

SP 40-1

Concrete Polymer Materials And Its Worldwide Development

By
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Synopsis: A wide range of concrete-polymer composite materials is under investigation in a number of laboratories around the world. For this materials development, the older technology of hydraulic cement concrete is combined with the newer technology of polymers to form new and improved materials of construction. Polymer impregnated precast concrete (PIC) is the more developed of the composites and exhibits the highest degree of strength and durability properties improvements. Polymer concrete (PC), an aggregate bound with polymer appears to be a promising material for cast-in-place applications. Numerous applications of PIC are presently under development which indicates a large potential for this material.

Keywords: aggregates; compressive strength; concrete durability; concretes; creep properties; modulus of elasticity; hydraulic cements; impregnating; polymer-cement concrete; polymer concrete; precast concrete; research; stress-strain relationships; tensile strength.

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INTRODUCTION

The first sample of polymer impregnated concrete was produced at Brookhaven National Laboratory in 1965 and the first measurements of the physical and durability properties were conducted in 1966 by the U.S. Bureau of Reclamation. The remarkable measurement of 20,000 psi (1410 Kg/cm²) in compressive strength and the large improvement in freeze-thaw durability becomes in retrospect impressive when considering that in the recorded history of concrete from 2000 BC to 1965 AD, the compressive strength was increased from 800 psi (56 Kg/cm²) to 5000 psi (353 Kg/cm²) and durability only in the order of hundreds of freeze-thaw cycles. Thus concrete-polymer materials represents a significant "quantum jump" in the development of concrete and its manufacture. Since 1965 mainly through the efforts of a joint U.S. government agency sponsorship, including the U.S. Atomic Energy Commission, the Bureau of Reclamation, the Office of Saline Water, and the Federal Highway Administration, materials and process information has been developed and is being evaluated for a number of applications in the U.S.

The development of concrete-polymer composite materials is directed at both improved and new concrete materials by combining the ancient technology of hydraulic cement concrete

formation with the more modern technology of polymer chemistry. A wide range of concrete-polymer composites is being investigated.

Material Properties

Polymer impregnated concrete (PIC) is a precast and cured hydrated cement concrete which has been impregnated with a low viscosity monomer and polymerized in-situ. This material is the more developed of the composites. The largest improvement in structural and durability properties have been obtained with PIC. With conventional concrete (28 day water cured), compressive strengths can be increased from 5000 psi (353 Kg/cm²) to as high as 20,000 psi (1410 Kg/cm²). Water absorption is reduced by 99% and the freeze-thaw resistance is enormously improved. With high silica cement, strong basaltic aggregate, and high temperature steam curing strength increases from 12,000 psi (845 Kg/cm²) to 38,000 psi (2680 Kg/cm²) can be obtained. The tensile strength of PIC is essentially one tenth of the compressive strength which is similar to conventional concrete. A maximum of 3500 psi (247 Kg/cm²) tensile strength has been obtained with the steam cured concrete. For steam cured concrete, polymer loadings (i.e. polymethyl methacrylate (PMMA)), of generally around 8% by weight of the dry concrete can be obtained. A photograph of a freeze-thaw test of PIC is shown in Figure 1.

In contrast to conventional concrete, PIC exhibits essentially zero creep properties. Furthermore by polymer impregnating concrete, conventional concrete is transformed from a plastic material to essentially an elastic material with an increase of at least two times in the modulus of elasticity. This is indicated by the linearity of the stress-strain for PIC in Figure 2. The ability to vary the shape of the stress-strain curve presents some interesting possibilities for tailoring desired properties of concrete for particular structural applications.

Methods of Manufacture

PIC is basically formed by drying cured conventional concrete by the most convenient and economical way (hot air,

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oven, steam, dielectric heating, etc.) removing or displacing the air in the open cell void volume (vacuum or monomer displacement and pressure), diffusing a low viscosity monomer (< 10 cps) through the open cell structure which saturates the concrete with the monomer and in-situ polymerizing the monomer to form a polymer by the most convenient and economical means (radiation, heat or chemical initiation). A schematic flow sheet of alternate processes is given in Figure 3. Mainly the free-radical vinyl type monomers, i.e. methyl methacrylate, styrene, acrylonitrile, t-butyl styrene, and other thermoplastic monomers are used. Good results are also obtained with crosslinked and thermosetting monomers such as styrene-trimethylol propane trimethacrylate (TMPTMA) and polyester-styrene. The more important criteria are that the monomer should be a relatively low cost, readily available material and have a relatively low viscosity. Much information on the formation and structural and durability properties of PIC have been accumulated over the past four years in the U.S. (1-4) Table I gives a summary classification of the PIC materials and properties. A U.S. patent has also been issued on the production of PIC. (7)

Polymer cement concrete (PCC) is a premixture of cement paste and aggregate to which a monomer is added prior to setting and curing. The introduction of various organic materials to a concrete mix has been tried numerous times in the past by others as well as by BNL. The results obtained are either disappointing or relatively modest in improvement of strength and durability. In many cases materials poorer than concrete are obtained. Under the best conditions compressive strength improvement over conventional concrete of $\sim 50\%$ are obtained with relatively high polymer concentrations of $\sim 30\%$. Polyester-styrene, epoxy-styrene, furans and vinylidene chloride have been used in PCC with limited success. This is explained by the fact that organic materials are incompatible with aqueous systems and in many cases, interfere with the alkaline cement hydration process. The incentive to attain improved premix concrete materials is that it can be cast in-place for field applications, whereas PIC requires a precast structure. The answer lies in PC development.

Polymer-concrete (PC) is an aggregate bound with a polymer binder. This material can be cast and formed in the field. It is called a concrete because by the general definition, concrete consists of any aggregate bound with a binder. The cheapest binder is portland cement, which costs in the U.S. about 1¢/lb. Polymer can also be a binder, however, it is more costly than hydrated cement, varying from 5¢/lb upwards to 30¢/lb for the majority of the polymer of commerce. Polymer filled with aggregate, for example, powdered walnut shells in plastics for table tops and furniture products has been known for a long time. What is referred to with PC is an aggregate filled with a polymer. The polymer acts as a binder for the aggregate. The main technique in producing PC is to minimize void volume in the aggregate mass so as to reduce the quantity of the relatively expensive polymer needed for binding the aggregate. This is accomplished by grading and mixing the aggregates to minimize void volume. For example to obtain less than 20% by volume voids, a stone aggregate mix of 3/8-1/2 in. stone (60.7% by wt.), 20-30 mesh sand (23.0%), 40-60 mesh sand (10.2%) and 170-270 sand (6.1%) are mixed and vibrated together in a form. Monomer is then diffused up through the mixed aggregate and the polymerization is initiated by either radiation or chemical means. There is also another reason for looking forward with interest to the development of this new class of PC materials. The problem with conventional concrete is the alkaline portland hydraulic cement which on curing, forms internal voids. Water can be entrapped which on freezing can readily crack the concrete. Furthermore the alkaline cement can be chemically attacked by acidic materials and concrete rapidly deteriorates under this condition. With polymer as a binder, most of these difficulties are overcome. The polymer can be made compact with a minimum of open voids and most polymers are hydrophobic and resistant to chemical attack. As shown in summary Table 1, PC compressive strengths can be obtained as high as with PIC (~20,000 psi (1410 Kg/cm²)). A silane coupling agent is added to the monomer to improve the bond strength between the polymer and the aggregate. The main problems arise from the viscoelastic properties of the polymer. Polymer usually has a low modulus of elasticity which means it is flexible and exhibits creep properties. This is mainly why plastics are not used alone in structural members. By using polymer

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as a binder with aggregates, some of these difficulties are overcome and there is much hope for developing an important new class of high benefit to cost ratio materials. It is interesting to note, from the open literature, that investigators in the USSR (6) have advanced the development of PC to a greater extent than in the U.S., whereas PIC is much more advanced in the U.S. than in the USSR. Much more investigation and experience is required with PC to make it a reliably acceptable material of construction.

Consideration can be given to the aggregate in the binder-aggregate concretes or composites. The definition of an aggregate is any readily available bulk material. The cheapest and most readily available aggregates are natural stone and sand and that is why they are used all over the world. There are many kinds of stone aggregates which basically relate to igneous (granite), metamorphic (slate) and sedimentary (sandstone) stone. Aggregates are also classified as standard weight, structural lightweight and insulating lightweight. Among the various lightweight polymer impregnated concrete materials, perlite and expanded shale which have poor structural properties, has been used to produce a material which is lighter than wood and compressively as strong as concrete. This opens up possibilities for producing lightweight structurally strong mortars and concretes which are buoyant and have a high strength-to-weight ratio. Table 1 briefly summarizes the properties of concrete-polymer materials produced to date including surface coated (SC) and partially penetrated PIC referred to as coated in-depth concrete (CID). An attempt at rating the improvement in strength and durability properties in relation to a cost of manufacture is indicated in the table as a relative benefit to cost ratio for each of the materials. The factors taken into account include cost of monomer, cost of manufacture, the degree of improvement of both strength and durability, and the weight.

Applications Development

A number of applications of concrete-polymers are being investigated in the U.S. For the U.S. Federal Highway Administration (FHWA) advanced prestressed-post tensioned bridge deck designs are being investigated. The U.S. Office

of Saline Water (OSW) is investigating corrosion resistant PIC for constructing economical distillation vessels used in producing fresh water from the sea. The U.S. Bureau of Mines (USBM) is investigating the chemical stabilization of coal mine roof supports by impregnation of rock (5) with monomers followed by in-situ polymerization and also in developing a pumpable roof bolt. Segmental PIC tunnel linings is another application under development by the U.S. Bureau of Reclamation (USBR). The U.S. Navy has been interested in the use of PIC for underwater buoys and habitats. PIC is also being investigated for beams and building blocks for durable housing. The American Concrete Pipe Association (ACPA) in cooperation with the U.S. Atomic Energy Commission (USAEC) and the USBR is investigating the use of PIC for sewer and pressure pipe. There is also interest in PIC for railroad crossties.

In Japan an industrial construction company together with a chemical company is reported to have constructed a 15 ton/day pilot plant for experimental production of PIC using thermal-catalytic initiation. The material is called powercrete and beams, panels, and pipe have been produced, and a number of structural and durability tests have been performed.

A firm in the Union of South Africa is reported to have constructed a pilot plant for the thermal-catalytic production of PIC using a special type of concrete with smooth surfaces called mirror concrete. In addition to pipe and building concrete, a market for domestic sanitaryware (i.e. wash basins, bathtubs, sinks, etc.) is being explored.

A cement association in Italy and the University of Rome is collaborating in developing a PIC using a high silica cement in high strength concrete. High pressure steam cured concrete using underwater polymer curing is being used. Possibilities for construction of ship plate, sewer pipe and building facings are being explored.

Investigators in Norway, Denmark, Belgium, France, Spain, and Israel are known to be exploring PIC applications.

Extensive work has been conducted in the USSR on developing and applying polymer-concrete (PC) which is aggregate bound

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with a polymer binder. The Russian literature (6) indicates significant advances in a number of applications including tunnel supports. PC is also being investigated in the U.S. however to a much less extent than PIC. Interestingly enough, the Russian literature indicates little work on PIC in the USSR.

A number of universities around the world have initiated studies on concrete-polymer materials.

In addition to conventional design procedures sophisticated three-dimensional finite element computer code structural analysis has been developed at Brookhaven National Laboratory (BNL) (8) and is being applied to aid in the design and analysis of structures utilizing these new concrete-polymer materials.

Preliminary cost estimates indicate that PIC materials cost could be competitive with other conventional materials of construction. The feeling is that concrete-polymer which mates an ancient materials technology (concrete) with a new materials technology (polymer) is a growing and exciting one. Given the opportunity of additional investigation, demonstration and experience it is believed that concrete-polymers can become an important class of construction materials.

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Table 1
Classification of Concrete-Polymer Materials

	Polymer loading, wt % PMMA	Density lbs/ft ³	Compressive strength, lbs/in. ²	Strength weight ratio	Durability	Benefit cost index
		(gm/cc)	(Kg/cm ²)			
1. Conventional concrete control	0.0	150 (2.40)	5,000 (353)	33	Poor	1.0
2. Surface Coating (SC) paint or overlay	0.0	150 (2.40)	5,000 (353)	33	Limited	1.1
3. Coating in Depth (CID)	1.0	150 (2.40)	6,000 (423)	40	Good	1.3
4. Polymer Cement Concrete (PCC) premix	35.0	130 (2.08)	7,500 (528)	58	Fair	0.4
5. Polymer Impregnated Con- crete (PIC)						
Standard aggregate						
a. Undried-dipped	2.0	153 (2.45)	10,000 (705)	49	Fair	1.4
b. Dried-evac.-filled	6.0	159 (2.55)	20,000 (1410)	126	Very good	2.0
c. Hi-Silica steam cured	8.0	159 (2.55)	38,000 (2680)	240	Very good	3.0
Lightweight aggregate						
a. Struct. lt. wt. concr.	15.0	130 (2.08)	25,000 (1760)	193	Very good	2.5
b. Insul. lt. wt. concr.	65.0	60 (0.96)	5,000 (353)	84	Very good	2.5
6. Polymer Concrete (PC) cementless	6.0	150 (2.40)	20,000 (1410)	133	Excellent	4.0

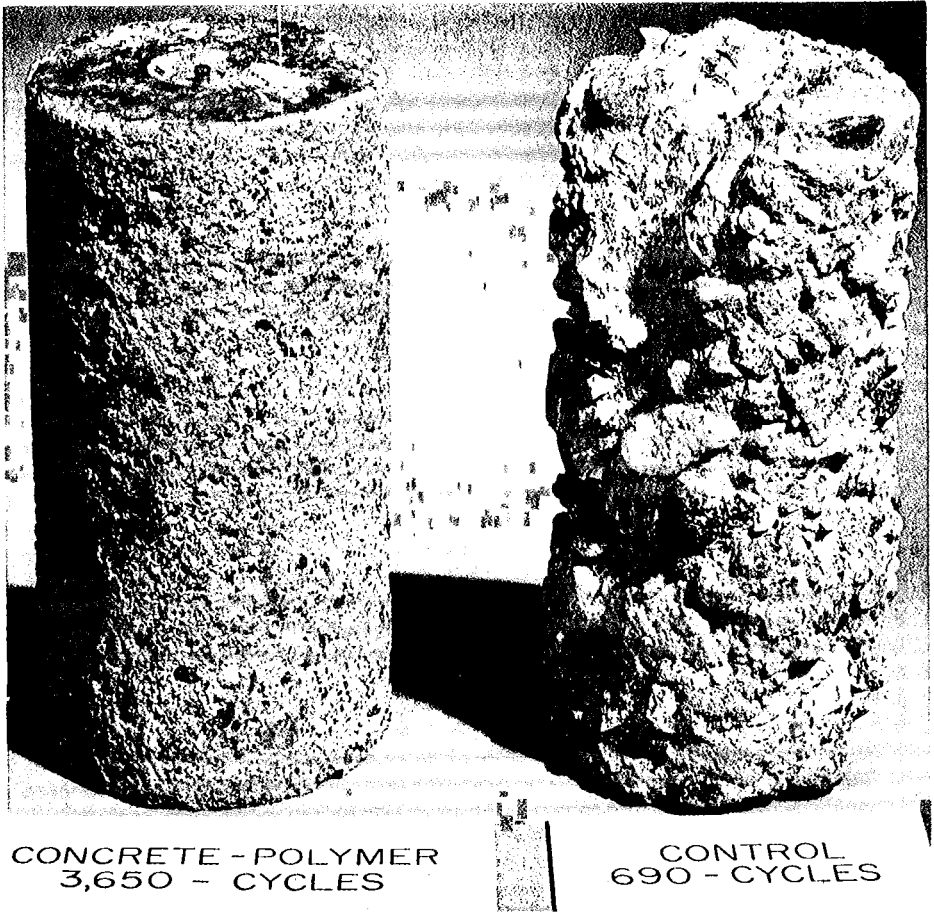


Fig. 1--Freeze thaw test on polymer impregnated concrete PIC (contains 6 percent by weight PMMA) lost 0.5 percent by weight. Control conventional concrete lost 26.5 percent by weight

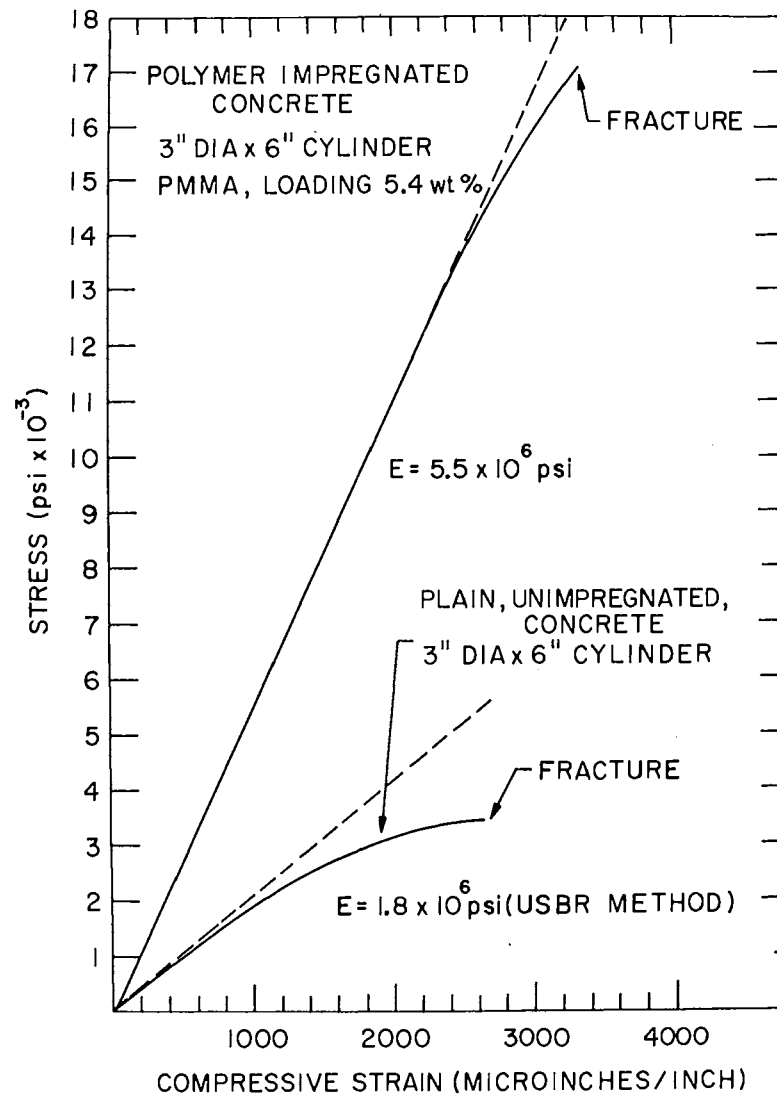
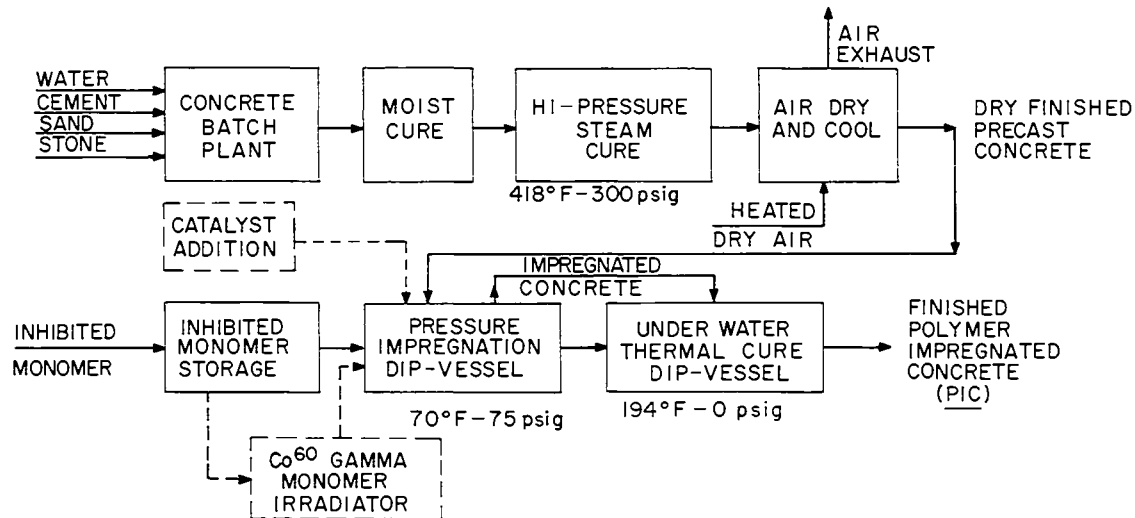


Fig. 2--Compressive stress-strain curve for PMMA-impregnated concrete. Impregnated shows elastic behavior. Unimpregnated shows plastic behavior



THERMAL PROCESS (WITH OPTIONAL MONOMER
IRRADIATION TREATMENT OR CATALYST ADDITION)
FOR PRODUCTION OF POLYMER IMPREGNATED CONCRETE
(PIC)

Fig. 3--Schematic of PIC process

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Process Techniques For Producing Polymer-Impregnated Concrete

By
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Synopsis: Techniques for producing polymer-impregnated concrete (PIC) are evaluated and a processing cycle recommended. A study of concrete mix variation indicates that this parameter has only a small effect on the final strength of the composite. The impregnation of high-pressure steam-cured concrete produces PIC with strengths greater than those obtained from fog-cured material.

Impregnation parameters such as vacuum, pressure, soaking time, and methods of encapsulation all have an effect on the strength of PIC. The degree of sample evacuation is one of the most important parameters. Complete saturation and therefore maximum improvement in strength and durability is accomplished only after prior evacuation to ≈ 30 in. Hg (760 mm).

The feasibility of using water as a means of reducing monomer losses due to evaporation and drainage has been demonstrated. Test data indicate that the underwater polymerization of methyl methacrylate has no detrimental effects on the properties of the composite and may even produce benefits due to the increased polymer content.

Keywords: admixtures; aggregates; air entrainment; autoclaving; compressive strength; concrete durability; curing; evaporation; hardening; hydration; impregnating; methyl methacrylate; mix proportioning; polymer cement concrete; polymer concrete; portland cement type 2; research; tensile strength; water-cement ratio.

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A. J. Romano is a chemical engineer at Brookhaven National Laboratory, Upton, New York. He has been associated with the Concrete Polymer Program for two years, assisting in the development of processing techniques. He was formerly associated with the Materials Science Division, where he assisted in the development of materials for nuclear coolants.

INTRODUCTION

Concrete-polymer composites are being developed as a new construction material which offers advantages of high strength and improved durability, as compared with conventional concrete. The program was initiated in 1967 by the Division of Isotopes Development, U.S. Atomic Energy Commission (AEC), now no longer a division but part of the AEC's new Division of Applied Technology, as a cooperative research and development program between the Department of Applied Science, Brookhaven National Laboratory (BNL), and the U.S. Department of the Interior's Bureau of Reclamation (USBR). The program has been supported by the AEC, the USBR, and the Office of Saline Water (OSW) since that time. In 1969 the U.S. Department of Transportation, Federal Highway Administration (FHWA), initiated support for work on the use of concrete-polymer materials for highway applications.

The long-range objectives of the program are the investigation and development of concrete-polymer composite materials for use as improved and new materials of construction. The investigation has progressed to the point where at least four

distinct types of material are being actively investigated. These include (a) polymer-impregnated concrete (PIC), consisting of a precast portland cement concrete impregnated by a monomer system which is immediately polymerized, (b) polymer-cement concrete (PCC), consisting of a monomer added to a water-portland cement-aggregate mix which is polymerized as the concrete hardens, (c) polymer-concrete (PC), an aggregate mixed with a monomer and subsequently polymerized in place, and (d) precast concrete, which is partially impregnated to produce an in-depth polymer coating. For each of these main types, process variations can be made to change the properties and characteristics of the materials.

The main effort has been directed toward the development of PIC, a material with enhanced structural and durability properties as compared to portland cement concrete. PIC is generally prepared by impregnating dry precast concrete with a liquid monomer and polymerizing the resin in situ by radiation or by thermal-catalytic techniques. The polymer tends to fill the porous void volume of the concrete, which results in significant improvement in strength and durability properties. For a concrete mix that produces specimens with a compressive strength of 5000 psi (352 kgf/cm²), compressive strengths >30,000 psi (>2120 kgf/cm²) have been measured after impregnation. Large improvements in tensile strength, modulus of elasticity, modulus of rupture, and hardness are also obtained. Water absorption and permeability are reduced to negligible values, and resistance to chemical attack by distilled water, sulfate brines, and acids is markedly improved. Descriptions of the preparation and testing methods for these materials have been published. (1-7) A detailed bibliography is given in Ref. 4.

The basic method of producing PIC consists of the fabrication of precast concrete specimens, oven-drying, saturation with monomer, and in-situ polymerization. Processing requirements for each of these steps are being developed.

A number of concrete preparation variables such as mix variations, method and duration of curing, and drying temperature have been investigated to determine the effects on the

properties of the composite material. Experiments are also being performed to determine the process conditions required to fully impregnate various types of concrete. Variables such as degree of vacuum, evacuation time, saturation time, pressure, and monomer viscosity have been studied. The effect of concrete composition on each of these parameters has also been studied, and techniques for reducing monomer losses due to evaporation and drainage during the polymerization reaction are being evaluated. The impregnation techniques are being used in conjunction with polymerization methods involving the use of radiation, chemical-initiator, and promoter-chemical initiator. Experimental methods for initiating the polymerization reactions have been described previously. (1-4) All results given here have been obtained by ^{60}Co gamma radiation-induced polymerization.

DISCUSSION OF RESULTS

Concrete Composition

A number of different concrete mixes have been impregnated to investigate the effects of concrete mix design variables on the compressive strength of PIC.

The first series of experiments consisted of 10 different mixes. The series was based on the USBR CP mix.* The concrete mix was varied to study the effects of water/cement ratio, entrained air content, slump, aggregate quality, and the use of admixtures, including fly ash. The concrete specimens were impregnated with methyl methacrylate (MMA) and radiation polymerized.

The results from these tests (Ref. 4) indicated control strengths that varied from 4200 psi (296 kgf/cm^2) for a mix having a 0.60 water/cement ratio to 7280 psi (510 kgf/cm^2) for the CP-type mix made without the addition of an air-entraining

* Type II portland cement, 5.5 cement factor, Clear Creek aggregate graded to 3/4-in. maximum size, 0.50 water/cement ratio, 3-in. slump, and 6 percent entrained air.

agent. After impregnation the average compressive strengths of the mixes, with the exception of one containing 25 percent fly ash as a replacement for cement, ranged between 19,000 psi (1335 kgf/cm²) and 23,100 psi (1620 kgf/cm²). The mix containing fly ash had a lower strength, 15,490 psi (1090 kgf/cm²), probably because the cement hydration reaction with fly ash is inhibited by drying the concrete. When fly ash is used in concrete, a considerably longer period of moist curing is needed to develop full strength.

Although large differences in concrete composition were not obtained in this test series, it would appear, on the basis of these limited data, that minor changes in composition do not significantly affect the compressive strength of PIC.

In an attempt to evaluate the effects of larger differences in composition, two additional studies were performed. All of these specimens were impregnated with MMA and polymerized by radiation. The mix variations based on the standard fog cured CP mix and test results are summarized in Table 1. Compared with the earlier tests, slightly higher strengths were obtained in this series although similar trends are indicated. The higher strengths are probably due to the use of improved impregnation techniques which reduced monomer evaporation and drainage losses. These techniques are discussed later.

As shown in Table 1, changes in air content from 2 to 10 percent had little effect on the final strength of the PIC. Compressive strengths of 24,200 psi (1700 kgf/cm²) and 23,400 psi (1650 kgf/cm²), respectively, were obtained. The impregnation of high-strength concrete [control strength, 10,000 psi (703 kgf/cm²)] produced composites with a strength of 25,300 psi (1780 kgf/cm²), essentially the same as those produced from low strength samples [2000 psi (141 kgf/cm²)].

In addition to the mixes listed in Table 1, concretes containing several other aggregates such as crushed diorite, quartzite gravel, expanded slate, and slag have been impregnated. All the materials produced high-strength, durable composites. (6) On the basis of these results it would seem that concretes prepared from locally available materials can be used in the production of PIC.

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Method and Duration of Curing

Three curing conditions, fog curing, low-pressure steam curing (LPS), and high-pressure steam curing (HPS), were studied to determine effects on MMA-impregnated concrete.

Fog curing consists of storage for 28 days in a moist room at 90 to 100 percent relative humidity at 73°F (23°C).

Low-pressure steam curing consists of subjecting specimens immediately after casting to fog curing or covering them with a water-saturated cloth for a period of 3 hours. The specimens are then placed in a steam room and the temperature is raised to 150°F (65°C) at a maximum rate of 31°F/hr (17°C/hr). Temperature is maintained at 150°F (65°C) for 24 hours, including the initial 3 hour of wet curing and the period of time required to reach 150°F (65°C). Specimens are then cooled at a maximum of 20°F/hr (11°C/hr) until the temperature is within 57°F (14°C) of the subsequent storage temperature.

The procedure used for high-pressure steam curing is as follows. After casting, specimens are fog-cured or covered with a water-saturated cloth for 4 hours. They are then placed in an autoclave and heat is applied at a rate that will bring the temperature to 350°F (177°C) in not less than 3 hours. Heating in saturated vapor is maintained for 8 hours, and the pressure is then released over a period of 20 to 30 minutes. Specimens are then cooled at a maximum of 20°F/hr (11°C/hr) until the temperature is within 57°F (14°C) of the subsequent storage temperature.

In an initial study, CP-type concrete cured by each method was impregnated and tested. The high-pressure steam-cured specimens achieved the highest compressive strength, 23,210 psi (1630 kgf/cm²). Low-pressure steam curing gave a strength of 22,930 psi (1610 kgf/cm²), and fog curing produced the lowest strength, 20,680 psi (1455 kgf/cm²).

Similar trends are apparent from the results of tests performed with other concrete mixes. These data are summarized in Table 1. In general the high-pressure steam-cured samples had higher polymer loadings and strengths than comparable

fog-cured specimens.

It has been shown that although steam curing does not change the total porosity of cement, the pore size distribution is changed. This results in an increase in the amount of porosity accessible to monomer. A higher percentage of the pores are filled with monomer therefore higher polymer loadings and strengths are produced. (3,8)

Preliminary tests to determine the effect of moist curing time have also been performed. Specimens cured in lime-saturated water for periods of 2, 7, and 28 days, were oven-dried, impregnated with MMA, and radiation polymerized. (3) Compressive strengths between 16,200 psi (1140 kgf/cm²) and 16,900 psi (1190 kgf/cm²) were obtained. The relatively low strengths were probably due to excessive monomer losses through evaporation, but the results indicate that the duration of moist curing does not significantly affect the final strength of the PIC.

Effect of Drying

The degree of dryness of concrete strongly affects the amount of monomer absorbed during impregnation. In a number of investigations, precast normal-weight concrete has been found to contain up to 5 weight percent free water depending on the prior treatment. Upon impregnation, normal weight dried specimens generally absorb 4 to 7 weight percent monomer. Undried specimens, equilibrated in air-conditioned laboratories, gain only 2 to 3 weight percent monomer upon impregnation.

Drying temperatures up to 482°F (250°C) have been evaluated. Earlier work (3) indicated that specimens dried at temperatures from 302°F (150°C) to 482°F (250°C), and subsequently impregnated with MMA, exhibited a slight decrease in compressive strength with increased drying temperature. Recent work (7) indicates that a drying temperature of 230°F (110°C) is not high enough to remove all the water. In these tests, constant weight is defined as the point at which two consecutive measurements over a 24-hour period indicate no change in weight.

It appears that a drying temperature of 302°F (150°C) is required to remove most of the free water without seriously affecting the strength of the PIC composite.

Impregnation Techniques

The effects of vacuum, pressure and soak time on the rate of saturation of 3x6-in. (7.5x16-cm) concrete specimens were studied. (7) Test specimens of CP concrete and three of its variations, all high-pressure steam-cured were compared. The mix variations were (a) high air content (10%), (b) structural lightweight (expanded-shale aggregate), and (c) low strength (low cement factor). All specimens were oven-dried at 230°F (110°C), impregnated with MMA, and radiation polymerized.

The effect of pressure on the filling rate of the high-pressure steam-cured (HPS) CP-type concrete specimens without prior vacuum treatment is shown in Fig. 1. Data are given for two pressure levels, 10 psig (1.7 kgf/cm²) and 100 psig (8 kgf/cm²). At 100 psig (8 kgf/cm²) the monomer loading approached equilibrium (≈6.2%) after about 10 minutes, whereas at 10 psig (1.7 kgf/cm²) equilibrium had not been achieved after 1000 minutes. Similar observations were made for the other concrete compositions tested, except that in each case equilibrium was achieved at other levels of monomer loading and at different rates. This will be discussed later. One of the disadvantages of soaking under high pressure without prior evacuation is that air is entrapped in the concrete. As a result, when the pressure is reduced to atmospheric conditions, a slight reduction in monomer loading occurs. This is caused by the expansion of air compressed during the filling step. For example, overnight soaking of a low-strength concrete sample at 100 psig (8 kgf/cm²) and subsequent depressurization resulted in a drop in monomer loading from 7.0 to 6.2 percent. This was observed to a lesser degree with samples soaked at 10 psig (1.7 kgf/cm²).

The effect of vacuum treatment on the rate of filling of CP concrete specimens, subsequently soaked at 10 psig (1.7 kgf/cm²) and 100 psig (8 kgf/cm²), is also shown in Fig. 1. The data indicate that holding a 3x6-in. (7.5x16-cm)

sample under vacuum for 15 min and then soaking at 10 psig (1.7 kgf/cm^2) for ~ 30 min is adequate to reach saturation. If the sample is pressurized to 100 psig (8 kgf/cm^2), saturation is achieved in considerably less time. The most significant improvement observed with evacuated samples is that the final monomer loading is higher. This would indicate that the application of soaking pressure following evacuation offers the most desirable impregnation process.

Similar observations were made for the other concrete compositions tested. A comparison of the filling rates at 10 psig (1.7 kgf/cm^2) after prior evacuation for the four materials tested is shown in Fig. 2. High air content, high water/cement ratio (low strength) and CP-type concrete samples essentially reached saturation in ~ 5 , 10, and 30 min, respectively, whereas the expanded shale specimen had not reached saturation after 60 min.

The effect of the degree of vacuum treatment was also studied. Data from experiments performed at 15 in. Hg (380 mm) indicate considerably longer saturation times are required and lower monomer loadings are obtained. After polymerization, compressive strengths measured on partially evacuated and un-evacuated samples were always lower than those of fully evacuated samples.

The effect of monomer viscosity on the saturation rate was also studied in experiments using MMA and pre-polymer solutions of MMA.* Compared with a saturation time of ~ 20 min with MMA, more than 360 min are required for 20 and 70 cps PMMA solutions. After saturation, all the samples had the same compressive strength, 26,000 psi (1830 kgf/cm^2).

Encapsulation Methods

One of the steps in the procedure for fully impregnating precast concrete has been to wrap the saturated sample in aluminum or polyethylene sheets in order to reduce monomer

* Polymethyl methacrylate dissolved in MMA

evaporation and drainage losses. In an attempt to further reduce these losses and to eliminate the necessity of wrapping, the following encapsulation techniques have been evaluated: (a) encapsulation in a form during processing, (b) polymerization with the specimen under water, and (c) application of a pre-polymer dip coating following impregnation of the specimen.

Experiments with CP-type concrete (7) indicate that maximum polymer loadings are obtained with the underwater method of encapsulation. This method consists of a standard vacuum-soak impregnation, placing the specimens in water, and radiation-polymerizing under water. Results indicate that evaporation and drainage are reduced considerably and the mechanical strengths are not affected by the presence of water.

Experiments have also been performed to determine the effectiveness of underwater thermal-catalytic polymerization. (7) Variables studied include water depth, temperature, and the use of primary encapsulating materials such as foil. It was found that MMA evaporation losses from concrete specimens polymerized at 167°F (75°C) could be essentially eliminated by the use of a 20-in. (50-cm) head of monomer saturated water. Specimens polymerized at 167°F (75°C) under 6 in. (15 cm) of unsaturated water exhibited surface depletions of $\sim 1/8$ in. (0.3 cm).

These results suggest that thermal-catalytic polymerization in hot water is also an effective and potentially economical method for use in the preparation of PIC.

Data obtained on highway-quality concrete (6) indicate that encapsulation in forms is superior to the underwater method when used for specimens containing slag or Solite (expanded slate). However, the underwater method is more effective with normal-weight [~ 150 pcf (~ 2400 kg/m³)] specimens containing limestone, White Marsh quartz gravel or diorite aggregate. A possible explanation is that the Solite and slag samples have a higher porosity than the higher density concretes and therefore are more susceptible to

drainage. However, the in-form method of encapsulation involves higher costs associated with the fabrication of forms and removal of excess polymer from the final product. In addition, excessively long drying times are required because of the limited surface area resulting from the use of tight-fitting forms.

The use of a pre-polymer dip, wrapping, and subsequent rotation of the specimen during polymerization has also been evaluated. (6) In general, although the strength results were similar to those obtained by other methods, the necessity of rotating large specimens would tend to make this method impractical.

CONCLUSIONS

The work with PIC has indicated that remarkable improvements in structural and durability properties of concrete can be obtained. Compressive strengths as high as 32,400 psi (2280 kgf/cm^2) have been measured.

Studies of concrete composition and method of curing indicate that each of these parameters has only a small effect on the strength of the PIC composite. Of the compositions tested, only the concretes containing fly ash and high-porosity limestone had strengths, after impregnation with MMA, that were discernably lower than the others. The average compressive strength of all the other specimens evaluated in this test series was $\approx 24,000 \text{ psi}$, ($\approx 1690 \text{ kgf/cm}^2$) and showed little correlation with concrete composition or initial strength.

The impregnation of high-pressure steam-cured concrete produced PIC with strengths greater than those obtained from fog-cured and low-pressure steam-cured material. In many cases the differences are not large and may not be sufficient to warrant the added processing cost.

The degree of dryness of a sample is an important impregnation parameter. The monomer loading of a specimen, and therefore its final strength, is related to its degree of dryness. Although a drying temperature of 230°F (110°C)

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seems adequate to remove enough moisture to produce high-strength PIC, 302°F (150°C) is recommended.

Impregnation parameters such as vacuum, pressure, soaking time, and methods of encapsulation were all found to have an effect on 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 (760 mm). Without prior evacuation, soak pressures of ≈ 100 psig (8 kgf/cm²) are required in order to approach saturation in a short period of time (≈ 60 min).

Concrete composition has a significant effect on the monomer filling rate. Samples of concrete having high air and water contents, were saturated with monomer in shorter periods of time than CP-type concrete. Samples containing the porous expanded shale aggregate absorbed monomer at a slower rate than CP-type concrete, containing dense aggregate.

The feasibility of using water as a means of reducing monomer losses due to evaporation and drainage has been demonstrated. This method appears more practical than the use of forms during impregnation and polymerization or rotation during polymerization. Test data indicate that underwater polymerization of MMA has no detrimental effects on the properties of the composite and may even produce benefits because of the increased polymer content. The method appears to have significant advantages over the other methods for impregnating high-density concretes.

RECOMMENDATIONS

High-quality PIC can be made from concretes with a wide variety of compositions. For best results, the use of standard-weight concretes containing a good quality aggregate is recommended. With this type of concrete, HPS curing appears advantageous.

For a high-pressure steam-cured, standard-weight concrete containing a low-porosity aggregate, the following processing cycle is recommended for sections up to ≈ 12 in. (30 cm) thick.

1. Oven-dry to constant weight at 302°F (150°C). Dryness should be achieved in ≈ 24 hr.
2. Evacuate section to ≈ 30 in. (760 mm) Hg and maintain for ≈ 30 min.
3. Introduce monomer under vacuum and subsequently pressurize to ≈ 10 psig (1.7 kgf/cm²). Pressure soak for ≈ 60 min.
4. Remove monomer.
5. Remove and place section in water or, for larger sections, back-fill impregnator with water.
6. Polymerize monomer in situ with radiation, hot water, or steam. The method of polymerization should be based on a detailed cost analysis for each specific product.
7. Remove water and clean section.

Data for larger sections are now being obtained.

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Table 1

Concrete Composition and Method of Curing

Concrete composition (a)	Method of curing	Polymer loading (b) wt %	Compressive strength, (c)	
			psi	(kgf/cm ²)
Standard CP mix, $\approx 6\%$ air	fog (d)	7.2	24,750	(1740)
CP mix, $\approx 2\%$ air	fog	5.9	24,200	(1700)
	HPS (e)	7.2	24,800	(1740)
CP mix, $\approx 10\%$ air	fog	9.5	23,400	(1650)
	HPS	10.0	22,000	(1550)
Low strength, ≈ 2000 psi	fog	7.2	25,000	(1760)
	HPS	8.3	27,260	(1915)
High strength, $\approx 10,000$ psi	fog	6.1	25,300	(1780)
	HPS	7.1	29,900	(2100)
CP mix with expanded shale aggregate	fog	25.5	24,300	(1710)
	HPS	29.8	26,000	(1830)
CP mix with pit run Clear Creek aggregate	fog	10.0	21,750	(1530)
	HPS	11.9	19,950	(1405)
CP mix with high porosity limestone aggregate	fog	18.1	16,700	(1170)
	HPS	20.2	17,150	(1205)
CP mix with low porosity limestone aggregate	fog	6.9	22,400	(1575)
	HPS	8.4	22,950	(1610)

(a) All mixes are variation of standard CP-type concrete (see Ref. 1).

(b) Monomer, MMA; radiation-induced polymerization under water. All specimens are 3x6-in. (7.5x16-cm) cylinders oven-dried at 230°F (110°C) prior to impregnation.

(c) Average of 8 specimens.

(d) Fog curing, 28 days.

(e) High-pressure steam curing at 350°F (177°C) for 3 hr.

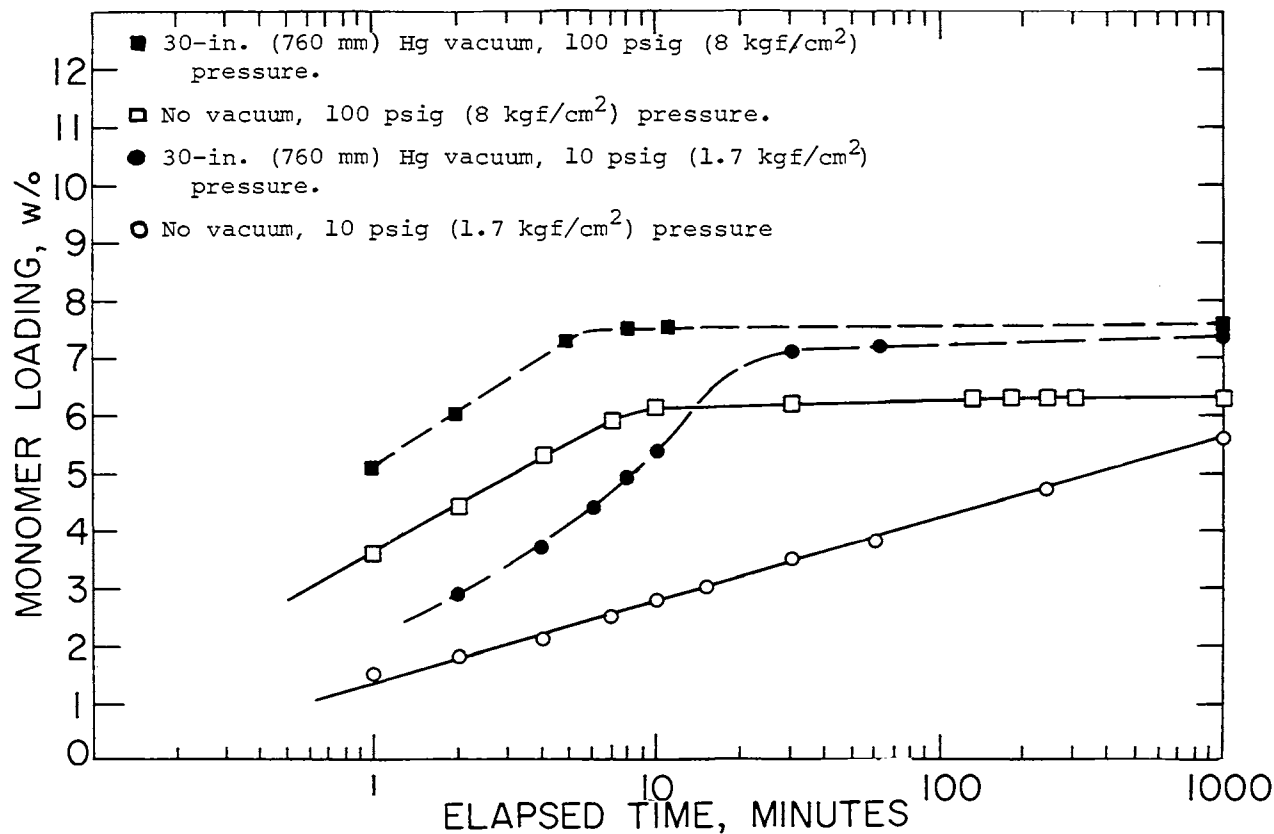


Fig. 1--The effect of vacuum and pressure on impregnation, using MMA, of 3x6-in. (7.5x16-cm) specimens of HPS cured CP concrete previously dried at 110°C (230°F)

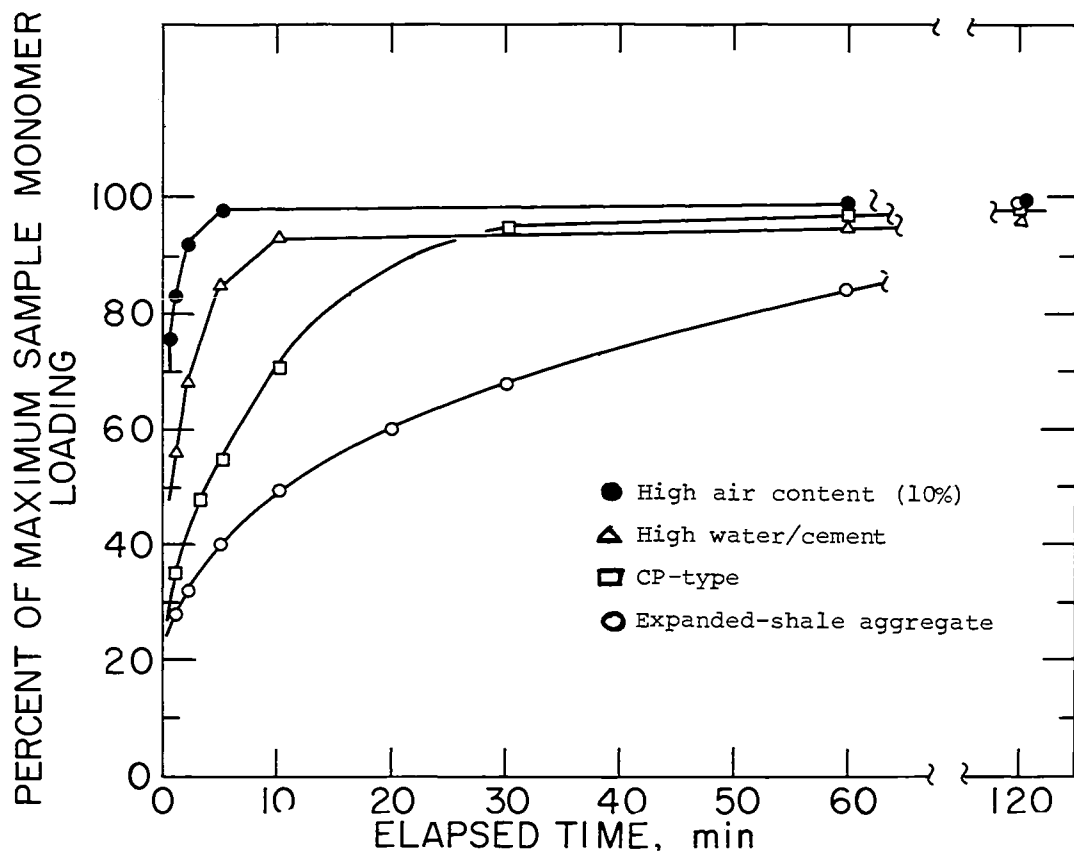


Fig. 2--The effect of concrete composition on impregnation, using MMA, of 3x6-in. (7.5 x 16-cm) concrete specimens previously dried at 110°C (230°F). All specimens were evacuated and pressure soaked at 10 psig (1.7 kgf/cm²)

SP 40-3

Development Of Polymer-Impregnated Concrete As A Construction Material For Engineering Projects

By

G. W. De Puy and J. T. Dikeou

Synopsis: The developmental program for polymer-impregnated concrete (PIC) has shown that a material of greatly improved properties, as compared with conventional concrete, can be routinely produced. Applications of this remarkable new material are now under active investigation. Typical structural properties at ambient and elevated temperatures are presented and results of durability tests are reviewed. The program has advanced from the stage of determining the basic characteristics and engineering properties of PIC to the gathering of statistically significant data for preliminary design purposes. Tests have shown that good quality PIC can be produced from precast concrete of widely varying quality and composition, and cured by different methods although some differences in the resultant properties can be expected due to porosity, composition of mix, curing conditions, and other factors affecting concrete properties. The main factor in producing high quality PIC is achieving a high degree of impregnation and complete polymerization. Potential applications currently under study for PIC include saline water distillation plants, precast tunnel liners and supports, concrete pipe, bridge decks, wall panels and beams, and marine structures. Field tests are in progress for polymer-impregnated drain tile and sewer pipe and are being planned for precast PIC tunnel liners.

Keywords: bridge decks; compressive strength; concrete durability; concrete pipes; concrete technology; creep properties; curing; impregnating; mix proportioning; modulus of elasticity; permeability; polymer-cement concrete; polymer concrete; precast concrete; stress-strain relationships; tensile strength; thermal properties; tunnel linings.

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INTRODUCTION

In 1966, the Bureau of Reclamation joined forces with Brookhaven National Laboratory to develop polymer-impregnated concrete as a new engineering material. Work on the program is funded by the Atomic Energy Commission and the Office of Saline Water, as well as the Bureau of Reclamation. More recently, other Federal agencies have sponsored work on applications of specific interest to their respective groups. Such agencies include the Federal Highway Administration, the Bureau of Mines, the Corps of Engineers Construction Engineering Research Laboratory, the Naval Civil Engineering Laboratory, and the Office of High Speed Ground Transportation. Private organizations sponsoring work in this field include the American Concrete Pipe Association and the Prestressed Concrete Institute. Work on the joint Bureau of Reclamation-Brookhaven National Laboratory program is conducted under 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
- (6) Performance of fundamental studies on concrete-polymer composites for the purpose of obtaining a basic understanding of their nature

The family of concrete-polymer materials includes the following three distinct types of materials: the first of these is polymer-impregnated concrete, called PIC, which is prepared by impregnating ordinary precast concrete with a monomer system, and subsequently polymerizing the monomer in situ. The monomers used in this work have very low viscosities and readily enter the voids of concrete. After the voids are filled, the monomer is converted to a solid plastic by the use of chemical promoters or by application of heat or radiation. The second material is polymer-cement concrete, called PCC. This material is produced by mixing water, cement, aggregate, and monomer together and polymerizing the monomer after placement of the concrete. The third material is polymer-concrete, called PC, which consists of aggregate and monomer mixed together with the monomer again polymerized following placement of the material. Recent developmental work with PC has shown the material can be easily fabricated, the processing cost should be much lower than for PIC, and the compressive and tensile strength is nearly equal to PIC.

To date, the greatest improvements in properties have been obtained with PIC; this material is therefore receiving the greatest emphasis in the program.

The basic procedure in producing polymer-impregnated precast concrete products involves drying the components, placing them in a vacuum to remove residual moisture and air, immersing them in a liquid monomer under pressure to achieve saturation, and polymerization of the monomer by heat or radiation. The procedure employed at USBR consists of the following steps:

1. Dry the concrete specimens to constant weight in a 300° F (149° C) oven.
2. Load specimens into impregnator and evacuate using a vacuum of approximately 24 inches (61 cm) Hg for one-half hour.
3. While the concrete specimens are under vacuum in the impregnator, catalyst is mixed with monomer in the transfer tank.
4. Maintain a partial vacuum in the impregnator and transfer the monomer from the transfer tank to the impregnator - fully covering the concrete specimens with monomer.
5. Release the vacuum and pressurize the impregnator to approximately 25 psi (nominal 1.8 kgf/cm²) with air for 2 hours.
6. Drain monomer from impregnator.
7. Polymerize to completion, thermal-catalytically, using the water jacket steam coil heat source or by injecting raw steam or water directly into the impregnator.

Improvement and simplification of the process is being investigated. The major developments in this area include polymerization of specimens while under water to eliminate wrapping, use of coupling agents to improve bonding, and polymerization at ambient temperatures with promoter-catalyst systems.

PROPERTIES

Polymer-impregnated concrete is very much like conventional concrete in appearance. Aside from some surface coatings of polymer which may be present, PIC is indistinguishable from conventional concrete with a casual observation. Upon closer inspection, PIC may be distinguished by the presence of polymer in air voids and by a slightly darker appearance somewhat similar to the appearance of moist conventional concrete. The polymer is distributed throughout the concrete in voids and microfractures and to some extent in the cement paste and aggregate particles. PIC made from conventional concrete usually contains 6 to 7 percent polymer by weight. The beneficial effects of polymer impregnation are largely a result of void and microfracture filling.

The improvements in durability of PIC are due to a reduction in permeability which tends to seal the interior of the concrete from aggressive agents. The polymers under study are fairly resistant to chemical attack, and cement paste is guarded from attack by the physical barrier presented by the polymer.

The reasons for increases in strength properties are not fully understood, especially in regards to the structural properties of the polymer itself. Factors contributing to strength improvement apparently include an improvement in the cement/aggregate bond and healing of microfractures by the polymer, which tend to eliminate fracture-propagating flaws and probably result in a more uniform distribution of stresses and strains within the concrete. Individual differences in properties of various polymers affect the degree to which the above changes take place. Another important property is the glass transition temperature of the polymer. Above this temperature the material becomes flexible or rubbery and results in corresponding changes in the composite material.

According to our understanding of the material, the degree of improvement in properties with a given polymer is a function of the degree to which available voids are filled. An important characteristic of the monomer in producing improved properties is its ability to penetrate concrete and be completely polymerized. Our standard vacuum-soak process fills most of the voids. With our present process, it probably is not possible to achieve much greater filling because some voids are either isolated or are too small to be penetrated by the monomer. Some improvements in polymer loading may be obtained through developing improvements in processing technique to reduce monomer evaporation and drainage, which occur during the

process in the period between impregnation and polymerization. A comparison of properties with polymer loadings should best be made on a basis of percentage of voids filled rather than on a strict weight or volume percent basis.

Types of PIC

The monomer systems and the production process used in the fabrication of PIC may be changed to produce a product to meet special requirements. For example, special monomer systems may be formulated to withstand high temperatures, the impregnation depth may be controlled to give a product having good durability rather than high strength, or the impregnated concrete may be given a seal coat to improve durability.

PIC under investigation may be grouped into four major categories:

PIC for normal temperature applications--This material is produced from a standard conventional concrete made with 517 lbs/cu yd (307 kg/m³) of Type II portland cement, a natural aggregate graded to 3/4-inch (1.9-cm) maximum size, 0.51 water/cement ratio, 3-inch (7.6-cm) slump, and 6 percent entrained air. Monomer systems under investigation have included methyl methacrylate (MMA), styrene, acrylonitrile, chlorostyrene, MMA - trimethylolpropane trimethacrylate (TMPTMA), and *(10-90) polyester - styrene. Most of the current testing is on MMA and (10-90) polyester - styrene impregnated concrete. Polymerization is initiated by radiation or thermal-catalytic methods.

PIC for desalting plant applications--This material is designed for use in a saline water distillation plant and is required to withstand temperatures up to 290° F (143° C) under exposure to brines and distilled water. Initial investigations used a special high-strength concrete made with a high-quality aggregate, Type V portland cement, and fly ash pozzolan. Subsequent studies have shown very little difference in the properties of PIC made with the high-strength concrete and standard mix concrete. Current studies on PIC for desalting plants are performed using the same standard mix concrete used in the normal temperature studies, adjusted to a 1-1/2 inch (3.8-cm) maximum-size aggregate. Two promising monomer systems currently under test are (60-40) styrene - TMPTMA and (70-30) MMA-TMPTMA. Polymerization is initiated thermal-catalytically.

Partially impregnated concrete--Partially impregnated concrete is designed for durability rather than high strength, which permits a saving in the amount of monomer as compared with fully impregnated concrete. The

* Numbers in parenthesis refer to percentages by weight of the respective components in the mixture.

concrete is impregnated by a process similar to that used for fully impregnated concrete but using specially formulated monomer systems to give controlled depths of penetration. The monomers should effectively seal the surface and penetrate to a sufficient depth to avoid 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. Monomer systems under investigation include polyester - styrene, epoxy-styrene, and a MMA prepolymer solution.

Surface impregnated concrete--This material is similar to partially impregnated concrete but is discussed separately because of its potential application and method of production. The surface impregnation and polymerization process is in the initial stages of investigation and is intended for field application on existing concrete highway bridge decks. The developmental program now underway includes the design of a portable impregnator to be used on an existing bridge deck, selection of an appropriate monomer system to achieve a nominal 1-inch (2.5 cm) depth of penetration, evaluation of polymerization by thermal-catalytic and ambient temperature promoter-catalyst systems, and evaluation of the method for highway applications.

Structural Properties

Typical mechanical and physical properties are given in Table 1 for unimpregnated and MMA-impregnated concrete polymerized by radiation and thermal-catalytic means. The values shown are relatively uniform when specimens are treated under a given set of process conditions. It should be noted that when the treatment process or the concrete mix is varied, an expected variation will occur in polymer loadings, degree to which voids are filled, and in test results. Properties listed include compressive and tensile strength, flexural strength, elasticity, hardness, abrasion and cavitation resistance, water absorption and permeability, thermal properties, and specific gravity.

The differences between radiation and thermal-catalytically polymerized specimens are minor with the radiation polymerized specimens generally showing slightly higher strengths. In general, MMA-impregnated concrete is about four times as strong in compression and tension as conventional concrete with a compressive strength of about 20,000 psi (1,406 kgf/cm²) and a tensile strength of 1,600 psi (112 kgf/cm²). In further comparisons of MMA-impregnated concrete with conventional concrete, modulus of elasticity is nearly twice as great, abrasion resistance is about 70 percent greater, cavitation resistance is nearly 90 percent more, water absorption and permeability are reduced by 80 to 90 percent, thermal properties are nearly the same, and the coefficient of expansion is about 30 percent larger. These results are considered as indicative of the properties of PIC and are

not intended to be used as the basis for final design of engineering structures. The current testing program includes tests on larger numbers of samples to determine the mean, standard deviation, and coefficient of variation. Preliminary design values are being determined as sufficient test data become available.

The effects of temperature on the strength and elastic properties of PIC are shown in Table 2. Preliminary results are given for MMA-impregnated concrete at 10° F (-12° C) and 70° F (21° C) and for (60-40) styrene - TMPTMA impregnated concrete at temperatures from 70° F (21° C) to 350° F (177° C). The results indicate some decrease in strength at the higher temperatures. The strength and elastic properties at cold temperatures are still considered as largely unknown and more extensive testing at high and low temperatures is in progress to determine the effects of long term exposure to different temperatures.

The stress - strain curve for MMA-impregnated concrete tested to failure at room temperature is shown in Figure 1. PIC has a nearly linear stress - strain relationship to failure. The stress - strain curve shows very little departure from linearity up to about 90 percent of ultimate strength and does not show an abrupt change at the proportional limit. The proportional limit was taken at 56 percent of ultimate strength. Stress - strain curves for (60-40) styrene - TMPTMA impregnated concrete are shown in Figure 2 for specimens tested to failure at room temperature, 250° F (121° C) and 290° F (143° C). These curves show the same characteristics as the curve for MMA-impregnated concrete tested at room temperature with some decrease in slope with increasing temperature.

Creep deformation of polymer-impregnated concrete is significantly lower than that of conventional concrete, generally being about one-tenth as much, when compared on a basis of deformation per unit load. Creep tests have been performed under compressive and tensile loadings ranging up to one-third of ultimate strength. Under relatively low loadings, several specimens have been observed to have negative creep, i.e., have shown expansion under compressive loading and contraction under tensile loading. Creep deformation generally stabilizes after 2 to 3 months under load.

The effects of concrete composition and method of curing the concrete on strength and polymer loading of polymer-impregnated concrete are under investigation. Results at this time are tentative, but it appears that strong polymer-impregnated concrete can be made with most any type of concrete and that, within some wide limits, variations in cement content, water/cement ratio, entrained air, and type of aggregate have relatively small effects on the strength of the final product. Determination of an optimum mix to produce a strong PIC at minimal cost is beyond the scope of these limited studies and would have to be based on the particular materials being used. The overall trend shows the more porous concretes require significantly more polymer for full impregnation, and that in some cases it

may be difficult to obtain the strength of PIC made from stronger and denser concrete. The main factor in producing high-quality PIC is achieving a high degree of impregnation and complete polymerization.

Results on two series of tests are given in Tables 3 and 4. These tests were based on variations of a standard concrete designed for a strength of 5,000 psi (352 kgf/cm²) at 28 days. Variations were made in the mix to study the effects produced by low and high water/cement ratios, low and high slump, low and high air contents, low and high strength mixes, use of a water reducing agent, replacement of cement by fly ash pozzolans, and various aggregates. The aggregates used were a high sand content, unprocessed pit run natural aggregate, a high-quality natural aggregate, a high-quality low-porosity crushed limestone coarse aggregate, a very poor quality high-porosity crushed limestone coarse aggregate, and expanded shale coarse aggregate. Compressive strengths for fog cured concrete impregnated with MMA ranged from 15,500 psi (1,090 kgf/cm²) for the mix employing fly ash pozzolan to 25,500 psi (1,793 kgf/cm²) for the high-strength mix. Polymer loadings ranged from 5.9 percent for the low-entrained air mix to 25.9 percent for the expanded shale concrete.

The method of curing portland cement produced some varied effects and does not appear to be highly significant. Experience to date indicates that prolonged curing is not required and that good quality PIC can be produced from rapid cured or partially cured concrete. This would be of great importance to the operation of a high production plant for PIC.

The concrete cures investigated were 28-day fog curing, low-pressure steam curing, and high-pressure steam curing. Low-pressure steam curing gave results similar to 28-day fog curing. PIC specimens cured by high-pressure steam were generally from 1,000 to 2,000 psi (70 to 140 kgf/cm²) higher or lower than comparable 28-day fog cured specimens with one notable exception. The high-strength high-pressure steam-cured PIC specimens had an average compressive strength of 30,700 psi (2,159 kgf/cm²) with an individual specimen breaking at 32,400 psi (2,278 kgf/cm²), which is the highest strength obtained to date in the program.

Durability

Durability tests have shown highly significant increases in durability of PIC as compared with conventional concrete. The testing program includes freeze-thaw, sulfate attack, and resistance to acids and bases for PIC designed for normal temperature applications, and exposure to brine and demineralized water at elevated temperatures for PIC designed for desalting plant applications. These are severe exposure conditions for conventional concrete. The polymers under study for these applications are stable under these exposure conditions, and the durability of PIC is largely dependent upon reduction of absorption and permeability to achieve an effective sealing of the concrete. A complete impregnation is more effective than a protective

coating on the surface as the protection extends with depth throughout the concrete and is not completely dependent upon the continuity of the surface layer. The durability testing has included partially impregnated specimens, which are impregnated with specially formulated monomers to give controlled depths of penetration, to determine the effectiveness of different penetration depths in improving durability.

Typical test results on fully and partially impregnated concrete for normal temperature applications are given in Table 5. These tests show excellent resistance to freeze-thaw, 15 percent HCl and sulfate attack, and some improvements in resistance to 5 percent and 15 percent H_2SO_4 . Durability tests have shown some erratic results which appear to be due to inadequate sealing of the surface. Although the porosity and permeability of concrete is significantly reduced by polymer-impregnation, PIC is not absolutely impermeable, and some deterioration of the material with time may be anticipated when exposed to aggressive environments. Improvements in the fabrication process, such as applying an impermeable seal coat would produce more uniform specimens which would be essentially immune to these severe exposure conditions.

Tests are in progress on PIC exposed to brine and deionized water. These are long term tests scheduled for 5 years' exposure. Results after 2 years' exposure to brine at temperatures of 250° F (121° C) and 290° F (143° C) indicate some loss of strength with increased temperatures for (60-40) styrene - TMPTMA impregnated concrete (Table 6).

CONCRETE-POLYMER MATERIALS APPLICATIONS UNDER STUDY AT THE BUREAU OF RECLAMATION

Tunnel Support-Lining Systems

In 1970, the Bureau of Reclamation initiated a program to study precast polymer-impregnated concrete tunnel support and lining systems. The study was undertaken in connection with development of new methods of rapid underground excavation for tunnels and improving the means of support and lining of the tunnel walls. In order to fully obtain the advantages that result from rapid excavation, a tunnel support and lining system must be developed to enable a contractor to support and line a tunnel as rapidly as the heading is advanced. With the utilization of a single system for support and lining, the construction time should be reduced and yield a savings in construction costs.

Such systems, utilizing precast reinforced and unreinforced segments made from conventional concrete have been used for over 30 years in Europe, and to some extent recently in the United States. The decision to evaluate polymer-impregnated concrete units is based upon anticipated benefits accruing from increased strengths which will allow use of thinner and lighter

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segments, improved resistance to abrasion, and almost a 95 percent reduction in water permeability and absorption properties.

The program involves full-scale tests using both precast conventional and polymer-impregnated concrete. Precast segments are erected inside a concrete-lined steel test chamber to form an 8-foot (2.4-m) internal diameter by 8-foot (2.4-m) long finished tunnel section. Twenty-one hydraulically activated diaphragms are located between the wall of the test chamber and the support lining system to provide invert, wall, and crown pressures of up to 1,500 psi (105 kgf/cm²). An objective of these tests is to obtain a comparison between conventional and polymer-impregnated concrete. Also, a check of analysis and design procedures will be made. The research program also includes testing single segments to determine physical and mechanical properties and developing construction procedures. Table 7 summarizes test results on full-scale and single-segment tests. Future work which is proposed, under sponsorship of the Bureau of Reclamation, Bureau of Mines, Federal Highway Administration, and Federal Railroad Administration, includes the following:

1. Performance of single-segment tests with other joint configurations and thicknesses and full-scale tests on polymer impregnated concrete segments with backpacking of granular and frangible material
2. Development of a high strength shotcrete system by adding polymeric materials to the shotcrete mixture to improve its load-carrying capacity and durability
3. Performance of full-scale tests on shotcrete, including both conventional and that which contains polymer
4. Performance of analytical studies of various joint and segment configurations including tunnels of larger diameter than the full-scale tests and shapes other than circular
5. Conduct of meaningful performance comparisons and economic studies of the systems investigated
6. Evaluation of steel fiber reinforcement to improve the ductility of polymer-impregnated concrete
7. Evaluation of fire resistance properties

Concrete Pipe

Starting in 1969, the American Concrete Pipe Association joined forces with the Bureau and Brookhaven National Laboratory in studies of PIC pipe applications. In this initial work, a series of three-edge bearing and hydrostatic pressure tests was made on 12- and 24-inch (30.5- and 61-cm) diameter unreinforced concrete pipe and 24-inch-diameter reinforced concrete pipe. The unreinforced pipe was made with thin and thick walls.

The results of three-edge bearing tests, Table 8, show that polymer impregnation increases the strength of unreinforced pipe by a factor of more

than two. For steel reinforced pipe, the effect of polymer impregnation is not as great, as indicated by an increase in strength of only 36 percent. However, a comparison of unreinforced polymer-impregnated concrete pipe, Specimen Group A24, with untreated reinforced concrete pipe having the same diameter and wall thickness, Specimen Group R24, indicates that polymer impregnation produces 20 percent greater strength than does steel reinforcement. Thus, it may be possible to eliminate steel to offset much of the increased cost of polymer impregnation.

Hydrostatic tests were also performed. The results showed that polymer-impregnated concrete pipe withstood about twice as much hydrostatic pressure as the unimpregnated pipe.

These results look impressive. Unreinforced polymer-impregnated concrete pipe, in addition to having strength comparable to that of untreated reinforced pipe, has the additional benefit of greatly increased durability. Before a system of polymer-impregnated concrete pipe can be specified for usage, thorough design data must be obtained and service requirement standards must be established. An expanded program is now underway to develop these criteria. The program will also determine optimum methods for pipe fabrication and production techniques for polymer impregnation. Economic evaluations will include cost comparisons of precast unreinforced polymer-impregnated concrete pipe against standard reinforced concrete pipe.

Tests are being made on both packer head and roller suspension pipe specimens 6 feet (1.8 m) long, 3 feet (0.9 m) inside diameter, and 4-inch (10.2 cm) wall thickness. As part of this program, U.S. Steel Corporation is supporting work on fabrication, treatment, and performance of three-edge bearing tests on unimpregnated and polymer-impregnated steel fiber reinforced concrete pipe. The specimens are impregnated and polymerized by both thermal-catalytic and radiation techniques. The work will include measuring deflections and stress - strain relationships as well as ultimate strength of specimens tested under three-edge bearing and hydrostatic pressure tests. Also, shear strength and durability will be evaluated.

Other research on concrete pipe includes field and laboratory tests of polymer-impregnated concrete draintile. Field tests were started in 1969, with an installation of polymer-impregnated concrete draintile in drainlines at the Westlands Experimental Drainage Plot near Tranquility, California. Untreated companion draintile were also installed for control purposes. Sulfate concentrations in this test plot are quite high, ranging up to 7-1/2 percent in the soil and 5.9 percent in water taken from the drainlines. The installation should, therefore, provide useful information on the performance of polymer-impregnated versus conventional concrete pipe in a severe sulfate field environment. To date, neither the conventional nor the polymer-impregnated concrete has shown deterioration. The test is expected to continue for several years.

Another field evaluation of polymer-impregnated concrete pipe is being conducted at the city of San Diego. Here, sections of 8-inch (20.3-cm) diameter polymer-impregnated pipe were placed in the city's sewage system, to evaluate their resistance to attack by hydrogen sulfide gas.

Future proposed research on PIC pipe includes design improvement studies, evaluation of the improved design, preparation of specifications for PIC pipe, and construction of a pilot plant for impregnation and polymerization of concrete pipe.

Studies are also proposed for PC pipe. Such pipe can be manufactured utilizing existing commercial concrete pipe production facilities. Objectives of this program are to determine optimum mix proportions and polymerization techniques, evaluate the product, study and evaluate possible improvements in pipe design, and prepare specifications for PC pipe.

Desalting Plants

In 1968, a program was initiated to develop polymer-impregnated concrete as a construction material for multistage flash distillation vessels for desalination of water. In such environments, materials must withstand the corrosive effects of distilled water, brine, and vapor at temperatures up to 290° F (143° C). Carbon steels are currently being used in the construction of such vessels; however, in addition to their comparatively high cost, these materials eventually deteriorate in prolonged use under severe exposure conditions.

The test program consists of selection of materials for high-temperature brine, vapor, and interface exposure, development of process techniques for their preparation, and structural and durability property measurements of such materials following exposure to environments similar to those which would be encountered in distillation plants.

To simulate the anticipated exposure conditions, three-phase loop tests have been developed, which expose concrete to salt-water brine, brine-vapor interface, vapor, and distilled water at temperatures ranging up to 290° F (143° C). Strength and elastic properties are determined as well as changes in physical properties for extended exposure times which will range from 6 months to 3 years. Based upon preliminary structural design of a desalting structure, a preliminary economic evaluation indicated a savings in construction costs over that of conventional concrete.

Another study which is being performed in connection with desalting plant applications is the development and evaluation of in situ surface impregnation techniques of concrete containment vessels to provide a protective coating against deterioration. In addition to laboratory studies, which are underway, field application has been made at OSW's Freeport Test

Facility, where distillation chambers and mortar-lined steel pipe have been treated and are under observation.

Bridge Decking

A serious problem exists in the United States in deterioration of concrete bridge decks. This deterioration is caused by the action of freezing and thawing and by the use of deicing salts which permeate the concrete, corrode the reinforcing steel, and result in spalling of the concrete. Because of the seriousness of the bridge deck deterioration problem, the Federal Highway Administration is very interested in exploring the feasibility of utilizing the greatly improved durability of polymer-impregnated concrete in the construction of precast bridge deck slabs. The annual cost of repairing or replacing deteriorated bridge decks now exceeds \$70 million. In addition to the cost, considerable inconvenience and safety hazards are caused to the traveling public.

As a result, a program was initiated in 1972 under joint sponsorship of the Federal Highway Administration, Bureau of Reclamation, and the Prestressed Concrete Institute. The program involves design, manufacture, polymer impregnation, and testing of test panels, approximately 16 feet (4.9 m) long by 4 feet (1.2 m) wide by 6 inches (15.2 cm) thick. Design details are concerned with (1) development of the deck for composite action with concrete girders, (2) deck panel to deck panel, and deck panel to girder connections, (3) load transfer between deck panels, and (4) control of surface smoothness at panel connections. The test program includes static load tests to failure, fatigue load test, and shear tests for development of composite action.

Another approach to solving the bridge deck deterioration problem is to develop methods for surface impregnation of existing bridge decks in place. Such a program was initiated in 1972 at the Bureau of Reclamation under sponsorship of the Federal Highway Administration. Overall objectives of this work include selection of appropriate chemical systems for surface impregnation of concrete, development of field techniques and apparatus for surface impregnation, evaluation of the effectiveness of the technique, and demonstration of the technique in the field on existing bridge decks.

SUMMARY

The concrete-polymer materials development program has progressed from the laboratory investigation stage to the point where large-scale applications are imminent. The developmental work with PIC has been highly successful, and the recent work with PC indicates a good potential for this material. The laboratory studies on monomer systems and process technology are still important and continuing, but the major emphasis is now being placed on testing programs to develop design data and engineering studies of specific applications. Included in these studies are the design and

scheduled construction of large impregnation-polymerization facilities for the commercial production of PIC. The basic properties and characteristics of PIC are now fairly well known. The material looks very good and appears quite suitable for a number of applications in which the high strength or excellent durability will provide definite advantages over the use of conventional concrete. The big questions remaining to be answered are if PIC is economically feasible to produce and if industry is willing to produce and accept the product. The construction and operation of the scheduled large impregnation-polymerization facilities within the next several years will provide the answers to these crucial questions. The work to date and the wide interest shown throughout the world indicate concrete-polymer materials will have a place as construction materials for engineering projects.

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Table 1

Typical Mechanical and Physical Properties
Polymer-impregnated Concrete for Normal Temperature Applications

Property	Unimpregnated Concrete	MMA-impregnated Concrete		% Improvement	
		R	T	R	T
Compressive strength, psi	5,300	20,300	18,200	285	244
Modulus of elasticity, 10^6 psi	3.5	6.3	6.2	80	77
*Tensile strength, psi	420	1,600	1,500	290	262
Modulus of rupture, psi	740	2,600	2,300	256	210
Flexural elasticity modulus, 10^6 psi	4.3	6.2	7.1	44	65
Hardness, "L"-type hammer	32	55	52	73	62
Abrasion loss, inches	0.050	0.016	0.015	67	70
Abrasion loss, grams	14	4	4	71	71
Cavitation, inches, 2 hours	0.320	0.064	0.020	80	94
Water absorption, percent	6.40	1.08	0.34	83	95
Water permeability, 10^4 ft/yr	5.3	0.8	1.4	85	73
Thermal conductivity, Btu/ft-hr-° F	1.332	1.306	1.265	2	5
Diffusivity, 73° F ft ² /hr	0.0387	0.0409	0.0385	6	0
Coef. of expansion, 10^{-6} in./in./° F	4.02	5.36	5.25	33	31
Specific heat, 73° F, Btu/lb/° F	0.241	0.214	0.220	11	9
Specific gravity	2.317	2.319	2.386	-	-

* Direct tensile strengths.

R = radiation polymerization.

MMA = methyl methacrylate.

T = thermal-catalytic polymerization.

Specimen sizes: Compressive strength, 3- by 6-inch (7.5- by 15-cm) cylinders

Tensile strength, 3- by 6-inch (7.5- by 15-cm) cylinders

Flexural strength, 3- by 3- by 16-inch (7.5- by 7.5- by 40.6-cm) bars

Other specimens sized according to test requirements.

Polymer loadings range from 4.6 to 6.7 percent by weight.

Conversion Factors

To Convert From	To	Multiply By
psi	kgf/cm ²	0.07031
inch	centimeter	2.54
ounce	gram	28.35
foot	meter	0.3048
ft ² /hr	cm ² /sec	0.2581
Btu/lb ° F	J/g ° C	4.1868
° F	° C	$(^\circ\text{F}-32)/1.8$
Btu/ft-hr-° F	kg cal m/hr m ² ° C	1.4880

Table 2
Strength and Elasticity at Various Temperatures
Polymer-impregnated Concrete

Type of Material	Test temp, °C	Compressive strength, psi	Elastic limit stress, psi	Ultimate strain μ in./in.	Modulus of elasticity 10^6 , psi	Poisson's ratio	Tensile splitting strength, psi	Modulus of rupture, psi	Shear strength, psi
Unimpregnated									
	-12	5,500	1,200	2,210	3.8	0.18	240	-	-
	21	5,300	1,600	2,240	3.8	.16	340	710	1,150
	121	5,200	1,380	2,390	3.2	.15	310	560	-
	143	5,100	1,180	2,590	3.0	.14	370	650	-
	177	5,000	1,140	2,630	2.9	.14	330	-	-
MMA impregnated									
	-12	16,700	8,000	2,720	6.9	.22	670	-	-
	21	16,800	8,000	2,840	6.7	.21	1,070	2,100	3,760
Styrene TMPMA impregnated									
	21	16,900	10,500	2,920	6.4	.21	1,090	1,480	2,900
	121	16,000	9,800	2,960	5.9	.21	890	1,180	-
	143	13,900	8,200	2,600	5.8	.19	850	1,250	1,400
	177	14,600	9,900	2,950	5.3	.18	790	-	-

Standard mix conventional concrete.

Specimen sizes: Compressive strength, 6- by 12-inch (approximately 15- by 30-cm) cylinders
Tensile splitting strength, 6- by 12-inch (approximately 15- by 30-cm) cylinders
Modulus of rupture, 4- by 4- by 30-inch (approximately 10- by 10- by 76-cm) bars
Shear strength, 2- by 4-inch (approximately 5- by 10-cm) cylinders.

Conversion Factors

To Convert From	To	Multiply By
psi	kgf/cm ²	0.07031
° F	° C	° C = (° F - 32)/1.8



Table 3

Effects of Concrete Composition
First Test Series

Concrete mix	Air content of mix percent	MMA-impregnated			Unimpregnated	
		Polymer loading, wt. %	Compressive strength,		Compressive strength,	
			psi	(kgf/cm ²)	psi	(kgf/cm ²)
1. Standard	6.5	8.0	22,200	(1,560)	5,200	(365)
2. Low w/c (0.40)	6.8	6.9	23,100	(1,625)	7,100	(500)
3. High w/c (0.60)	6.5	7.9	20,300	(1,425)	4,200	(295)
4. High quality aggregate	4.7	6.2	19,900	(1,400)	6,100	(430)
5. Low slump (1-inch (2.5-cm))	5.8	6.5	21,100	(1,485)	6,200	(435)
6. High slump (5-inch (12.7 cm))	6.6	7.2	22,500	(1,580)	6,100	(430)
7. No AEA	2.3	6.2	19,000	(1,335)	7,300	(515)
8. WRA added	6.1	6.7	21,800	(1,530)	6,400	(450)
9. High sand (35%)	6.8	7.2	20,200	(1,420)	5,000	(350)
10. Fly ash pozzolan (25% replace- ment of cement)	6.3	7.0	15,500	(1,090)	4,600	(325)

3- by 6-inch (7.5- by 15-cm) cylinders fog cured 28 days.
Radiation-induced polymerization.
Values are averages of three specimens.

Table 4
Effects of Concrete Composition and Curing
Second Test Series

Concrete mix	Concrete cure	Air content of mix, %	MMA-impregnated				Unimpregnated		
			Absorption, wt %	Polymer loading, wt %	Compressive strength		Absorption, wt %	Compressive strength	
					psi	(kgf/cm ²)		psi	(kgf/cm ²)
**11a. Standard mix	Fog	6.5	0.84	7.4	20,700	(1,455)	8.63	3,200	(225)
	HPS	6.5	1.19	7.1	23,200	(1,630)	8.15	4,300	(300)
	LPS	6.5	0.72	7.1	22,900	(1,610)	7.99	4,100	(290)
***11b. Standard mix	Fog	5.9	-	7.3	24,400	(1,715)	-	6,100	(430)
	*HPS	5.9	-	6.6	21,200	(1,490)	-	4,100	(290)
	LPS	5.9	-	7.0	24,700	(1,735)	-	5,000	(350)
12. Low-entrained air	Fog	1.6	0.36	5.9	24,600	(1,730)	6.32	8,200	(575)
	HPS	1.6	0.48	7.3	23,700	(1,665)	7.36	2,900	(205)
13. High-entrained air	Fog	11.2	0.50	9.9	24,200	(1,700)	8.02	1,800	(125)
	HPS	11.2	0.53	10.4	21,800	(1,530)	8.34	1,800	(125)
14. Low strength	Fog	5.3	0.32	7.4	24,800	(1,745)	6.49	5,900	(415)
	HPS	5.3	0.55	8.4	27,000	(1,900)	7.30	4,200	(295)
15. High strength	Fog	3.6	0.26	6.1	25,500	(1,790)	6.21	9,000	(635)
	HPS	3.6	0.30	7.2	30,700	(2,160)	5.78	8,400	(590)
16. Pit run aggregate	Fog	4.3	0.34	10.2	21,800	(1,530)	9.95	5,100	(360)
	HPS	4.3	0.92	12.2	19,900	(1,400)	10.22	2,600	(185)
17. Low-porosity limestone aggregate	Fog	5.0	0.29	6.9	22,500	(1,580)	6.48	6,300	(445)
	HPS	5.0	0.60	8.5	23,200	(1,630)	7.75	2,600	(185)
18. High-porosity limestone aggregate	Fog	7.2	1.05	18.0	17,100	(1,200)	17.56	2,500	(175)
	HPS	7.2	1.17	20.3	17,100	(1,200)	11.45	2,300	(160)
19. Expanded shale aggregate	Fog	10.2	0.69	25.9	24,000	(1,690)	12.90	7,800	(550)
	HPS	10.2	0.93	30.3	26,200	(1,840)	16.24	5,200	(365)

3- by 6-inch (7.5- by 15-cm) specimens.

Radiation-induced polymerization in air for Mix 11a.; all other mixes polymerized under water with radiation.

MMA = Methyl methacrylate.

Fog = 28-day fog cure.

HPS = High-pressure steam cure.

LPS = Low-pressure steam cure.

*HPS = Nonstandard HPS cure; specimens steam cured after 24 hours' fog cure.

Values are averages of three specimens except as noted:

** = average of five specimens.

*** = Average of 10 specimens.



Table 5

Durability of Fully Impregnated
and Partially Impregnated Concrete

Property	Unimpregnated concrete	MMA-impregnated		Partially impregnated	
		R	T	P-S R	PMMA R
Freeze-thaw					
No. of cycles	*740	8,110	**3,650	2,310	1,900
Percent wt loss	25	8	2	10	0
Percent improvement		>996	>393	>212	>157
Sulfate attack					
Test cycle days	*480	1,436	1,436	908	300
Percent expansion	0.467	0.032	0.017	0.077	0.015
Percent improvement		>199	>199	>89	-
Acid, 15% HCl					
Exposure, days	*105	1,395	1,395	940	-
Percent wt loss	27	13	10	8	-
Percent improvement		>1,229	>1,229	>795	-
Acid, 15% H ₂ SO ₄					
Exposure, days	*49	*126	*119	-	-
Percent wt loss	35	29	26	-	-
Percent improvement		157	143	-	-
Acid, 5% H ₂ SO ₄					
Exposure, days	*210	210	-	252	252
Percent wt loss	33	14	-	21	18
Percent improvement		-	-	20	20

3- by 6-inch (7.5- by 15-cm) cylinders.

MMA = methyl methacrylate.

R = radiation polymerization.

T = thermal-catalytic polymerization.

Results are for tests still in progress, except as noted:

* = test completed; failure criteria is 25% weight loss for acid immersion and freeze-thaw test and 0.5% expansion for sulfate attack test.

** = test discontinued; specimen removed for examination.

Table 6

Exposure to Brine and Demineralized Water
at High Temperatures

Exposure condition	Exposure time	Exposure temp,		*Test temp	Compressive strength,		Length change 10 ⁻⁶ , in./in.
		° F	(° C)		psi	(kgf/cm ²)	
Brine	215 days	250	(121)	121	16,200	(1,140)	593
	1 year	250	(121)	121	14,900	(1,050)	955
	2 years	250	(121)	121	13,300	(935)	1,272
Brine	180 days	290	(143)	143	12,900	(905)	1,141
	1 year	290	(143)	143	11,100	(780)	1,452
	2 years	290	(143)	143	10,300	(725)	1,704
Air	1 year	73	(23)	121	17,200	(1,210)	94
	2 years	73	(23)	121	15,900	(1,120)	107
Air	1 year	73	(23)	143	14,600	(1,025)	94
	2 years	73	(23)	143	16,000	(1,125)	107
Deionized water	6 months	290	(143)	143	12,300	(865)	-

* Compressive strengths are determined on specimens at the indicated temperatures; length change measurements are at room temperature.