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Polymer-Concrete Composites
for
Energy Related Systems

Progress Report No. 5
April-June 1975

Radiation Division

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INFORMAL REPORT

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I. Introduction

The BNL research effort to develop polymer-concrete composites for use in energy related systems was started in April 1974. The work is a direct outgrowth of the Concrete-Polymer Materials Program which was conducted at BNL for several years. During that program, the feasibility for several energy related applications became apparent. These include the following: (1) polymer-concrete (PC) linings for pipe and vessels used in geothermal power systems, (2) PC as a material to cement well casings in oil and geothermal wells, (3) the incorporation of waste products into PC which can be used as construction materials and (4) the use of polymer-impregnated concrete (PIC) for pilings, pipe, railroad ties, arctic structures subject to ice abrasion, and devices to prevent the formation of ice on canal lock walls. Recently the advantages of using the composites in thermal storage systems for residential and commercial buildings have become apparent.

II. Polymer-Concrete Materials for Geothermal Applications

A. Field Tests

Field testing of PC materials at The Geysers was started during the current report period. Thirty-six 2-in. cube PC specimens were placed in a test chamber mounted at the top of a well where they were exposed to dry steam at a temperature of 238°C. The test series consisted of two PC formulations, 60 wt % styrene - 40 wt % trimethylolpropane trimethacrylate (TMPTMA) and 50 wt % styrene - 17 wt % TMPTMA - 33 wt % acrylonitrile (AN). Three methods of polymerization, radiation, thermal-catalytic, and promoter-catalyst were utilized.

The first examination of the specimens was performed after a 30 day exposure. At that time, swelling and cracking of 4 samples was apparent. The remainder were crack-free and no deterioration was observed. Testing of the crack-free specimens was then resumed for another 30-day period.

The four defective specimens (identified No. 9, 23, 34, and 45 in Table 1 of Progress Report No. 4) were returned to BNL for examination. All of these samples contained the styrene-TMPTMA monomer mixture and had been polymerized by promoter-catalytic techniques using 1 wt % dimethyl aniline and 1.5 wt % benzoyl peroxide. Similar results with this system have subsequently been obtained in laboratory autoclave tests at 218°C.

The 60 day exposure test was completed in mid June and the results from a visual examination are available.¹ No cracking was apparent. The only sign of deterioration was slight erosion of the top surface of styrene-TMPTMA-AN specimen No. 18. Seven cubes (one representative of each experimental condition) will be sent to BNL for determination of weight and dimensional changes, water absorption, and compressive strength. The remaining 25 cubes will be placed back in test at The Geysers by early August.

Tests at the Bacca Wells in New Mexico are presently scheduled to commence on September 1. In the initial series of tests, twelve 2-in. cube specimens, similar to those in test at The Geysers, will be exposed. The samples are identified as No. 1-6 and 25-30 in Table 1 of the previous progress report. The expected test environment will be a ~ 2 % brine solution at a temperature of ~ 200°C. The initial observation will be after 90 days.

Attempts will be made to expand the field testing program by placing concrete-polymer materials in as many geothermal sites as possible. A list of potential test sites

¹Verbal communication from J. P. Gallus, Union Oil Company of California, July 15, 1975.

in the U.S. has been prepared. During the next report period, attempts to establish cooperative testing programs will be made. Similar efforts in foreign countries will also be pursued.

B. Laboratory Tests

Laboratory tests are being performed in support of the field test program and to screen other candidate materials.

Long term testing of PC specimens in autoclaves containing a synthetic Imperial Valley geothermal brine (25% salt concentration) at temperatures of 177° and 218°C is continuing. Data obtained to date are summarized in Table 1. To date, the higher temperature appears to have a lesser effect on the styrene - TMPTMA system than on the styrene-TMPTMA-ACN.

Compared to a control strength of 9600 psi, the styrene-TMPTMA PC exhibited a reduction in strength to ~4100 psi after exposure to brine at 218°C for 12 days. Little additional loss in strength has been observed and after 104 days the strength was 3500 psi.

After exposure to brine at 177°C for 63 days, the PC prepared with styrene-TMPTMA-ACN had a compressive strength of 7000 psi. The strength of the control was 10,900 psi.

Table 1

Compressive Strength of PC After Exposure

to a

25% Geothermal Brine^e

PC Material ^{a,b}	Control strength, psi	Brine temperature, °C	Compressive strength, psi ^c			
			Exposure time, 12 days	Exposure time, 28 days	Exposure time, 63 days	Exposure time, 104 days
60 wt % styrene - 40 wt % TMPTMA	9600	218	4100	3900	3800	3500
"	9600	177	--	--	4450	--
50 wt % styrene - 33 wt % ACN- 17 wt % TMPTMA	10,900	218	5500	4400	1500	1000
"	10,900	177	10,000	10,000 ^d	7000	--

a, specimens 0.75-in.-diam x 1.5-in. long

b, thermal-catalytic polymerization

c, tested at room temperature

d, 30 day exposure

e, simulated Imperial Valley brine

After exposure at 218°C for 63 days, the strength was reduced to 1500 psi. A continued reduction to 1000 psi after 104 days was also noted.

Autoclave testing at the temperature condition expected at the New Mexico test site (200°C) has been started. In an attempt to accelerate any deterioration that may occur and due to the uncertainty of the brine concentration in the well, a 10% solution is being used. The first observation will be made after 30 days.

The results from differential thermal analysis (DTA) evaluation of styrene-TMPTMA, before and after exposure to brine at 218°C, were given in the previous progress report. It was stated that the results from the material exposed to brine showed exothermic decomposition reactions. This was in error. The samples that showed exotherms were retested and the DTA results showed normal endothermic decomposition similar to that of the unexposed polymer (see curve a in Figure 1 of the previous progress report). The erroneous results were obtained due to the system inadvertently being contaminated with air.

The testing of a 4.5-in.-i.d. steel pipe into which a 1-in.-thick PC liner was placed was described in the previous progress report. The section was exposed to the 25%

brine at 218°C for 83 days. Visual inspection at that time indicated that the top and bottom surfaces which were cut prior to commencing the test were unchanged and that there was no apparent loss of bond to the steel nor gross deterioration of the PC. Preparations are being made to measure the bond strength at the PC/steel interface.

In support of the field tests being performed at The Geysers, autoclave tests in which 2-in. PC cubes are exposed to wet steam have been started. As a result of pressure limitations imposed by the autoclaves, initial tests are being conducted at a temperature of 218°C. A new autoclave capable of operating at steam temperatures up to 290°C has recently been placed into operation and tests have been started at The Geysers' temperature of 238°C.

Specimens with compositions identical to those in test at The Geysers (see Section II A) are being evaluated. The data obtained after 42 days in test are summarized in Table 2. Control data are also given.

With the exception of the radiation-polymerized styrene-TMPTMA-ACN specimens, the control strengths were in the range 10,000 to 11,000 psi. The radiation polymerized specimen had a strength of 20,000 psi. These results are in good agreement with the results given in the previous

Table 2

Compressive Strength of PC After Exposure to
Wet Steam at 218°C

<u>PC Material^a</u>	<u>Polymerization method</u>	<u>Control strength^b, psi</u>	<u>Exposure time, days</u>	<u>Test strength, psi</u>
60 wt % styrene- 40 wt % TMPTMA	A	10,250	42	7600
"	B	10,900	42	7740
"	C	10,150	42	5590
50 wt % styrene- 33 wt % ACN- 17 wt % TMPTMA	D	20,000	42	12700
"	E	10,200	42	6800
"	C	10,600	42	3712

a, specimens 2 x 2 x 2-in.

b, tested at room temperature

A, thermal-catalytic polymerization using 1.5 wt % benzoyl peroxide

B, promoter-catalytic polymerization using 1 wt % dimethyl aniline and 1.5 wt % benzoyl peroxide

C, thermal-catalytic using 1 wt % tert butyl perbenzoate

D, radiation induced polymerization

E, promoter-catalytic polymerization using 1 wt % dimethyl aniline, 0.5 wt % dimethyl toluidine, and 2 wt % benzoyl peroxide

progress report and may reflect a greater polymer loading in the radiation sample, a higher molecular weight polymer, or a higher degree of crosslinking.

After exposure to the wet steam, the styrene-TMPTMA system retained a greater percentage of its initial strength than the styrene-TMPTMA-ACN material. This observation was noted earlier for samples exposed to brine at 218°C. The poorest results for each material were obtained when the monomers were polymerized at 115°C using tert butyl perbenzoate. The reason for the poor results obtained with this initiator is not known at this time. A reaction between catalyst fragments in the polymer and moisture is one possible explanation.

Cracking of some styrene-TMPTMA specimens polymerized by promoter-catalyst techniques was noted after exposure at 218°C for 14 days. The crack pattern was the same as that observed in specimens at The Geysers. DTA evaluation of polymer extracted from these samples will be made.

In conjunction with the above work, thermal stability tests are being performed at 238°C in an air-circulating oven. This is the temperature of the steam at The Geysers and is greater than the anticipated temperature conditions at the Bacca Wells in New Mexico.

The thermal stability tests described in the previous report were completed. After 30 days exposure to a temperature

of 238°C, the 50 wt % styrene - 17 wt % TMPTMA - 33 wt % AN system was found to be more stable than the 60 wt % styrene - 40 wt % TMPTMA. This is opposite to the stability upon exposure to hot brine and steam and indicates that an optimization of TMPTMA and AN concentrations should be performed. Radiation polymerized specimens exhibited the smallest weight loss (2.8%) and had the highest strength (565 psi) after heating.

In an attempt to improve upon the stability of the PC in hot brine and steam, experiments are being performed in which the compositions of the styrene, TMPTMA, and AN are varied. Also, Clear Creek aggregate is being used as a replacement for the crushed limestone which had been used in earlier work.

Two monomer compositions, 60 wt % styrene - 40 wt % AN and 57.2 wt % styrene - 4.7 wt % TMPTMA - 38.1 wt % AN have been tested to date in this series. After 30 days exposure in air at 238°C, both monomer mixtures exhibited properties superior to those obtained in the earlier work. A weight loss of 1.65% and an average compressive strength of 4900 psi were measured for the styrene-TMPTMA-AN system. The styrene-AN mixture produced a PC which lost 2.4% weight and had a final strength of 2285 psi. PC specimens containing each of these materials are presently being tested in wet steam at a temperature of 238°C and in brine at 218°C.

Two epoxy resins have been selected for evaluation as high temperature binders in PC. One material is reported to withstand temperatures up to 427°C. The materials have been ordered and testing will be started during the next report period.

Tests to determine the effect of thermal shock on PC lined steel pipe were continued. The section being tested consists of an 8-in.-diam steel pipe containing a 0.5-in.-thick PC liner composed of 60 wt % styrene - 40 wt % TMPTMA. To date the section has been exposed to 18 temperature cycles between 0° and 100°C, 11 cycles from -57° to 100°C, and 7 cycles from -57° to 150°C. No cracking or loss of bond is apparent. This test is being continued.

III. Solid Waste Utilization

A problem of great concern to municipal and other governmental units is that of solid waste disposal. Since it is becoming very expensive for a municipality to land-fill its waste material, a great deal of activity is in progress to develop waste management systems. While uses for recycled ferrous and non-ferrous metals are readily apparent, efficient methods for utilizing waste paper and glass are needed. In addition, electric utilities that convert from oil to coal as a result of the energy crises will also be faced with severe

problems to find ecologically and economically acceptable methods for disposing of fly ash. The disposal of sulfur resulting from oil and coal desulfurization processes is also of increasing concern.

The techniques for utilizing solid waste as aggregate in PC are being developed. As the initial part of this effort, waste glass of the type obtained by a "head-end" separation process is being investigated. Emphasis is being placed on converting the waste glass into a glass-polymer composite (GPC) sewer pipe which could compete with asbestos cement or vitreous clay as a corrosion resistant material. The excellent durability may also make the use of GPC feasible for a number of applications in geothermal energy systems.

The cooperative research program between BNL and Teledyne National continued to function during the report period. Emphasis is currently being placed on the fabrication and testing of 5-ft sections of 12-in.-diam pipe. Several pipes containing glass separated from Washington, D. C. municipal waste by the Bureau of Mines at College Park, Maryland have been fabricated. The pipes contained 12.5 wt % of a 90 wt % styrene - 10 wt % polyester mix and 87.5 wt % glass. Polymerization was initiated thermal-catalytically. All of the sections separated from the mold easily when an internal

release agent (Frekote²) was used in conjunction with an external release agent (Zelec UN³).

Three-edge bearing strength tests performed on several pipes indicated values ranging from 7400 lb/ft to 11,467 lb/ft. These strengths are considerably greater than the 1000 to 3000 lb/ft given in ASTM specification C-76-72A for reinforced concrete pipe. Therefore, it appears that reductions in the wall thickness of glass polymer pipe can be made while still meeting the strength specifications.

During the next report period additional pipe will be produced for field testing in a sewer system. Laboratory tests to determine the long-term durability characteristics will also be initiated.

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3, E. I. DuPont material.

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