wt % styrene; curve *d*, 98 wt % MMA - 2 wt % styrene; curve *e*, 95 wt % MMA - 5 wt % styrene.

with normal-weight and structural lightweight concretes supplied by the FHWA.⁸

The effectiveness of underwater thermal-catalytic polymerization is also being determined. Variables studied include water depth, temperature, and the use of primary encapsulating materials such as foil. It was observed that MMA evaporation losses from concrete specimens polymerized at 75°C could be essentially eliminated by the use of a 20-in. head of monomer-saturated water (MMA solubility in water at 30°C is 1.5%). PIC produced by immersing monomer-saturated samples in water preheated to 75°C was similar to that obtained by using 20°C water and subsequently heating it to 75°C. Specimens polymerized at 75°C under 6 in. of unsaturated water exhibited surface depletions of $\approx \frac{1}{8}$ in. Cross sections of PIC specimens produced by several techniques are compared in Figure 18.

Figure 18. Cross sections of CP-type concrete specimens impregnated with MMA and thermal-catalytically polymerized. GPI-1A1: wrapped in foil and polymerized under a 20-in. head of water at 75°C, with no surface depletion; GPI-1B3: wrapped in foil, immersed under a 20-in. head of water at 20°C and subsequently polymerized at 75°C, with no surface depletion; GPI-1A2: wrapped in foil, polymerized in an oven at 75°C, with surface depletion $\approx \frac{1}{8}$ in.; GPI-1B2: unwrapped, polymerized under a 20-in. head of unsaturated water at 75°C, with surface depletion $\approx \frac{1}{8}$ in.; GPI-1A3: unwrapped, polymerized under a 6-in. head of water at 75°C, with surface depletion $\approx \frac{1}{8}$ in.

On the basis of these results, the use of warm water to reduce evaporation and drainage during thermal-catalytic polymerization is completely feasible.

It should be noted that the underwater method for the radiation and thermal-catalytic processes re-

sults in the formation of polymer in the water. On draining, some polymer may adhere to the walls of the impregnator and collect in piping and valves. The problem is essentially one of design and arises primarily from the polymerization of nondrainable monomer. However, less polymer is formed in the

Table 9

Polymerization Techniques^a

Series No.	Thermal-catalytic polymerization technique	Polymerization temperature, °C	Specimen No.	Polymer loading, wt %	Compressive strength, psi
1	Steam in vessel and water jacket	80	5372	5.5	17,700
			100	5.6	16,270
			76	5.4	17,500
			86	5.0	19,100
			5322	5.0	16,450
2	Steam in vessel and water jacket	80	5206	4.5	16,900
			5226	6.2	17,500
3	Steam in vessel and water jacket, with atomization	75	5220	5.2	18,500
			5259	5.3	18,000
			5276	4.9	17,300
4	Steam in vessel and water jacket	75	SC1	10.9	17,000
			SC2	10.0	16,900
			Can 6	9.5	18,600
			Can 7	8.7	18,500
5	Steam in water jacket	60	72.209.18	5.0	17,000
			72.209.71	5.9	16,900
			72.209.77	4.7	16,700
			72.209.85	4.6	15,900
6	Wrapped and placed in oven	75	TE-47	5.5	20,860
			TE-6	5.9	21,230
7	Wrapped and placed in oven	75	TE-12	6.0	21,210
			TE-56	5.4	20,820
8	Wrapped and placed in oven	75	TE-16	5.4	21,140
			TE-27	5.9	20,960
9	Wrapped and placed in oven	75	TE-4	5.5	20,960
			TE-64	5.8	20,610
10	Wrapped and placed in oven	75	TE-33	5.8	19,890
			TE-58	4.8	19,890
11	Wrapped and placed in oven	75	TE-13	5.2	20,860
			TE-21	5.3	18,710
12	Wrapped and placed in oven	75	TE-37	5.4	18,960
			TE-38	5.9	18,960
13	Wrapped and placed in oven	75	TE-5	5.4	18,820
			TE-10	5.3	21,070
14	Wrapped and placed in oven	75	72.209.42	5.9	20,100
			72.209.69	6.0	19,800

^a 6-in.-diam × 12-in.-long cylinders impregnated with MMA and catalyzed with tert.-butylazoisobutyronitrile (D-A79).

thermal-catalytic than in the radiation process, probably because of the decreased solubility of MMA in water at the elevated temperature. The problem can be minimized by proper design, and reduced evaporation and drainage losses more than compensate for it.

Large-scale testing of underwater polymerization is being done in the preparation of pipe specimens for the ACPA and in the USBR tunnel support and lining program. These studies are discussed in Sections 8.1.2 and 8.2, respectively.

4.5.4 Thermal-Catalytic Process, Using Steam.

Experiments were conducted to evaluate the feasibility of thermal-catalytic polymerization of tert-butylazoisobutyronitrile-catalyzed MMA-impregnated concrete specimens by filling the impregnation vessel with steam. This method eliminates the wrapping of specimens for the polymerization process and reduces handling of specimens. Polymerization heat was applied to the specimens by two procedures: (1) injecting steam directly into the impregnation vessel (inner tank steam) and steam-heating the water in the water jacket surrounding the vessel, and (2) steam-heating only the water in the water jacket. Results to date indicate that compressive strengths for both steam-heating methods are lower than those obtained with wrapped specimens polymerized in an oven. These data are shown in Table 9. Polymerization times for steam heating and oven heating are nearly the same.

Solenoids controlled by thermostats were used to automatically open and close steam valves in order to reach and maintain the desired vessel temperature. After this temperature had been maintained for an hour, the controls were switched off and steam valves closed. The insulation around the vessel helped to maintain the temperature until polymerization had started. The polymerization reaction is exothermic; thus the temperature in the vessel increased.

Temperature controls for specimens polymerized by using the inner tank steam and water jacket simultaneously were set for 75° and 80°C, respectively. In one experiment, only the water in the jacket was steam-heated, with the temperature control set at 60°C. The oven temperature during polymerization was controlled at 75°C by a thermostat.

Specimens polymerized by both steam techniques showed a monomer loss from the exterior surfaces varying from about $\frac{1}{16}$ to $\frac{1}{4}$ in. in depth. This loss

is greater than that normally obtained with wrapped specimens and is assumed to result from evaporation during heating and polymerization.

An attempt was made to reduce MMA monomer loss by atomizing MMA monomer vapor into the top of the impregnation vessel during the polymerization cycle. By saturating the air inside the vessel with monomer vapor, it was hoped that evaporation from the surfaces would be reduced. The technique reduced monomer loss from exterior surfaces in some instances, but was difficult to control and in general gave inconsistent results.

The compressive strengths for steam-polymerized specimens are lower than those for wrapped and oven-polymerized specimens (see Table 9). This is probably because of the increased evaporation losses. The average compressive strength of 6-in.-diam $\times$ 12-in.-long oven-polymerized specimens was 20,000 psi. Specimens polymerized with the combined inner-vessel steam and water-jacket heat gave an average strength of 17,800 psi. In one test in which only the steam-heated water jacket was used as a source of heat, the strengths averaged 16,600 psi. Specimens from this test showed large amounts of monomer depletion from the exterior surfaces.

Since wrapping large specimens is impractical and expensive, work will continue to develop improved steam polymerization techniques. At present the use of steam to heat water in which the monomer-saturated specimens are immersed (see Section 4.5.3) appears to be the best method of reducing monomer depletion in a practical manner.

5. TEST RESULTS ON POLYMER-IMPREGNATED CONCRETE

Tests of structural and durability properties are conducted on PIC for normal-temperature applications and for high-temperature desalting plant applications. PIC for these two applications is currently made from one basic type of concrete, but different monomer systems are used. Those for desalting plant applications produce polymers that withstand high temperature and exposure to brine and water without softening or decomposing. Monomers for normal-temperature applications are generally polymerized by γ radiation from a ^{60}Co source, and monomers for high-temperature applications are thermal-catalytically polymerized. In addition, tests are performed on partially impregnated CP-type concrete to develop a tech-

Table 10

Property	Unimpregnated concrete			MMA impregnated, ^a CP-1 series		S impregnated, ^a CP-2 series	
	Controls, CP-0 series	CP-3 series		R	T	R	T
		R ^b	T ^b				
Compressive strength, psi	5,270	4,950	5,260	20,260	18,160	14,140	8,790
% improvement	—	—6	0	285	244	168	67
Modulus of elasticity, 10 ⁶ psi	3.5	2.7	2.9	6.3	6.2	6.3	5.2
% improvement	—	—23	—17	80	77	83	48
Tensile strength, ^c psi	420	335	388	1,630	1,510	1,100	720
% improvement	—	—19	—7	290	262	165	73
Modulus of rupture, psi	740	632	666	2,640	2,290	2,300	1,060
% improvement	—	—15	—10	256	210	211	44
Flexural elasticity modulus, 10 ⁶ psi	4.3	3.0	3.4	6.2	7.1	6.3	5.1
% improvement	—	—30	—21	44	65	47	19
Creep, ^d μ in./in.	200 ^e	117 ^f	42 ^f	6 ^g	141 ^{g,h}	141	222 ⁱ
Hardness, "L" type impact hammer	32	27	27	55	52	48	50
% improvement	—	—15	—15	73	62	51	56
Abrasion loss, in.	0.0497	0.0352	0.0357	0.0163	0.0147	0.0400	0.0365
% improvement	—	35	28	67	70	19	27
Loss in weight, g	14	6	7	4	4	9	6
% improvement	—	57	50	71	71	36	57
Cavitation, in., 2-hr exposure	0.320	0.368	0.262	0.064	0.020	0.035	0.009
% improvement	—	—15	18	80	94	89	97
Water absorption, %	6.40	6.5	6.2	1.08	0.34	0.51	0.70
% decrease	—	—2	3	83	95	92	89
Water permeability, 10 ⁴ ft/yr	5.3	32.0	29.0	0.8	1.4	8.2	1.5
% decrease	—	—500	—450	85	73	—55	72
Thermal conductivity, 23°C, Btu/ft-hr-°C	2.398	1.915	1.989	2.351	2.277	2.246	2.349
% decrease	—	20	17	2	5	4	2
Diffusivity at 23°C, ft ² /hr	0.0697	0.0637	0.0704	0.0736	0.0693	0.0715	0.0734
% increase	—	—9	1	6	0	3	5
Coefficient of expansion, μ in./in.-°C	7.24	7.60	7.70	9.65	9.45	9.16	9.00
% increase	—	5	6	33	31	27	24
Specific heat, 23°C, Btu/lb-°C	0.434	—	—	0.385	0.396	0.382	0.398
% reduction	—	—	—	11	9	12	8
Specific gravity	4.171	—	—	4.304	4.295	4.419	4.261

Results are representative values, based on 3 or more specimens, for each property.

Specimens oven-dried at 150°C prior to impregnation.

Specimen sizes: compressive strength, 3×6-in. cylinders; tensile strength, 3×6-in. cylinders; flexural strength, 3×3×14-in. bars; creep tests, 6×12-in. cylinders. Other specimens sized according to test requirements.

^aMMA = methyl methacrylate; S = styrene; TMPTMA = trimethylolpropane trimethacrylate; AN = acrylonitrile; CS = chloro-styrene; PE = polyester.

^bR = radiation treatment; T = thermal-catalytic treatment.

^cTensile strengths are obtained by the direct tension method.

^dCreep under sustained compressive load of 800 psi.

^eLoaded for 1482 days.

Summary of Mechanical and Physical Properties of Polymer-Impregnated Concrete

MMA + 10 TMPTMA CP-4 series		AN impregnated, ^a CP-5 series		CS impregnated, ^a CP-6 series		PE + 10 S, ^a CP-7 series	MMA impregnated, ^a polymerized under water, CP-8 series
R	T	R	T	R	T	R	R
21,590	19,000	14,410	10,750	16,090	14,800	20,500	23,800
310	260	174	104	205	173	289	352
6.1	4.8	5.9	4.2	5.6	5.6	6.5	6.4
75	38	67	20	60	60	86	83
1,510	1,250	1,040	870	1,120	1,200	1,530	1,700
261	200	150	113	167	190	264	305
2,220	—	1,470	620	2,380	1,580	3,300	2,100
200	—	99	—16	223	114	346	184
6.1	—	4.5	3.5	6.3	5.0	6.4	7.6
40	—	5	—19	47	16	49	77
32 ^k	—	45 ^l	73 ^l	50 ^m	47 ^m	3 ⁿ	28 ⁿ
54	—	47	34	30	28	—	—
69	—	48	5	—6	—11	—	—
0.044	0.019	0.030	0.026	—	—	0.024	0.025
10	61	40	49	—	—	52	50
10	5	8	6	—	—	3	2
29	64	45	57	—	—	79	86
0.074	—	0.099	0.092	0.072	0.115	0.019	0.016
77	—	69	71	77	64	94	95
1.09	0.21	2.95	5.68	0.88	1.97	0.67	0.06
83	97	54	11	86	69	90	—
0.01	1.2	—	—	—	—	0	0
99	77	—	—	—	—	100	100
2.381	—	2.243	2.245	2.340	2.394	—	2.279
1	—	6	6	2	0	—	5
0.0792	—	0.0738	0.0702	0.0792	0.0720	—	0.0754
14	—	6	0	13	3	—	8
9.11	9.11	8.84	8.24	8.41	8.59	—	8.80
26	26	22	14	16	19	—	22
0.373	—	0.376	0.396	0.362	0.405	—	0.369
14	—	1.3	9	17	6	—	15
4.219	—	4.185	4.192	4.248	4.271	4.207	4.261

^f Loaded for 1451 days.^g Loaded for 1552 days.^h Specimens exhibit negative creep, i.e., an expansion in length under compressive load.ⁱ Loaded for 1534 days.^j Radiation-polymerized styrene-impregnated specimens show a large difference in creep. One specimen has 17 $\mu\text{in./in.}$ creep improvement of 89% as compared with control concrete; the other has a negative creep of 150 $\mu\text{in./in.}$ ^k Loaded for 344 days.^l Loaded for 1056 days.^m Loaded for 1010 days.ⁿ Loaded for 204 days.

nique for impregnating the surfaces of concrete to a controlled depth.

Originally, two types of concrete were tested, one designed for normal-temperature applications (CP-type concrete), and the other for high-temperature applications (OSW-type concrete). Tests have shown that CP-type concrete, impregnated with the same monomers for high-temperature applications as those used with OSW-type concrete, has strength comparable to that of OSW-type PIC. References to the OSW-type concrete will be found throughout the text because long-term tests are still in progress.

Concrete designated as CP-type is of a standard mix made with 5.5 sacks/cu yd of type II laboratory-blend portland cement, Clear Creek aggregate graded to 3/4-in. maximum size, 0.51 water-to-cement ratio, 3-in. slump, and 6% entrained air. When the specimen size is such that 1 1/2-in. maximum-sized aggregate should be used, the mix is adjusted accordingly.

Concrete designated as OSW-type is a special high-strength mix designed for use in desalting plants. It is made with 6 sacks/cu yd of type V portland cement, 1.8 sacks/cu yd of fly ash pozzolan, 0.35 water-to-cement plus pozzolan ratio a water-reducing agent, air entrainment, and a high-quality aggregate graded to 1 1/2-in. maximum size.

Tests are usually made on concrete at 120 days of age. In monomer survey tests, both undried concrete (exposed to air following removal from the 28-day fog cure) and oven-dried concrete are monomer impregnated. Experience with the monomer systems tested has shown that oven-dried concrete is more fully impregnated by monomer and has greater improvements in properties than the undried concrete. Unless otherwise stated, test results on PIC are for concrete oven-dried prior to impregnation.

The majority of the test results are obtained from relatively few specimens and are to be considered indicative of the properties of PIC. They are not intended to be used as a basis for final design of engineering structures.

Preliminary design values for both the unimpregnated control and the impregnated concrete have been determined where sufficient test data are available. The design values were obtained on the assumption that the group of specimens tested represented a random sample of all future specimens of a given type made under the same con-

ditions. The mean value, standard deviation, and coefficient of variation were obtained in each group of tests. If the coefficient of variation is $\leq 15\%$, the design value equals the mean value minus the standard deviation. If the coefficient of variation is $> 15\%$, the value reported is the same as the design value, but it is noted that in this area more test data are needed. Design values for preliminary design purposes are presented in Section 5.1.2 for normal-temperature applications, and in Section 5.2.1 for high-temperature applications. These are initial values and will be refined as additional data become available.

5.1 POLYMER-IMPREGNATED CONCRETE FOR AMBIENT-TEMPERATURE APPLICATIONS

5.1.1 CP Test Series. The program consists of a series of structural and durability tests on CP-type concrete impregnated with various monomers. Each test series consists of 38 specimens. Descriptions of specimen preparation and test procedures are given in Ref. 1.

The CP test series are designated as follows:

CP-0	Control (unimpregnated concrete).
CP-1A	MMA, radiation polymerized.
CP-1B	MMA, thermal-catalytically polymerized.
CP-2A	Styrene, radiation polymerized.
CP-2B	Styrene, thermal-catalytically polymerized.
CP-3A	Unimpregnated, radiation treated.
CP-3B	Unimpregnated, thermally treated.
CP-4A	MMA - 10 wt % TMPTMA, radiation polymerized.
CP-4B	MMA - 10 wt % TMPTMA, thermal-catalytically polymerized.
CP-5A	Acrylonitrile, radiation polymerized.
CP-5B	Acrylonitrile, thermal-catalytically polymerized.
CP-6A	Chlorostyrene, radiation polymerized.
CP-6B	Chlorostyrene, thermal-catalytically polymerized.
CP-7A	10 wt % polyester - 90 wt % styrene, radiation polymerized.
CP-8A and CP-UA	MMA, radiation polymerized under water.

Test results for all but the CP-7A series have been presented in previous topical reports¹⁻⁴ and are summarized in Table 10. Tests on CP-7A specimens are in progress and results to date are reported below.

5.1.1.1 STRUCTURAL AND PHYSICAL PROPERTIES OF 10 WT % POLYESTER - 90 WT % STYRENE IMPREGNATED CONCRETE. The CP-7A test specimens were prepared from CP-type concrete, impregnated with 10 wt % polyester - 90 wt % styrene by the standard vacuum-soak method and polymerized by radiation. The series includes

Table 11

**Compressive and Tensile Strengths of CP-Type Concrete
Impregnated With 10 wt % Polyester - 90 wt % Styrene**

CP-7 Test Series

Compression tests					Direct tension tests			
Specimen No., CP-7-	Polymer loading, wt %	Treatment	Compressive strength, psi	Modulus of elasticity, 10^6 psi	Specimen No., CP-7-	Polymer loading, wt %	Treatment	Tensile strength, psi
1A ^a	4.1	U	9,480	4.5	2B ^b	4.6	U	480
1B ^a	3.9	U	8,910	4.8	2C	4.0	U	540
1C ^a	4.9	U	9,280	4.4				
Av	4.3		9,220	4.6		4.3		510
1D	6.8	D	20,820	6.4	2D	6.8	D	1,680
1E	6.3	D	19,940	6.7	2E	6.7	D	1,120
1F	7.0	D	20,760	6.3	2F	6.8	D	1,800
Av	6.7		20,510	6.5		6.8		1,530

3×6-in. specimens, radiation polymerized.

U = specimens not oven-dried prior to impregnation.

D = specimens oven-dried at 110°C prior to impregnation.

^aOnly about two-thirds of cross section appeared impregnated on visual inspection after testing.

^bSpecimen cracked prior to testing.

Table 12

**Flexural Strength of CP-Type Concrete
Impregnated With 10 wt % Polyester - 90 wt % Styrene**

CP Test Series

Specimen No., CP-7-	Polymer loading, wt %	Specimen treatment	Modulus of rupture, psi	Modulus of elasticity, 10^6 psi
5A	3.2 ^a	U	1400	6.1
5B	3.6 ^a	U	1730	6.4
5C	2.6 ^a	U	1480	6.3
Av	3.1		1540	6.3
5E	7.4	D	3350	7.0
5F	6.9	D	3300	5.8
Av	7.2		3330	6.4

3×3×16¼-in. beams.

Radiation-initiated polymerization.

U = specimens not oven-dried prior to impregnation.

D = specimens oven-dried at 110°C prior to impregnation.

^aSpecimens not fully impregnated; unimpregnated zones were observed in the center of the beams.

Table 13

**Shotblast Abrasion
CP-7 and CP-8 Test Series**

		Abrasion ¹¹	
Specimen No.	Polymer loading, wt %	Depth, in.	Weight loss, g
CP-7-10A	6.8	0.020	3
10B	6.7	0.033	3
10C	6.5	0.020	2
Av	6.7	0.024	3
CP-UA-10A	6.8	0.025	2
10B	6.7	0.029	2
10C	6.7	0.020	1
Av	6.7	0.025	2

CP-type concrete, 2×3×7-in. specimens.

CP-7 specimens oven-dried at 110°C and impregnated with 10 wt % polyester - 90 wt % styrene.

CP-UA specimens (CP-8 test series) oven-dried at 105°C, impregnated with MMA, dipped in PMMA, and polymerized under water.

All specimens polymerized by radiation.

undried specimens and specimens oven-dried at 105°C prior to impregnation.

(a) COMPRESSIVE STRENGTH AND MODULUS OF ELASTICITY. The oven-dried PIC specimens had an average compressive strength of 20,500 psi and a modulus of elasticity of 6.5×10^6 psi as compared with 9200 psi and 4.6×10^6 psi for the undried PIC specimens. The compressive strength of oven-dried specimens is comparable with that of the oven-dried MMA-impregnated (CP-1), MMA - 10 wt % TMPTMA impregnated (CP-4), and MMA-impregnated, underwater-polymerized (CP-8) specimens, and is an improvement of 289% over the strength of unimpregnated concrete. Visual

examination of specimens after testing disclosed that the undried specimens were not fully impregnated. Test results are given in Table 11.

(b) TENSILE STRENGTH. Direct tensile strengths averaged 1530 psi for oven-dried and 510 psi for undried PIC specimens (Table 11). The oven-dried specimens are comparable with the corresponding specimens from the CP-1, CP-4, and CP-8 series and show an improvement of 264% over unimpregnated concrete.

(c) FLEXURAL STRENGTH. Modulus of rupture averaged 3330 psi for oven-dried and 1540 psi for undried PIC specimens (Table 12). The modulus for the oven-dried specimens is the highest obtained so

Table 14

Property	Unimpregnated concrete			MMA impregnated, ^a CP-1 test series		S impregnated, ^a CP-2 test series	
	Controls, CP-0 test series	CP-3 test series		R	T	R	T
		R ^b	T ^b				
Freeze-thaw durability							
Polymer loading, %	-	-	-	5.9	6.8	4.9	4.4
No. of cycles	740	440	440	10,340	3,650	2,635	6,015
% weight loss	25	28	35	12	2	25	25
% improvement	-	-	-	>1,297	>393	256	713
Sulfate attack							
Polymer loading, %	-	-	-	6.6 ^d	6.4	5.4	4.5 ^d
Test cycle, days	480	750	605	1,436	1,436	1,420	1,420
% expansion	0.467	0.553	0.522	0.032	0.017	0.039	0.042
% improvement	-	56	26	>199	>199	>196	>196
Resistance to acid (15% HCl)							
Polymer loading, %	-	-	-	6.1 ^b	6.4 ^d	4.9	4.6
Exposure, days	105	103	106	1,395	1,395	1,395	1,395
% weight loss	27	26	26	13	10	17	14
% improvement	-	-	-	>1,229	>1,229	>1,229	>1,229
Resistance to acid (15% H ₂ SO ₄)							
Polymer loading, %	-	-	-	5.7	5.7 ^d	5.4	4.0
Exposure, days	49	63	77	126	119	91	77
% weight loss	35	30	30	29	26	27	29
% improvement	-	29	17	157	143	86	57
Resistance to acid (5% H ₂ SO ₄)							
Polymer loading, %	-	-	-	5.9 ^l	-	-	-
Exposure, days	210	-	-	210	-	-	-
% weight loss	33	-	-	14	-	-	-
% improvement	-	-	-	-	-	-	-

3×6-in. specimens, oven-dried at 105°C prior to impregnation.

Results are averages for two specimens, except as noted.

^a MMA = methyl methacrylate; S = styrene; TMPTMA = trimethylolpropane trimethacrylate; AN = acrylonitrile; CS = chloro-styrene; PE = polyester.

^b R = radiation treatment; T = thermal-catalytic treatment.

^c Single specimen; companion failed (25% weight loss) at 3350 cycles.

far in the CP test series. The previous high value (2640 psi) was for MMA-impregnated and radiation-polymerized specimens. Unimpregnated conventional concrete had a modulus of rupture of 740 psi.

(d) ABRASION RESISTANCE. Shotblast abrasion test results, given in Table 13, show good abrasion resistance for CP-7 specimens. Abrasion losses averaged 0.024 in. and 3 g. CP-8 specimens had comparable abrasion resistance, with losses averaging 0.025 in. and 2 g.

(e) PERMEABILITY. Water permeability tests, conducted under a pressure of 400 psi, showed no measurable permeability for both CP-7 and CP-8 specimens.

5.1.1.2 DURABILITY TESTS. Tests were made of freeze-thaw durability and resistance to chemical attack by sulfates, acids, and sodium hydroxide. The acid tests have included 15% HCl and 15% H₂SO₄; current testing is with 5% H₂SO₄, which was selected as being more representative of a severe exposure for sewer pipe. Test results to date are summarized in Table 14.

(a) FREEZE-THAW DURABILITY. In this test, specimens are immersed in water and alternately frozen at -1°C and thawed at 20°C at a rate of about 50 cycles per week. The criterion for failure is 25% weight loss. According to past experience, conventional concrete withstanding 500 to 700 cycles is

Summary of Durability Properties of Polymer-Impregnated Concrete, CP Test Series

MMA + 10 TMPTMA impregnated, ^a CP-4 test series		AN impregnated, ^a CP-5 test series		CS impregnated, ^a CP-6 test series		PE + 10 S impregnated, ^a CP-7 test series	MMA impregnated, ^a polymerized under water, CP-8 test series
R	T	R	T	R	T		
6.2 ^c	7.2 ^d	5.1	5.5 ^e	6.2	6.4	7.0	7.0
7,870	9,450	1,690	8,910	1,900	4,660	1,530	2,780
25	0	25	11	25	25	1	2
964	>1,177	128	>1,104	157	530	>107	>276
6.5 ^d	7.3	5.1 ^f	6.0 ^g	6.0	6.4	6.7	6.9
1,326	1,326	540	1,100	732	905	62	320
0.024	0.012	0.462	0.032	0.632	0.024	0.002	0.012
>176	>176	12	>129	53	>89	-	-
6.1	7.1 ^d	5.2	5.4	6.0	6.4	-	-
1,289	1,289	1,213	1,213	882	882	-	-
14	9	17	13	13	12	-	-
>1,128	>1,128	>1,055	>1,055	>740	>740	-	-
6.1	-	4.4 ^d	3.8	6.4	5.7	-	-
126	-	77	70	84	77	-	-
27	-	28	33	28	26	-	-
157	-	57	43	71	57	-	-
-	-	-	-	-	-	6.8	7.2
-	-	-	-	-	-	252	252
-	-	-	-	-	-	17	17
-	-	-	-	-	-	-	-

Single specimen; companion removed for display.

Single specimen; companion failed (25% weight loss) at 8710 cycles.

Single specimen; companion removed at 180 days because of excessive deterioration.

Single specimen; companion removed at 390 days because of excessive deterioration.

Single specimen; companion removed at 1216 days with 13% weight loss.

Average of six specimens.

considered to be of good quality, and that withstanding 1000 cycles is considered of excellent quality. The unimpregnated concrete used as a control failed at 740 cycles. All CP-series PIC specimens show greatly improved resistance to freezing and thawing, ranging from 128 to >1279% improvement as compared with conventional con-

crete (Table 15). The PIC specimen with the greatest improvement in freeze-thaw durability is an MMA-impregnated and radiation-polymerized specimen from an earlier survey. This specimen has a weight loss of only 0.5% after 12,010 cycles, an improvement of >1523% over unimpregnated concrete. CP-series specimens that have

Table 15
Resistance to Freezing and Thawing of Polymer-Impregnated Concrete
CP Test Series

Specimen No.	Monomer ^a	Polymer loading, wt %	Method of polymerization ^b	Number of test cycles	Weight loss, %
Control	-	-	-	590 ^d	26.5
BNL-1-3 ^c	MMA	6.7	R	12,010	0.5
CP-0-3A	-	-	-	490 ^d	25.0
CP-0-3B	-	-	-	990 ^d	26.0
CP-1A-3A	MMA	5.9	R	8,310 ^e	9.0
CP-1A-3B	MMA	5.9	R	10,340 ^f	12.5
CP-1B-3A	MMA	6.9	T	3,650 ^e	1.5
CP-1B-3B	MMA	6.6	T	3,650 ^e	2.0
CP-2A-3A	S	4.8	R	2,010 ^d	25.0
CP-2A-3B	S	4.9	R	3,260 ^d	26.0
CP-2B-3A	S	4.5	T	6,290 ^d	25.0
CP-2B-3B	S	4.3	T	5,740 ^d	26.0
CP-3A-3A	-	-	R	360 ^d	30.0
CP-3A-3B	-	-	R	490 ^d	26.0
CP-3B-3A	-	-	T	440 ^d	40.0
CP-3B-3B	-	-	T	440 ^d	30.0
CP-4A-3A	MMA + TMPTMA	6.2	R	3,350 ^d	33.0
CP-4A-3B	MMA + TMPTMA	6.2	R	7,870 ^d	24.5
CP-4B-3A	MMA + TMPTMA	7.2	T	1,230 ^d	0.5
CP-4B-3B	MMA + TMPTMA	7.1	T	9,450	0
CP-5A-3A	AN	5.1	R	1,840 ^d	25.0
CP-5A-3B	AN	5.0	R	1,540 ^d	25.0
CP-5B-3A	AN	5.6	T	8,910	11.0
CP-5B-3B	AN	5.3	T	8,710 ^d	25.0
CP-6A-3A	CS	6.3	R	2,000 ^d	25.0
CP-6A-3B	CS	6.2	R	1,800 ^d	25.0
CP-6B-3A	CS	6.3	T	4,710 ^d	25.0
CP-6B-3B	CS	6.5	T	4,610 ^d	25.0
CP-UA-3A	MMA	7.1	R	2,780	1.0
CP-UA-3B	MMA	6.9	R	2,780	3.0
CP-7-3A	PE-S	7.0	R	1,530	1.0
CP-7-3B	PE-S	6.9	R	1,530	1.5

3×6-in. cylinders, oven-dried at 105°C prior to impregnation.

^a MMA = methyl methacrylate; S = styrene; TMPTMA = trimethylolpropane trimethacrylate; MMA + TMPTMA = MMA - 10 wt % TMPTMA; AN = acrylonitrile; CS = chlorostyrene; PE-S = 10 wt % polyester - 90 wt % styrene.

^b R = radiation; T = thermal-catalytic.

^c Specimen not oven-dried prior to impregnation.

^d Removed from test.

^e Failed (weight loss >25%) and removed from test.

^f Specimen split into two pieces.

not reached failure and are still under test include a thermal-catalytically polymerized MMA - 10 wt % TMPTMA specimen with no weight loss after 9450 cycles, a thermal-catalytically polymerized acrylonitrile specimen with 11% weight loss after 8910 cycles, two underwater radiation-polymerized MMA specimens (CP-UA series) with

2% weight loss after 2780 cycles, and two radiation-polymerized polyester-styrene specimens (CP-7 series) with 1% weight loss at 1530 cycles. A radiation-polymerized specimen (CP-1 series) split in half at 10,340 cycles with a weight loss of 12.5%.

(b) RESISTANCE TO SULFATE ATTACK. Results of accelerated sulfate attack tests are updated in Table 16. The

Table 16
Resistance to Sulfate Attack of Polymer-Impregnated Concrete
CP Test Series

Specimen No.	Monomer ^a	Polymer loading, wt %	Method of polymerization ^b	Test cycles, days	Net expansion, %
Control	-	-	-	1486	0.550 ^d
MMA-10 ^c	MMA	6.3	R	1486	-0.030
S-14 ^c	S	6.2	R	1477	0.006
CP-0-4A	-	-	-	480	0.502 ^d
CP-0-4B	-	-	-	480	0.432 ^d
CP-1A-4A	MMA	6.1	R	540	0.016 ^e
CP-1A-4B	MMA	6.6	R	1436	0.032
CP-1B-4A	MMA	6.3	T	1436	0.018
CP-1B-4B	MMA	6.6	T	1436	0.016
CP-2A-4A	S	5.1	R	1420	0.036
CP-2A-4B	S	5.7	R	1420	0.042
CP-2B-4B	S	4.5	T	1420	0.042
CP-3A-4A	-	-	R	750	0.580 ^d
CP-3A-4B	-	-	R	750	0.536 ^d
CP-3B-4A	-	-	T	605	0.496 ^d
CP-3B-4B	-	-	T	605	0.548 ^d
CP-4A-4A	MMA + TMPTMA	6.1	R	360	0.004 ^e
CP-4A-4B	MMA + TMPTMA	6.5	R	1326	0.024
CP-4B-4A	MMA + TMPTMA	7.4	T	1326	0.018
CP-4B-4B	MMA + TMPTMA	7.2	T	1326	0.006
CP-5A-4A	AN	5.1	R	540	0.462 ^d
CP-5A-4B	AN	5.3	R	180	0.096 ^f
CP-5B-4A	AN	5.0	T	390	0.150 ^g
CP-5B-4B	AN	6.0	T	1100	0.034
CP-6A-4A	CS	6.1	R	732	0.466 ^d
CP-6A-4B	CS	5.8	R	732	0.798 ^d
CP-6B-4A	CS	6.3	T	905	0.028
CP-6B-4B	CS	6.6	T	905	0.020
CP7-4A	PE-S	6.6	R	62	0
CP7-4B	PE-S	6.8	R	62	0.004
CP-UA-4A	MMA	7.1	R	390	0.016
CP-UA-4B	MMA	6.7	R	390	0.014

3×6-in. specimens, oven-dried at 105°C prior to impregnation.

^aMMA = methyl methacrylate; S = styrene; TMPTMA = trimethylolpropane trimethacrylate; MMA + TMPTMA = MMA - 10 wt % TMPTMA; AN = acrylonitrile; CS = chlorostyrene; PE-S = 10 wt % polyester - 90 wt % styrene.

^bR = radiation; T = thermal-catalytic.

^cSpecimen not oven-dried.

^dSpecimen failed, removed from test.

^eRemoved from test for display.

^fLoose insert from specimen deterioration, removed from test.

Table 17
Compressive Strength of Polymer-Impregnated Concrete After Exposure to 5% NaOH
CP-Type Concrete

Monomer	Specimen No.	Polymer loading, wt %	Exposure in 5% NaOH		Compressive strength, psi
			Days	Weight change, %	
Unimpregnated controls	17	—	382	+0.4	6,800
	18	—	382	+0.5	6,700
PE-S	7	7.1	382	+0.8	15,700
	8	5.7	382	+1.0	9,000
MMA	2	7.3	382	+0.6	18,900
	6	5.6	382	+0.6	16,300
Unimpregnated controls	20	—	382	+0.5	6,400
	21	—	382	+0.4	6,200
S-TMPTMA	5	7.1	382	+0.4	19,300
	12	7.5	382	+0.5	16,000
DAP-MMA	4	8.5	382	+0.8	16,300
	13	7.9	382	+0.8	12,200

3×6-in. specimens, oven-dried at 150°C prior to impregnation.

PE-S = 10 wt % polyester - 90 wt % styrene, radiation polymerized.

MMA = methyl methacrylate, radiation polymerized.

S-TMPTMA = 60 wt % styrene - 40 wt % TMPTMA, thermal-catalytically polymerized.

DAP-MMA = 90 wt % DAP - 10 wt % MMA, thermal-catalytically polymerized.

Table 18
Resistance of Polymer-Impregnated Concrete to 5% H₂SO₄

Monomer	Specimen No.	Polymer loading, wt %	Exposure, days	Weight loss, %
PE-S	CP-7-17A	6.6	252	17.5
	19B	6.9	252	16.3
MMA ^a	CP-UA-19A	7.3	252	13.2
	19B	7.1	252	21.3
PE-S	CP-R- 2	6.5	210	14.5
	22	6.6	210	14.2
	23	6.4	210	14.6
	51	6.5	210	13.4
	64	6.3	210	15.0
	72	6.4	210	16.4
MMA	CP-4B-15A	6.5	210	10.2
	4B-15D	5.6	210	18.5
	5B-11A	6.3	210	15.9
	5B-12D	5.6	210	13.0
	5B-14A	5.4	210	14.7
	5B-15B	6.0	210	13.3
Unimpregnated	CP-DP-76	—	210	33.6 ^b
	82	—	210	32.4 ^b

3×6-in. specimens, oven-dried at 110°C prior to impregnation.

Radiation polymerization.

PE-S = 10 wt % polyester - 90 wt % styrene.

MMA = methyl methacrylate.

^aRadiation polymerization under water.

^bFailed (weight loss >25%).

Table 19

Resistance of Polymer-Impregnated Concrete to 15% HCl

CP Test Series

Specimen No.	Monomer ^a	Polymer loading, wt %	Method of polymerization ^b	Days in test	Weight loss, %	Compressive strength, psi
CP-0-17A	-	-	-	105	27.0 ^c	-
CP-0-17B	-	-	-	105	26.1 ^c	-
CP-1A-17A	MMA	6.1	R	1395	12.5	2300
CP-1A-17B	MMA	6.0	R	1216	13.4 ^d	2300
CP-1B-17A	MMA	6.6	T	1395	10.2	1780
CP-1B-17B	MMA	6.1	T	497	7.6 ^d	-
CP-2A-17A	S	4.9	R	1395	17.2	1400
CP-2A-17B	S	4.9	R	1395	17.6	1300
CP-2B-17A	S	4.6	T	1395	12.6	850
CP-2B-17B	S	4.6	T	1395	14.5	820
CP-3A-17A	-	-	R	96	25.0 ^c	-
CP-3A-17B	-	-	R	110	28.3 ^c	-
CP-3B-17A	-	-	T	102	26.7 ^c	-
CP-3B-17B	-	-	T	110	26.1 ^c	-
CP-4A-17A	MMA+TMPTMA	6.2	R	1289	13.8	2400
CP-4A-17B	MMA+TMPTMA	6.0	R	1289	15.1	2200
CP-4B-17A	MMA+TMPTMA	7.2	T	1289	8.6	2100
CP-4B-17B	MMA+TMPTMA	7.1	T	391	5.7 ^d	-
CP-5A-17A	AN	5.2	R	1213	17.1	1500
CP-5A-17B	AN	5.3	R	1213	16.8	1500
CP-5B-17A	AN	5.4	T	1213	13.4	1100
CP-5B-17B	AN	5.4	T	1213	12.6	1000
CP-6A-17A	CS	6.0	R	882	13.4	1600
CP-6A-17B	CS	6.1	R	882	13.2	1800
CP-6B-17A	CS	6.5	T	882	12.3	1800
CP-6B-17B	CS	6.3	T	882	11.2	1800

3×6-in. cylinders, oven-dried at 105°C prior to impregnation.

^aMMA = methyl methacrylate; S = styrene; TMPTMA = trimethylolpropane trimethacrylate; MMA+TMPTMA = MMA - 10 wt % TMPTMA; AN = acrylonitrile; CS = chlorostyrene.

^bR = radiation; T = thermal-catalytic.

^cFailed (weight loss >25%), removed from test.

^dRemoved from test.

Table 20

Weatherometer Tests

Polymer-Impregnated Concrete

Sample No.	Monomer	Polymer loading, wt %	Exposure time, hr	Remarks
2.5.2-B-1	MMA	6.5	3000	No deterioration
-2	PE-S	6.5	3000	No deterioration
2.5.3.5.5-1	S-TMPTMA	4.4	5900	Minor scaling (<10% of surface area)
-2	DAP-MMA	4.1	5900	Polymer in voids is yellowing and shrinking
-3	Unimpregnated	-	5900	Entire surface area leached to depth of 1/8 in.
OSW-CP				
1,2,3	Unimpregnated	-	6000	Entire surface area leached
4,5,6	S-TMPTMA	6.5	6000	Minor scaling (<10% of surface area)

MMA = methyl methacrylate, radiation polymerized.

PE-S = 10 wt % polyester - 90 wt % styrene, radiation polymerized.

S-TMPTMA = 60 wt % styrene - 40 wt % trimethylolpropane trimethacrylate, thermal-catalytically polymerized.

DAP-MMA = 90 wt % diallyl phthalate - 10 wt % MMA, thermal-catalytically polymerized.

accelerated test consists of 1 cycle per day of soaking in a 2.1% Na_2SO_4 solution at 22°C and drying in air at 54°C. Net expansion of 0.5% is the criterion for failure. The unimpregnated concrete serving as a control was removed at 480 cycles with a net expansion of 0.467%.

The PIC specimens have shown moderately to greatly improved resistance to sulfate attack as compared with the unimpregnated concrete. After 1436 cycles, the MMA-impregnated specimens show from 0.016 to 0.032% expansion, an improvement of >199% over the unimpregnated concrete. The styrene specimens have expansions of 0.036 to 0.042% at 1420 cycles. The MMA-TMPTMA specimens have expansions of 0.006 to 0.024% at 1326 cycles. The remaining acrylonitrile specimen has an expansion of 0.034% at 1100 cycles, and the remaining chlorostyrene specimens have expansions of 0.020 to 0.028% at 705 cycles. The CP-7 polyester-styrene and CP-UA MMA underwater-polymerized specimens have low expansions and have not been in test long enough for results to be significant.

(c) EXPOSURE TO 5% NaOH. Specimens were tested for resistance to exposure in 5% NaOH at room temperature for 382 days. Unimpregnated concrete, 10 wt % polyester - 90 wt % styrene impregnated and radiation-polymerized specimens, and MMA-impregnated specimens dipped in a PMMA solution and radiation-polymerized were tested. Also tested were thermal-catalytically polymerized 60 wt % styrene - 40 wt % TMPTMA and 90 wt % DAP - 10 wt % MMA specimens, which were prepared for the high-temperature applications. The test results (Table 17) indicate no adverse effect from exposure to 5% NaOH. All specimens showed a slight gain in weight and no visible signs of deterioration. The specimens were removed from test and compressive strengths were determined. These averaged 6500 psi for the unimpregnated concrete specimens and were generally in the range of about 16,000 to 19,000 psi for the PIC specimens, with one specimen of polyester-styrene having a low strength of 9000 psi and one DAP-MMA specimen a low strength of 12,200 psi.

(d) RESISTANCE TO CHEMICAL ATTACK FROM ACIDS. Test specimens are immersed in 5% H_2SO_4 and 15% HCl at room temperature. The criterion for failure is 25% weight loss. In the 5% H_2SO_4 test (Table 18) the unimpregnated specimens had a weight loss of >32% at 210 days. The CP-7 polyester-styrene specimens and the CP-UA underwater polymer-

ized MMA specimens show somewhat greater acid resistance, with a weight loss of about 17% after 252 days. The other polyester-styrene and MMA specimens show a weight loss of about 15% after 210 days. Test results from exposure to 15% HCl, given in Table 19, show significantly greater resistance for PIC specimens than for unimpregnated concrete. Weight losses ranged from 10 to 12% for MMA specimens and 12 to 17% for styrene specimens at 1395 days, 9 to 15% at 1287 days for MMA-TMPTMA specimens, 13 to 17% at 1213 days for acrylonitrile specimens, and 11 to 13% at 882 days for chlorostyrene specimens. The unimpregnated concrete control specimens failed after 105 days. The weight loss data indicate improvements in acid resistance ranging from >740% to >1229% as compared with unimpregnated concrete.

Although these data indicate that in general PIC has far greater resistance to acids than unimpregnated concrete, the specimens are slightly absorptive and the cement paste is slowly attacked by acid. To obtain some data on loss of strength after prolonged exposure to acid, the PIC specimens still exposed to 15% HCl were removed from the acid and tested for compressive strength (see Table 19). Acid exposure periods ranged from 882 to 1395 days, with weight losses of about 9 to 17%. Compressive strengths ranged from about 800 to 2400 psi. No corrections were made for cross-sectional areas reduced through deterioration, and the strengths are to be considered approximations only.

(e) WEATHEROMETER TESTS. Unimpregnated concrete and concrete impregnated with MMA, 10 wt % polyester - 90 wt % styrene, 60 wt % styrene - 40 wt % TMPTMA, and 90 wt % DAP - 10 wt % MMA are under test in a Weatherometer apparatus. The apparatus is used primarily for accelerated exposure tests of paints and protective coatings and simulates exposure to sunlight and rain. Samples are exposed to a total of 20 hr/day of light from 2 carbon arc lamps and receive a 12-min cold, demineralized water spray each hour. Test results to date are given in Table 20. The MMA and the polyester-styrene impregnated specimens have shown no visual indications of deterioration after 3000 hr of exposure. Samples of PIC for desalting plant applications, which include styrene-TMPTMA after exposure for 5900 and 6000 hr and DAP-MMA after 5900 hr of exposure, show some surface scaling affecting <10% of the surface

area. Unimpregnated samples show fairly uniform leaching of cement paste over the entire surface area to a depth of about $\frac{1}{16}$ in.

(e) **EFFECT OF SOIL MICROORGANISMS.** Samples of unimpregnated concrete and PIC are under test to determine whether soil microorganisms have an adverse effect on the materials. Samples are buried in compost-enriched soil at 27°C and 80% relative humidity, which are optimum conditions for soil microorganism growth. The specimens were examined visually after 18 months' burial for evidence of soil microorganism growth and surface appearance (Table 21). The samples, which contain MMA, 10 wt % polyester - 90 wt % styrene, 90 wt % DAP - 10 wt % MMA, and 60 wt % styrene - 40 wt % TMPTMA-impregnated concrete, had no microorganism growths and showed no changes in surface appearance. These observations indicate that the materials are highly resistant to soil microorganisms.

5.1.1.3 FLAMMABILITY TESTS. Standard fire resistance tests for plastics and various building materials have been reviewed for application to concrete-polymer materials. The existing test methods are designed to measure burning characteristics or fire resistance of specific materials, such as plastics, roofing materials, painted surfaces, and lumber, and are not intended for evaluating all materials. The only generally accepted procedure is conducted under ASTM E 84-68, Surface Burning Characteristics of Building Materials, which requires

a specimen 25 ft long and 20 in. wide. Final evaluation of a concrete-polymer material should be made by this procedure; however, the method is expensive and not suitable for screening tests. In preliminary studies⁴ several samples of PIC exposed to a gas flame ignited, appeared to contribute fuel to support combustion, and emitted smoke in varying amounts. The results of these studies apparently were affected by the presence of excess polymer on the surface. Additional studies on a limited basis were performed at BNL and the USBR to gather more information on flammability and to plan for a more comprehensive and meaningful test in next year's program.

(a) **BNL STUDIES.** A study was undertaken to determine the flammability of the polymers currently used in the program and of the composite materials containing them. The purpose of the study was to measure the relative burning rates for PIC and PC composites and to determine whether the addition of flame retardants was necessary.

The apparatus for determining the relative flammabilities of these materials under ASTM D 635-68, Flammability of Self-Supporting Plastics, is shown in Figures 19 and 20. In Figure 19 the flame source is being applied to a test specimen, and in Figure 20 it has been removed.

The relative burning rates for some bulk polymers are given in Table 22. Of the polymers tested, only chlorostyrene did not support combustion after removal of the flame source. Its noncombustion

Table 21
Effect of Soil Microorganisms
on Polymer-Impregnated Concrete Buried in Compost-Enriched Soil

Sample No.	Monomer	Polymer loading, wt %	Exposure time, months	Observations
2.5.2-3	MMA	6.9	18	No microorganism growths. Surface appearance unchanged - no pitting, good gloss retention.
-5	MMA	5.7	18	
-9	PE-S	7.0	18	
-11	PE-S	6.7	18	
-13	Unimpregnated	-	18	
-15	Unimpregnated	-	18	No microorganism growths. Surface appearance unchanged - no pitting, good gloss retention.
2.5.3.5.5-10	DAP-MMA	8.1	18	
-15	S-TMPTMA	7.4	18	
-19	Unimpregnated	-	18	

MMA = methyl methacrylate, radiation polymerized.

PE-S = 10 wt % polyester - 90 wt % styrene, radiation polymerized.

DAP-MMA = 90 wt % diallyl phthalate - 10 wt % MMA, thermal-catalytically polymerized.

S-TMPTMA = 60 wt % styrene - 40 wt % trimethylolpropane trimethacrylate, thermal-catalytically polymerized.

Figure 19. Flammability test of PIC specimen containing MMA. Specimen burns while flame is applied.

Figure 20. Flammability test of PIC specimen containing MMA. On removal of flame source, flame dies out almost immediately.

Table 22

Determination of the Relative Flammability of Plastics,^a
Polymer-Impregnated Concrete, and Polymer-Concrete Composites

Polymer	Composite	Polymer conc., wt %	Burning rate, in min	Remarks
Methyl methacrylate	—	100	1.2	Burning by this test
Styrene	—	100	1.0	Burning by this test
tert.-butyl styrene	—	100	0.9	Burning by this test
Chlorostyrene	—	100	0	Self-extinguishing by this test
10% Polyester - 90% styrene	—	100	0.9	Burning by this test
60% Styrene - 40% TMPTMA	—	100	0.8	Burning by this test
Methyl methacrylate	PIC	6.5	—	Self-extinguishing in 45 sec; two 30-sec ignitions
Styrene	PIC	6.3	—	Self-extinguishing in 30 sec; two 30-sec ignitions
tert.-butyl styrene	PIC	6.5	—	Does not support combustion; two ignitions
Chlorostyrene	PIC	6.2	—	Does not support combustion; two ignitions
60% Styrene - 40% TMPTMA	PIC	6.5	—	Self-extinguishing in 10 sec; two ignitions
Methyl methacrylate	PC	8.0	—	Self-extinguishing flame; travels 2 in. in 2.5 min
Styrene	PC	7.6	—	Self-extinguishing; <1 in. flame travel in 2.5 min
tert.-butyl styrene	PC	7.4	—	Does not support combustion
Chlorostyrene	PC	7.6	—	Does not support combustion
10% Polyester - 90% styrene	PC	6.9	—	Self-extinguishing; burns for 1.5 sec
60% Styrene - 40% TMPTMA	PC	7.0	—	Self-extinguishing; burns for 15 sec

^aASTM D 635-68, Flammability of Self-Supporting Plastics.

tibility is probably due to the chlorine portion of the monomer molecule, which acts as a flame retardant.

When these polymers are incorporated into concrete, the burning characteristics change drastically. As shown in Table 22, under the conditions of this test all the PIC composites are either self-extinguishing or do not burn at all. This may be due to the small amount (≈ 6 wt %) of polymer in the composite. The surface polymer exposed to the flame burns or is pyrolyzed quickly and leaves a charred residue which acts as a protective blanket for polymer beneath the surface. In addition, the concrete acts as a heat sink, and the heat resulting from combustion is not sufficient to sustain pyrolysis.

The burning rates obtained for PC were similar to those for PIC. In some cases, however, deformation and disintegration took place at the point of burning. Composites containing MMA, styrene, tert.-butyl styrene and chlorostyrene showed disintegration at the point of application when the flame was sustained for 30 sec. A portion of the polymer pyrolyzed, and the remainder melted and dropped off the test specimen along with the

aggregate. After removal of the flame, deformation was noted in the heated area. The softening points for the polymers tested range between $\approx 80^\circ$ and 120°C . Melting was not observed in composites containing 10 wt % polyester - 90 wt % styrene and 60 wt % styrene - 40 wt % TMPTMA, although slight deformation at the point where the flame was applied was observed in the former. The absence of melting and the resistance to deformation in these two systems can be attributed to cross-linking within the polymer network. Cross-linked polymers do not flow-melt and are more resistant to thermal deformation.

(b) USBR STUDIES. Flammability studies patterned after ASTM D 635-68, Flammability of Self-Supporting Plastics, were performed on six 60 wt % styrene - 40 wt % TMPTMA and six 70 wt % MMA - 30 wt % TMPTMA PIC specimens. Specimens measuring $1 \times 2 \times 12$ in. were mounted on a ringstand with the 12-in. axis horizontal and the 2-in. axis inclined 45° . The extended end of the sample was heated for 30 sec with a Bunsen burner flame showing a 1-in. inner blue cone. The burner was removed for 30 sec, then reapplied to the specimen for an additional 60 sec. To ensure

that PIC and not the excess polymer frequently observed on the surface of PIC specimens was being tested, surface coatings of polymer were removed with a grinding wheel. The following results were obtained.

i. No sustained combustion was observed. The PIC specimens are classified "nonburning" by this test.

ii. During the second, more prolonged heating period, a small flame was observed playing on the vertical surface of the test specimen. The flame went out almost immediately on removal of the flame source. PIC is nonburning by this test.

iii. For comparison, a specimen with a surface layer of 70 wt % MMA - 30 wt % TMPTMA polymer was tested. It burned with a yellow,

Table 23

Ultimate Design Tensile Strength and Elastic Properties
Polymer-Impregnated Concrete for Ambient-Temperature Applications

Type of material ^a	Test temperature, °C	Design values ^b		Average values ^c		
		Tensile strength, psi	Modulus of elasticity, 10 ⁶ psi	Polymer loading, wt %	Poisson's ratio ^d	Ultimate strain, μ in./in.
Unimpregnated	-12	210	2.9	-	0.15	177
	21	250	3.3	-	0.13	121
MMA	-12	600	6.1	5.5	0.18	117
	21	980	6.9	5.7	0.22	156
PE-S	-12	860	6.6	5.2	0.18	151
	21	1250	6.9	5.2	0.26	210

Direct tension tests on $4\frac{1}{2} \times 12\frac{1}{2}$ -in. cylinders.

^aMMA = methyl methacrylate, radiation polymerized; PE-S = 10 wt % polyester - 90 wt % styrene, radiation polymerized.

^bDesign values = mean minus standard deviation.

^cAverage values = mean of 4 or 5 specimens.

^dPoisson's ratio determined on one specimen only.

Table 24

Ultimate Design Compressive Strength and Elastic Properties
Polymer-Impregnated Concrete for Ambient-Temperature Applications

Type of material	Test temperature, °C	Design values			Average values		
		Compressive strength (f'_c), psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Polymer loading, wt %	Elastic limit stress, psi	Ultimate strain, in./in.
Unimpregnated	-12	5,100	0.16	3.6	-	1,200	0.0022
Unimpregnated	21	4,900	0.13 ^a	3.8	-	1,400	0.0022
MMA	-12	15,400	0.20	6.7	5.6	8,000	0.0027
MMA	21	14,100 ^a	0.19	6.5	5.6	8,000	0.0028
PE-S	-12	18,900	0.18 ^a	6.9	5.4	3,400	0.0032
PE-S	21	18,900	0.19	6.9	5.4	6,800	0.0031

6 $\times$ 12-in. cylinders oven-dried at 75°C prior to impregnation.

MMA = methyl methacrylate.

PE-S = 10 wt % polyester - 90 wt % styrene.

Radiation polymerization.

^aCP-type-concrete coefficient of variation of measurements was >15%.

smoky flame, and molten, burning polymer splattered from the surface. The flame died out within 5 sec after removal of the burner.

Several fragments of PC (containing 8 wt % MMA) were similarly tested and were observed to have similar flammability characteristics in that no sustained combustion was observed. The heated portion of the sample decomposed into a mixture of fine and coarse aggregate which could be brushed away with the fingers. A very thin fragment (measuring $\approx 2 \times 6 \times \frac{1}{8}$ in.) burned with a pale yellow flame for about 50 sec after removal of the burner and left a loose pile of aggregate beneath the test specimen.

Flammability appears to be less important than loss of strength upon exposure to fire. PC is completely destroyed, and it may be assumed that PIC loses strength.

5.1.2 Structural Properties Tests. Tests of structural properties during the past year have included direct tension tests at -12° and 20°C , single- and double-shear tests, a continuation of the long-term 800-psi compressive creep studies tests of flexural strength of concrete beams partially impregnated from one and from two sides, flexure and shear tests of steel-reinforced PIC, and preliminary work on a fatigue testing program for PIC beams.

Preliminary design values for tensile strength and modulus of elasticity at -12° and 21°C were obtained (see Section 5.1.2.1 and Tables 25 to 27). These design values for the MMA and 10 wt % polyester - 90 wt % styrene systems, radiation polymerized, are given in Table 23. For comparison with the tensile values, the preliminary design values for compressive strength, modulus of elasticity, and Poisson's ratio determined earlier⁴ are reproduced in Table 24.

Shear tests (see Section 5.1.2.2) showed an average ultimate shear stress of about 3700 psi for MMA-impregnated concrete in both the single-shear and the double-shear test. The test procedure apparently has little effect on the results because PIC is sufficiently strong to resist the small bending moment induced in the single-shear test. The shear strength of MMA-impregnated concrete is some 2 to 3 times greater than that of unimpregnated concrete.

Creep tests on CP-series specimens under 800-psi sustained load and on MMA-impregnated and chlorostyrene-impregnated concrete under low- and high-stress tensile and compressive loads are

continuing. These tests are discussed in Section 5.1.2.3. Results to date indicate that PIC undergoes significantly lower creep deformation than unimpregnated concrete.

Flexural strength tests were conducted on partially impregnated beams (see Section 5.1.2.4). The beams were impregnated from one and two sides to determine the effects of polymer impregnation on tension and compression of beams in flexure. Beams impregnated only on the tension side sustained an average ultimate load nearly twice as great as that for unimpregnated beams. The tests with beams impregnated on both the tension and compression sides were inconclusive.

Flexural and shear tests of steel-reinforced PIC beams are discussed in Section 5.1.2.5. The PIC beams carried more load than unimpregnated beams, but the difference was not considered significant. A check of the results indicated that the beams were underreinforced and that what had been tested was the reinforcement rather than the concrete.

5.1.2.1 TENSILE STRENGTH. Direct tensile strength has been determined for concrete impregnated with MMA and 10 wt % polyester - 90 wt % styrene, both radiation polymerized (Tables 25 and 26)

Figure 21. Schematic diagram of direct tension test.

Table 25

Low-Temperature Tensile Strength, Short Term

MMA-Impregnated Concrete^a

Test temperature, °C	Specimen No., 6.1.1-	Polymer loading, wt %	Tensile strength, psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Ultimate strain, (μin./in.)	Type of failure ^b
-12	53	5.7	740	-	7.0	111	EF
	54	5.4	710	-	6.8	126	OF
	56	5.3	550	0.18	5.8	140	MF
	59	5.4	680	-	6.4	111	EF
	65	5.8	670	-	6.9	100	EF
	Mean	5.5	670	0.18	6.6	117	
	S.D.	-	70	-	0.5	-	
20	57	5.8	1180	-	6.9	176	EF
	61	5.3	1060	0.22	7.0	153	MF
	62	5.7	950	-	7.0	140	EF
	69	6.2	1080	-	7.0	154	EF
	75 ^c	5.4	-	-	-	-	MF
	Mean	5.7	1070	0.22	7.0	156	
	S.D.	-	90	-	0.1	-	

^aMMA = methyl methacrylate, radiation polymerized.^bFailure occurring (1) in middle of specimen (MF); (2) outside recessed portion of end plate (OF); (3) inside of end plate (EF).^cHalf of cross section was impregnated and polymerized.

Table 26

Low-Temperature Tensile Strength, Short Term

10 wt % Polyester - 90 wt % Styrene Impregnated Concrete

Test temperature, °C	Specimen No., 6.1.1-	Polymer loading, wt %	Tensile strength, psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Ultimate strain, μin./in.	Type of failure ^a
-12	58	5.4	1080	-	6.9	161	EF
	60	5.0	790	0.18	6.4	129	MF
	67	5.0	1020	-	7.0	158	EF
	68	5.0	970	-	7.6	143	EF
	73	5.4	1150	-	7.2	166	EF
	Mean	5.2	1000	0.18	7.0	151	
	S.D.	-	140	-	0.4	-	
20	63	5.0	1550	-	7.0	238	EF
	66	5.0	1400	0.26	7.2	205	MF
	70	5.4	1380	-	7.1	199	EF
	71	5.3	1160	-	7.3	168	EF
	72	5.4	1460	-	6.9	240	EF
	Mean	5.2	1390	0.26	7.1	210	
	S.D.	-	140	-	0.2	-	

Radiation-induced polymerization.

^aFailure occurring (1) in middle of specimen (MF); (2) inside of end plate (EF).

Table 27

Low-Temperature Tensile Strength, Short Term
Unimpregnated Concrete

Test temperature, °C	Specimen No., 6.1.1-	Tensile strength, psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Ultimate strain, μ in./in.	Type of failure ^a
-12	76	210	-	2.8	104	MF
	80	280	-	3.1	206	OF
	81	270	0.15	3.1	281	MF
	82	210	-	3.7	66	EF
	85	220	-	3.2	230	MF
	Mean	240	0.15	3.2	177	
	S.D.	30	-	0.3	-	
20	77	230	0.13	3.9	68	MF
	78 ^b	-	-	-	-	MF
	79	300	-	3.8	111	OF
	83	290	-	4.0	100	OF
	84	300	-	3.2	205	OF
	Mean	280	0.13	3.7	121	
	S.D.	30	-	0.4	-	

^a Failure occurring (1) in middle of specimen (MF); (2) outside recessed portion of end plate (OF); (3) inside of end plate (EF).

^b Specimen failed during preload cycle.

Table 28

Comparison of Average Elastic Properties Determined
in Direct Tension and Compression Tests
(Low temperature, short term.)

Type of material	Test temperature, °C	Direct tension		Compression	
		Modulus of elasticity, 10 ⁶ psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Poisson's ratio
Control	-12	3.2	0.15	3.8	0.18
Control	20	3.7	0.13	3.8	0.16
MMA	-12	6.6	0.18	6.9	0.22
MMA	20	7.0	0.22	6.7	0.21
PE-S ^a	-12	7.0	0.18	7.0	0.22
PE-S	20	7.1	0.26	7.0	0.22

Polymer loadings in both test series were similar for each monomer system.

^a 10 wt % polyester - 90 wt % styrene, radiation polymerized.

and for unimpregnated concrete (Table 27). Measurements were made at -12° and 20°C. Modulus of elasticity and a few Poisson's ratios were obtained from electrical resistant strain gages bonded to the cylinders. A schematic diagram of the test is shown in Figure 21. The numbers of

end failures (EF) and failures within 4 in. of the end plates (OF) that occurred during the tests were not considered significant because these strengths were not much different from those found with middle failures (MF). (See Tables 25 to 27 for definition of types of failure.)

Figure 22. Schematic diagram of single-shear test.

Figure 23. Schematic diagram of double-shear test.

Three tests were made on each cylinder. The first two were used to obtain values of Poisson's ratio and modulus of elasticity. The third run was made to obtain stress-strain plots to failure. Study of these plots shows the stress-strain relationship of impregnated concrete to be much more linear than that of plain concrete.

A comparison of average values for each type of PIC indicates a lower tensile strength at the lower temperature. However, when these same materials were tested in compression, the average compressive strengths at the two temperatures were approximately the same.⁴ The reason for the apparent decrease in tensile strength with decreased temperature is not known. Additional work to investigate this point is planned.

Elastic properties at -12° and 20°C have been determined in both direct tension and compression tests. As can be seen in Table 28, the elastic properties under direct tension are very similar to those under compression.

5.1.2.2 SHEAR STRENGTH. Shear tests were conducted on 2×4 -in. cylinders of both unimpregnated con-

Table 29

Shear Tests, Single- and Double-Shear Methods
MMA-Impregnated and Unimpregnated Concrete

Single-shear method			Double-shear method		
Specimen No., 72-	Polymer loading, wt %	Shear stress, psi	Specimen No., 72-	Polymer loading, wt %	Shear stress, psi
119-8	7.9	3580	119-1	8.5	6620
9	8.0	2970	2	8.1	3980
10	7.5	4230	3	8.7	3210
11	8.2	3840	4	8.6	3610
12	8.5	4170	5	7.9	2080
Mean	8.0	3760	6	7.6	3160
			7	8.2	3010
			Mean	8.2	3670
120-1	-	920	120-6	-	1480
2	-	1180	7	-	1450
3	-	1200	8	-	1830
4	-	1260	9	-	1550
5	-	1160	10	-	2310
Mean	-	1140	11	-	1920
			12	-	1560
			Mean	-	1730

2×4 -in. cylinders, tested at room temperature.

MMA = methyl methacrylate, radiation-polymerized under water.

crete and MMA-impregnated concrete prepared by the underwater radiation-initiated polymerization method. The specimens were tested with use of a USBR standard single-shear apparatus and a newly constructed double-shear apparatus. The latter was developed to eliminate a bending moment that may be induced when the single-shear apparatus is used. The single-shear and double-shear methods are illustrated in Figures 22 and 23, and test results are given in Table 29.

MMA-impregnated specimens tested in single- and double-shear tests showed no significant differences. An average ultimate shear stress of 3760 psi was obtained in the single-shear test, and 3670 psi in the double-shear test. However, the unimpregnated concrete specimens tested in double shear showed $\approx 51\%$ greater ultimate shear stress than those tested in single shear, averaging 1730 psi in double shear and 1140 psi in single shear.

The orientation and location of large aggregate particles has more effect on shear strength in unimpregnated concrete than in PIC. In addition, PIC has a higher tensile strength which resists the bending moment introduced by the test method. These tests are as close to a pure shear test as could be performed at this time.

Single-shear test results on 60 wt % styrene - 40 wt % TMPTMA and 70 wt % MMA - 30 wt % TMPTMA impregnated concrete (specimens tested for desalting plant applications) and a comparison with MMA-impregnated concrete are discussed in Section 5.2.1.4.

5.1.2.3 CREEP. Long-term creep deformation studies made on PIC specimens at room temperature include tests on CP-series specimens under a sustained compressive load of 800 psi, and a high-stress test on MMA and chlorostyrene-impregnated specimens under sustained compressive and tensile loads.

(a) **800-PSI COMPRESSIVE CREEP.** Results on CP-series specimens under load for periods of 270 to 1500 days are given in Table 30. Creep deformation is given in terms of millionths of an inch per inch under 800-psi load. All tests have been terminated, except for the CP-7 and CP-8 (CP-UA) series. After 1500 days under load, MMA-impregnated specimens show a small negative creep (an elongation in length under the compressive load) ranging from 17 to 25 $\mu\text{in./in.}$, which with some minor fluctuations has been fairly constant since the test began. The styrene specimens have shown the

greatest amount and the most variation of creep deformation, ranging from 267 $\mu\text{in./in.}$ to a negative creep of 183 $\mu\text{in./in.}$; these values are somewhat questionable because the measurements were made on only one gage line. The MMA - 10 wt % TMPTMA specimens were under test for only 1 year and underwent a very minor creep deformation of 0 and 32 $\mu\text{in./in.}$ Acrylonitrile specimens were removed from test after 1000 days under load with creep deformation of 28 to 117 $\mu\text{in./in.}$ Chlorostyrene specimens were removed from test after 1000 days under load with a creep deformation of 31 to 69 $\mu\text{in./in.}$ Tests of CP-7 (polyester-styrene) and CP-8 (CP-UA, MMA radiation-polymerized under water) specimens are continuing and show creep of 3 $\mu\text{in./in.}$ for CP-7 and 28 $\mu\text{in./in.}$ for CP-8 specimens. Creep measurements on unimpregnated concrete after 1500 days under load show a deformation of 233 $\mu\text{in./in.}$ on the control specimens, 97 $\mu\text{in./in.}$ on radiation-treated concrete, and 58 $\mu\text{in./in.}$ on thermally treated concrete.

After completion of the creep study, measurements of compressive strength were made on two specimens of each type of concrete that had been under the 800-psi sustained compressive load, and an unloaded control specimen of each type (Table 31). The compressive strengths of the loaded specimens were comparable to that of the corresponding unloaded control specimen. These results indicate no decrease in strength due to the 800-psi loading over periods of time ranging from 3 to 4½ years.

(b) **HIGH-STRESS TENSILE AND COMPRESSIVE CREEP.** Results at about 2½ years under continuous loads from 345 psi tension to 7000 psi compression on PIC and unimpregnated concrete are presented in Table 32. Trends in these tests continue to be the same as those reported in Ref. 4. MMA and chlorostyrene specimens under tensile loads show negative creep (a contraction in length under tension) ranging from a unit deformation ($\mu\text{in./in. per psi}$) of 0.024 to one of 0.515. Under the compressive loads, unit deformation of MMA and chlorostyrene specimens generally ranges from about 0.08 $\mu\text{in./in.-psi}$ under the low load of 690 psi to about 0.05 $\mu\text{in./in.-psi}$ under the high load of 7000 psi, or a decrease in unit deformation per psi with increasing load. The unit deformation per psi for unimpregnated concrete is nearly the same for the two loadings of 690 and 2313 psi used in this test,

with possibly a slight increase at the higher loading. In comparing MMA and chlorostyrene specimens with unimpregnated specimens under the same load, the PIC specimens undergo about 5 times less creep at 690 psi and about 7 times less creep at 2313 psi. At the high load of 7000 psi, the PIC specimens have about 10 times less creep deformation per psi than unimpregnated concrete at 2313 psi.

Negative creep has been observed in PIC specimens only under low tensile and compressive loads and is not considered significant in the design of a structure.

5.1.2.4 FLEXURAL STRENGTH OF PARTIALLY IMPREGNATED CONCRETE.

The flexural strength of conventional concrete beams is limited by the amount of tensile stress that can be carried by the extreme tension fibers. A study was made to determine the effect of polymer impregnation of the extreme fibers on the flexural strength. Conventional concrete beams, 3×5 in. in cross section and 54 in. long, were partially impregnated with MMA and radiation-polymerized. The bottom surface of one set of bars was impregnated to a depth of $\approx 1\frac{1}{4}$ in. to determine the effects of polymer impregnation of the tension fibers. Both the top and bottom surfaces of another

Table 30
800-psi Compressive Creep Tests
CP Test Series Specimens

Sample No., CP-	Monomer ^a	Polymer loading, wt %	Polymerization method ^b	Creep strain, $\mu\text{in./in.}$							
				Days under 800-psi compressive load							
				6	30	90	270	360	1000	1500	
1A-7A	MMA	5.7	R	34 ^c	21 ^c	29 ^c	3 ^c	17 ^c	0	17 ^{c,d}	
1A-7C	MMA	5.9	R	42 ^c	54 ^c	38 ^c	12 ^c	2 ^c	25 ^c	33 ^{c,d}	
1B-7A	MMA	6.2	T	8 ^c	25 ^c	49 ^c	90 ^c	67 ^c	75 ^c	67 ^{c,d}	
1B-7B	MMA	6.2	T	50 ^c	86 ^c	111 ^c	84 ^c	84 ^c	58 ^c	75 ^{c,d}	
2A-7A	S	5.6	R	0	101 ^c	127 ^c	90 ^c	142 ^c	92 ^c	183 ^{c,d}	
2A-7B ^e	S	6.0	R	50	18 ^c	7	17	18	191	17 ^{c,d}	
2B-7B ^e	S	5.1	T	66	51	68	156	160	200	267 ^d	
2B-7X ^e	S	3.5	T	8	43	52	135	148	184	233 ^d	
4A-7A	MMA-TMPTMA	6.2	R	27 ^c	0	12	17	0 ^d	—	—	
4A-7B	MMA-TMPTMA	6.2	R	2	32	17	37	32 ^d	—	—	
5A-7A	AN	5.7	R	5	18	28	50	33	39 ^d	—	
5A-7B	AN	5.4	R	20	36	47	67	50	50 ^d	—	
5B-7A	AN	4.4	T	0	0	0	66	49	117 ^d	—	
5B-7B	AN	5.4	T	0	0	0	16	33	28 ^d	—	
6A-7A	CS	6.7	R	0	10	33	33	33	64 ^d	—	
6A-7B	CS	6.9	R	0	7	49	33	50	69 ^d	—	
6B-7A	CS	6.2	T	0	15	34	34	17	31 ^d	—	
6B-7B	CS	6.5	T	0	24	50	50	33	67 ^d	—	
7-7A, 7B	S-P	6.9	R	0	0	0	3				
UA-7A, 7B	MMA	6.9	R	0	3	17	28				
0-7C, 7B	—	—	—	77	95	132	157	184	209	233 ^d	
3A-7A, 7B	—	—	R	40	64	87	87	91	101	97 ^d	
3B-7A, 7B	—	—	T	12	27	31	37	50	50	58 ^d	

6×12 -in. cylinders, oven-dried at 105°C prior to impregnation.

^aMMA = methyl methacrylate; TMPTMA = trimethylolpropane trimethacrylate; S = styrene; MMA-TMPTMA = 90 wt % MMA - 10 wt % TMPTMA; AN = acrylonitrile; CS = monochlorostyrene; S-P = 90 wt % styrene - 10 wt % polyester.

^bR = radiation; T = thermal-catalytic.

^cNegative creep; length change is in the direction opposing the load.

^dSpecimen removed from test.

^eMeasurements could be made on only one gage line; therefore values are questionable.

set of bars were impregnated to determine the effects of polymer impregnation on the tension and compression fibers. A set of unimpregnated bars was used as a control.

The test loading was applied as shown in Figure 24. The test results indicate an average ultimate load of 1905 pounds for singly (tension fiber) impregnated beams, 1875 pounds for doubly (tension

and compression fiber) impregnated beams, and 1610 pounds for unimpregnated beams (see Table 33). The results for doubly impregnated beams are inconclusive, since after the test most of the beams were found to be incompletely impregnated or polymerized. The reason for this is not known.

Tension and compression fiber strain measurements were made during the testing of each beam

Table 31
Compressive Strength of Creep Test Specimens
3 to 4½ Years Under 800-psi Sustained Compressive Load

Specimen No., CP-	Monomer ^a	Polymer loading, wt %	Polymerization method ^b	Time under load, yr	Compressive strength, psi	
					Loaded specimens	Unloaded control specimens
1A-7A	MMA	5.7	R	4½	21,800	—
1A-7C	MMA	5.9	R	4½	22,800	—
1A-7B	MMA	5.7	R	0	—	23,400
1B-7A	MMA	6.2	T	4½	19,600	—
1B-7B	MMA	6.2	T	4½	19,700	—
1B-7C	MMA	6.4	T	0	—	20,200
2A-7A	S	5.6	R	4½	17,400	—
2A-7B	S	6.0	R	4½	16,300	—
2A-7C	S	6.0	R	0	—	16,600
2B-7B	S	5.1	T	4½	13,500	—
2B-7X	S	3.5	T	4½	10,800	—
2B-7C	S	5.3	T	0	—	—
5A-7A	AN	5.7	R	3	16,900	—
5A-7B	AN	5.4	R	3	18,100	—
5A-7C	AN	4.9	R	0	—	16,300
5B-7A	AN	4.4	T	3	7,100	—
5B-7B	AN	5.4	T	3	7,300	—
5B-7C	AN	4.7	T	0	—	7,860
6A-7A	CS	6.7	R	3	19,700	—
6A-7B	CS	6.9	R	3	19,400	—
6A-7C	CS	7.2	R	0	—	19,100
6B-7A	CS	6.2	T	3	15,400	—
6B-7B	CS	6.5	T	3	15,600	—
6B-7C	CS	7.2	T	0	—	14,900
0 -7B	—	—	—	4½	6,600	—
0 -7C	—	—	—	4½	6,500	—
0 -7A	—	—	—	0	—	6,400
3A-7A	—	—	R	4½	6,400	—
3A-7B	—	—	R	4½	6,100	—
3A-7C	—	—	R	0	—	6,000
3B-7A	—	—	T	4½	6,300	—
3B-7B	—	—	T	4½	5,400	—
3B-7C	—	—	T	0	—	6,000

6×12-in. cylinders, tested for compressive strength after completion of creep study.

Specimens oven-dried at 105°C prior to impregnation.

^aMMA = methyl methacrylate; S = styrene; AN = acrylonitrile; CS = monochlorostyrene.

^bR = radiation; T = thermal-catalytic.

with use of 4-in. strain gages. The neutral axes of the beams were calculated from the strain measurements for each increment of load. The neutral axes of the control beams and the doubly impregnated beams started at the midpoint of the section because the compression and tension strains were equal. As the load increased the neutral axes moved ≈ 0.10 in. toward the compression fiber. These calculations are based on the assumption that the strain varies linearly across the section. The neutral axes of singly impregnated beams started at a point 2.80 in. from the extreme compression fiber and remained in this position until failure. This proves that a transformed section does exist. The following ratios of the modulus of elasticity of impregnated concrete to that of concrete were computed.

Specimen No.	$n = E_{imp}/E_c$
1502	1.70
1507	1.95
1509	1.64
1511	1.76
1512	1.89

These ratios are comparable to results found in structural property testing of other materials.

5.1.2.5 REINFORCED POLYMER-IMPREGNATED CONCRETE IN FLEXURE AND SHEAR. Eleven $3 \times 5 \times 54$ -in. reinforced concrete beams were tested in flexure. The reinforcing consisted of one No. 4 bar placed longitudinally in the center of the 3-in. dimension on the bottom side of the beam. The bar was placed to allow $\frac{1}{2}$ in. clear cover. Five of the beams were unimpregnated controls and six were impregnated with MMA and dipped in PMMA. Polymerization was

Table 32
High-Stress Tensile and Compressive Creep
Polymer-Impregnated CP-Type Concrete

Monomer ^a	Cylinder No., CP-	Polymer loading, wt %	Sustained load, psi	Creep deformation, $\mu\text{in./in.-psi}$						
				Days under load						
				8	31	70	261	562	744	836
Tensile creep										
MMA	3	4.6	178	0.230 ^b	0.051 ^b	0.185 ^b	0.191 ^b	0.398 ^b	0.421 ^b	0.515 ^b
	13	4.6	345	0.049 ^b	0.023 ^b	0.069 ^b	0.049 ^b	0.181 ^b	0.205 ^b	0.242 ^b
CS	4	6.1	178	0.090 ^b	0.090 ^b	0.191 ^b	0.163 ^b	0.234 ^b	0.164 ^b	0.257 ^b
	8	6.1	345	0.003 ^b	0	0.052 ^b	0.026 ^b	0.024 ^b	0.024 ^b	0.024 ^b
Control	5	—	59	0.424	0.288	0.492	0.271	—	—	—
	6	—	178	0.051	0.191	0.258	0.331	0.257	0.257	0.164
Compressive creep										
MMA	11	5.4	690	0.006	0.011	0.039	0.029	0.066	0.072	0.085
	20	5.5	690	0	0.030	0.068	0.054	0.079	0.070	0.085
	31	5.4	2313	0.015	0.023	0.036	0.038	0.049	0.054	0.058
	32	5.4	2313	0.014	0.022	0.033	0.033	0.043	0.047	0.054
	37	5.4	7000	0.019	0.025	0.035	0.041	0.049	0.051	0.054
	44	5.4	7000	0.019	0.027	0.034	0.039	0.047	0.048	0.049
CS	12	6.1	690	0.049	0.074	0.074	0.055	0.127	0.121	0.163
	14	6.2	690	0.007	0.019	0.025	0.017	0.060	0.060	0.085
	15	6.2	2313	0.010	0.022	0.024	0.032	0.047	0.050	0.067
	16	6.1	2313	0.013	0.018	0.024	0.027	0.043	0.049	0.054
	17	6.5	7000	0.014	0.020	0.022	0.030	0.041	0.045	0.049
	18	6.5	7000	0.016	0.022	0.025	0.031	0.040	0.043	0.045
Control	22	—	690	0.091	0.139	0.168	0.271	0.368	0.380	0.380
	23	—	690	0.084	0.127	0.155	0.258	0.356	0.405	0.423
	25	—	2313	0.131	0.198	0.239	0.336	0.336	0.416	0.423
	24	—	2313	0.134	0.198	0.243	0.336	0.400	0.425	0.432

$4\frac{1}{2} \times 12$ -in. cylinders oven-dried at 150°C prior to impregnation.

Radiation polymerization.

^aMMA = methyl methacrylate; CS = chlorostyrene.

^bNegative creep; length change is in direction opposing applied load.

Figure 24. Schematic diagram of flexure test for partially impregnated 3×5×54-in. beams.

Figure 25. Schematic diagram of flexure test for steel-reinforced 3×5×54-in. beams.

Table 33

Partially Impregnated Concrete in Flexure
Ultimate Load

Unimpregnated controls		Singly impregnated (tension fiber)		Doubly impregnated (tension and compression fibers)	
Specimen No., 6.1.5-	Ultimate load, lb	Specimen No., 6.1.5-	Ultimate load, lb	Specimen No., 6.1.5-	Ultimate load, lb
1513	1100	1502	2135	1503	1240*
1514	1230	1507	1750	1504	2000
1515	1095	1509	1935	1505	1110*
1516	1135	1511	1945	1508	1580*
1517	1250	1512	1755	1510	1750
Mean	1160		1905		1875

3×5×54-in. beams partially impregnated with MMA, radiation polymerized. Specimens singly impregnated on bottom surfaces and doubly impregnated on top and bottom surfaces, to a depth of 1¼ in.

*Beams incompletely impregnated or polymerized; excluded from mean.

Table 34

Reinforced Concrete Beams in Flexure

Specimen No., 6.1.6-	Polymer loading, wt %	Ultimate load, lb	Ultimate compressive strain, in./in.	Ultimate moment, in.-lb	Modulus of elasticity (from av strain), 10 ⁶ psi	Modulus of rupture, psi
1602	6.7	6,600	0.0023	52,800	6.43	4,220
1603	6.9	6,600	0.0023	52,800	6.62	4,220
1604	7.0	7,320	0.0020	58,560	6.49	4,680
1605	7.3	6,700	0.0033	53,600	6.43	4,290
1606	7.4	6,750	0.0022	54,000	6.52	4,320
1607	6.8	6,560	0.0027	52,480	6.49	4,200
Mean	7.0	6,760	0.0025	54,040	6.50	4,320
1608	—	5,650	0.0023	45,200	2.28	3,620
1609	—	5,275	0.0042	42,200	2.26	3,380
1610	—	5,430	0.0029	43,400	2.26	3,480
1611	—	5,450	0.0034	43,600	2.12	3,490
1612	—	5,550	0.0020	44,400	2.02	3,550
Mean	—	5,470	0.0029	43,760	2.19	3,500

Monomer, MMA with PMMA dip coat.
Radiation-induced polymerization.

Specimens, 3×5×54-in. beams.
Test temperature, 20°C.

Figure 26. Schematic diagram of shear test for steel-reinforced $3 \times 5 \times 54$ -in. beams.

induced by radiation. The test loading was applied as shown in Figure 25. Four-in.-gage-length strain gages were placed longitudinally on the centerlines of the top and bottom surfaces to record strain. Results of the tests are shown in Table 34.

The ultimate moment of $3 \times 5 \times 54$ -in. beams in flexure was checked in accordance with ACI Code 318-63. A measured yield strength for the steel reinforcement of 48 ksi was used. From this check it was determined that the test beams were inadequately reinforced. Consequently the reinforcement rather than the concrete had been tested.

Table 35

Reinforced Concrete Beams in Shear

Specimen No., 6.1.6-	Polymer loading, wt %	Ultimate load, lb	Ultimate shear, lb	Shear stress, psi	Ultimate moment, in.-lb
1621	6.6	15,860	10,570	830	52,870
1622	6.7	15,840	10,560	830	52,800
1623	6.7	16,480	10,990	860	54,930
1626	6.6	16,340	10,890	855	54,470
1627	7.4	15,200	10,130	795	50,670
Mean	6.8	15,940	10,630	835	53,150
1628	-	12,200	8,130	640	40,670
1629	-	10,500	7,000	550	35,000
1630	-	11,500	7,670	600	38,330
1631	-	10,220	6,810	535	34,070
1632	-	11,420	7,610	595	33,070
Mean	-	11,170	7,440		37,230

Monomer, MMA with PMMA dip coat.
Radiation-induced polymerization.

Specimens, $3 \times 5 \times 54$ -in. beams.
Test temperature, 20°C.

Table 36

Flexure Tests

MMA-Impregnated Concrete

Specimen No., 6.1.6-	Polymer loading, wt %	Ultimate load, lb	Modulus of rupture, psi	Modulus of elasticity, 10^6 psi
1641	8.0	5830	2270	6.6
1642	8.3	5325	2070	6.1
1643	8.1	5165	2010	6.1
1644	7.5	5230	2030	6.5
Mean	8.0	5390	2100	6.3
1645	-	2155	840	4.2
1646	-	2180	840	3.9
Mean		2168	840	4.1

Radiation-induced polymerization.

Specimens, $3 \times 3 \times 16$ -in. beams.

Test temperature, 21°C.

Ten $3 \times 5 \times 54$ -in. reinforced concrete beams were tested in shear. A No. 4 reinforcing rod was placed at the top and bottom of each beam. The steel reinforcement was placed to allow $\frac{1}{2}$ in. clear cover. MMA with a PMMA dip coat was used to impregnate five of the beams, and polymerization was induced by radiation. Five unimpregnated beams were used as controls. The test loading was applied as shown in Figure 26. As indicated in the figure, the shear load applied to the beam was determined by load cells. Test results are given in Table 35. All the controls failed in shear. However, all the impregnated specimens failed in flexure. The loading setup will be revised in an attempt to produce shear failure in the impregnated specimens.

Additional specimens – $3 \times 3 \times 16$ -in. unreinforced bars and 3×6 -in. cylinders – were prepared to determine the basic properties of unreinforced concrete for comparison with the reinforced concrete. Four impregnated and two unimpregnated bars were tested (see Table 36). Six impregnated and six unimpregnated 3×6 -in. companion cylinders were also tested. Three of each type were tested under compression and three under direct tension. Table 37 shows the results of these tests.

5.1.2.6 FATIGUE TESTS. A fatigue-testing machine was installed, checked out, and put into operation. Fatigue tests were started on six $3 \times 5 \times 54$ -in. concrete beams. Three of the beams were unimpregnated controls and three were impregnated with MMA. Polymerization was induced by radiation. Results are not yet available.

5.1.3 Durability Properties of Partially Impregnated Concrete. Partially impregnated concrete is under investigation as a less costly alternative to fully impregnated concrete in applications where durability rather than high strength is required. The monomer should effectively seal the surface and penetrate deeply enough to prevent separation of the impregnated layer and premature failure. Viscous monomer systems are used because penetration depths are more easily controlled, voids in the penetrated portion remain filled, and monomer losses due to evaporation and drainage during the time between impregnation and complete polymerization are lower.

The preparation of partially impregnated concrete has been discussed in Refs. 2 to 4. The first series of partial impregnation tests utilized epoxy- and polyester-styrene monomer mixtures. The specimens were impregnated to depths of $\frac{1}{16}$, $\frac{1}{8}$, and $\frac{1}{4}$ in. Difficulties were encountered in obtain-

ing uniform penetrations within the desired closely spaced depths. Work on developing better systems for controlled penetration continued with a second series of tests using polyester-styrene monomer and PMMA prepolymer. A third series of tests was started to evaluate the effects that the use of high-pressure steam-cured concrete and high-entrained-air concrete might have on the durability of partially impregnated concrete.

First Test Series. This series is nearing completion, with only the sulfate attack tests continuing. Freeze-thaw tests were completed and the results incorporated in the Fourth Topical Report.⁴

The test for resistance to 15% HCl was concluded after 940 days of exposure to the acid (see Table 38). Specimens were removed from test and compressive strengths were determined. After 940 days of exposure, weight losses of partially impregnated specimens ranged from about 6 to 22% as compared with a weight loss of $>25\%$ at 257 days for unimpregnated concrete. Although these specimens were exposed to acid for more than $3\frac{1}{2}$ times

Table 37

Compressive and Direct Tensile Strength Tests
MMA-Impregnated Concrete

Specimen No., 6.1.6-	Polymer loading, wt %	Test	Strength, psi
1651	7.3	Tension	1,170
1653	7.6	Tension	1,310
1656	7.5	Tension	1,130
Mean	7.5		1,200
1657	—	Tension	330
1658	—	Tension	340
1659	—	Tension	360
Mean			350
1652	7.6	Compression	19,500
1654	7.4	Compression	18,400
1655	7.8	Compression	20,900
Mean	7.6		19,600
1660	—	Compression	4,580
1661	—	Compression	4,810
1662	—	Compression	4,500
Mean			4,630

Radiation-induced polymerization.
Specimens, 3-in.-diam $\times$ 6-in.-long cylinders.
Test temperature, 21°C.

Table 38

Resistance to 15% HCl
Partially Impregnated Concrete – First Test Series

Specimen No., CP-DP-	Monomer	Nominal depth of penetration, in.	Polymer loading, wt %	Water absorption, wt %	Acid exposure, days	Weight loss, %	Compressive strength, ^a psi
53	—	—	—	6.8	259	27.3 ^b	—
43	—	—	—	6.9	259	35.2 ^b	—
6	E-S	1/16	1.9	3.1	940	10.3	310
45	E-S	1/16	2.0	3.2	940	9.5	300
38	E-S	1/8	2.1	4.4	940	18.0	200
44	E-S	1/8	2.1	4.5	940	18.4	210
33	E-S	1/4	2.0	3.9	940	11.3	290
40	E-S	1/4	2.0	4.8	940	22.4	180
1	PE-S	1/16	1.1	3.0	940	20.5	210
28	PE-S	1/16	1.5	3.7	940	14.9	230
8	PE-S	1/8	1.6	0.6	940	8.4	270
48	PE-S	1/8	1.7	1.7	940	9.2	250
29	PE-S	1/4	1.8	1.1	940	9.3	290
35	PE-S	1/4	1.9	0.3	940	6.5	320

3×6-in. cylinders oven-dried at 150°C prior to impregnation.
Radiation-initiated polymerization.
E-S = epoxy-styrene; PE-S = polyester-styrene.

^aAfter exposure to HCl for 940 days.
^bFailed (weight loss >25%), removed from test.

Table 39

Resistance to Sulfate Attack
Partially Impregnated Concrete – First Test Series

Specimen No.	Monomer	Nominal depth of penetration, in.	Test cycles, days	Net expansion, %
CP-DP-49	—	—	908	0.456
CP-DP-50	—	—	908	0.450
CP-DP-20	E-S	1/16	908	0.162
CP-DP-11	E-S	1/16	908	0.166
CP-DP-39	E-S	1/8	908	0.126
CP-DP-12	E-S	1/8	908	0.098
CP-DP-24	E-S	1/4	908	0.498
CP-DP-43	E-S	1/4	908	0.204
CP-DP-22	PE-S	1/16	908	0.534
CP-DP-15	PE-S	1/16	908	0.340
CP-DP-2	PE-S	1/8	908	0.204
CP-DP-34	PE-S	1/8	908	0.084
CP-DP-9	PE-S	1/4	908	0.080
CP-DP-26	PE-S	1/4	908	0.074

3×6-in. specimens oven-dried at 150°C prior to impregnation.
Radiation-initiated polymerization.
E-S = epoxy styrene; PE-S = polyester-styrene.

Table 40

Compressive Strength

Partially Impregnated Concrete - Second Test Series

Specimen No., CP-DP-	Polymer	Nominal depth of penetration, in.	Polymer loading, wt %	Water absorption, %	Compressive strength, psi	Modulus of elasticity, 10 ⁶ psi
121	PE-S	½	5.4	0.2	13,900	5.4
123	PE-S	½	5.5	0.2	14,400	5.7
111	PE-S	¾	3.4	0.4	8,600	4.3
116	PE-S	¾	3.6	0.3	9,600	4.4
114	PE-S	¼	2.8	0.6	7,800	4.1
120	PE-S	¼	3.1	0.7	8,300	3.8
117	PMMA	½	5.0	0.2	13,500	5.7
119	PMMA	½	5.3	0.1	13,900	5.3
105	PMMA	¾	5.1	0.3	10,700	4.7
106	PMMA	¾	3.9	0.6	7,700	4.4
103	PMMA	¼	4.5	0.1	10,400	5.1
104	PMMA	¼	4.7	0.1	11,200	5.0
112	-	-	-	-	4,600	3.0

3×6-in. specimens oven-dried at 105°C.

PE-S = 50 wt % polyester (Plaskon) - 50 wt % styrene; viscosity, ≈70 cP.

PMMA = PMMA prepolymer, produced by irradiating MMA to a viscosity of ≈70 cP.

Table 41

Resistance to Freezing and Thawing

Partially Impregnated Concrete - Second Test Series

Specimen No., CP-DP-	Polymer	Nominal depth of penetration, in.	Polymer loading, wt %	Water absorption, %	Number of cycles	Weight loss, %
83	PE-S	½	5.3	0.2	1900	1.5 ^a
95	PE-S	½	6.0	0.2	1900	0.5 ^a
79	PE-S	¾	4.0	0.3	1900	2.0 ^a
81	PE-S	¾	3.5	0.4	1900	1.5 ^a
80	PE-S	¼	3.0	0.4	1900	3.0 ^a
93	PE-S	¼	3.0	0.3	1900	1.0 ^a
91	PMMA	½	5.6	0.2	1900	0
100	PMMA	½	4.9	0.3	1900	1.5
74	PMMA	¾	5.3	0.2	1900 ^b	1.0
77	PMMA	¾	4.5	0.5	1900 ^b	7.0
75	PMMA	¼	4.4	0.1	1900	3.0 ^a
88	PMMA	¼	4.3	0.1	1900	3.0 ^a
92	Control	-	-	-	1900 ^c	15
101	Control	-	-	-	1900	14

3×6-in. cylinders oven-dried at 105°C prior to impregnation.

Radiation-initiated polymerization.

PE-S = 50 wt % polyester (Plaskon) - 50 wt % styrene; viscosity, ≈70 cP.

PMMA = PMMA prepolymer, produced by irradiating MMA to a viscosity of ≈70 cP.

^aGain in weight.

^bOuter shell scaling off.

^cTop ½ separated at 13% loss.

Table 42
Resistance to 5% H₂SO₄
Partially Impregnated Concrete – Second Test Series

Monomer	Specimen No., CP-DP-	Nominal penetration depth, in.	Polymer loading, wt %	Absorption, wt %	Exposure, days	Weight loss, %
PE-S	115	½	5.4	0.1	252	26.8 ^a
	118	½	5.0	0.2	252	24.9
	96	⅜	3.8	0.4	252	24.6
	110	⅜	3.9	0.4	252	24.6
	94	¼	3.2	0.6	252	22.6
	108	¼	3.0	0.5	252	20.4
PMMA	109	½	5.0	0.2	252	20.0
	113	½	5.2	0.2	252	22.3
	90	⅜	3.3	0.3	252	27.6 ^a
	97	⅜	4.5	0.4	252	28.3 ^a
	89	¼	4.1	0.1	252	20.9
	98	¼	4.9	0.1	252	16.4
Unimpregnated	76	—	—	—	210	33.8 ^a
	82	—	—	—	210	32.4 ^a

3×6-in. specimens oven-dried at 105°C prior to impregnation.

PE-S = 50 wt % polyester (Plaskon) – 50 wt % styrene; viscosity, ≈70 cP.

PMMA = methyl methacrylate prepolymer, produced by irradiating MMA to a viscosity of ≈70 cP.

Radiation polymerization.

^aFailed (weight loss >25%).

Table 43
Resistance to Sulfate Attack
Partially Impregnated Concrete – Second Test Series

Specimen No., CP-DP-	Polymer	Nominal depth of penetration, in.	Polymer loading, wt %	Absorption, %	Test cycles, days	Net expansion, %
60	PE-S	½	5.1	0.3	300	0.006
72	PE-S	½	5.2	0.2	300	0.008
68	PE-S	⅜	3.3	0.3	300	0.010
69	PE-S	⅜	3.4	0.6	300	0.054 ^a
59	PE-S	¼	3.1	0.6	300	0.066 ^a
70	PE-S	¼	2.6	0.8	300	0.056
58	PMMA	½	5.5	0.3	300	0.036
62	PMMA	½	6.1	0.2	300	0.016
66	PMMA	⅜	4.3	0.4	300	0.034
73	PMMA	⅜	4.5	0.4	300	0.030
57	PMMA	¼	4.6	0.2	300	0.014
71	PMMA	¼	4.6	0.1	300	0.016
63	None	—	—	—	300	0.076
67	None	—	—	—	300	0.040

3×6-in. specimens oven-dried at 105°C.

PE-S = 50 wt % polyester (Plaskon) – 50 wt % styrene; viscosity, ≈70 cP.

PMMA = methyl methacrylate prepolymer, produced by irradiating MMA to a viscosity of ≈70 cP.

^aFine cracks appeared at 60 days.

Table 44
Resistance to 5% H₂SO₄
Partially Impregnated CP-Type Concrete - Third Test Series

Monomer	Specimen No.	Nominal penetration depth, in.	Polymer loading, wt %	Absorption, wt %	Exposure, days	Weight loss, %
PE-S	72.16-7	¼	2.5	5.2	52	0.4
	8	¼	2.3	5.5	52	0.9
	9	¼	2.2	5.0	52	0.8
	4	¾	4.9	2.6	52	1.2
	5	¾	4.6	1.9	52	1.6
	6	¾	4.7	2.5	52	1.3
	1	½	5.7	1.7	52	2.4
	2	½	5.2	2.1	52	2.0
	3	½	5.8	1.3	52	1.3
	17	¼	2.3	5.2	52	0.6 ^a
	19	¼	3.0	0.8	52	0.8 ^a
	20	¼	2.6	3.0	52	0.2 ^a
PMMA	11	¾	3.9	2.3	52	0.4
	13	¾	3.3	1.7	52	1.4
	15	¾	3.7	3.0	52	0.5
	10	½	4.1	1.1	52	0.9
	12	½	4.6	1.2	52	0.9
	14	½	4.5	2.1	52	1.5
Unimpregnated	72.17-1	—	—	6.6	52	2.6 ^a
	2	—	—	6.9	52	4.8 ^a
	3	—	—	6.7	52	4.3 ^a
	4	—	—	6.3	52	1.1 ^a
	5	—	—	6.9	52	4.8 ^a
	6	—	—	6.3	52	1.0 ^a

3×6-in. specimens oven-dried at 110°C.

Radiation-initiated polymerization.

PE-S = 50 wt % polyester - 50 wt % styrene; viscosity, ≈40 cP.

PMMA = 20% solution of PMMA in methyl methacrylate; viscosity, ≈60 cP.

^aGain in weight.

as long as unimpregnated concrete, with about one-half as much weight loss, the compressive strength of the specimens after exposure was in the 200 to 300-psi range. The acid slowly penetrates the specimens and attacks the cement paste.

Sulfate-attack test results are shown in Table 39. Specimens impregnated with epoxy-styrene are erratic in performance, ranging from about 0.10% to about 0.5% net expansion after 908 cycle-days, as compared with 0.45% expansion for unimpregnated concrete. Specimens impregnated with polyester-styrene had expansions ranging between 0.07% and 0.53%. A correlation with depth of monomer penetration is apparent.

Second Test Series. Compressive strengths (Table 40) ranged from about 7700 psi to 14,400 psi and in general increased with polymer loading and depth of penetration for the polyester-styrene specimens and to a lesser extent with PMMA specimens.

Freeze-thaw tests show excellent durability after 1900 cycles (Table 41). All polyester-styrene specimens show a slight increase in weight which is due to absorption of water. The ¾-in.-depth PMMA specimens are showing some deterioration.

Results after 252 days of exposure to 5% H₂SO₄ are given in Table 42. This is a severe test, and the specimens are deteriorating more rapidly than those in the first test series, which were exposed to

Table 45

Resistance to 5% H₂SO₄
Partially Impregnated High-Entrained-Air Concrete - Third Test Series

Monomer	Specimen No.	Nominal penetration depth, in.	Polymer loading, wt %	Absorption, wt %	Exposure, days	Weight loss, %
PE-S	72.45-5	¼	4.6	6.4	52	0.5
	6	¼	4.2	6.0	52	0.3
	7	¼	4.7	5.5	52	0.9
	1	⅜	5.1	4.4	52	1.4
	2	⅜	4.9	5.3	52	1.4
	4	⅜	5.1	4.7	52	1.3
	8	½	7.7	0.7	52	3.2
	9	½	7.8	0.6	52	3.2
	10	½	8.0	0.7	52	3.5
	20	¼	3.7	7.5	52	0.8 ^a
PMMA	21	¼	3.7	8.2	52	1.1 ^a
	24	¼	3.9	6.4	52	0.2 ^a
	17	⅜	5.5	1.3	52	1.0
	18	⅜	5.7	2.4	52	0.8 ^a
	19	⅜	5.5	2.4	52	0.1 ^a
	12	½	7.8	1.9	52	0.5 ^a
	13	½	7.9	1.4	52	0.1
	15	½	8.0	1.7	52	0.5 ^a
	Unimpregnated	72.46-1	-	6.2	52	12.7
		2	-	5.7	52	11.6
		3	-	6.3	52	9.9
		5	-	6.4	52	13.2
		6	-	6.3	52	8.6

High-entrained-air concrete, CP-type concrete mix adjusted to give 11.2% entrained air, 3 × 6-in. specimens oven-dried at 110°C.

Radiation-initiated polymerization.

PE-S = 50 wt % polyester - 50 wt % styrene; viscosity, ≈40 cP.

PMMA = 20% solution of PMMA in methyl methacrylate; viscosity, ≈60 cP.

^aGain in weight.

HCl. Weight losses ranged from about 16% to 28% at 252 days for partially impregnated specimens. Both monomer systems gave similar results and no correlation with penetration depth was apparent. Unimpregnated specimens had >30% weight loss at 210 days. An improved specimen-preparation technique, such as treatment with a seal coat to obtain an impermeable specimen, will be required to produce a material with high durability when exposed to sulfuric acid. This technique has been used successfully with sewer pipe (see Section 8.1.3).

Sulfate-attack tests (Table 43) show generally low expansions after 300 test cycles. This is not

a sufficient exposure time to produce significant results.

Third Test Series. Partially impregnated specimens were prepared from the standard CP-mix concrete and from a CP mix adjusted to give a high entrained air content (11% vs 6% for standard CP mix). Both types of concrete were cured with high-pressure steam and then impregnated with polyester-styrene and PMMA solutions. Specimens in this series were tested only for absorption and resistance to 5% H₂SO₄ (see Tables 44 and 45).

Partially impregnated specimens generally showed a decrease in absorption with increased depth of penetration; however, absorption was

fairly high as compared with that found in previous tests of partially impregnated concrete. After 52 days of exposure to 5% H_2SO_4 , the partially impregnated specimens are deteriorating slightly, with several specimens showing weight gains due to absorption. The unimpregnated steam-cured CP-type concrete specimens are showing good durability, and the steam-cured high-air-content specimens are showing significant weight loss.

5.2 POLYMER-IMPREGNATED CONCRETE FOR DESALTING PLANT APPLICATIONS AT TEMPERATURES UP TO 143°C

5.2.1 Structural Properties and Design Criteria.

Tests of structural properties were conducted on unimpregnated CP-type concrete and on CP-type concrete impregnated with 60 wt % styrene - 40 wt % TMPTMA and 70 wt % MMA - 30 wt % TMPTMA. The tests included compressive, tensile, flexural, and shear strengths, and were conducted at room temperature (taken here as 21°C), 121°C, and 143°C. In addition, several tests of compressive and tensile strength were conducted

at -23°C and 177°C. The long-term tests in progress on creep deformation and brine-loop exposure were continued.

Preliminary design values were calculated for compressive strength, Poisson's ratio, and modulus of elasticity of the MMA-TMPTMA impregnated concrete at -23°, 21°, 121°, and 143°C, and for unimpregnated concrete and the styrene-TMPTMA impregnated concrete at 177°C. The design values are equal to the mean compressive strength minus the standard deviation and were obtained from compressive strength tests described in Section 5.2.1.1. These values are for short-term exposure at the various temperatures. Results are given in Table 46, which also contains a summary of design values for unimpregnated concrete and 60 wt % styrene - 40 wt % TMPTMA impregnated concrete presented in Ref. 4. The design values for PIC show a downward trend with increasing temperature. The lowest value for compressive strength of the styrene-TMPTMA impregnated concrete is 13,700 psi at 143°C, and for the MMA-TMPTMA concrete the lowest value is 11,900 psi

Table 46

Ultimate Design Compressive Strength and Elastic Properties
Polymer-Impregnated Concrete for High-Temperature Applications

Type of material ^a	Test temperature, °C	No. of specimens	Design values ^b			Average values ^c		
			Compressive strength (f'_c), psi	Poisson's ratio	Modulus of elasticity, 10^6 psi	Polymer loading, wt %	Elastic limit stress, psi	Ultimate strain, in./in.
Unimpregnated	21	10	4,700	0.14	3.4	-	1,200	0.0023
	121	10	4,800	0.13	3.0	-	1,400	0.0024
	143	15	4,500	0.12	2.9	-	1,300	0.0025
	177	10	4,800	0.11	2.7	-	1,100	0.0026
S-TMPTMA	21	12	15,300	0.20	6.1	5.7	10,500	0.0029
	121	12	15,000	0.20	5.7	5.6	9,800	0.0030
	143	12	13,700	0.17	5.5	5.5	8,200	0.0026
	177	10	14,200	0.15	5.1	5.6	9,900	0.0030
MMA-TMPTMA	-23	10	17,200	0.17	5.7	6.4	13,600	0.0033
	21	15	17,100	0.18	5.8	5.8	12,400	0.0032
	121	25	12,500	0.16	4.8	5.8	9,200	0.0030
	143	20	11,900	0.14	4.3	5.8	8,900	0.0030

Compressive strength tests on 6×12-in. cylinders.

Thermal-catalytic polymerization.

^aS-TMPTMA = 60 wt % styrene - 40 wt % TMPTMA; MMA-TMPTMA = 70 wt % MMA - 30 wt % TMPTMA.

^bDesign values = mean minus standard deviation.

^cAverage values = mean of 10 to 25 specimens.

Table 47

Ultimate Design Direct Tensile Strength and Elastic Properties
Polymer-Impregnated Concrete for High-Temperature Applications

Type of material	Test temperature, °C	Design values		Average values		
		Tensile strength, psi	Modulus of elasticity, 10 ⁶ psi	Polymer loading, wt %	Ultimate strain, μ in./in.	Poisson's ratio
Unimpregnated	21	260	3.8	~	136	0.14
	121	170	2.9	~	162	0.10
	143	210	2.6	~	156	-
S-TMPTMA	21	980	6.6	5.5	172	0.20
	121	800	5.9	5.5	146	0.22
	143	760	5.5	5.5	161	0.19

Direct tension tests on $4\frac{1}{2} \times 12\frac{1}{2}$ -in. cylinders.

Average values = mean of 4 or 5 specimens.

Design values = mean minus standard deviation.

S-TMPTMA = 60 wt % styrene - 40 wt % TMPTMA.

Thermal-catalytic polymerization.

Table 48

Comparison of Tensile Strength Average and Design Values Determined
in Direct Tension and Tensile Splitting Tests

Type of material ^a	Test temperature, °C	Average values from							
		Design values from		Direct tension ^d			Tensile splitting ^c		
		Direct tension, ^b psi	Tensile splitting, ^c psi	No. of specimens	Tensile strength, psi	Standard deviation, psi	No. of specimens	Tensile strength, psi	Standard deviation, psi
Unimpregnated	21	260	250	4	310	50	10	340	50
	121	170	230	5	220	50	10	310	40
	143	210	280	4	230	20	10	370	40
	177	-	260	-	-	-	10	330	30
S-TMPTMA	21	980	660	5	1090	110	10	890	110
	121	800	650	5	890	90	10	880	110
	143	760	620 ^d	5	850	90	10	920	190
	177	-	540 ^d	-	-	-	10	790	150
MMA-TMPTMA	-23	-	820	-	-	-	10	1040	70
	21	-	780	-	-	-	20	1000	80
	121	-	780	-	-	-	20	990	70
	143	-	640	-	-	-	20	870	110

Direct tension tests on $4\frac{1}{2} \times 12\frac{1}{2}$ -in. cylinders; tensile splitting tests on 6×12 -in. cylinders.

Thermal-catalytic polymerization.

^aS-TMPTMA = 60 wt % styrene - 40 wt % TMPTMA; MMA-TMPTMA = 70 wt % MMA - 30 wt % TMPTMA.

^bDesign values = mean minus standard deviation.

^cDesign values = 0.85(mean - standard deviation).

^dCoefficient of variation was >15%.

at 143°C. On the basis of these tests, these values should be used as the upper limit of ultimate compressive strength design stresses.

Preliminary tensile strength design values for styrene-TMPTMA impregnated concrete tested in direct tension at 21°, 121°, and 143°C are given in Table 47. Design values calculated from tensile splitting tests on styrene-TMPTMA and MMA-TMPTMA impregnated concrete, and a comparison of direct tension and tensile splitting strengths, are given in Table 48. These data were obtained from tests discussed in Section 5.2.1.2 and from Ref. 4. Test temperatures ranged from -23°C to 177°C. Design values from direct tension tests are equal to the mean tensile strength minus the standard deviation; those from tensile splitting

tests are calculated by multiplying the mean tensile splitting strength minus the standard deviation by an empirical factor of 0.85 (see discussion in Section 5.2.1.2).

The tensile strength design values for PIC, like those for compressive strength, generally show a decrease with increasing temperature. The lowest tensile strength design value for styrene-TMPTMA impregnated concrete from direct tension tests was 760 psi at 143°C. Such tests have not yet been performed on the MMA-TMPTMA impregnated concrete. The lowest tensile strength design values from tensile splitting tests were 620 psi at 143°C and 540 psi at 177°C for the styrene-TMPTMA impregnated concrete, and 640 psi at 143°C for the MMA-TMPTMA impregnated

Table 49
Compressive Strength of Unimpregnated and Styrene-TMPTMA
Impregnated Concrete After Short-Term Exposure at 177°C

Specimen No.	Polymer loading, wt %	Compressive strength, psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Elastic limit stress, psi	Ultimate strain, μ in./in.
72.3-1	5.8	14,900	0.21	5.2	9,000	3,100
2	5.9	14,600	0.17	5.1	10,000	2,900
5	5.3	14,500	0.19	5.7	11,500	2,760
6	5.9	14,000	0.22	5.2	9,500	2,800
7	6.2	15,000	0.19	5.2	9,500	3,190
8	5.0	14,800	0.19	5.3	10,000	3,050
9	5.0	14,600	0.14	5.4	10,000	3,000
10	5.7	14,700	0.15	5.3	9,500	2,960
11	5.8	14,800	0.17	5.2	9,000	3,100
12	5.3	14,000	0.15	5.1	11,000	2,600
Mean	5.6	14,600	0.18	5.3	9,900	2,950
S.D.	-	300	0.03	0.2	810	-
72.4-1	-	5,200	0.08	2.8	1,150	2,700
2	-	5,000	0.18	2.9	1,100	2,800
3	-	5,100	0.21	3.1	1,100	2,700
4	-	5,000	0.18	2.9	1,100	2,600
5	-	5,000	0.12	2.8	1,150	2,600
6	-	5,100	0.14	2.8	1,150	2,700
7	-	4,600	-	2.5	1,100	2,700
8	-	5,000	0.16	3.0	1,250	2,550
9	-	5,100	0.08	2.9	1,100	2,550
10	-	4,600	0.10	3.0	1,150	2,400
Mean	-	5,000	0.14	2.9	1,140	2,630
S.D.	-	200	0.05	0.2	50	-

Specimens, 6-in.-diam $\times$ 12-in.-long cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 177°C.

concrete. These values should be considered the upper limit of ultimate tensile strength stress for use as a preliminary design aid.

5.2.1.1 COMPRESSIVE STRENGTH. Compressive strength and elastic properties have been obtained for unimpregnated concrete and for concrete impreg-

nated with 60 wt % styrene - 40 wt % TMPTMA and 70 wt % MMA - 30 wt % TMPTMA. Test temperatures ranged from -23°C to 177°C . Results at the various temperatures are considered to be short-term effects, since the specimens are exposed only long enough to obtain a uniform tem-

Table 50

Compressive Strength of MMA-TMPTMA Impregnated Concrete
After Short-Term Exposure at 21° , 121° , and 143°C

Test temperature, $^{\circ}\text{C}$	Specimen No., 72.93-	Polymer loading, wt %	Ultimate strength, psi	Poisson's ratio	Modulus of elasticity, 10^6 psi	Elastic limit stress, psi	Ultimate strain, $\mu\text{in./in.}$
21	1	5.7	17,900	0.21	5.8	13,000	3,160
	2	5.6	17,400	0.20	5.9	12,500	3,000
	5	6.1	17,900	0.20	5.9	12,500	3,400
	14	5.9	18,100	0.19	5.8	13,500	3,400
	15	5.8	17,400	0.19	5.7	13,000	3,040
	17	6.1	17,100	0.18	5.9	12,500	3,380
	23	5.6	17,300	0.23	6.1	11,000	2,960
	29	5.8	18,000	0.19	5.8	12,000	3,420
	31	5.3	17,400	0.18	6.0	10,000	2,910
	33	5.8	16,900	0.21	6.4	11,500	2,820
	Mean	5.8	17,500	0.20	5.9	12,150	3,150
	S.D.	-	400	0.02	0.2	-	-
121	4	5.9	13,100	0.13	4.9	8,500	3,190
	7	5.6	14,800	0.17	4.9	10,000	3,460
	13	6.1	13,000	0.18	4.6	10,000	3,400
	16	5.8	13,600	0.19	4.9	9,500	3,030
	20	6.1	13,800	0.21	5.2	8,500	3,370
	21	5.8	12,800	0.16	4.3	10,000	3,220
	25	5.7	14,600	0.20	5.3	9,500	3,030
	27	5.6	13,500	0.20	4.9	9,000	3,020
	30	5.8	13,400	0.17	5.3	9,000	3,030
	35	5.4	14,000	0.17	5.6	9,500	2,700
	Mean	5.8	13,700	0.18	5.0	9,350	3,150
	S.D.	-	700	0.02	0.4	-	-
143	3	5.9	12,300	0.13	4.5	8,500	2,900
	6	5.8	13,000	0.20	5.1	8,000	2,960
	10	5.1	12,100	0.16	4.6	9,500	2,530
	18	5.8	13,100	0.17	4.8	9,500	2,840
	19	5.7	12,300	0.13	5.0	9,000	2,760
	22	5.6	12,700	0.16	4.8	9,000	2,750
	24	6.1	12,000	0.17	4.8	9,500	3,020
	26	6.1	11,900	0.20	4.5	9,000	2,710
	32	5.7	13,600	0.19	5.1	9,000	3,040
	34	5.7	12,800	0.18	5.0	9,000	2,950
	Mean	5.8	12,600	0.17	4.8	9,000	2,850
	S.D.	-	500	0.03	0.2	-	-

Specimens, 6×12 -in. cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt % TMPTMA.

perature. The test specimens are 6×12-in. cylinders. Elastic properties are determined with use of electrical resistance strain gages bonded to the test cylinders, and three test runs are made. In the first two, PIC is stressed to 2000 psi and unimpregnated concrete is stressed to 1000 psi. Data from these runs are used to determine Poisson's ratio

and modulus of elasticity. The third run is used to obtain stress-strain data to failure.

Compressive strength and elastic properties at 177°C of unimpregnated concrete and styrene-TMPTMA impregnated concrete are given in Table 49. The unimpregnated concrete had an average compressive strength of 5000 psi and the

Table 51

Compressive Strength of MMA-TMPTMA Impregnated Concrete
Initial Tests for Long-Term Exposure Tests at -23°, 21°, 121°, and 143°C

Test temperature, °C	Specimen No., 72.194-	Polymer loading, wt %	Ultimate strength, psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Elastic limit stress, psi	Ultimate strain, in./in.
-23	1	6.4	18,400	0.16	5.9	14,000	3,520
	6	6.4	18,200	0.21	5.7	14,000	3,420
	8	6.7	18,500	0.20	5.8	14,000	3,400
	11	6.3	17,500	0.19	5.9	13,000	3,266
	13	6.1	17,900	0.21	6.0	13,000	3,320
	15	7.2	17,000	0.22	5.6	13,000	3,380
	17	6.6	17,800	0.19	6.1	13,500	3,080
	19	6.7	18,700	0.18	6.1	14,000	3,150
	22	5.3	18,900	0.16	6.2	13,500	3,180
	24	6.6	18,000	0.18	6.1	14,000	3,080
	Mean	6.4	18,100	0.19	5.9	13,600	3,280
	S.D.	-	600	0.02	0.2	-	-
21	5	6.3	18,000	0.22	5.9	13,000	3,480
	7	6.4	17,300	0.22	6.0	13,000	3,080
	9	6.7	17,900	0.23	6.1	13,000	3,300
	12	6.6	18,500	0.24	6.2	13,000	3,160
	21	6.3	18,000	0.16	6.4	13,000	3,100
	Mean	6.5	17,900	0.21	6.1	13,000	3,220
	S.D.	-	500	0.03	0.2	-	-
121	2	6.6	11,100	0.20	5.2	8,000	2,400
	4	6.3	12,200	0.20	5.4	8,000	2,580
	8	6.4	13,500	0.16	4.9	9,000	3,200
	20	5.6	13,200	0.16	5.2	9,000	2,660
	26	6.9	14,100	0.18	5.1	9,000	3,680
	Mean	6.4	12,800	0.18	5.2	8,600	2,900
	S.D.	-	1,200	0.02	0.2	-	-
143	3	6.3	12,500	0.15	4.6	9,500	3,400
	10	6.6	12,700	0.12	3.9	9,000	3,240
	14	6.6	12,200	0.16	4.7	9,000	3,200
	16	6.1	11,500	0.16	4.2	8,500	2,950
	25	6.4	12,400	0.16	4.1	8,000	3,180
	Mean	6.4	12,300	0.15	4.3	8,800	3,190
	S.D.	-	400	0.02	0.4	-	-

Specimens, 6×12-in. cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt % TMPTMA.

Table 52

Compressive Strength of Unimpregnated and MMA-TMPTMA Impregnated Concrete
Initial Tests at 121° and 143°C for Three-Phase Brine Loop Exposure

Test temperature, °C	Specimen No.	Polymer loading, wt %	Ultimate strength, psi	Poisson's ratio	Modulus of elasticity, 10 ³ psi	Elastic limit stress, psi	Ultimate strain, in./in.
121	72.189-1	5.8	12,800	0.20	5.3	9,000	2,710
	2	6.1	14,500	0.21	5.9	10,000	2,980
	4	5.8	14,300	0.18	5.6	9,500	2,990
	6	5.9	15,000	0.20	5.7	9,000	2,900
	7	5.8	13,600	0.26	5.7	9,000	2,680
	72.123-61X	5.5	13,300	-	-	-	-
	62S	5.8	13,100	-	-	-	-
	63X	6.1	15,400	-	-	-	-
	64X	5.8	12,700	-	-	-	-
	65X	6.1	11,500	-	-	-	-
	Mean	5.9	13,600	0.21	5.6	9,300	2,850
	S.D.	-	1,200	0.03	0.2	400	150
143	72.189-3	5.9	12,900	0.21	5.1	8,500	3,220
	5	6.0	12,900	0.16	5.0	9,000	2,750
	8	6.1	12,900	0.21	5.2	9,000	3,230
	9	5.9	12,900	0.21	4.6	8,000	3,120
	10	6.3	11,400	0.20	4.8	8,500	2,680
	Mean	6.0	12,600	0.20	5.0	8,600	3,000
	S.D.	-	600	0.02	0.2	400	260
143	72.199-1	-	4,500	0.17	3.3	1,400	1,660
	2	-	4,600	0.19	3.0	1,500	2,560
	3	-	4,500	0.12	3.2	1,600	1,810
	4	-	4,900	0.16	3.3	1,600	-
	5	-	4,400	0.15	3.3	1,600	2,340
	Mean	-	4,600	0.16	3.2	1,500	2,090
	S.D.	-	200	0.03	0.1	90	430

Specimens, 6 × 12-in. cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt TMPTMA.

styrene-TMPTMA impregnated concrete averaged 14,600 psi.

Compressive strength and elastic properties of the MMA-TMPTMA impregnated concrete at 21°, 121°, and 143°C are given in Table 50. Compressive strengths showed a decrease with increased temperature, averaging 17,500 psi at 21°C, 13,700 psi at 121°C, and 12,600 psi at 143°C.

Additional tests of compressive strength and elastic properties of MMA-TMPTMA impregnated concrete have been performed. Initial results from a series of tests to determine long-term effects of exposure at -23°, 21°, 121°, and 143°C are given in Table 51. These specimens showed a similar decrease in compressive strength with

increased temperature, averaging 18,100 psi at -23°C, 17,900 psi at 21°C, 12,800 psi at 121°C, and 12,300 psi at 143°C. Initial results on specimens selected for long-term exposure in the three-phase brine loops are given in Table 52. These specimens had an average compressive strength of 13,600 psi at 121°C, and 12,600 psi at 143°C.

A summary of average values for compressive strength and elastic properties for unimpregnated, styrene-TMPTMA impregnated, and MMA-TMPTMA impregnated concretes is given in Table 53. This table summarizes the data presented in Tables 49 to 52 and data on unimpregnated and 60 wt % styrene - 40 wt % TMPTMA impregnated concrete from Ref. 4.

Table 53

Average Values for Compressive Strength and Elastic Properties
Unimpregnated, Styrene-TMPTMA Impregnated, and MMA-TMPTMA Impregnated Concrete

Concrete type	Polymer loading, wt %	Test temperature, °C	No. of specimens	Compressive strength, psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Elastic limit stress, psi	Ultimate strain, μ in./in.
Unimpregnated	—	21	10	5,000	0.16	3.5	1,200	2,320
	—	121	10	5,200	0.15	3.2	1,380	2,390
	—	143	15	4,900	0.15	3.1	1,290	2,450
	—	177	10	5,000	0.14	2.9	1,140	2,630
Styrene-TMPTMA	5.7	21	12	16,900	0.21	6.4	10,500	2,920
	5.6	121	12	16,100	0.21	6.0	9,800	2,960
	5.5	143	12	15,000	0.19	5.3	8,200	2,600
	5.6	177	10	14,600	0.18	5.3	9,900	2,950
MMA-TMPTMA	6.4	—23	10	18,100	0.19	5.9	13,600	3,280
	6.0	21	15	17,700	0.20	6.0	12,400	3,170
	6.0	121	25	13,500	0.19	5.2	9,200	3,020
	6.0	143	20	12,500	0.17	4.7	8,900	2,970

Specimens, 6×12-in. cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomers, 60 wt % styrene – 40 wt % TMPTMA; 70 wt % MMA – 30 wt % TMPTMA.

Table 54

Direct Tensile Strength of Unimpregnated Concrete After Short-Term Exposure at 21°, 121°, and 143°C

Test temperature, °C	Specimen No., 6.2.1–	Tensile strength, psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Ultimate strain, μ in./in.	Type of failure ^a
21	4021	320	—	3.9	148	OF
	4029	250	0.14	3.8	78	MF
	4030	300	—	4.5	162	MF
	4032	360	—	4.1	154	MF
	Mean	310	0.14	4.1	136	
	S.D.	50	—	0.3	—	
121	4024	280	—	2.9	169	MF
	4028	240	—	3.2	184	MF
	4031	150	0.10	2.9	89	OF
	4033	230	—	3.0	205	MF
	Mean	220	0.10	3.0	162	
	S.D.	50	—	0.1	—	
143	4022	230	—	2.5	152	OF
	4023	230	—	2.8	153	MF
	4025	260	—	3.0	177	MF
	4026	200	—	2.7	141	MF
	Mean	230	—	2.8	156	
	S.D.	20	—	0.2	—	

Direct tension test.

Specimens, 4½×12½-in. cylinders of CP-type concrete.

^aMF = failed in middle of specimen; OF = failed outside recessed portion of end plate.

Table 55

Direct Tensile Strength of Styrene-TMPTMA Impregnated Concrete
After Short-Term Exposure at 21°, 121°, and 143°C

Test temperature, °C	Specimen No., 6.2.1-	Polymer loading, wt %	Tensile strength, psi	Poisson's ratio	Modulus of elasticity, 10 ⁶ psi	Ultimate strain, μ in./in.	Type of failure ^a
21	4001	5.4	960	0.20	7.2	159	OF
	4007	5.4	1130	—	6.7	178	EF
	4011	5.4	1190	—	7.1	184	OF
	4013	5.8	1180	—	6.8	180	OF
	4016	5.4	990	—	6.6	159	OF
	Mean	5.5	1090	0.20	6.9	172	
	S.D.	—	110	—	0.3	—	
121	4002	5.8	860	—	6.2	144	EF
	4004	5.4	880	0.22	6.4	140	OF
	4008	5.4	1040	—	6.4	129	EF
	4012	5.4	800	—	5.8	158	MF
	4017	5.4	890	—	6.0	158	EF
	Mean	5.5	890	0.22	6.2	146	
	S.D.	—	90	—	0.3	—	
143	4005	5.4	800	0.19	5.9	152	EF
	4006	5.8	900	—	5.9	152	EF
	4010	5.4	970	—	6.1	178	EF
	4015	5.4	870	—	5.7	155	EF
	4019	5.4	730	—	5.4	157	MF
	Mean	5.5	850	0.19	5.8	161	
	S.D.	—	90	—	0.3	—	

Direct tension test.

Specimens, 4½ × 12½-in. cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

*MF = failed in middle of specimen; OF = failed outside recessed portion of end plate; EF = failed inside end plate.

5.2.1.2 TENSILE STRENGTH. Tensile strengths from direct tension tests and tensile splitting tests have been obtained for PIC and unimpregnated concrete at various temperatures ranging from -21° to 177°C. Test results at the various temperatures are considered to be short-term effects, since the specimens are exposed only long enough to obtain a uniform temperature. The direct tension tests are performed on 4½ × 12½-in. cylinders, and the tensile splitting tests are performed on 6 × 12-in. cylinders. A summary of direct tensile and tensile splitting strengths, and design values obtained from these results, is given in Table 48.

Tensile strength and elastic properties from direct tension tests of unimpregnated and 60 wt % styrene - 40 wt % TMPTMA impregnated con-

crete at 21°, 121° and 143°C are given in Tables 54 and 55. Elastic properties were determined by electrical resistance strain gages bonded to the test cylinders, and three test runs were made on each cylinder. Data from the first two were used to determine Poisson's ratio and modulus of elasticity. Poisson's ratio was determined for only a few specimens because of the low strain level of direct tension tests. The third run was used to obtain stress-strain data to failure.

A cross-sectional view of the direct tension test and types of failure are shown in Figure 21. The end failures and failures within 4-in. of the end plate were not considered significant, since the strengths of these specimens were not greatly different from those of specimens with middle failures.

Table 56

Comparison of Direct Tensile Strength With Tensile Splitting Strength, Unimpregnated and Styrene-TMPTMA Impregnated Concrete

Type of concrete	Test temperature, °C	Tensile strength, ^a psi		
		Tensile splitting	85% of tensile splitting ^b	Direct tension
S-TMPTMA ^c	21	890	760	1090
	121	880	750	890
	143	920	780	850
Unimpregnated	21	340	290	310
	121	310	260	220
	143	370	310	230

Specimens, $4\frac{1}{2} \times 12\frac{1}{2}$ -in. cylinders for direct tension tests; 6×12 -in. cylinders for tensile splitting tests.

^a Values are averages for 4 or 5 specimens for direct tension tests and 10 specimens for tensile splitting tests.

^b Empirical factor sometimes used with unimpregnated concrete to approximate direct strength from tensile splitting tests.

^c 60 wt % styrene - 40 wt % TMPTMA, thermal-catalytically polymerized.

The direct tension tests for unimpregnated concrete and the styrene-TMPTMA impregnated concrete show a loss of tensile strength and a lower modulus of elasticity with an increase in test temperature. Tensile strength of the impregnated concrete averaged 1090 psi at 21°C, 890 psi at 121°C, and 850 psi at 143°C. Tensile strength of unimpregnated concrete averaged 310 psi at 21°C, 220 psi at 121°C, and 230 psi at 143°C.

A comparison of the direct tension tests with previously reported⁴ tensile splitting tests at 21°, 121°, and 143°C is given in Table 56. Tensile splitting strengths for unimpregnated concrete run consistently higher than the direct tensile strengths. For the styrene-TMPTMA impregnated concrete, tensile splitting strengths showed no significant variation with temperature and were closely grouped at about 900 psi, whereas the direct tensile strengths ranged from 1090 psi at 21°C to 850 psi at 143°C. Table 56 also lists a computed value for tensile strength determined by multiplying the tensile splitting strength by 0.85, which is used to approximate the direct tensile strength of unimpregnated concrete from tensile splitting strength tests. These computed values for styrene-TMPTMA impregnated concrete are consistently low-

Table 57

Tensile Splitting Strength After Short-Term Exposure at 177°C, Unimpregnated and Styrene-TMPTMA Impregnated CP-Type Concrete

Specimen No.	Polymer loading, wt %	Tensile splitting strength, psi
72.8-1	-	310
2	-	310
3	-	370
4	-	320
5	-	360
6	-	370
7	-	320
8	-	290
9	-	310
10	-	320
Mean		330
S.D.		30
72.7-1	5.9	930
3	5.7	870
4	6.7	810
5	5.7	900
6	5.9	650
7	5.9	930
9	5.9	930
10	6.4	700
11	6.5	670
12	6.2	520
Mean	6.1	790
S.D.	-	150

Specimens, 6×12 -in. cylinders, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization. Monomer, 60 wt % styrene - 40 wt % TMPTMA.

er (by 70 to 330 psi) than comparable direct tensile strengths, and use of the 0.85 factor does not appear to be valid for PIC. Further tests are required to determine whether a factor should be applied to approximate direct tensile strength from tensile splitting tests.

Tensile splitting test results at 177°C are shown in Table 57 for unimpregnated and styrene-TMPTMA concrete. Tensile splitting strength averaged 790 psi for the impregnated concrete, and 330 psi for the unimpregnated.

Tensile splitting test results at 21°, 121°, and 143°C for MMA-TMPTMA impregnated concrete are given in Table 53. These tests show a decrease in tensile splitting strength with an increase in temperature, from 1030 psi at 21°C, to 990 psi at 121°C, and 880 psi at 143°C.

Additional tensile splitting tests were performed at -23°, 21°, 121°, and 143°C on another group

of specimens also impregnated with MMA-TMP-TMA (Table 59). These are initial tests on specimens selected for long-term exposure at these four temperatures. Tensile splitting strength averaged 1040 psi at -23°C , 970 psi at 21°C , 990 psi at 121°C , and 860 psi at 143°C .

Table 58

Tensile Splitting Strength After Short-Term Exposure at Various Temperatures, MMA-TMPTMA Impregnated Concrete

Test temperature, $^{\circ}\text{C}$	Specimen No., 72.95-	Polymer loading, wt %	Tensile splitting strength, psi
21	1	5.9	850
	2	6.1	1030
	4	6.4	1100
	5	5.9	1090
	10	5.9	1000
	11	5.9	1010
	12	5.8	1080
	15	6.4	940
	29	6.2	1020
	32	5.6	1120
	Mean	6.0	1030
	S.D.	-	96
121	6	6.2	960
	13	6.1	920
	17	5.9	1060
	18	6.1	970
	20	5.9	1100
	23	5.9	960
	24	6.4	970
	25	6.1	1050
	28	5.9	1030
	34	6.2	900
	Mean	6.1	990
	S.D.	-	60
143	7	6.1	950
	14	5.6	990
	16	6.1	970
	21	6.7	940
	26	5.9	710
	27	5.6	770
	30	5.6	990
	33	5.9	740
	35	5.9	770
	36	6.4	1020
	Mean	6.0	880
	S.D.	-	120

Specimens, 6×12 -in. cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt % TMPTMA.

Table 59

Tensile Splitting Strength After Short-Term Exposure of MMA-TMPTMA Impregnated Concrete at Various Temperatures - Initial Tests for Long-Term Exposure

Test temperature, $^{\circ}\text{C}$	Specimen No., 72.196-	Polymer loading, wt %	Tensile splitting strength, psi
-23	3	5.8	950
	4	7.2	940
	6	6.3	1070
	10	6.6	1140
	18	6.6	1060
	22	6.7	1090
	26	6.1	1120
	30	6.7	1020
	31	6.3	970
	42	6.5	1030
	Mean	6.5	1040
	S.D.	-	70
21	2	6.4	970
	5	6.6	1000
	11	6.7	940
	12	6.3	1090
	15	6.9	1010
	19	6.6	980
	20	6.7	950
	28	6.3	790
	34	6.1	1040
	37	6.6	970
	Mean	6.5	970
	S.D.	-	80
121	1	7.2	1080
	7	6.4	1070
	8	7.0	930
	9	6.6	860
	17	6.9	1050
	21	6.6	1130
	24	6.3	990
	35	6.1	920
	36	5.8	950
	41	6.1	960
	Mean	6.5	990
	S.D.	-	90
143	13	6.3	640
	14	6.1	810
	16	7.1	930
	23	6.7	810
	25	6.6	800
	27	6.9	800
	29	6.1	1020
	32	6.0	990
	33	6.3	890
	40	6.9	860
	Mean	6.5	860
	S.D.	-	110

Specimens, 6×12 -in. cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt % TMPTMA.

Table 60

Flexural Strength of Unimpregnated Concrete and Styrene-TMPTMA Impregnated Concrete at 21°C

Specimen No.	Polymer loading, wt %	Ultimate load, lb	Modulus of rupture, psi	Modulus of elasticity, 10 ⁶ psi	Shear, lb	Nominal shear stress, psi
72.27-1	-	3960	745	4.39	1980	124
2	-	3580	675	4.25	1790	112
3	-	3820	720	4.40	1910	119
4	-	3550	665	3.99	1775	111
5	-	3960	745	4.63	1980	124
Mean	-	3775	710	4.33	1888	118
72.26-1	5.9	8980	1690	6.24	4490	281
5	6.2	8400	1580	6.36	4200	262
8	7.0	6900	1300	6.22	3450	216
10	7.0	6800	1280	6.36	3400	212
16	5.8	8060	1515	5.95	4030	252
Mean	6.4	7830	1475	6.23	3915	245

Specimens, 4×4×30-in. bars of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Table 61

Flexural Strength of Unimpregnated Concrete and Styrene-TMPTMA Impregnated Concrete After Short-Term Exposure at 121°C

72.27-6	-	3210	605	3.26	1605	100
7	-	1985	375	2.88	993	62
8	-	3370	635	3.38	1685	105
9	-	3280	615	3.11	1640	103
10	-	2895	545	3.28	1448	91
Mean	-	2950	555	3.18	1474	92
72.26-2	6.6	5920	1115	4.84	2960	185
4	6.3	7080	1130	4.81	3540	221
6	5.9	7020	1320	5.52	3510	219
11	6.5	5300	995	5.40	2650	166
13	6.5	6000	1130	5.48	3000	188
Mean	6.4	6265	1180	5.21	3132	196

Specimens, 4×4×30-in. bars of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 121°C.

Table 62

Flexural Strength of Unimpregnated Concrete and Styrene-TMPTMA Impregnated Concrete After Short-Term Exposure at 143°C

72.27-11	-	3815	715	3.42	1908	119
12	-	3130	590	3.29	1565	98
X	-	3570	670	3.21	1785	112
14	-	3250	610	3.13	1625	102
15	-	3510	660	3.43	1755	110
Mean	-	3455	650	3.30	1728	108
72.26-7	6.8	6760	1270	5.21	3380	211
9	6.4	7060	1330	5.05	3530	221
12	6.4	5920	1115	5.72	2960	185
14	6.3	6320	1190	5.38	3160	198
15	6.0	7080	1330	5.13	3540	221
Mean	6.4	6630	1245	5.30	3315	207

Specimens, 4×4×30-in. bars of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 143°C.

Figure 27. Flexure test of 4×4×30-in. bars of unimpregnated and 60 wt % styrene - 40 wt % TMPTMA impregnated CP-type concrete.

Figure 28. Flexure test of 4×4×30-in. bars of 70 wt % MMA - 30 wt % TMPTMA impregnated CP-type concrete.

Table 63

Flexural Strength of MMA-TMPTMA Impregnated Concrete at 21°C

Specimen No., 72.110-	Polymer loading, wt %	Ultimate load, lb	Modulus of rupture, psi	Modulus of elasticity, 10 ⁶ psi	Shear, lb	Nominal shear stress, psi
1	6.1	a	-	6.34	-	-
2	6.3	3900	1650	5.64	1950	122
3	6.2	3765	1590	5.81	1880	118
4	6.9	4255	1800	6.39	2130	133
14	6.0	4175	1760	5.41	2090	131
Mean	6.3	4020	1700	5.92	2010	126

Specimens, 4×4×30-in. bars of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt % TMPTMA.

*Accidentally failed.

Table 64

Flexural Strength of MMA-TMPTMA Impregnated Concrete
After Short-Term Exposure at 121°C

6	6.7	2850	1200	4.35	1425	89
7	6.5	2630	1110	4.74	1315	82
8	6.5	2715	1150	4.76	1360	85
9	6.5	2810	1190	4.89	1405	88
10	5.2	2550	1080	4.61	1280	80
Mean	6.3	2710	1150	4.67	1360	85

Specimens, 4×4×30-in. bars of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt % TMPTMA.

Test temperature, 121°C.

Table 65

Flexural Strength of MMA-TMPTMA Impregnated Concrete
After Short-Term Exposure at 143°C

5	6.6	2225	940	4.35	1110	69
11	6.0	2810	1190	4.52	1405	88
12	6.8	2720	1150	4.52	1360	85
13	6.3	2900	1220	4.84	1450	91
15	5.8	2805	1180	4.80	1400	88
Mean	6.3	2690	1140	4.61	1345	84

Specimens, 4×4×30-in. bars of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt % TMPTMA.

Test temperature, 143°C.

Table 66
Average Values for Strength and Modulus of Elasticity
as Determined From Flexure Tests

Type of material	Test temperature, °C	Flexure tests				Compressive tests		
		Polymer loading, wt %	No. of specimens	Modulus of rupture, psi	Modulus of elasticity, 10 ⁶ psi	Polymer loading, wt %	No. of specimens	Modulus of elasticity, 10 ⁶ psi
Control	21	—	5	710	4.3	—	10	3.5
	121	—	5	555	3.2	—	10	3.2
	143	—	5	650	3.3	—	10	3.0
S-TMPTMA ^a	21	6.4	5	1475	6.3	5.7	12	6.4
	121	6.4	5	1180	5.2	5.6	12	6.0
	143	6.4	5	1245	5.3	5.5	12	5.3
MMA-TMPTMA ^b	21	6.3	5	1700	5.9	6.0	15	6.0
	121	6.3	5	1150	4.7	6.0	15	5.1
	143	6.3	5	1140	4.6	6.0	15	4.6

Specimens, 4×4×30-in. bars of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

^a60 wt % styrene – 40 wt % TMPTMA.

^b70 wt % MMA – 30 wt % TMPTMA.

5.2.1.3 FLEXURAL STRENGTH. Flexure tests were performed at 21°, 121°, and 143°C on 4×4×30-in. bars to obtain the modulus of rupture (extreme tension fiber stress at failure) and the modulus of elasticity for unimpregnated concrete and concrete impregnated with 60 wt % styrene – 40 wt % TMPTMA (see Tables 60 to 62). All elevated-temperature testing is considered as short-term temperature exposure because the specimens are heated only long enough to obtain a uniform temperature. Figure 27 shows the test arrangement and loading locations.

The modulus of elasticity was determined from electrical resistance strain gages bonded to the top and bottom surfaces of the bars at midspan. Given the strain and moment, the modulus can be calculated. A comparison between the modulus of elasticity as determined from the deflection and that determined from strain measurements was made for the bars tested at 21°C. The values of modulus of elasticity were essentially the same, and therefore the strain method was adopted as a standard method.

Test results for concrete impregnated with 70 wt % MMA – 30 wt % TMPTMA are summarized in Tables 63 to 65. Data for three temperatures, 21°, 121°, and 143°C, are listed. A comparison of average values of modulus of rupture and modulus

of elasticity and a comparison of modulus of elasticity obtained from compressive strength testing has been made. These results are summarized in Table 66. The loading arrangement is shown in Figure 28.

5.2.1.4 SHEAR STRENGTH. Shear strengths have been obtained for unimpregnated concrete and concrete impregnated with 60 wt % styrene – 40 wt % TMPTMA and 70 wt % MMA – 30 wt % TMPTMA, both thermal-catalytically polymerized. The tests were performed in accordance with the USBR standard single-shear method on 2-in.-diam × 4-in.-long cylinders at 21°C. Section 5.1.2.2 contains an illustration and discussion of single-shear as well as double-shear methods. Examination of the test results summarized in Tables 67 to 69 indicates that both types of impregnated concrete produced a shear strength 3 times as great as that of unimpregnated concrete.

The shear strength of unimpregnated control specimens averaged 940 psi, which is slightly lower but generally comparable with that of unimpregnated control specimens in the study of normal-temperature applications discussed in Section 5.1.2.2. Shear strengths averaged 2880 psi for styrene-TMPTMA specimens and 2510 psi for MMA-TMPTMA specimens. These strengths were somewhat lower than the 3760 psi obtained

Table 67

Shear Strength of Unimpregnated Concrete Single-Shear Test Method		
Specimen No., 72.29-	Load, lb	Shear stress, psi
3	3420	980
4	3260	930
5	2550	720
6	3570	1020
7	3420	980
8	3240	920
9	2890	830
10	3370	960
11	3620	1030
12	3440	980
Mean	3280	940

Specimens, 2-in.-diam $\times$ 4-in.-long cylinders of CP-type concrete.

Test temperature, 21°C (room temperature).

Table 69

Shear Strength of MMA-TMPTMA Impregnated Concrete Single-Shear Test Method			
Specimen No., 72.111-	Polymer loading, wt %	Load, lb	Shear stress, psi
2	7.4	9,740	2,780
3	7.4	7,960	2,270
5	7.2	7,600	2,160
6	7.0	10,400	2,960
7	7.0	10,440	2,990
8	7.2	9,480	2,720
9	7.0	8,840	2,550
10	7.2	7,800	2,240
11	7.1	8,040	2,280
12	7.0	7,600	2,170
Mean	7.1	8,790	2,510

Specimens, 2-in.-diam $\times$ 4-in.-long cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 70 wt % MMA - 30 wt % TMPTMA.

Test temperature, 21°C.

with MMA-impregnated specimens in the single-shear test (Section 5.1.2.2). A comparison of all shear tests is given in Table 70.

5.2.1.5 HIGH-TEMPERATURE CREEP. Two series of tests have been conducted at elevated temperatures: (1) an earlier test series with OSW-type concrete impregnated with 60 wt % styrene - 40 wt % TMPTMA and 90 wt % DAP - 10 wt % MMA (the

Table 68

Shear Strength of Styrene-TMPTMA Impregnated Concrete Single-Shear Test Method			
Specimen No., 72.28-	Polymer loading, wt %	Load, lb	Shear stress, psi
2	7.7	11,180	3,180
3	8.3	9,330	2,650
4	7.6	10,960	3,130
5	7.6	9,180	2,630
6	7.6	12,160	3,460
7	7.6	7,140	2,040
8	7.8	8,830	2,510
9	7.8	9,920	2,810
10	7.8	12,020	3,410
12	7.6	10,460	2,980
Mean	7.7	10,120	2,880

Specimens, 2-in.-diam $\times$ 4-in.-long cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 21°C.

Table 70

Comparison of Shear Test Results Single-Shear and Double-Shear Methods		
Specimen	Test method	Shear stress, psi
Unimpregnated	Single shear	940
Styrene-TMPTMA ^a	Single shear	2880
MMA-TMPTMA ^b	Single shear	2540
Unimpregnated	Single shear	1140
MMA	Single shear	3760
Unimpregnated	Double shear	1730
MMA	Double shear	3670

Specimens, 2-in.-diam $\times$ 4-in.-long cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Test temperature, 21°C.

^a60 wt % styrene - 40 wt % TMPTMA.

^b70 wt % MMA - 30 wt % TMPTMA.

DAP-MMA test results are given; however, the system is no longer being considered for desalting plant applications⁴), and (2) a test series with CP-type concrete impregnated with 60 wt % styrene - 40 wt % TMPTMA and 70 wt % MMA - 30 wt % TMPTMA.

(a) OSW-TYPE CONCRETE. Compressive creep tests on OSW-type concrete at 143°C have been termi-

Table 71
High-Temperature High-Stress Creep
Polymer-Impregnated OSW-Type Concrete

Time under load, days	Creep strain, $\mu\text{in./in.}$ -psi at 143°C					
	S-TMPTMA ^a		DAP-MMA ^b		Unimpregnated	
	Spec. 5 ^c	Spec. 2 ^d	Spec. 19 ^c	Spec. 6 ^d	Spec. 7 ^c	Spec. 8 ^d
1	0.026	0	0.026	0	0.454	0
5	0.062	0.020	0.061	0.029	0.630	0.178
30	0.074	0.030	0.081	0.049	0.735	0.304
55	0.076	0.032	0.094	0.058	0.751	0.328
121	0.084	0.042	0.111	0.080	0.778	0.351
184	0.089	0.043	0.124	0.092	0.782	0.353
348	0.082	0.035	0.120	0.093	0.811	0.389
498	0.091	0.048	0.158	0.129	0.816	0.402
694	0.096	0.048	0.242	0.149	0.827	0.418
798	0.104	0.051	0.248	0.161	0.832	0.425
889	0.092	0.042	0.252	0.157	0.814	0.413

4½×12-in. cylinders loaded to ≈37% of ultimate strength.

Impregnated concrete under 7000 psi and unimpregnated concrete under 2313 psi sustained compressive load at 143°C.

^aS-TMPTMA = 60 wt % styrene - 40 wt % TMPTMA; specimens have polymer loading of 4.7 wt %.

^bDAP-MMA = 90 wt % DAP - 10 wt % MMA; specimens have polymer loading of 5.4 wt %.

^cSpecimen loaded at 24°C, then heated to 143°C.

^dSpecimen heated to 143°C before loading.

nated after nearly 2½ years (Table 71). The compressive loads are 7000 psi for PIC specimens and 2313 psi for unimpregnated specimens. These loadings were estimated to be about 37% of the ultimate strength at room temperature for each type of concrete. Initially specimens were either loaded at room temperature and then heated to 143°C for testing, or heated to 143°C and then loaded. PIC and unimpregnated specimens loaded at 143°C have about one-half the deformation of companion specimens loaded at room temperature and then heated to 143°C. The styrene-TMPTMA specimens have about one-tenth the unit deformation per psi shown by comparable unimpregnated specimens. After 889 days under load, the styrene-TMPTMA specimen loaded at 143°C had a deformation of 0.043 $\mu\text{in./in.}$ -psi, and the specimen loaded at room temperature and then heated to 143°C had a deformation of 0.092 $\mu\text{in./in.}$ -psi. Most of the deformation of the styrene-TMPTMA and unimpregnated specimens occurred soon after loading. After about 1 month under load there was very little additional movement aside from minor fluctuations. The DAP-MMA

specimens showed continued movement throughout the test. After completion of the test, the compressive strength and modulus of elasticity of all specimens was determined (Table 72). For both styrene-TMPTMA and unimpregnated specimens, no loss in strength due to exposure at 143°C or sustained compressive loading at 143°C was noted, although there was some decrease in modulus of elasticity.

(b) CP-TYPE CONCRETE. Compressive creep tests at 121° and 143°C are in progress on 60 wt % styrene - 40 wt % TMPTMA, 70 wt % MMA - 30 wt % TMPTMA, and unimpregnated CP-type concrete (Table 73). PIC specimens are under compressive loads of 2313 and 7000 psi, and unimpregnated concrete is under compressive loads of 800 and 2313 psi. All specimens were heated to the test temperature before the load was applied. Styrene-TMPTMA and the unimpregnated specimens have been under load for 400 days. The MMA-TMPTMA specimens were started at a later date and have been under load for only 46 days.

The styrene-TMPTMA specimens show that most of the deformation occurs during the first 120

Table 72
High-Temperature Strength of Creep Test Specimens
Polymer-Impregnated OSW-Type Concrete

Specimen No., OSW-10-	Polymer	Polymer loading, wt %	Temperature exposure time, days	Compressive strength, psi	Modulus of elasticity, 10 ⁶ psi
28 ^a	-	-	1	6,000	4.3
29	-	-	1	6,400	4.1
30	-	-	7	6,200	3.5
31	-	-	7	6,900	3.3
32	-	-	70	6,200	4.2
33	-	-	70	6,300	3.3
34	-	-	457	4,400	2.2
35	-	-	457	3,800	2.4
9	-	-	890	6,600	-
7 ^b	-	-	890	6,100	-
8 ^b	-	-	890	6,000	-
4 ^a	S+TMPTMA ^c	4.3	1	20,400	8.0
1	S+TMPTMA	5.1	1	14,200	6.7
11	S+TMPTMA	4.6	7	16,200	6.6
14	S+TMPTMA	5.1	7	15,300	6.7
16	S+TMPTMA	4.7	70	15,300	6.8
20	S+TMPTMA	5.0	70	15,600	7.9
12	S+TMPTMA	4.6	457	12,300	3.4
21	S+TMPTMA	4.6	457	14,200	5.0
26	S+TMPTMA	5.1	457	15,000	6.4
27	S+TMPTMA	5.1	457	16,500	5.4
12	S+TMPTMA	4.6	890	16,700	-
5 ^d	S+TMPTMA	4.7	890	15,900	-
2 ^d	S+TMPTMA	4.7	890	16,000	-
13 ^a	DAP+MMA ^e	5.4	1	17,200	6.8
15	DAP+MMA	4.9	1	13,000	6.0
17	DAP+MMA	5.0	7	11,400	6.0
18	DAP+MMA	5.0	7	14,900	6.2
3	DAP+MMA	5.0	70	14,700	5.9
22	DAP+MMA	5.4	70	14,300	6.0
23	DAP+MMA	5.4	457	13,700	4.0
24	DAP+MMA	5.4	457	13,500	5.2
25	DAP+MMA	5.0	457	10,400	4.1
10	DAP+MMA	5.4	890	12,300	3.4
19 ^d	DAP+MMA	5.4	890	11,800	-
6 ^d	DAP+MMA	5.4	890	14,400	-

4½ × 12½-in. specimens ($L/d=2.8$); compressive strengths have been corrected to approximate a cylinder of $L/d=2$. Specimens exposed to a temperature of 143°C and tested at 143°C, except as noted.

^aSpecimen tested at room temperature (24°C).

^bSpecimen under 2313 psi compressive load at 143°C for 890 days.

^cS+TMPTMA = 60 wt % styrene - 40 wt % TMPTMA; catalyst, 1 wt % benzoyl peroxide.

^dSpecimen under 7000 psi compressive load at 143°C for 890 days.

^eDAP+MMA = 90 wt % diallyl phthalate - 10 wt % MMA; catalyst, 5 wt % tert.-butyl perbenzoate; thermal-catalytic polymerization.

Table 73

High-Temperature High-Stress Creep
Polymer-Impregnated CP-Type Concrete

Time under load, days	Average creep strain, $\mu\text{in./in.}\cdot\text{psi}$									
	S-TMPTMA				Unimpregnated				MMA-TMPTMA	
	121°C		143°C		121°C		143°C		121°C	143°C
	2313 psi	7000 psi	2313 psi	7000 psi	800 psi	2313 psi	800 psi	2313 psi	2313 psi	7000 psi
2	0.028	0.044	0.053	0.068	0.174	0.104	0.224	0.179	0.113	0.078
4	-	-	-	-	-	-	-	-	0.132	0.099
6	0.033	0.045	0.064	0.079	0.164	0.115	0.258	0.237	0.128	0.098
46	-	-	-	-	-	-	-	-	0.173	0.138
62	0.070	0.082	0.125	0.139	0.243	0.197	0.417	0.357	-	-
126	0.102	0.099	0.151	0.155	0.294	0.217	0.508	0.408	-	-
204	0.102	0.100	0.151	0.153	0.320	0.230	0.570	0.436	-	-
308	0.104	0.101	0.195	0.174	0.375	0.270	0.570	0.454	-	-
348	0.113	0.114	0.192	0.184	0.388	0.291	0.602	0.476	-	-
400	0.105	0.100	0.173	0.174	0.370	0.262	0.622	0.467	-	-

Values are average creep strain of two $4\frac{1}{2} \times 12$ -in. cylindrical specimens.

Specimens heated to test temperatures of 121° and 143°C prior to loading. Impregnated specimens subjected to 2313 and 7000 psi sustained compressive load; unimpregnated specimens subjected to 800 and 2313 psi sustained compressive load. MMA-TMPTMA specimens have been under load for only 46 days.

S-TMPTMA = 60 wt % styrene - 40 wt % TMPTMA.

MMA-TMPTMA = 70 wt % MMA - 30 wt % TMPTMA.

Table 74

High-Temperature Strength of Companion Specimens for Creep Test
Polymer-Impregnated CP-Type Concrete

Test temperature, °C	Styrene-TMPTMA ^a				MMA-TMPTMA ^b				Unimpregnated		
	Specimen No.	Polymer loading, wt %	Compressive strength, psi	Modulus of elasticity, 10 ⁶ psi	Specimen No.	Polymer loading, wt %	Compressive strength, psi	Modulus of elasticity, 10 ⁶ psi	Specimen No.	Compressive strength, psi	Modulus of elasticity, 10 ⁶ psi
Initial Tests											
23	14	6.3	18,500	6.2	12	5.0	17,000	5.5	3	5,000	3.6
	57	5.8	18,400	6.4	13	5.2	19,800	6.4	50	5,300	3.6
	56	5.8	17,400	6.6	14	5.0	18,500	6.5	52	5,500	3.6
	Av	-	18,100	6.4	Av	5.1	18,500	6.2	-	5,300	3.6
121	4	6.3	16,700	6.6	15	5.3	-	5.0	15	4,900	3.1
	97	5.4	17,600	6.2	16	4.5	13,600	5.1	32	4,900	3.1
	87	5.8	16,600	6.4	18	4.9	-	5.0	84	5,700	3.0
	Av	-	17,000	6.4	Av	5.6	13,900	-	Av	5,200	3.1
143	29	6.3	14,800	5.2	19	4.9	11,100	3.9	46	5,800	3.2
	6	5.8	16,800	5.5	20	4.6	17,600	4.2	98	4,500	2.9
	68	5.8	14,600	5.0	21	5.3	11,800	4.0	101	5,100	2.6
	Av	-	15,400	5.2	Av	4.9	11,300	4.0	Av	5,500	2.9
Tests After 1-Year Exposure at Test Temperatures^c											
23	61	5.8	18,900	6.1	-	-	-	-	30	5,700	3.7
	102	5.8	19,300	7.0	-	-	-	-	34	5,500	3.9
	Av	-	19,000	6.5	-	-	-	-	Av	5,600	3.8
121	21	6.3	71,000	5.7	-	-	-	-	45	4,900	3.0
	2	5.8	15,400	5.8	-	-	-	-	46	5,300	3.0
	5	5.8	16,100	5.4	-	-	-	-	96	5,400	2.4
	Av	-	16,100	5.7	-	-	-	-	Av	5,200	2.8
143	69	6.3	15,700	4.9	-	-	-	-	7	5,200	2.6
	73	5.8	15,100	4.9	-	-	-	-	38	5,000	2.8
	37	5.8	15,200	5.1	-	-	-	-	83	5,700	2.7
	Av	-	15,300	5.0	-	-	-	-	Av	5,300	2.7

$4\frac{1}{2} \times 12\frac{1}{2}$ -in. cylinders, $L/d = 2.8$. Compressive strengths have been corrected to approximate the strength of a cylinder of $L/d = 2$.

^aStyrene-TMPTMA = 60 wt % styrene - 40 wt % TMPTMA.

^bMMA-TMPTMA = 70 wt % MMA - 30 wt % TMPTMA.

^cMMA-TMPTMA specimens have not been exposed long enough for 1-year tests.

Table 75
Flexural Strength of Reinforced Concrete and Reinforced
Impregnated Concrete After Short-Term Exposure at 143°C

Specimen No., 6.2.6-	Polymer loading, wt %	Ultimate load, lb	Ultimate moment, in.-lb	Ultimate compressive strain, in./in.	Shear at ultimate load, lb	Nominal shear stress, ^a psi
10028	-	4,770	38,160	0.0014	2,385	187
10029	-	4,700	37,600	0.0012	2,350	184
10030	-	4,600	36,800	0.0020	2,300	180
10031	-	4,825	38,600	0.0014	2,410	189
10032	-	4,625	37,000	0.0014	2,310	181
Mean	-	4,700	37,630	0.0015	2,350	184
10022	6.6	4,775	38,200	0.0008	2,390	187
10023	6.5	4,590	36,720	0.0009	2,295	180
10024	6.7	4,970	39,760	0.0009	2,485	195
10025	6.9	4,940	39,520	0.0014	2,470	194
10026	6.7	4,630	37,040	0.0010	2,315	182
Mean	6.7	4,780	38,250	0.0010	2,390	188

Specimens, 3×5×54-in. beams of CP-type concrete, reinforced with a single No. 4 deformed bar in tension area and oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 143°C.

^aNominal shear stress = shear/3×4.25.

Table 76
Shear Strength of Reinforced Concrete and Reinforced
Impregnated Concrete After Short-Term Exposure at 143°C

Specimen No., 6.2.6-	Polymer loading, wt %	Ultimate load, lb	Ultimate shear, lb	Nominal shear stress, ^a psi	Moment at ultimate load, in.-lb	Type of failure
10048	-	9,200	6,130	481	30,670	Shear
10049	-	10,750	7,170	562	35,830	"
10050	-	11,200	7,470	586	37,330	"
10051	-	10,400	6,930	544	34,670	"
10052	-	10,240	6,830	536	34,130	"
Mean	-	10,360	6,910	542	34,530	
10041	7.1	15,200	10,130	795	50,670	Flexure
10042	6.9	14,500	9,670	758	48,330	"
10043	6.6	16,620	11,080	869	55,400	"
10045	6.9	16,400	10,930	857	54,670	Shear
10046	6.6	16,700	11,130	873	55,670	Flexure
Mean	6.8	15,880	10,590	830	52,950	

Specimens, 3×5×54-in. beams of CP-type concrete, reinforced with two No. 4 deformed bars and oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 143°C.

^aNominal shear stress = shear/3×4.25.

days under load and that specimens under 2313 and 7000 psi load have about the same creep deformation per psi. Styrene-TMPTMA specimens tested at 121°C for 400 days have a creep deformation of about 0.10 $\mu\text{in./in.-psi}$; specimens tested at 143°C have a somewhat greater creep deformation, about 0.17 $\mu\text{in./in.-psi}$. The unimpregnated specimens show about 3 to 6 times more creep strain per psi than comparable styrene-TMPTMA specimens. The unimpregnated specimens under 800 psi load show about one-third more creep strain per psi than comparable specimens under 2313 psi, and specimens tested at 143°C have about one-half more creep strain per psi than specimens tested at 121°C. The CP-type concrete creeps slightly more than the OSW type. At about 400 days under 7000 psi at 143°C, styrene-TMPTMA CP-type concrete has a creep strain of 0.17 $\mu\text{in./in.-psi}$, as compared with 0.04 for styrene-TMPTMA OSW-type concrete (Table 71). Compressive strengths of companion specimens at room temperature and at the elevated temperatures are given in Table 74. Styrene-TMPTMA and unimpregnated specimens show no decrease in strength after exposure to high temperature for 1 year. The styrene-TMPTMA specimens show some decrease in strength with increasing exposure temperature, averaging about 19,000 psi at room temperature, 16,100 psi at 121°C, and 15,300 psi at 143°C. The initial strengths of MMA-TMPTMA specimens were slightly lower at the high temperatures; they averaged 18,500 psi at room temperature, 13,900 psi at 121°C, and 11,900 psi at 143°C.

5.2.1.6 FLEXURAL AND SHEAR STRENGTHS OF REINFORCED BEAMS. Flexural strengths and shear strengths were obtained for reinforced unimpregnated concrete and reinforced concrete impregnated with 60 wt % styrene - 40 wt % TMPTMA, thermal-catalytically polymerized. These tests were conducted at 143°C on 3×5×54-in. beams each having one No. 4 deformed reinforcement bar in the tension area. Figures 25 and 26 show the flexure and shear test configurations, and the test results are summarized in Tables 75 and 76. None of the beams that failed in flexure failed because of a compression failure; this indicates that all beams were underreinforced.

The ultimate load was taken as the amount of load that the beam could support without failing. Comparison of Tables 75 and 76 shows that the shear specimens achieved higher moments at ultimate load. This is because the shear beams were doubly reinforced and the arrangement did not

Table 77

Flexural Strength of Unreinforced and Polymer-Impregnated Concrete After Short-Term Exposure at 143°C

Specimen No., 6,2,6-	Polymer loading, wt %	Ultimate load, lb	Modulus of rupture, psi	Modulus of elasticity, 10 ⁶ psi
10065	-	1770	690	3.03
10066	-	1760	680	3.20
Mean	-	1765	685	3.12
10061	7.0	3660	1420	5.56
10062	7.1	3860	1500	5.26
10063	6.9	3620	1410	5.58
10064	7.1	3240	1260	5.28
Mean	7.0	3595	1400	5.42

Specimens, 3×3×16-in. bars of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 143°C.

allow a large deflection, such as was obtained in the flexure arrangement. Only one impregnated beam in the shear arrangement developed an actual shear failure. Even though the majority of the shear beams failed in flexure, the increase in the nominal shear stress is evident from the test results.

The flexural strengths of unreinforced unimpregnated bars and concrete impregnated with 60 wt % styrene - 40 wt % TMPTMA were obtained at 143°C (see Table 77). These bars were tested on a 14-in. span with a two-point loading of 4 in. between load points centered on the bar. A correlation between modulus of rupture and appearance of the first crack in the 3×5×54-in. beams could not be made, since the beams were covered with insulation to maintain the test temperature.

Compressive and tensile strengths for unimpregnated concrete and concrete impregnated with 60 wt % styrene - 40 wt % TMPTMA were obtained at 143°C. The data are summarized in Table 78. These values are higher than those obtained for 6×12-in. cylinders, probably because the aggregate used in a 3×6-in. cylinder has a smaller maximum size.

5.2.1.7 HIGH-TEMPERATURE LOOP TESTS. Long-term loop tests are conducted to evaluate the behavior of PIC under exposure to simulated desalting plant conditions. The test results discussed in this

Table 78

Compressive and Tensile Strengths of Unimpregnated and Styrene-TMPTMA Impregnated Concrete After Short-Term Exposure at 143°C

Specimen No., 6.2.6-	Polymer loading, wt %	Test	Ultimate load, lb	Strength, psi
10077	-	Tensile	2,400	340
10078	-		2,600	370
10079	-		2,200	310
Mean			2,400	340
10074	7.0	Tensile	8,300	1,173
10076	7.0		7,140	1,010
Mean	7.0		7,720	1,090
10080	-	Compressive	32,300	4,570
10081	-		42,100	5,950
10082	-		42,000	5,940
Mean			38,800	5,490
10071	6.9	Compressive	129,000	18,250
10073	7.2		119,000	16,830
10075	7.2		100,000	14,140
Mean	7.1		116,000	16,410

Specimens, 3-in.-diam $\times$ 6-in.-long cylinders of CP-type concrete, oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 143°C.

section pertain to structural properties. A discussion of test results pertaining to durability, as well as a description of the loop tests, is given in Section 5.2.2.3.

(a) SINGLE-PHASE LOOPS. Compressive strength tests were performed on three 60 wt % styrene - 40 wt % TMPTMA impregnated 6 $\times$ 12-in. cylinders after 2 years of exposure in the 121°C brine loop. Two companion cylinders that had been exposed to air at 23°C and 50% relative humidity during this period were also tested after being heated to 121°C. As shown in Table 79, the specimens not exposed to the brine had both a greater strength and a higher modulus of elasticity than those exposed to the brine.

The effect of exposure time in the 121°C brine loop is shown in Table 88 in Section 5.2.2.3. Tests on brine-exposed specimens indicated a gradual loss in strength from an average of 16,200 psi after 215 days of exposure to 13,300 psi after

2 years. A reduction in the modulus of elasticity from 5.7×10^6 to 5.0×10^6 psi was noted in this time interval. A fairly consistent increase in unit length was observed from an initial 0 to 0.001272 in./in. in 2 years. No definite trend in length change is evident in the specimens exposed to air at 23°C and 50% relative humidity.

Test results on 6 $\times$ 12-in. cylinders and 4 $\times$ 4 $\times$ 30-in. bars after 2 years of exposure in 143°C brine are summarized in Table 80 and in Table 88 in Section 5.2.2.3. Compared with initial and 6-month measurements, some decrease in compressive strength and modulus of elasticity and an increase in length were noted. Three additional cylinders were removed from the loops and tested after 15 months to verify these changes. The same trend was noted for modulus of elasticity and change in unit length, but the compressive strength was not significantly different.

Tests were conducted on impregnated 6 $\times$ 12-in. specimens after 2 years of exposure in 143°C brine. Companion specimens that had been stored at 21°C and 50% relative humidity were also tested after being heated to 143°C. The strength and modulus of elasticity of the brine-exposed specimens were only about 65% of the values for specimens not exposed. An analysis was made to determine the effect of exposure time in 143°C brine. A definite loss of strength was noted for both unimpregnated and styrene-TMPTMA impregnated concrete. This loss appears to continue with increased exposure time.

(b) THREE-PHASE BRINE LOOPS. Tests were made on unimpregnated and 60 wt % styrene - 40 wt % TMPTMA impregnated CP-type concrete after exposure for 6 months and 1 year in the 121°C three-phase loops (see Table 89 in Section 5.2.2.3). Compressive strengths of the impregnated specimens were not significantly different for any environment. After 1 year's exposure, compressive strengths averaged 14,700 psi for both vapor and brine-vapor interface exposures and 15,300 psi for brine exposures. The average for all three environments was 14,900 psi, the same as that obtained for the impregnated OSW-type concrete specimens after 1 year of exposure in the single-phase brine loop at the same temperature. The average compressive strength of all impregnated specimens in the three-phase loops after 6 months' exposure was about 15,250. The difference between results for 1 year and 6 months are not significant enough to arrive at any definite conclusion. Examination

Table 79

**Compressive Strength and Elasticity of Styrene-TMPTMA Impregnated Concrete
After Two-Year Exposure to Brine at 121°C**

Specimen No.	Polymer loading, wt %	Ultimate strength, psi	Modulus of elasticity, 10 ⁶ psi	Poisson's ratio	Elastic limit stress, psi	Ultimate strain, μ in./in.
OSW-8-1	4.6	13,210	4.66	0.08	12,000	2,660
10	4.7	13,360	5.32	0.08	9,500	2,600
8	4.4	13,300	5.08	0.13	10,000	3,000
Mean	4.6	13,290	5.02	0.10	10,500	2,730
OSW-10-5	5.1	17,610	6.78	0.23	12,000	2,860
36	4.6	14,180	7.47	0.22	10,000	2,040
Mean	4.9	15,900	7.13	0.23	11,000	2,450

Specimens, 6-in.-diam $\times$ 12-in.-long cylinders of OSW-type concrete, oven-dried at 150°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

OSW-8 specimens exposed to brine at 121°C for 2 years.

OSW-10 specimens exposed to air at 23°C and 50% relative humidity for 2 years.

Test temperature, 121°C.

Table 80

**Compressive Strength and Elasticity of Styrene-TMPTMA Impregnated Concrete
After Two-Year Exposure to Brine at 143°C**

Specimen No.	Polymer loading, wt %	Ultimate strength, psi	Modulus of elasticity, 10 ⁶ psi	Poisson's ratio	Elastic limit stress, psi	Ultimate strain, μ in./in.
OSW-9-8	4.6	10,500	4.35	0.13	7,500	2,580
15	4.4	9,390	4.10	0.14	7,000	2,740
25	4.8	11,100	4.84	0.17	7,500	2,800
Mean	4.6	10,330	4.43	0.15	7,330	2,710
OSW-10-17	4.8	16,320	6.98	0.22	11,000	2,560
24	5.0	15,570	6.75	0.19	11,000	2,700
Mean	4.9	15,950	6.86	0.20	11,000	2,630

Specimens, 6-in.-diam $\times$ 12-in.-long cylinders of OSW-type concrete, oven-dried at 150°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

OSW-9 specimens exposed to brine at 143°C for 2 years.

OSW-10 specimens exposed to air at 23°C and 50% relative humidity for 2 years.

Test temperature, 143°C.

of unit length change at 6 months and 1 year does indicate a trend to greater expansion with increased exposure time.

Results after 6 months and 1 year of exposure in the 143°C three-phase loops show more pronounced effects of exposure. (See Tables 81 and 82 and Table 89 in Section 5.2.2.3.) Compressive strengths of impregnated concrete ranged from

11,700 psi for the vapor-exposure specimens to 13,000 psi for the brine-exposure specimens. The average compressive strength of all impregnated CP-type concrete specimens tested in the three-phase loops at 143°C is 12,400 psi, compared with 14,900 psi for 121°C three-phase specimens and 11,100 psi for impregnated OSW-type concrete in the 143°C single-phase loops. Unit length

Table 81
Compressive Strength and Elasticity of Styrene-TMPTMA Impregnated Concrete
After One-Year Exposure at 143°C in Three-Phase Test Loops

Specimen No., 72.174-	Exposure ^a	Polymer loading, wt %	Ultimate strength, psi	Modulus of elasticity, 10 ⁶ psi	Poisson's ratio	Elastic limit, psi	Ultimate strain, $\mu\text{in./in.}$
357	V	6.9	9,890	4.17	0.19	9,000	2,640
279	V	5.9	12,460	4.55	0.12	10,000	3,100
350	V	5.6	12,880	4.13	0.11	11,000	3,100
Mean		6.1	11,740	4.28	0.14	10,000	2,950
234	BV	6.4	12,710	4.21	0.15	11,000	3,300
341	BV	5.7	12,780	5.00	0.14	11,000	2,840
261	BV	5.4	12,360	4.89	0.15	10,500	2,330
Mean		5.7	12,620	4.70	0.14	10,830	2,990
349	B	6.2	13,110	3.89	0.15	11,000	3,420
366	B	5.7	12,910	4.67	0.14	11,000	2,840
252	B	5.6	13,000	4.52	0.18	11,000	3,100
Mean		5.8	13,010	4.36	0.16	11,000	3,120

Specimens, 6-in.-diam $\times$ 12-in.-long cylinders of CP-type concrete, oven-dried at 150°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 143°C.

^aB, exposure to brine; V, in vapor; BV, at brine-vapor interface.

Table 82
Compressive Strength and Elasticity of Unimpregnated Concrete
After One-Year Exposure at 143°C in Three-Phase Test Loops

Specimen No., 72.175-	Exposure ^a	Ultimate strength, psi	Modulus of elasticity, 10 ⁶ psi	Poisson's ratio	Elastic limit, psi	Ultimate strain, $\mu\text{in./in.}$
403	V	9,540	4.56	0.11	7,000	2,330
409	V	9,540	4.50	0.12	7,000	2,300
333	V	10,920	4.94	0.16	6,500	2,460
Mean		10,000	4.67	0.13	6,833	2,360
318	BV	7,460	4.31	0.18	4,500	2,280
398	BV	8,040	4.47	0.18	5,500	2,670
379	BV	9,210	4.59	0.16	6,000	2,720
Mean		8,240	4.46	0.17	5,330	2,560
310	B	8,710	4.20	0.20	5,000	3,340
402	B	8,320	4.57	0.20	5,500	2,280
387	B	7,790	4.42	0.18	5,500	2,440
Mean		8,270	4.40	0.19	5,330	2,690

Specimens, 6-in.-diam $\times$ 12-in.-long cylinders of CP-type concrete.

Test temperature, 143°C.

^aB, exposure to brine; V, in vapor; BV, at brine-vapor interface.

Table 83

Effect of Length of Exposure in Three-Phase Loops at 143°C on the Compressive Strength of Unimpregnated and Styrene-TMPTMA Impregnated Concrete

Exposure time, mo	Exposure environment ^a	Polymer loading, wt %	Ultimate strength, psi	Elastic modulus, 10 ⁶ psi
6	B	6.0	12,640	4.30
12	B	5.8	13,010	4.36
6	BV	5.8	14,810	4.50
12	BV	5.7	12,620	4.70
6	V	5.8	13,417	4.40
12	V	6.1	11,740	4.28
6	B	-	7,080	4.67
12	B	-	8,270	4.40
6	BV	-	6,810	4.33
12	BV	-	8,240	4.46
6	V	-	8,180	4.67
12	V	-	10,000	4.67

Specimens, 6-in.-diam × 12-in.-long cylinders of CP-type concrete, oven-dried at 150°C prior to impregnation and thermal-catalytic polymerization.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Test temperature, 143°C.

^aB, exposure to brine; V, in vapor; BV, at brine-vapor interface.

change is nearly 2.5 times as great in these tests as it was after the same length of time in the 121°C three-phase loops. The reason for the extremely high compressive strengths observed for unimpregnated concrete is not known. However, a comparison of results of tests at 6 months and 1 year (see Table 83) does show a tendency for unimpregnated concrete to increase in strength with time in all three environments.

A series of 70 wt % MMA - 30 wt % TMPTMA specimens is being prepared for testing in the three-phase loops.

5.2.1.8 THERMAL PROPERTIES. Measurements of the thermal coefficient of expansion of 60 wt % styrene - 40 wt % TMPTMA impregnated CP-type concrete are given in Table 84. An increase in the linear coefficient of expansion was observed with an increase in the temperature range. The coefficient of expansion varied from 9.7 $\mu\text{in./in.}^\circ\text{C}$ in the temperature range 24° to 66°C to 10.4 $\mu\text{in./in.}^\circ\text{C}$ in the range 24° to 127°C, and 11 $\mu\text{in./in.}^\circ\text{C}$ in the range 24° to 178°C.

The thermal diffusivity of 60 wt % styrene - 40 wt % TMPTMA impregnated OSW-type concrete at temperatures of 21°, 66°, and 149°C is

Table 84

Thermal Coefficient of Expansion of Styrene-TMPTMA Impregnated CP-Type Concrete

Specimen No.	Polymer loading, wt %	Temperature range, °C	Average temp., °C	Coefficient of linear expansion, $\mu\text{in./in.}^\circ\text{C}$
10603	7.0	24-66	45	9.7±0.2
		24-127	75	10.4±0.1
		24-178	101	11.0±0.1

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Specimen oven-dried at 177°C prior to impregnation and thermal-catalytic polymerization.

Table 85

High-Temperature Thermal Properties of Unimpregnated and Styrene-TMPTMA Impregnated OSW-Type Concrete

Samples	Average thermal diffusivity, ft ² /hr, at		
	21°C	66°C	149°C
Impregnated concrete			
Three 8×16-in. cylinders	0.044	0.041	0.035 ^a
Two 6×12-in. cylinders	—	—	0.024
Unimpregnated concrete			
Two 8×16-in. cylinders	0.044	0.042	0.039 ^a
One 6×12-in. cylinder	—	—	0.021

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

Specimens oven-dried at 150°C prior to impregnation and thermal-catalytic polymerization.

^aExtrapolated value.

essentially the same as that of unimpregnated concrete (see Table 85). The impregnated and unimpregnated concrete specimens exhibit some reduction in diffusivity with increasing temperature.

5.2.2 Durability and Resistance to Chemical Attack by Hot Brine and Distilled Water. Durability testing at the USBR and BNL of PIC for desalting plant applications includes exposure to brine and distilled water at elevated temperatures and environmental testing. At the USBR, exposure to brine is conducted in a series of enclosed recirculating loops maintained at 121°C and 143°C, and exposure to distilled water is conducted at 143°C in a closed autoclave system through which deionized water is circulated. At BNL, hot-brine and distilled-water exposures are conducted

in autoclaves modified to provide for testing specimens under water, in vapor, at the water-vapor interface, and when subjected to a dripping condensate. The BNL autoclave tests, USBR brine-loop tests, and exposure tests in different environments are described in the following sections.

5.2.2.1 AUTOCLAVE TESTS. The autoclave tests at BNL are intended to provide rapid evaluation of the resistance of concrete and concrete-polymer materials to attack by hot brine and distilled water. The facility has been described in detail in previous topical reports.^{3,4} Briefly, it consists of 12 steel pressure vessels lined with a baked phenolic coating. The vessels are capable of operation at a steam pressure of up to 350 psi (220°C). Sample holders in the vessels are designed to hold eighteen 1½-in.-diam × 3-in.-long concrete cylinders. The cylinders may be in water, at the water-vapor interface, or in the vapor phase. In addition, the vessels contain condensers that permit the condensate to drip on the surface of short concrete specimens. The pressure vessels usually run at three temperatures, 121°, 143°, and 177°C.

An extensive screening program was completed this year to find a suitable polymer system to replace the 90 wt % DAP – 10 wt % MMA system, which had failed. The DAP-MMA system was a backup system for the primary 60 wt % styrene – 40 wt % TMPTMA system. Failure of the DAP-MMA system was indicated by rapid loss of material when exposed to condensate drip and by loss of strength at 143°C.

Three candidate PIC systems were evaluated for 87 days in 143°C brine: isodiallyl phthalate (ISODAP), 50 wt % ethylene glycol dimethacrylate – 50 wt % MMA, and 70 wt % MMA – 30 wt % TMPTMA. The MMA-TMPTMA system was chosen for further evaluation, on the basis of compressive strength and weight loss after exposure to condensate drip. PIC was prepared with this polymer for further long-term evaluation in the pressure vessels at 121°, 143°, and 177°C.

Continued observations of the PIC condensate drip sample of the MMA-TMPTMA system were made. After 270 days in the pressure vessel (90 days under condensate) at 143°C, the sample disintegrated completely. At 177°C the larger 1½ × 3-in.-long samples started to disintegrate after 83 days. This system is still under evaluation at 121°C. It should be noted that the types of failure exhibited by the condensate drip samples containing 90 wt % DAP – 10 wt % MMA and those con-

Figure 29. Compressive strength of PIC containing 60 wt % styrene – 40 wt % TMPTMA after immersion in brine at 143°C.

taining 70 wt % MMA – 30 wt % TMPTMA are entirely different. The former fail by continuous erosion of the mortar phase. The latter exhibit a sound appearing surface until they start disintegrating. Once started, disintegration continues even at room temperature.

The main test program now consists of evaluating PIC prepared with 60 wt % styrene – 40 wt % TMPTMA. Weight and length changes are being measured at 121°, 143°, and 177°C, and compressive strength measurements are made periodically at 143°C. The compressive strengths as a function of time are shown in Figure 29. Although the polymer in this system is the most stable used so far, the PIC has undergone a strength decrease of nearly 50%. After about 180 days, the decrease in strength has almost stopped. In Table 86 the changes in weight and length are tabulated for samples immersed in brine at the three test temperatures. The changes in both weight and length are positive, an indication of absorption and swelling. The rates of weight and length change after exposure for 1 year are positive, although the standard deviations of the measurements are large.

Because the concrete being tested is water- or fog-cured, exposure to high-pressure steam or water, even after polymer impregnation, can result in changes in its pore structure (as reported previously³ and discussed in Section 6 of this report). Since these changes in the cement microstructure may be detrimental to the strength of the system, it was decided to try to avoid them by steam-curing the concrete prior to impregnation. Some preliminary tests were made using 60 wt %

Table 86
Dimensional and Weight Changes in Polymer-Impregnated Concrete
After Exposure to Hot Brine

Temperature, °C	Weight change, ^a %	Rate of weight change, ^b %/yr	Length change, ^a %	Rate of length change, ^b %/yr
121	+2.3±0.08 ^c	0.4±0.4	+0.31±0.05	0.4±0.6
143	+2.8±0.2	0.6±1.7	+0.57±0.08	0.7±0.8
177	+3.1±0.2	1.2±1.7	+0.89±0.09	0 ±0.2

Specimens, 1.5-in.-diam × 3-in.-long cylinders.

Monomer, 60 wt % styrene - 40 wt % TMPTMA.

^a Change at temperature less change of controls in brine at room temperature, after about one year.

^b Based on the last 70 days.

^c Estimated standard deviation based on two samples.

Table 87
Compressive Strength and Weight Loss
Polymer-Impregnated Concrete Exposed to Deionized Water at 143°C

Specimen No.	Polymer loading, wt %	Exposure time, months	Weight change, %	Compressive strength, psi	Remarks
Unimpregnated concrete					
41	-	6	-0.55	5,700	Concrete appears to be in good condition. No signs of deterioration.
42	-	6	-0.52	5,500	
43	-	6	-0.38	5,200	
Av	-		-0.48	5,500	
44	-	12	-3.98	4,000	Concrete appears to be <i>very</i> unsound. Surface spalling to depth of ¾ in. on No. 45.
45	-	12	-13.96	3,700	
46	-	12	-2.12	6,500	
Av	-		-6.69	4,700	
60 wt % styrene - 40 wt % TMPTMA impregnated concrete					
2	7.7	6	+0.58	12,900	Concrete appears to be in good condition. No signs of deterioration.
11	8.0	6	+0.47	12,200	
28	7.6	6	+0.36	11,800	
Av	7.8		+0.47	12,300	
12	7.5	12	+0.19	10,500	Concrete appears to be in good condition. No signs of deterioration.
21	7.6	12	+0.32	10,500	
26	7.6	12	+0.55	9,800	
Av	7.6		+0.35	10,300	
70 wt % MMA - 30 wt % TMPTMA impregnated concrete					
72.109-1	7.3	6	+0.78	11,300	Concrete appears to be in good condition. No signs of deterioration.
3	7.0	6	+1.21	13,000	
5	7.0	6	+1.95	13,000	
Av	7.1		+1.31	12,400	

3×6-in. CP-type concrete cylinders oven-dried at 177°C prior to impregnation.
Thermal-catalytic polymerization.

styrene - 40 wt % TMPTMA impregnated steam-cured concrete. Initial results showed that the rate of decrease in strength was less for the steam-cured concrete than for the water-cured. A more extensive testing program with steam-cured concretes is in progress.

5.2.2.2 DEIONIZED WATER TESTS. Unimpregnated and PIC specimens are tested for resistance to deionized water at 143°C in a closed recirculating autoclave system. Specimens are removed periodically, visually examined, and tested for weight change and compressive strength. Unimpregnated and 60 wt % styrene - 40 wt % TMPTMA impregnated concretes have been tested after 6 months and 1 year of exposure, and 70 wt % MMA - 30 wt % TMPTMA impregnated concrete has been tested after 6 months' exposure. Test results are given in Table 87.

Unimpregnated concrete showed little deterioration after 6 months' exposure and had a compressive strength of 5500 psi. After 12 months' exposure, specimens appeared unsound, with some surface disintegration, and averaged about 7% weight loss; however, compressive strengths showed only a small decrease and averaged 4700 psi. The styrene-TMPTMA specimens appear to be in good condition after 12 months' exposure, showing only a slight weight increase. Compressive strengths seem to be declining, from an average of 12,300 psi after 6 months' exposure to 10,300 psi after 12 months. The MMA-TMPTMA specimens appear to be in good condition after 6 months' exposure. Compressive strengths after 6 months were comparable to those for the styrene-TMPTMA specimens (12,400 vs 12,300 psi). The MMA-TMPTMA specimens are showing a small weight gain of 1.3%, which suggests that these specimens are a little more absorptive than the styrene-TMPTMA specimens.

5.2.2.3 LOOP TESTS. Loop-test specimens are exposed to concentrated synthetic seawater at high temperatures in enclosed recirculating systems. Two series of loop tests are in progress: the first is a single-phase test in which polymer impregnated OSW-type concrete is exposed to brine at 121° and 143°C; the second is a three-phase system in which polymer-impregnated CP-type concrete is exposed to brine, to the brine-vapor interface, and to vapor at 121° and 143°C. The brine in the 121°C loops is concentrated synthetic seawater containing 73,000 ppm dissolved salt, and the brine in the 143°C loops contains 38,400 ppm dis-

solved salt. The loop exposures are long-term tests; the single-phase system has been in test for 2 years, and the three-phase system, for 1 year. Early failures aside, the final observations on durability will await completion of the test. Measurements are made on specimens prior to exposure and periodically during the test.

Compressive strength, modulus of elasticity, Poisson's ratio, specific gravity, and ultrasonic pulse velocity are determined on 6-in.-diam $\times$ 12-in.-long cylinders. Resonant frequency and length and weight changes are measured on 4 $\times$ 4 $\times$ 30-in. bars. Corrosion measurements are also made on 4 $\times$ 4 $\times$ 30-in. bars containing reinforcing steel. A more detailed discussion of structural properties of loop-test specimens is given in Section 5.2.1.7.

(b) **SINGLE-PHASE BRINE-LOOP TESTS.** The single-phase brine loops are being used to test OSW-type concrete impregnated with 60 wt % styrene - 40 wt % TMPTMA, thermal-catalytically polymerized. Tests have been in progress for more than 2 years and results are summarized in Table 88.

Previous investigations⁴ have shown that concrete impregnated with 90 wt % DAP - 10 wt % MMA deteriorates when exposed to hot brine and distilled water.

Styrene-TMPTMA specimens exposed to brine at 121° and 143°C show a trend toward lower compressive strengths with an increase in exposure time and temperature. Compressive strengths ranged from 16,200 psi at 121°C for specimens exposed for 215 days in 121°C brine to 10,300 psi for specimens exposed for 2 years in 143°C brine. The modulus of elasticity shows a similar decrease, from 5.7×10^6 psi for a 215-day exposure in 121°C brine to 4.4×10^6 psi for 2 years of exposure in 143°C brine. Length change measurements show a progressive expansion with an increase in exposure time and temperature, ranging from 593 μ in./in. for 215 days of exposure at 121°C to 1704 μ in./in. for 2 years of exposure at 143°C. Tests of other properties show less definite changes with exposure time and temperature. Ultrasonic pulse velocity measurements show a decrease from about 18,000 ft/sec to about 14,000 to 16,000 ft/sec after exposure to brine, but the decrease in velocity does not appear to be a function of brine exposure time or temperature. Weight changes are minor and show an increase of about 2%, due to moisture absorption. Resonant frequency measurements (resonant frequency squared) show an initial increase of 9.8% for specimens exposed in 121°C

brine for 215 days, followed by a gradual decrease with exposure time to a 5.3% increase at 2 years. Specimens exposed in 143°C brine show decreases in resonant frequency of 3.4% at 180 days, 10.8% at 1 year, and 5.7% at 2 years.

The results of brine exposure tests on unimpregnated concrete in Table 88 are from a previous test¹⁶ and are included for a general comparison of the behavior of unimpregnated concrete. Some of the test conditions varied somewhat, chiefly in that the concrete was allowed to dry in air for up to 1½ years before exposure in brine and compressive strengths were determined at room temperature. The general conclusions from this study¹⁶ were that 2½ years of exposure in 121°C brine does not detrimentally affect concrete, although minor surface alteration has occurred. Exposure in 143°C brine for 40 months produced loss of strength and deterioration in the surface of the concrete to an average depth of 15 mm. Examination of 143°C test specimens revealed chemical alteration and microfracturing in the deteriorated zone. However, the interior of the concrete appeared sound. On the basis of these tests, the report recommended that unimpregnated concrete should not be used in contact with 143°C brine.

(b) **THREE-PHASE LOOPS.** Unimpregnated and 60 wt % styrene - 40 wt % TMPTMA impregnated CP-type concretes have been in test at 121° and 143°C in the three-phase brine loops for 1 year. A number of observations on test results have been made, but these tests have not been in progress long enough for definite conclusions to be made on the suitability of the materials. Test results are given in Table 89. A 70 wt % MMA - 30 wt % TMP-TMA monomer system has been selected as a second system for high-temperature applications, and testing has begun. To date the test has not been in progress long enough to give meaningful results.

Styrene-TMPTMA impregnated specimens show little difference in compressive strength after 6 months and 1 year of exposure to brine, the brine-vapor interface, and vapor at 121°C. Compressive strengths averaged about 15,000 psi and are comparable to the strength of styrene-TMP-TMA impregnated OSW-type concrete specimens exposed in the 121°C single-phase brine loops for 1 year. The compressive strengths of styrene-TMPTMA CP-type specimens in the 143°C three-phase system were a little lower and indicate a trend toward lower strengths with increased

exposure time; small differences among specimens from the three test environments in the 143°C system were also apparent. Specimens exposed to 143°C brine for 1 year had an average compressive strength of 13,000 psi, brine-vapor interface specimens averaged 12,600 psi, and vapor specimens averaged 11,700 psi. Modulus of elasticity values were comparable to previous results with styrene-TMPTMA impregnated OSW-type concrete in the single-phase brine loops; specimens exposed at 121°C in the three-phase loops ranged from 5.1 to 5.6 × 10⁶ psi and from 4.1 to 5.1 × 10⁶ psi in the 143°C three-phase loops.

Measurements of length change and resonant frequency indicate some changes within the specimens. These measurements have not been correlated with other physical and mechanical properties of PIC but are useful as indications of reductions in the quality of the materials. Length change measurements show a gradual expansion with time and temperature in all three phases. Expansions were not as large for the styrene-TMPTMA impregnated OSW-type concrete specimens in the single-phase loops, and at one year were 486 µin./in. in the 121°C brine exposure and 1296 µin./in. in the 143°C brine exposure. Resonant frequency measurements (resonant frequency squared) showed small losses of 5% and 6% at 1 year for specimens in the 121°C brine and vapor exposures, respectively, and a 20% loss in the brine-vapor interface exposure. In the 143°C loops, losses were about 18% after 1 year for all three exposures. The initial resonant frequency measurements for the 143°C impregnated specimens are roughly 10% higher than those usually obtained with impregnated specimens, but the readings after 1 year's exposure are roughly similar to 1-year measurements on 143°C single-phase loop specimens.

The reasons for the expansion in length and decrease in resonant frequency, as well as loss in compressive strength, are not known. Although it would be speculative to try to evaluate the possible cause in view of the limited data and relatively short exposures, moisture in the specimens may be a contributing factor. Absorption of moisture is evident from the small increase in weight and has also been observed in some compressive strength specimens. Several such specimens have emitted a small amount of vapor on fracturing, which in some cases condensed in small droplets of water on the test machines' load plates.

Table 88

**Properties of Styrene-TMPTMA^a Impregnated OSW-Type Concrete
Exposed to Brine^b at Elevated Temperatures**

Exposure	Initial measurements					Measurements after exposure									
	Polymer loading, wt %	Specific gravity	Unit weight, lb/cu ft	Resonant frequency squared, 10 ³ cP	Pulse velocity, ft/sec	Exposure time	Specific gravity ^c	Unit weight lb/cu ft	Resonant frequency, ^d % change	Pulse velocity, ^c ft/sec	Weight change, ^d %	Unit length change, ^d μ in./in.	Strength test temperature, °C	Compressive strength, ^c psi	Modulus of elasticity, ^c 10 ⁶ psi
Impregnated concrete															
121°C brine	4.5	2.53	157.8	551	18,300	215 days	2.55	159.0	+9.8	16,400	+1.4	+593	121	16,200	5.7
	4.5	2.57	160.0	551	17,900	1 yr	2.57	160.1	+7.0	16,000	+1.8	+955	121	14,900	5.3
	4.6	2.53	157.7	551	17,500	2 yr	2.56	159.5	+5.3	15,900	+2.0	+1,272	121	13,300	5.0
143°C brine	4.6	2.57	159.7	585	18,300	180 days	2.59	161.5	-3.4	15,600	+2.1	+1,141	143	12,900	4.7
	4.6	2.56	159.3	585	17,700	1 yr	2.56	159.5	-10.8	13,800	+1.1	+1,451	143	11,100	4.4
	4.6	2.55	-	-	18,300	1½ yr	2.57	-	-	16,400	-	-	143	11,400	4.1
	4.6	2.56	159.2	585	17,700	2 yr	2.59	161.0	-5.7	16,700	+2.2	+1,704	143	10,300	4.4
PIC control specimens															
23°C air (50% R.H.)	4.9	2.54	158.6	608	18,200	1 yr	-	-	+1.3	18,200	+0.1	+94	121	17,200	7.2
	4.9	2.55	158.8	608	17,900	2 yr	2.55	158.7	+1.9	17,600	-0.4	+107	121	15,900	7.1
	4.9	2.53	157.7	-	18,100	1 yr	-	-	-	17,800	-	-	143	14,600	6.6
	4.9	2.54	157.9	-	17,500	2 yr	2.54	157.9	-	17,600	-	-	143	15,900	6.9
Unimpregnated concrete^e															
121°C brine	-	-	155.3	449	15,800	-	-	155.3	-	15,800	-	-	Room	8,300	4.9
	-	-	-	449	-	180 days	-	159.5	+12.2	16,100	+2.4	+412	Room	7,900	5.7
	-	-	-	449	-	1 yr	-	159.1	+12.9	16,500	+2.6	+408	Room	8,500	5.9
	-	-	-	449	-	1½ yr	-	155.5	+6.0	15,600	+3.2	+510	Room	8,600	6.3
	-	-	-	449	-	2 yr	-	157.4	+12.7	16,000	+3.7	+578	Room	8,000	6.2
	-	-	-	449	-	2½ yr	-	158.6	+9.1	16,100	+4.3	+573	Room	7,600	6.1
	-	-	-	-	-	3 yr	-	158.3	+19.1	15,200	+4.7	+702	Room	7,300	6.2
	-	-	-	-	-	3½ yr	-	157.2	+8.6	16,400	+5.5	+717	Room	7,400	5.6
143°C brine	-	-	156.2	445	15,600	-	-	156.2	-	15,600	-	-	Room	7,900	4.4
	-	-	-	445	-	180 days	-	159.9	+3.8	16,800	+2.6	+471	Room	7,200	5.6
	-	-	-	445	-	1 yr	-	162.2	-3.6	15,700	+4.5	+626	Room	5,400	4.8
	-	-	-	445	-	1½ yr	-	161.5	-6.5	15,700	+5.4	+826	Room	6,200	4.5
	-	-	-	445	-	2 yr	-	-	-13.0	-	+6.2	+855	Room	-	-
	-	-	-	445	-	2½ yr	-	156.9	-19.6	14,900	+7.1	+924	Room	4,900	3.2
	-	-	-	445	-	3 yr	-	-	-34.4	-	-	+987	Room	-	-

^a60 wt % styrene - 40 wt % TMPTMA, thermal-catalytically polymerized.

^bSynthetic seawater concentrated to 73,000 ppm tds for 143°C exposure and 38,400 ppm tds for 121°C exposure.

^cValues are averages for three 6×12-in. cylinders.

^dValues are averages for two 4×4×30-in. prisms.

^eResults for unimpregnated concrete are from a previous study.¹⁶

Table 89

**Properties of Styrene-TMPTMA* Impregnated CP-Type Concrete Exposed to Brine,^b
Vapor, and Brine-Vapor Interface at Elevated Temperatures**

Exposure	Initial measurements					Measurements after exposure								
	Polymer loading, wt %	Specific gravity	Unit weight, lb/cu ft	Resonant frequency squared, 10 ³ cP	Pulse velocity, ft/sec	Exposure time	Specific gravity ^c	Unit weight, ^c lb/cu ft	Resonant frequency, ^d % change	Pulse velocity, ^c ft/sec	Weight change, ^d %	Unit length change, ^d μ in./in.	Compressive strength, ^{c,e} psi	Modulus of elasticity, ^c 10 ⁴ psi
Impregnated concrete														
121°C brine	6.3	2.38	148.3	570	16,800	6 mo	2.40	149.2	-1.3	15,900	+0.3	+280	14,600	5.5
	6.7	2.37	147.8	570	17,000	1 yr	2.28	148.4	-6.4	15,300	+0.4	+486	15,300	5.5
121°C brine/vapor	6.0	2.40	150.0	574	17,300	6 mo	2.40	149.5	-7.3	15,900	+1.0	+407	15,200	5.6
	6.2	2.37	148.1	574	17,200	1 yr	2.38	148.7	-20.2	15,700	+0.8	+522	14,700	5.5
121°C vapor	6.2	2.39	148.8	570	17,300	6 mo	2.39	149.0	-1.2	16,400	+0.8	+291	15,900	5.4
	6.5	2.37	147.7	570	17,200	1 yr	2.39	148.4	-5.2	15,800	+1.1	+436	14,700	5.1
143°C brine	6.0	2.39	148.6	656	17,100	6 mo	2.39	149.1	-13.8	15,300	+1.2	+800	13,200	4.1
	5.8	2.40	149.9	656	16,500	1 yr	-	-	-18.8	-	+0.3	+1296	13,000	4.4
143°C brine/vapor	5.8	2.39	148.9	620	16,900	6 mo	2.39	149.1	-12.8	15,400	+1.4	+703	14,800	4.5
	5.7	2.40	149.1	620	16,900	1 yr	-	-	-18.6	-	+1.4	+1264	12,600	4.7
143°C vapor	5.8	2.38	148.5	632	16,800	6 mo	2.39	149.1	-13.4	15,800	+1.6	+728	13,400	4.4
	6.1	2.38	148.4	632	16,300	1 yr	-	-	-18.0	-	+1.7	+1275	11,700	4.3
Unimpregnated concrete														
121°C brine	-	2.33	145.4	397	14,300	6 mo	2.38	148.4	-4.7	13,300	+2.3	+717	5,700	4.2
	-	2.31	143.9	397	14,300	1 yr	2.36	147.2	-3.7	13,400	+1.9	+623	6,100	4.7
121°C brine/vapor	-	2.32	144.6	403	14,400	6 mo	2.37	148.1	-4.4	13,700	+2.8	+707	5,100	4.2
	-	2.33	145.2	403	14,000	1 yr	2.37	147.4	-4.7	13,500	+1.8	+486	5,900	4.9
121°C vapor	-	2.33	145.1	397	14,600	6 mo	2.36	147.2	+3.9	13,800	+2.0	+361	6,700	4.3
	-	2.31	143.8	397	13,800	1 yr	2.34	145.4	+8.2	14,500	+1.9	+374	7,400	5.1
143°C brine	-	2.36	146.8	456	14,200	6 mo	2.37	147.5	-18.4	13,100	+2.4	+821	7,100	4.6
	-	2.32	144.9	456	14,000	1 yr	-	-	-23.7	-	+2.7	+1157	8,300	4.4
143°C brine/vapor	-	2.37	147.6	436	14,100	6 mo	2.38	148.3	-18.8	13,400	+2.1	+839	6,800	4.3
	-	2.35	146.6	436	14,200	1 yr	-	-	-24.1	-	+3.0	+961	8,200	4.4
143°C vapor	-	2.33	145.1	442	14,100	6 mo	2.33	145.3	-6.6	14,100	+0.2	+475	8,200	4.7
	-	2.33	145.0	442	13,500	1 yr	-	-	-11.5	-	+1.7	+732	9,800	4.8

*60 wt % styrene - 40 wt % TMPTMA, thermal-catalytically polymerized.

^bSynthetic seawater concentrated to 73,000 ppm tds for 143°C exposure and 38,000 ppm tds for 121°C exposure.

^cValues are averages for three 6×12-in. cylinders.

^dValues are averages for two 4×4×30-in. prisms.

^eTested at exposure temperature.

5.2.2.4 ENVIRONMENTAL TESTS. (a) **EXPOSURE TO 5% NaOH.** Specimens of unimpregnated concrete, 60 wt % styrene – 40 wt % TMPTMA, and 90 wt % DAP – 10 wt % MMA impregnated concrete showed no signs of deterioration after immersion for 382 days in a 5% NaOH solution. The specimens showed small weight gains of about 0.5% for unimpregnated concrete, 0.5% for styrene-TMPTMA impregnated concrete, and 0.8% for DAP-MMA impregnated concrete. Compressive strengths after exposure were about 6300 psi for unimpregnated concrete, 16,000 to 19,300 psi for styrene-TMPTMA specimens, and 12,200 to 16,300 psi for DAP-MMA specimens. Test results are given in Table 17.

(b) **WEATHEROMETER TESTS.** Unimpregnated concrete and concrete impregnated with 60 wt % styrene – 40 wt % TMPTMA and 90 wt % DAP – 10 wt % MMA have been exposed in a Weatherometer apparatus. The apparatus (Ref. 3) simulates exposure to sunlight and rain and is primarily used for accelerated testing of paints and protective coatings. Samples are exposed to a total of 20 hr/day of light from two carbon arc lamps with a 12-min cold demineralized water spray each hour. After 6000 hr of exposure the styrene-TMPTMA specimens and the DAP-MMA specimens show some surface scaling affecting <10% of the surface area. Unimpregnated samples show a fairly uniform leaching of cement paste over the entire surface area to a depth of about $\frac{1}{16}$ in. Test results are given in Table 20.

(c) **EFFECT OF SOIL MICROORGANISMS.** Samples of unimpregnated concrete and PIC are under test for effects

of soil microorganisms. The specimens are buried in compost-enriched soil with continuous exposure to a temperature of 27°C and 80% relative humidity, which are optimum conditions for soil microorganism growth. The specimens were examined visually after 18 months' burial for surface appearance and evidence of soil microorganism growth. The unimpregnated concrete, 60 wt % styrene – 40 wt % TMPTMA, and 90 wt % DAP – 10 wt % MMA impregnated concrete showed no changes in surface appearance and no microorganism growth. These observations indicate that the materials are highly resistant to soil microorganisms. Test results are given in Table 21.

6. FUNDAMENTAL STUDIES

Fundamental studies during the past year were conducted in the areas of application of composite materials theory to calculation of the modulus of elasticity for concrete-polymer materials, a porosimetry study of high-pressure steam-cured cement paste, the stability of 60 wt % styrene – 40 wt % TMPTMA polymer exposed to brine at high temperature, and chemical reactions of monomers and polymers with cement paste. Studies on negative creep were not continued during the year.

6.1 POLYMER-IMPREGNATED CONCRETE AS A COMPOSITE MATERIAL

Concrete can be considered a composite material consisting of a dispersed phase (coarse aggregate) and a matrix phase (mortar). The theory of composite materials permits the elastic properties of the composite to be computed from the elastic properties and concentrations of the components.

Figure 30. Predicted and experimental variation of Young's modulus for mortar with a water-to-cement ratio of 0.5 as a function of sand content.

Figure 31. Predicted and experimental variation of Young's modulus for mortar with a $-\frac{3}{8}$ -in. to +4 mesh aggregate content.

Composite theory is most advanced for fiber-reinforced composites, in which the fibers are parallel and continuous. For particulate composites like concrete the theory is less well developed. However, a number of models are available which appear to predict the modulus of elasticity reasonably well for concrete.

In concrete the mortar phase is also a composite material, consisting of sand particles dispersed in a matrix of hardened cement paste. Thus, to predict the modulus of a mortar, the moduli of the hydrated cement and sand phases must be known, along with their concentrations.

The material becomes more complex when polymer is added to the system. The polymer fills the pores of the hardened cement paste phase and creates still another composite material. Earlier studies^{2,17} showed that the polymer raised the strength of the cement phase and improved the bond between matrix and aggregate. It appeared that the role of polymer could be more clearly brought out by applying composite theory to a simple composite system, and then to successively more complex systems. Elastic properties were calculated from a composite model for concrete developed by Hobbs¹⁸ and compared with experimental results.

Hobbs' model states that

$$\frac{E}{E_m} = 1 + \frac{2V_a(r-1)}{(r+1) - V_a(r-1)}, \quad (1)$$

where E refers to the composite modulus of elasticity, V is the volume fraction, the subscripts m and a refer to matrix and aggregate (filler), respectively, and r is the modulus ratio E_a/E_m .

Equation (1) may be used to predict the increase in modulus of elasticity when the pores of the cement become filled. Assuming that the porosity of cement is about 0.45, Young's modulus of cement is about 1×10^6 psi, and that of the polymer (the filler phase) is about 0.4×10^6 psi, Eq. (1) predicts an increase in modulus by a factor of 2.4 when the cement is impregnated. Experimentally an increase of 2.8 times was observed. Another independent empirical model predicted an increase of between 1.8 and 3.3 times.¹⁹

From both theoretical and experimental considerations it is seen that the incorporation of rigid polymer in the pores of the cement phase results in a cement phase of greatly increased stiffness.

Hobbs' model (Eq. 1) was next applied to mortar. A series of mortar specimens was prepared

with an 0.40 to 0.65 volume fraction of sand. The experimental moduli for the normal and unimpregnated mortars were compared with the computed ones. The modulus of the unfilled hardened cement paste matrix was 1×10^6 psi, the polymer-filled matrix modulus was 2.8×10^6 psi, and the aggregate (silica sand) modulus was 10×10^6 psi. The results are shown in Figure 30. The calculated results are in fairly good agreement with the experimental results. Both indicate that the only effect polymer has is to increase the modulus of the cement phase and create a stiffer matrix.

The work was next extended to concretes. A $-\frac{3}{8}$ -in. to +4 mesh limestone aggregate was added to a mortar in concentrations of 0.1 to 0.5 by volume. The expected moduli of the composite materials were calculated from Eq. (1) using 8×10^6 psi as the modulus for limestone aggregate (estimated from sonic velocity measurements), 2×10^6 psi for the unfilled mortar matrix, and 4.3×10^6 for the polymer-filled mortar matrix. The results are shown in Figure 31. Here the experimental results lie below the calculated curve and indicate an extrapolated mortar modulus (0% aggregate) much lower than that used for the calculation. The reason for this discrepancy is not clear.

The results do, however, show some interesting features. For the unfilled concrete, there is very little compositional dependence of the modulus until the aggregate volume reaches 50%. The polymer-filled concrete indicates a compositional dependence of approximately the proper magnitude. This suggests that in the unfilled material the adhesion between the aggregate and the matrix is poor.

In another extension of the composite model, the normal limestone aggregate with a modulus of about 8×10^6 psi was replaced with a comparable volume of steel bolts (modulus, 30×10^6 psi). The modulus of the polymer-impregnated steel-aggregate concrete predicted by Eq. (1) is about 8×10^6 psi. Measurements indicated a modulus of 7.8 to 8.2×10^6 psi. For the unfilled concrete the experimental modulus ($\approx 1 \times 10^6$ psi) was much lower than that predicted ($\approx 5 \times 10^6$ psi).

All the measurements so far indicate that the improvement in the elastic modulus of polymer-impregnated mortars and concretes arises from the filling of the pores of the cement phase with the rigid polymer. With concrete, the improvement in bond between the matrix and aggregate also increases the modulus of elasticity.

Figure 32. Polymer-impregnated concrete (left) and normal concrete after failure (3-in.-diam $\times$ 6-in.-long cylinders).

Figure 33. Polymer-impregnated steel-aggregate concrete (left) and unimpregnated steel-aggregate concrete after failure (1 1/2-in.-diam $\times$ 3-in.-long cylinders).

As noted earlier,³ the fracture modes of concrete and PIC are different (see Figure 32). PIC shatters on failure; the fracture surface passes through the aggregate particles, and thus the strength of the aggregate is utilized completely. Normal concrete fails primarily by failure of the matrix-aggregate bond, and failure is less abrupt. One way to alter the relatively brittle fracture mode of PIC is to use a stronger and tougher aggregate. If the aggregate is strong enough the crack will be diverted around the aggregate rather than through it. This is the case when concrete is made with steel bolts as the aggregate. The failure mode is no longer brittle, but much like that of normal concrete. After maximum stress the concrete is still capable of supporting a considerable load. At a strain of 1% the concrete sustained a load of 14,000 psi. Fractured polymer-impregnated steel-aggregate concrete is illustrated in Figure 33. In Figure 34 the stress-strain curve for polymer-impregnated steel-aggregate concrete is shown.

The fracture mode of PIC can also be made like that of normal concrete by incorporating a small quantity ($\approx 1\%$ by volume) of fiber in the matrix. The fiber does not alter the concrete's modulus because its volume concentration is so low, but it does inhibit the propagation of cracks. The stress-strain curve for steel-wire-reinforced mortar is also shown in Figure 34. At 1% strain the material still supports 17,000 psi. The fact that a small concentration of fiber can have such an appreciable effect at the high stress level suggests that the fiber is very well bonded to the matrix.

All the experimental evidence so far indicates that PIC behaves more like a true composite material than does normal concrete. This is probably because of the improved bonding between phases. Conversely, the improvement in the modulus of PIC results from the improved modulus of the hardened cement paste after impregnation.

6.2 PORE STRUCTURE OF HARDENED CEMENT AND POLYMER-IMPREGNATED CEMENT

As an aid in understanding the relationships between cement cure, pore structure, rate of monomer loading, and polymer loading, the pore size distribution of hardened cement paste has been studied. The distributions are measured by high-pressure mercury porosimetry. This technique is capable of measuring pores with diameters as small as 35 Å. Earlier porosimetry work has been summarized in previous topical reports.^{3,4} During

the present report period an extended study of the effect of the water-to-cement ratio (w/c) and cure time for water-cured cements was completed and a report was published.²⁰ Most of the conclusions drawn from the study bear directly on models of cement hydration developed by Powers and co-workers.²¹ One important observation is that the difference in capillary pore structure between pastes of different w/c ratios lies mainly in the region of large pores; pastes with higher w/c ratios have a group of large pores not present in the lower w/c pastes. This holds approximately true at all stages of hydration. This is illustrated in Figure 35 for w/c = 0.35 and 0.55 pastes cured for 2½ days.

A small-scale porosimetry study was made to see whether changes in porosity occurred when water-cured polymer-impregnated cement was subsequently exposed to a high-pressure steam environment. Steam-cured polymer-impregnated cements were also included in the test. Steam curing and steam treating were done for 24 hr at 150 psi. All samples were impregnated with 60 wt % styrene - 40 wt % TMPTMA.

The porosity changes resulting from the steam treatment were much greater for the water-cured than for the steam-cured cement (see Table 90). The results indicate that the polymer does not completely seal either water- or steam-cured cements, and that steam-cured cement is much more stable in a high-pressure steam environment than is water-cured cement. The changes in the pore structure of water-cured cement may be a factor in the continuous strength decrease observed in PIC filled with 60 wt % styrene - 40 wt % TMPTMA (see Section 5.2.2.1).

Additional porosimetry studies are in progress on steam-cured cements, cements cured with use of accelerators, and cements cured with water-reducing agents.

6.3 STABILITY OF 60 WT % STYRENE - 40 WT % TMPTMA AND 70 WT % MMA - 30 WT % TMPTMA POLYMERS

Differential thermal analysis (DTA) studies were performed on polymer extracted from PIC that had been exposed to high-temperature brine. The analyzed polymer samples were taken from the larger filled void spaces of crushed PIC fragments. Changes in the DTA curves could indicate degradation of the polymer.

Figure 36 shows some DTA results for 60 wt % styrene - 40 wt % TMPTMA. After 5740 hr (239 days) at 143°C, the thermal analysis of the polymer after removal from the concrete was essentially identical to that of the original, as-prepared, bulk polymer, with prominent endotherms at 415° and 460°C. This indicates that 60 wt % styrene - 40 wt % TMPTMA is a very stable polymer system in concrete. The fact that the strength of PIC containing this monomer mixture decreases with prolonged exposure in 143°C brine suggests that the decrease is due to changes in the concrete, rather than the polymer. This was discussed in Section 5.2.2.1.

In Figure 37 some DTA results for 70 wt % MMA - 30 wt % TMPTMA are given. This polymer system shows continuous changes with exposure to hot brine. The as-prepared pure polymer thermogram is characterized by prominent endotherms at 305°, 365°, and 470°C. After exposing the PIC for 2000 hr in 143°C brine, the DTA thermogram

Figure 34. Stress-strain curve for polymer-impregnated steel-aggregate concrete and polymer-impregnated steel-wire-reinforced mortar.

Figure 35. Comparison of pore size distributions for cement pastes with water-to-cement ratios of 0.35 and 0.55, cured for 2½ days.

shows that changes have occurred in the polymer, as indicated by the disappearance of the 305° and 365°C endotherms, development of a large endotherm at 400°C, and a decrease in the 470°C endotherm. Further exposure in 143°C brine shows the development of an exotherm at about 460°C and the development of an endotherm at 110°C, probably indicative of free water. After 2000 hr of exposure at 177°C, the thermogram shows a large endotherm at 110°C, the endotherm at 400°C is no longer present, the exotherm at 460°C is still present, and a small endotherm at 470°C is partially masked by the 460°C exotherm. Although the chemistry of these changes has not been developed, the changes in the thermograms show that the original 70 wt % MMA – 30 wt % TMPTMA polymer system has changed considerably. PIC prepared with this polymer has failed under certain experimental conditions (see Section 5.2.2.1), so apparently the DTA changes reflect degradation of the polymer.

A limited investigation was conducted at the USBR to study the stability of 60 wt % styrene – 40 wt % TMPTMA polymer exposed at 150°C to air, water, brine, and $\text{Ca}(\text{OH})_2$ solutions. Test specimens of polymer were cut and machined into cylinders $\approx \frac{1}{2}$ in. in diameter and $\frac{5}{8}$ in. long. Two specimens were stored at room temperature to serve as controls, and eight specimens were sealed in stainless steel pressure vessels under the following conditions: Two specimens were sealed in air, two in distilled water, two in 38,000 ppm seawater brine, and two in $\text{Ca}(\text{OH})_2$ slurry.

The specimens were measured and weighed before exposure and after exposure at 150°C for 7 days, 31 days, and 6 months (see Figure 38). The exposure was terminated after 6 months, and the specimens were tested for compressive strength. Test results are summarized in Table 91.

Table 90

Pore Content of Polymer-Impregnated Concrete^a

	Water-cured	Steam-cured
Porosity before steam exposure, cc/g	0.0075	0.0204
Porosity after steam exposure, ^b cc/g	0.0370	0.0262
Change in porosity, %	+350	+28

^aMonomer, 60 wt % styrene – 40 wt % TMPTMA.

^bTreatment conditions, 150 psi steam for 24 hr.

There were no significant changes in dimension or weight. Samples immersed in liquids expanded about 0.002 in. in both diameter and length at the 7-day measurement and did not appreciably change after that. The samples also showed a small increase in weight due to absorption of water. Specimens exposed to air at 150°C showed a correspondingly small contraction and slight decrease in weight. No evidence of deterioration or corrosion was seen. After 6 months' exposure, the specimens were generally darkened in color near the outer surfaces. The brine, air, and $\text{Ca}(\text{OH})_2$ specimens were a deep brown, and the water specimens were amber.

The effects of exposure on compressive strength could not be accurately evaluated because of small cracks inherent in the specimens. Compressive strengths averaged 23,900 psi for controls, 26,000

Figure 36. Differential thermal analysis of 60 wt % styrene – 40 wt % TMPTMA, after various exposures. *a*, as prepared, bulk polymer; *b*, 48 hr at 143°C, bulk polymer; *c*, 5740 hr at 143°C, from PIC. Argon atm, 10°C/min.

Figure 37. Differential thermal analysis of 70 wt % MMA – 30 wt % TMPTMA, after various exposures. *a*, as prepared, bulk polymer; *b*, 2000 hr at 143°C, from PIC; *c*, 6500 hr at 143°C, from PIC; *d*, 2000 hr at 177°C, from PIC. Argon atm, 10°C/min.

ture and 105°C. The MMA monomer was uninhibited and contained no initiators.

X-ray diffraction analysis disclosed two distinct crystalline reaction products. One was identified as hydrated calcium methacrylate with an estimated 3 H₂O per molecule, which is very loosely held and easily removed by vacuum drying, oven-drying, and even air-drying at a low relative humidity. The other reaction product appears when the amount of water in the system is limited to about 1 to 5% by volume of monomer. This compound is thermally more stable than the hydrated calcium methacrylate and persists at a temperature of 105°C in air. The compound has not been positively identified but appears to be anhydrous calcium hydroxymethacrylate rather than an anhydrous form of calcium methacrylate.

The two reaction products are very soluble in water but, no matter which one is dissolved, only the hydrous form is recrystallized from solution. The hydrous form does not convert to the anhydrous reaction product on heating or drying.

The anhydrous reaction product is not formed as a result of reaction with dry monomer and dry Ca(OH)₂. No reaction could be detected in a dry reaction system; even with the addition of methanol (a liquid reaction product), no reaction occurred. The anhydrous form apparently crystallizes from some mixture of monomer, methanol,

anhydrous water, and the water must be present only in very low concentration or the hydrous salt will form instead.

DTA patterns of the reaction products are shown in Figure 39. The calcite endotherm at 800° to 900°C is prominent in both reaction products. Since only minor calcite (<2% by x-ray analysis) is present in these preparations, the large amounts indicated by DTA must form during the analysis by reaction of carbon dioxide (formed by oxidation of the sample) with calcium from the salt or unreacted calcium hydroxide.

No reaction between polymerized MMA and calcium hydroxide in an aqueous system was detected. X-ray analysis of the solids present after the reaction period found only Ca(OH)₂. A limited reaction might have built up some concentration of calcium methacrylate in solution, but this was not considered at the time, and the liquid was not evaporated to check this. Such a reaction may proceed slowly in a long exposure but does not compare with the rapid reaction of the monomer. This suggests that the loss of Ca(OH)₂ when pre-cured concrete is impregnated with MMA actually occurs before polymerization takes place.

Batching of the reaction systems was done on the basis of the reaction of two mols of methyl methacrylate with one of calcium hydroxide, with water added to produce one mol of hydrated salt and 2 mols of methyl alcohol:

Figure 39. Differential thermal analysis of calcium methacrylate reaction products: (1) calcium methacrylate hydrate, preparation No. 5; (2) calcium (hydroxy?) methacrylate, preparation No. 9. Sample (2) contains 10 to 20% of unreacted calcium hydroxide. Analyses were made at 10°C/min with limited access of air to samples.

Systems of this composition appeared to react almost completely, the Ca(OH)₂ being completely or nearly absent in the solid reaction products and the odor of monomer not very strong. The odor of methanol was very evident. Systems batched with double the amount of Ca(OH)₂ in an effort to form the hydroxy salt simply used up the monomer completely and the excess Ca(OH)₂ remained, except when a very limited amount of water, say 1 to 5% of the volume of monomer, was used. In this case the anhydrous salt formed but was generally accompanied by a little of the hydrated salt and never completely used up the

$\text{Ca}(\text{OH})_2$ or monomer. It is suggested, but not proved, that the reaction is

Temperatures of 25°, 70°, and 105°C were used with no effect on the different types of product, but the reaction was more rapid at the higher temperatures. In several cases some of the monomer succeeded in polymerizing in spite of the lack of initiator.

Findings are summarized below.

(1) MMA monomer reacts rapidly with $\text{Ca}(\text{OH})_2$ in the presence of water (water appears essential) to form calcium methacrylate and methyl alcohol. With less water present (≈ 1 to 5%), the solid product formed is not calcium methacrylate. This product has not been positively identified but may be calcium hydroxymethacrylate.

(2) The reaction is fairly rapid and goes to completion.

(3) PMMA does not react, or at least does not react to any comparable degree. The reaction of $\text{Ca}(\text{OH})_2$ when concrete is impregnated actually occurs before polymerization takes place.

(4) The calcium methacrylate salts are highly soluble in water. In themselves they do not appear harmful to concrete but possibly are subject to leaching by water in PIC.

7. QUALITY AND PROCESS CONTROL

7.1 QUALITY CONTROL

The objective of the effort in quality control is to develop nondestructive techniques that will simply and rapidly indicate the degree to which concrete has been polymer filled. In past topical reports,²⁻⁴ sonic velocity, impact hammer measurements, and other techniques have been reported and discussed. Both sonic velocity and impact hammer tests indicate that significant changes occur in the measured parameters when concrete is polymer filled. However, both methods suffer from inherent limitations. Impact hammer measurements indicate the condition of the concrete in regions within 1 to 2 in. of the surface. If the regions are polymer filled, there is a significant increase (by a factor of ≈ 1.6) in rebound number. Regions near the surface that are monomer filled show no increase in rebound number. As previously mentioned,⁴ the

impact hammer may have application to thin-wall concrete sections.

Sonic velocity measurements, on the other hand, show the condition of the whole sample. In polymer-filled concrete the sonic velocity is increased by a few thousand feet per second over that in unfilled concrete. However, since the sonic velocity is very sensitive to the presence of moisture or liquid monomer, such an increase is not unambiguously related to polymer content.

Considerable effort was spent at BNL during the past year in evaluating resonant frequency techniques for testing polymer-impregnated concrete. The resonant frequency approach evolved from the acoustic impact technique, which was briefly discussed in Ref. 4. In the acoustic impact technique the specimen is mechanically struck and the intensity of the transmitted sonic signal is measured. Preliminary measurements indicated large differences in the received acoustic impact signals which correlated with polymer loadings. Subsequent work showed that the acoustic impact instrumentation was indeed more suitable for determining the vibration frequencies than the relative damping of transmitted signals. When used to measure the vibration spectrum of concrete, the acoustic impact instrumentation gives the same information as the ASTM standard technique described in ASTM C 215-60. In Figure 40 the acoustic impact equipment is illus-

Figure 40. Acoustic impact testing unit with a concrete beam set in the transverse mode. The hammer is taped to the center of the beam, and the pickup is at the end.

Figure 41. Vibration spectrum of a 4½-in.-diam × 12½-in.-long concrete cylinder in the longitudinal mode, showing the fundamental and first-harmonic frequencies.

trated. Figure 41 shows the vibration spectrum, in the longitudinal mode, of a concrete cylinder; the fundamental and the first-harmonic frequencies are present. An extensive series of measurements using the standard ASTM C 215-60 instrumentation and the acoustic impact instrumentation showed that the two methods were identical. This work has been summarized.²²

Measurements of the resonant frequencies of unimpregnated and polymer-impregnated bars and cylinders showed significant increases in the resonant frequency of the impregnated samples, in accordance with theory. For example, 6-in.-diam × 12-in.-long cylinders of CP-type concrete have the fundamental resonant frequency at 6000 Hz. After polymer impregnation the fundamental changes to 7300 Hz. Measurements of water-saturated cylinders indicated no change in resonant frequency. It thus appears that the technique of resonant frequency analysis may be valuable for nondestructive testing of PIC. It has the important advantages of responding to the total sample and of being unaffected by liquid (water or monomer) in the pores.

It is conceivable that a specimen of PIC may not be completely polymer filled. Partial filling may be due to incomplete drying, partial polymerization, evaporation, etc. An investigation is under way utilizing sonic velocity, impact hammer, and resonant frequency techniques to identify various types of partially loaded concrete test cylinders.

A preliminary investigation at the USBR indicated that the use of electrical resistivity and dielectric measurements showed some promise as a nondestructive quality control test for PIC.⁴ The test results revealed significant differences in dielectric constant and resistivity between unim-

Table 92

Dielectric Tests
MMA-Impregnated Concrete

Specimen No.	Polymer loading, wt %	Dielectric constant	Electrical resistivity, 10 ⁶ ohmmeters
1	6.7	7.23	46.9
2	7.9	6.56	69.0
3	7.3	6.82	62.0
4	6.3	7.13	52.2
5	8.0	6.87	63.8
6	8.0	6.94	63.2
7	6.7	6.84	58.4
8	7.4	7.18	54.2
9	7.6	7.00	57.0
16 ^a	4.5	6.87	56.9
17 ^a	3.9	7.18	50.1
18 ^a	5.2	7.00	54.7
10	—	10.81	7.2
11	—	46.33	1.5
12	—	60.76	1.9

^a Specimen only partially impregnated.

pregnated concrete and PIC. A subsequent investigation with specially prepared samples of MMA-impregnated concrete indicated that the observed values for dielectric constant and electrical resistance (Table 92) showed poor correlation with variations in polymer loading. A set of nine fully impregnated specimens with polymer loadings of 6.7 to 8.0 wt % had dielectric constants ranging from 6.56 to 7.23 and resistivities ranging from 46.9 to 69.0 million ohmmeters. A set of three partially impregnated specimens with polymer loadings of 3.9 to 5.2 wt % had dielectric constants from 6.87 to 7.18 and resistivities of 50.1 to 56.9 million ohmmeters. Since the results indicated that dielectric constant and electrical resistance had poor correlation with polymer loading, development of dielectric methods as a quality control test has been discontinued.

7.2 PROCESS CONTROL

Experiments have been performed to determine the stability of catalyzed MMA systems after repeated contact with concrete. For comparison, the shelf life of uncontacted catalyzed MMA was also measured. Chemical initiators studied were 2,2-azobisisobutyronitrile (AIBN), tert.-butylazoisobutyronitrile (D-A79), and benzoyl peroxide (BP). The results of this study are summarized in Table 93.

Table 93

Stability of Various Chemical Initiators in Methyl Methacrylate at $23^{\circ} \pm 2^{\circ}\text{C}$

Storage time, days	Shelf life			Storage time, hr	Shelf life after concrete contact			
	Peak exotherm time, min ^a AIBN ^b D-A79 ^c BP ^d				Peak exotherm time, min ^a			Peak exotherm time, min ^{a,e}
					AIBN ^b	D-A79 ^c	BP ^d	
0	46	160	94	0	46	160	94	94
6	—	—	83	22	48	159	87	95
7	43	159	85	24	43	137	87	96
8	38	161	84	66	—	—	85	—
10	33 ^f	—	—	88	—	—	84	—
14	—	159	83	114	38	128	—	92
16	—	160	78	136	38	128	—	—
21	—	—	78	153	32 ^f	119	73	—
23	—	144	76	175	—	120	68	—
				197	—	119	64 ^f	—

^aMeasurements conducted at $70^{\circ} \pm 0.1^{\circ}\text{C}$.^b2,2' azobisisobutyronitrile (conc., 1 wt %).^ctert.-butylazoisobutyronitrile (conc., 1 wt %).^dBenzoyl peroxide (conc., 1 wt %).^eBenzoyl peroxide catalyst added after contact of monomer with concrete.^fOnset of polymerization.

The stability of the catalyzed MMA was determined by measuring the peak exotherm time. This procedure was described in Ref. 3.

The uncontacted monomer containing AIBN showed a 30% decrease in peak exotherm time and onset of polymerization after 10 days. The D-A79 and BP systems remained essentially stable for a period exceeding 23 days, although decreases in peak exotherm time of 10 and 21%, respectively, occurred. These data are tabulated in Table 93. All MMA systems contained 1 wt % catalyst and 35 ppm hydroquinone inhibitor.

The same monomer systems were contacted with concrete. In these tests, a different concrete specimen was used during each contacting. After a contact period of 153 hr, the MMA containing AIBN showed onset of polymerization. With D-A79 the MMA had not started to polymerize after 197 hr, although the peak exotherm time had decreased by 26%. The BP showed onset of polymerization at 197 hr. The data indicate that the stability of MMA-catalyst systems is decreased with repeated concrete contact. However, they also indicate that the catalyzed monomer can be used repeatedly in a process plant for rather long periods of contact time, depending on the catalyst used. Additions of inhibitor will also further extend the service time.

To determine whether the decrease in peak exotherm time for monomer-contacted concrete was due to instability of catalyst or of inhibitor, a series of experiments was performed. MMA containing inhibitor was contacted with concrete for a total of 114 hr. Periodically catalyst was added to samples of the monomer and peak exotherm time measurements were made. The peak exotherm time remained essentially the same for the time periods listed in Table 93. This indicates that the inhibitor remains stable and that the decrease in stability observed in the earlier experiments is due to catalyst instability.

8. APPLICATIONS DEVELOPMENT

8.1 PIPE APPLICATIONS

8.1.1 Concrete Draintile. Field and laboratory tests started in 1968 to evaluate PIC draintile are continuing. The following draintiles are under investigation: (1) 30 lengths of poor quality (PQ) made with type I cement, not acceptable for use in USBR projects; (2) 20 lengths of average quality (AQ) made with type II cement, meeting the requirements of ASTM Designation C 118; and (3) 30 lengths of high quality (HQ) made with type V cement and fly ash, meeting USBR special re-

quirements for exposure to high-sulfate environments. From each class of pipe, 10 lengths were fully impregnated with MMA, 10 were fully impregnated with epoxy-styrene, and the remainder served as controls. The average polymer content for each experimental condition is given below.

Class of pipe	Monomer	Polymer loading, wt %
PQ	MMA	6.8
AQ	MMA	6.3
HQ	MMA	5.8
PQ	epoxy-styrene	9.1
AQ	epoxy-styrene	7.7
HQ	epoxy-styrene	5.0

Nine sections of drain tile, each representative of a different experimental condition, are continuing to undergo laboratory testing at the USBR in Denver. The remaining sections are installed in drainage lines at the Westlands Experimental Drainage Plot, Tranquillity, California. Sulfate

concentrations in this area are extremely high; analyses indicate concentrations ranging up to 7.5% in the soil and 5.9% in water taken from the drainage lines. The first periodic inspection of the lines was made after 2 years of exposure. A borehole TV camera was used, and the results were included in the Fourth Topical Report.⁴ All drain tiles were in good condition and no signs of deterioration were observed. Further inspections will be made at appropriate intervals.

The laboratory tests include three-edge bearing strengths, water absorption, and resistance to sulfate attack in both the accelerated sulfate test and the continuous soaking test in 10% Na₂SO₄ solution.

Results of three-edge bearing and water absorption tests can be found in the Third Topical Report.³ They indicated that impregnation with MMA gave increases in strength ranging from 73 to 121%, depending on the combined effect of quality of pipe and the resultant polymer loading. With epoxy-styrene, increases in strength over those for unimpregnated pipe ranged from 100

Table 94
Resistance to Sulfate Attack
Polymer-Impregnated Concrete Drain tile

Class of pipe ^a	Monomer ^b	Polymer loading, %	Sample No.	Immersion test ^c		Accelerated test ^d	
				Days	Expansion, %	Cycles	Expansion, %
PQ	—	—	A1	931	0.287	361	0.536 ^f
PQ	—	—	B1	931	0.213	615	0.500 ^f
AQ	—	—	A2	931	0.195	300	0.580 ^f
AQ	—	—	B2	931	0.099	300	0.634 ^f
HQ	—	—	A3	931	0.075	931	0.036
HQ	—	—	B3	931	0.091	931	0.416
PQ	MMA	7.4	1-5	549	0.538	225	0.536 ^f
PQ	ES	9.5	1-12	931	0.226	931	0.064
AQ	MMA	7.1	2-3	931	0.308	931	0.205*
AQ	ES	8.6	2-13	931	0.254	931	0.160
HQ	MMA	6.6	3-2	931	0.394	931	0.344*
HQ	ES	5.8	3-19	931	0.105	931	0.106

Specimens cut from 4-in.-diam drain tile to $\approx 1 \times 1 \times 6$ -in. size, oven-dried at 150°C prior to impregnation, and radiation polymerized.

^aPQ = poor quality; AQ = average quality; HQ = high quality.

^bMMA = methyl methacrylate; ES = epoxy-styrene.

^cContinuous soaking in 10% Na₂SO₄ solution.

^dSoaking in 2.1% Na₂SO₄ solution at 22°C and drying at 54°C; 1 cycle/day.

*Values are averages for three specimens.

^fRemoved from test (expansion >0.5%).

*Average net expansion for two specimens (third specimen removed from test for examination).

to 281%. In water absorption tests, epoxy-styrene impregnated PQ, AQ, and HQ samples exhibited less absorption than the corresponding MMA-impregnated samples. Compared with unimpregnated specimens, reductions in absorption ranging from 73 to 85% were obtained for MMA specimens, and from 86 to 95% for specimens impregnated with epoxy-styrene.

Results are given in Table 94 for the 10% Na_2SO_4 immersion test and the accelerated (1-day wetting and drying cycle) 2.1% Na_2SO_4 test. In both tests, the resistance to sulfate of unimpregnated control specimens is generally related to the quality of the tile, with the accelerated test showing a generally more severe effect.

In the accelerated test, epoxy-styrene specimens show greater resistance than MMA-impregnated or unimpregnated specimens. All the impregnated specimens are about two to three times more resistant than the unimpregnated specimens, although the MMA specimens are somewhat erratic in performance and in general somewhat less resistant than the epoxy-styrene specimens. In the immersion test the trend is reversed, with the unimpregnated specimens showing less expansion than impregnated specimens. The reason for this discrepancy has not been ascertained.

8.1.2 Sewer and Culvert Pipe: Cooperative Program With American Concrete Pipe Association. A PIC pipe research program was initiated as a cooperative effort of the American Concrete Pipe Association (ACPA), the AEC, BNL, and the USBR. Results of the initial study were given in Ref. 3. The current program is designed to compare unreinforced PIC pipe with reinforced precast concrete pipe. Steel-fiber reinforced concrete pipe has also been included in the program. Goals of the program are to obtain complete design information, service requirements, manufacturing techniques, and an evaluation of the economic benefits.

The test program includes three-edge bearing and hydrostatic burst tests of full-size pipe sections to provide basic design data, and durability test on cores drilled from pipe sections to determine resistance to attack by sulfate and sulfuric acid. Cores will also be tested to determine shear strength and water absorption.

Following completion of tests, the development of an impregnation facility at an existing pipe plant will be studied jointly by ACPA, BNL, and USBR. An economic reconnaissance evaluation

of polymer-impregnated concrete pipe will then be made.

A total of 56 pipe sections have been commercially manufactured by the packerhead and roller suspension methods. The pipe sections are 36-in. in i.d. and 6 ft long, with a wall thickness of 4 in. The test series consists of 36 sections of nonreinforced pipe for polymer impregnation, 12 sections of steel-reinforced pipe, and 8 sections of steel-fiber reinforced pipe. An equal number of each type of pipe was made by each manufacturing method.

The steel-reinforced pipes were manufactured in accordance with ASTM D C76 Class III Reinforced Pipe. These pipes are to be used as controls and will not be impregnated.

The steel-fiber reinforced pipe contains 198 lb of fiber/cu yd of concrete (about 1.5 vol %). The fibers are $0.010 \times 0.022 \times 1$ in. in size. Six sections will be impregnated at BNL and the remaining two will be left unimpregnated.

Thirty-six sections of the unreinforced pipe are to be impregnated and polymerized. Thirty sections are now being impregnated at the BNL facility.⁴ Fifteen will be polymerized by radiation and 15 by thermal-catalytic methods. This work is in progress (see Figures 42 to 46).

Six pipe sections have been impregnated at the USBR facility⁴ (Figures 47 to 52) with MMA by the vacuum-soak process and thermal-catalytically polymerized while in the impregnation vessel. The first section was polymerized in air and the other five sections were polymerized under water. Steam was used as a source of heat. Polymer loadings of the pipe sections are given in Table 95.

Table 95

Preliminary Impregnation Data for ACPA Test Program

Manufacturing method	Specimen No.	Oven-dry weight, lb	Polymer loading, wt %
Roller suspension	412 N*	3272	2.4
	422 NT	3306	2.5
	432 NT	3219	2.9
Packerhead	151 N	3044	-
	161 NT	3056	4.2
	171 NT	3074	3.9

Monomer, MMA.

Specimens, 36-in.-i.d. $\times$ 6-ft-long sections with walls $\frac{1}{4}$ in. thick, thermal-catalytically polymerized under water.

* Polymerized in air.

Figure 42. ACPA pipe being removed from drying oven prior to impregnation at BNL.

Figure 43. ACPA pipe being placed in steel container prior to impregnation at BNL.

Figure 44. ACPA pipe and steel container being lowered into BNL impregnation facility.

Figure 45. ACPA pipe and container being lowered into BNL irradiation facility.

Figure 46. ACPA pipe after impregnation with MMA and radiation polymerization. Core samples have been taken from top end for use in strength and durability tests.

being removed from
pregnation at BNL.

Figure 43. ACPA pipe being placed in steel
container prior to impregnation at BNL.

Figure 44. ACPA pipe and steel container
being lowered into BNL impregnation facility

Figure 45. ACPA pipe and container being lowered
into BNL irradiation facility.

Figure 46. ACPA pipe after impregnation with MMA
and radiation polymerization. Core samples have been
taken from top end for use in strength and durability tests.

Figure 47. Weighing 36-in.-i.d. concrete pipe.

Figure 48. Concrete pipe placed in 7×4×4-ft oven for drying.

Figure 49. Concrete pipe with lifting bracket next to 34.5-in.-o.d. spacer.

Figure 50. Concrete pipe on volume displacement spacer being lowered into impregnator.

Figure 51. Impregnator lid being lowered on top of impregnator tank.

Figure 52. Bolting impregnator lid on tank.

Table 96
San Diego Sewer Pipe
Summary of Results

Specimen No.	Polymer loading, % of dried weight	Coating, % of impregnated weight
SD- 2	5.8	2.4
3	5.0	2.4
4	5.0	2.0
5	5.6	2.1
6	5.8	2.7
7	5.8	2.0
8	5.8	2.1
9	5.1	2.4
10	5.0	2.1
11	5.9	2.4
12	6.1	2.2
13	6.1	2.9
16	6.3	2.4
17	5.8	2.1
18	6.7	2.4

Monomer, 90 wt % styrene - 10 wt % polyester.

Specimens, 8-in.-i.d. $\times$ 4-ft-long sections, oven-dried at 110°C; vacuum-soak impregnation and radiation-induced polymerization.

Coating material, 42 wt % resin 623, 42 wt % resin 624, 15 wt % resin 511 (manufacturer, W.R. Grace).

Catalyst, 1 wt % methyl ethyl ketone peroxide.

8.1.3 Sewer Pipe: Cooperative Program With City of San Diego. Based on the improvements found in structural and durability properties in laboratory experiments, field tests of PIC pipe were undertaken in the city of San Diego sewage system. In the initial test, six pieces of 8-in.-diam $\times$ 24-in.-long pipe were impregnated with tert.-butyl styrene and radiation polymerized. Three of the sections are in test at San Diego and a fourth is being used as a control. Details of this work were given in Refs. 3 and 4. The test was started in January 1971 and data are not yet available.

A laboratory test of an additional piece of tert.-butyl styrene impregnated pipe in 5 wt % sulfuric acid indicated severe attack after a 57-day exposure. Because of this poor result, a program was initiated to select an improved monomer system and impregnation method for use in the preparation of additional specimens to be tested under laboratory and field conditions. On the basis of results from previous tests,⁴ fifteen 4-ft lengths of pipe were impregnated and doubly coated with polyester-styrene. In February 1972 nine lengths

were installed in the city of San Diego sewage system at a location with a high hydrogen sulfide concentration. Another length was installed in the Alvarado Filtration Plant, where it will be compared with the tert.-butyl styrene impregnated pipe that has been in service for $\approx$ 18 months. Five other lengths are being laboratory tested. Impregnation data for all specimens are given in Table 96.

A 30-in.-long section of an impregnated length of sewer pipe (specimen SD-3 in Table 96) was subjected to a three-edge bearing test. Compared with a control strength of 2260 lb/linear ft, the impregnated specimen failed at a load of 5460 lb/linear ft. This corresponds to improvement by a factor of 2.4 and is in agreement with earlier work.³

Two lengths of pipe (specimens SD-6 and SD-13) were sent to a consulting firm for evaluation. Upon receipt by the consultant, examination of SD-13 indicated that an 8-in.-long longitudinal hairline crack in the polymer coating on the end opposite the bell-end had developed during shipping. No defects were found in specimen SD-6.

Testing of both sections in 5 % H_2SO_4 was started on December 14, 1971. As of July 1972, no evidence of attack was apparent on sample SD-6. Surface blistering and discoloration near the hairline crack in sample SD-13 had progressively increased to the point where the coating was considered to have failed.²³

Laboratory testing of two 1.5-ft lengths and one 4-ft length of sewer pipe is in progress at BNL. Initial data were given in Ref. 4. After the test specimens had been exposed to 5% H_2SO_4 for 150 days, the acid was removed and the specimens were visually examined. Compared with earlier work in which unimpregnated sewer pipe showed severe attack after exposure for 17 days, no attack was apparent on the walls of the PIC pipe. However, peeling of the coating and some deterioration were apparent at the bottom end of each specimen (see Figure 53). Since in all cases the attack occurred at corners or joints, it was decided to repair the specimens, using a polyester-styrene resin that would produce a tougher and more flexible polymer.

A mixture consisting of 50 wt % W.R. Grace Co. resin 210, 15 wt % W.R. Grace Co. resin 511, and 35% Hetron 197 was used to repair the attacked area on the 4-ft length and to completely recoat the specimens shown in Figure 53. Testing

Figure 53. Concrete sewer pipes fully impregnated with 10 wt % polyester - 90 wt % styrene and the inner surfaces coated with two coats of polyester-styrene. After exposure to 5% H_2SO_4 for 150 days, both specimens show no attack on the walls, but the coating has lifted and blistered at the joint between the pipe and the stainless steel bottom plate.

in 5% H_2SO_4 has been resumed and the completely recoated sections have shown no attack after exposure for an additional 120 days. The pipe with only the deteriorated areas recoated has been in test for 45 days. No further attack is apparent. These tests are continuing.

8.2 PRECAST TUNNEL SUPPORTS AND LININGS

The USBR has conducted a research program to investigate, develop, and test PIC tunnel support and lining systems for gravity flow, circular-cross-section, water conveyance tunnels. The system consists of segmented precast rings, backfilled with concrete.

A description of the experimental program and the facility used to impregnate the precast segments is given in Ref. 4. Sixty-three tunnel liner segments were impregnated with MMA by the vacuum-soak method and thermal-catalytically polymerized. Tests were performed on single seg-

ments and on an 8-ft-diam full-scale segment system. The results of the investigation²⁴ are summarized below.

Individual tests on single segments indicate that PIC segments have an ultimate strength 2.25 times that of conventional concrete segments. Full-scale tests showed that a system comprised of 2-in.-thick PIC segments and 3.5 in. of conventional backfill concrete can support 60% more load than a similar system comprised entirely of conventional concrete.

The feasibility of using PIC for tunnel support lining systems can be determined only by continued investigation. Results to date as to strength, durability, and economics are favorable.

8.3 HIGHWAY APPLICATIONS

The FHWA is interested in the potential use of concrete-polymer materials for a number of highway applications and is sponsoring research and development efforts at BNL and the USBR. Highest priority has been assigned to the development of techniques for repairing deteriorated bridge decks and improving the durability of sound bridge decks. A materials development program to yield data for use in the design of precast prestressed, or post-tensioned, PIC bridge

decks is also in progress. Two reports describing this work have recently been published.^{8,9}

9. CONCLUSIONS AND RECOMMENDATIONS

Remarkable improvements in the structural properties and durability of concrete can be achieved by monomer impregnation and *in situ* polymerization by either radiation or thermal-catalytic means. The impregnation and polymerization process has been developed to the point where polymer-impregnated concrete is no longer limited to small-scale production in the laboratory; it can now be successfully produced in a technically feasible large-scale facility. New developments in process technology have demonstrated the feasibility of polymerizing MMA-impregnated concrete within the impregnation vessel (by the thermal-catalytic method) or in a separate suitable container (by the radiation method). These processing improvements have eliminated the need for specimen wrapping and have greatly assisted in the development of PIC as a practical construction material.

A notable achievement in the development of PC as a practical construction material was the successful fabrication of PC with use of conventional concrete mixing and placing equipment. The new process produces PC having about the same polymer content and compressive strength as standard PIC.

Investigations of PCC have been limited and so far have not shown improvements comparable to those achieved with PIC and PC. A preliminary study of furfuryl alcohol PCC has shown it to have some promise, and investigations are continuing on a limited basis.

Investigations of the structural properties and durability of PIC for ambient-temperature applications have included testing of seven monomer systems: MMA, styrene, MMA - 10 wt % TMP-TMA, acrylonitrile, chlorostyrene, 10 wt % polyester - 90 wt % styrene, and MMA polymerized in contact with water. These systems have produced PIC with improved structural properties and durability as compared with unimpregnated concrete. Improvements in the properties of concrete impregnated with MMA, MMA - 10 wt % TMP-TMA, 10 wt % polyester - 90 wt % styrene, and MMA polymerized in contact with water are particularly good. Investigations have shown that good-quality PIC can be made with concrete that

varies widely in composition and quality. The primary factors in producing good-quality high-strength PIC appear to be achievement of a high degree of impregnation and complete polymerization. The highest compressive strength obtained to date was 32,400 psi for an MMA-impregnated specimen made from a high-strength, high-pressure steam-cured concrete mix.

Data on structural properties have been obtained from direct tension tests at -12°C and 20°C , shear tests, long-term tensile and compressive creep tests, tests of flexural strength of beams impregnated from one and two sides, and flexure and shear tests of steel-reinforced PIC beams. Preliminary tensile strength design values were obtained at -12° and 20°C for concrete impregnated with MMA and 10 wt % polyester - 90 wt % styrene PIC.

Durability tests of PIC continue to give generally excellent results. MMA-impregnated concrete, which shows good performance and has been under test longer than PIC made with other monomer systems, has shown improvements over unimpregnated concrete of $>1523\%$ for freeze-thaw durability, 1200% for resistance to attack by 15% HCl, and 200% for resistance to sulfate attack. PIC exposed to 5% sodium hydroxide exhibits no sign of deterioration after 1 year's exposure. Specimens exposed to sulfuric acid have shown moderate improvements, but it appears that a suitable surface seal coat in addition to complete impregnation will be required for good durability.

Development of PIC for desalting plant applications continued with work on the structural properties and durability of 60 wt % styrene - 40 wt % TMPTMA and 70 wt % MMA - 30 wt % TMPTMA impregnated concrete. Tests include compressive strength, tensile strength, flexural strength, shear strength, thermal properties, creep deformation, and long-term exposure to hot distilled water, brine, and vapor. Tests were conducted at temperatures ranging from -23° to 177°C . Preliminary design values have been calculated for compressive strength, modulus of elasticity, and Poisson's ratio at the various temperatures. A trend toward lower values with increasing temperature was observed. The preliminary design values for compressive strength at 143°C are 13,700 psi for the styrene-TMPTMA and 12,000 for the MMA-TMPTMA impregnated concrete.

Resistance to chemical attack by hot brine and distilled water is being measured in autoclave ex-

periments and recirculating loops. Tests have been in progress on styrene-TMPTMA PIC for 2 years in brine and for 1 year in brine and vapor at temperatures of 121° and 143°C. The PIC specimens show a trend toward lower compressive strength with an increase in exposure time and temperature, ranging downward to 10,300 psi for specimens exposed 2 years in 143°C brine. Tests with MMA-TMPTMA PIC were started, but results are not yet available. Autoclave tests disclosed a failure of MMA-TMPTMA PIC, and the desirability of continued testing is being determined.

Experiments are being conducted to improve the process technology for producing PIC and to determine the process requirements for full impregnation of various types of concrete. These studies include determination of the effects of concrete composition and methods for curing concrete, monomer impregnation methods, the use of different catalysts and polymerization techniques, and methods to reduce monomer evaporation and drainage losses. A recommended process has been developed for impregnation of standard weight, high-pressure steam-cured concrete specimens of up to 12-in. thickness.

A number of potential applications for PIC are being evaluated in cooperative programs with several governmental and industrial organizations. The applications include desalting plants, concrete pipe, bridge decks, housing construction, underwater structures, and tunnel lining and support systems. Concrete culvert and sewer pipe sections 3 ft in diameter and 6 ft long are being impregnated and tested in a cooperative program with the American Concrete Pipe Association. PIC draintiles have been under field test for three years at the Westlands Experimental Drainage Plot in California, where the soil has a high concentration of sulfate. Field tests of PIC sewer pipe are being conducted in cooperation with the city of San Diego. A cooperative program with the Federal Highway Administration is investigating the repair of deteriorated bridge decks, treatment of new bridge decks to improve durability, and, in a joint effort with the Prestressed Concrete Institute, the design of a precast, prestressed PIC bridge-deck system. A PIC tunnel lining and support system is under development in a joint program with the Bureau of Mines and the Department of Transportation. This program involves design of the system and full-scale laboratory testing.

The following recommendations are made for continuation of the program.

1. Efforts to improve process technology should be continued, in order to produce a product of optimum quality at minimum cost.

2. Studies should be continued to obtain a better understanding of the major factors controlling the physical and chemical properties of PIC. Information on the effects of variations in concrete composition, concrete curing conditions, aggregate type and gradation, and polymer loadings provides a basis for establishing product specifications.

3. The testing program on PIC for ambient-temperature applications should be continued, to develop structural properties data and design criteria over a range of temperatures. Durability tests in progress should be continued, and a study should be made to determine the rate of loss in strength of specimens exposed to freezing and thawing and to acid.

4. Development of PIC for desalting plant applications should be continued for the determination of structural properties and design criteria based on long-term exposure to air, brine, and vapor at elevated temperatures.

5. Periodic inspections should be made of the surface treatment work performed (partial impregnation and coating techniques were used to protect mortar-lined distillation chambers and pipe sections) at the OSW Water Desalting Facility, Freeport, Texas.

6. Experiments should be performed to determine the effects of coupling agents, wetting agents, fire retardants, plasticizers, and thixotropic materials.

7. A standard flame resistance test should be performed and the effects of exposure to fire should be determined.

8. Preliminary process and product designs and economic studies for specific applications should be made with use of test data for prototype and full-scale units. Such applications would include precast concrete pipe, tunnel linings and supports, bridge decks, and piling.

9. Development of PC should be accelerated and testing performed to determine structural properties over a range of temperature conditions and durability on exposure to adverse conditions.

10. Potential applications for PIC and PC should be identified and evaluated in laboratory and field investigations. These applications include the use of PIC and PC in the treatment or repair of existing concrete to improve durability,

marine applications, shotcrete, and panels and structural elements in building construction.

11. Construction methods for the utilization of concrete-polymer materials for specific applications should be developed and tested.

12. The major emphasis in the program should now be shifted from the laboratory to the field. With the development of technically feasible processes for the production of PIC and PC, and the determination of design criteria and performance data, these materials are ready for field installation. The ultimate success or failure of these materials will depend upon demonstration of feasible production methods and actual performance under field service conditions.

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