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DEPARTMENT of APPLIED SCIENCE

Polymer-Concrete Composites
for
Energy Related Systems

Progress Report No. 4
January-March 1975

Radiation Division

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M. Steinberg, Associate Head
L. E. Kukacka, Project Leader

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INFORMAL REPORT

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Polymer-Concrete Composites
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I. Introduction

Concrete-polymer materials have been under development at BNL for several years. The work has progressed to the point that the feasibility for several energy related applications has become 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, (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. Development work has been started on these applications.

II. Polymer-Concrete Materials for Geothermal Applications

A. Field Tests

Work to initiate field testing of two polymer-concrete (PC) materials at geothermal sites is progressing. The tests

will be performed in conjunction with the Union Oil Company at three locations; The Geysers, Imperial Valley, and in New Mexico. Descriptions of the tests to be performed were given in the previous progress report.

Forty-eight 2-in. cube PC specimens were fabricated and shipped to the Union Oil Company for use in a series of preliminary field tests at The Geysers and in New Mexico to determine the feasibility of using PC as a material for cementing well casings into the hole. Two PC systems, 60 wt % styrene-40 wt % trimethylolpropane trimethacrylate (TMPTMA) and 50 wt % styrene-17 wt % TMPTMA-33 wt % acrylonitrile (ACN), polymerized by three methods, radiation, thermal-catalytic, and promoter-catalyst, will be evaluated initially. Radiation polymerization is of interest for this application due to the potential for improved control of the reaction during the placement of the grout. Experimental data for the specimens are given in Table 1.

Testing at The Geysers is scheduled to start on April 1. In this test, the specimens will be exposed to dry steam at a temperature of 238°C . The first scheduled observation will be made after exposure for 30 days.

A starting date for the New Mexico test has not yet been established. In this test the specimens will be exposed to a 2% brine solution at a temperature of $\sim 200^{\circ}\text{C}$.

Table 1

Polymer Concrete Specimens For Exposure to
Geothermal Environments

* Specimen size, 2x2x2-in
Polymer concentration, 12 wt%
Monomer systems and polymerization
conditions listed below.

<u>Sample No.</u>	<u>Monomer system</u>	<u>Specimen weight, g</u>	<u>Polymerization method</u>	<u>Polymerization temperature, °C</u>
1	S-T	293.3	R	25
2	S-T-A	275.6	B	82
3	S-T	292.4	B	82
4	S-T-A	287.4	C	115
5	S-T	291.8	D	20
6	S-T-A	296.4	E	20
7	S-T-A	282.4	R	25
8	S-T	284.7	C	115
9	S-T	293.8	D	20
10	S-T	290.0	B	82
11	S-T-A	285.8	C	115
12	S-T-A	296.5	E	20
13	S-T-A	288.1	R	25
14	S-T-A	278.9	B	82
15	S-T	285.6	R	25
16	S-T	283.9	C	115
17	S-T	291.0	B	82
18	S-T-A	289.1	C	115
19	S-T-A	285.2	R	25
20	S-T-A	303.3	E	20
21	S-T-A	278.9	B	82

Table 1 (Continued)

<u>Sample No.</u>	<u>Monomer system</u>	<u>Specimen weight, g</u>	<u>Polymerization method</u>	<u>Polymerization temperature, °C</u>
22	S-T	283.8	C	115
23	S-T	293.8	D	20
24	S-T	285.9	R	25
25	S-T	286.0	R	25
26	S-T	283.7	C	115
27	S-T-A	295.2	E	20
28	S-T-A	278.9	R	25
29	S-T	287.7	D	20
30	S-T	293.1	B	82
31	S-T-A	287.9	C	115
32	S-T-A	277.5	B	82
33	S-T-A	278.5	R	25
34	S-T	292.4	D	20
35	S-T	287.6	C	115
36	S-T-A	284.9	C	115
37	S-T-A	276.1	B	82
38	S-T	282.4	R	25
39	S-T-A	295.6	E	20
40	S-T	289.3	B	82
41	S-T	281.6	C	115
42	S-T-A	287.8	C	115
43	S-T	280.0	R	25
44	S-T-A	276.3	B	82
45	S-T	294.6	D	20
46	S-T-A	290.4	E	20
47	S-T	293.3	B	82
48	S-T-A	288.6	R	25

Table 1 (Continued)

S-T, 60 wt% styrene - 40 wt% trimethylolpropane trimethacrylate (TMPTMA)

S-T-A, 50 wt% styrene - 17 wt% TMPTMA - 33 wt% acrylonitrile

R, radiation induced polymerization. Total gamma exposure 2.5×10^7 rad

B, thermal-catalytic polymerization using 1.5 wt% benzoyl peroxide.

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

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

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

Planning for field experiments in which PC structural members and PC lined pipe will be exposed to geothermal conditions was delayed due to a strike at the Union Oil Company. Drawings of the desired test sections are currently being prepared by Union Oil.

B. Laboratory Tests

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

Initial autoclave tests in which PC specimens were exposed to brine at 177°C for 100 days indicated that the styrene-TMPTMA and styrene-ACN-TMPTMA systems showed promise. These results were given in the previous progress report. During the current report period more extensive testing of these systems has been started. A second series of tests at 177°C was initiated in order to obtain data for exposures >100 days. Tests in which specimens are being exposed to concentrated brine ($\sim 25\%$) and wet steam at 218°C have also been started.

Results are available for 28 day exposures to brine at 218°C . The data, summarized in Table 2, indicate an $\sim 50\%$ decrease in compressive strength during the first twelve days followed by a more gradual decrease. The relative decrease in strength is greater than that observed at 177°C (see previous progress report).

Table 2

Compressive Strength of PC After Exposure
to
Concentrated Geothermal Brine at 218°C

<u>PC Material</u>	<u>Control</u>	Compressive strength, psi ^c	
		<u>Exposure time, 12 days</u>	<u>Exposure time, 28 days</u>
60wt% styrene-40wt% TMPTMA	9600	4100	3900
50wt% styrene-33wt% ACN-17wt% TMPTMA	10900	5500	4400

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

b, thermal-catalytic polymerization

c, tested at room temperature, control average of 4 specimens,
others average of 2 specimens

The results from examination of the polymers by differential thermal analysis (DTA) indicate considerable differences between material exposed at 218°C and 177°C. Styrene-TMPTMA polymer after exposure to brine at 177°C for 100 days was not appreciably different from the control. The DTA curve for styrene-TMPTMA exposed at 218°C for 12 days was very different and complex. At least two exothermic reactions were indicated compared to one endothermic decomposition reaction for the lower temperature exposure. DTA curves for styrene-TMPTMA polymer before and after exposure to brine at 218°C are given in Figure 1. Similar results were obtained for the styrene-ACN-TMPTMA polymer.

The nature of the changes in the structure of the polymers that cause the thermal effect are not known. However, the thermal stability of the systems has been lowered. For styrene-TMPTMA the temperature at which the maximum rate of decomposition occurs has been reduced by 40 to 50°C. The styrene-ACN-TMPTMA system exhibits considerable decomposition at temperatures as low as 315°C compared to a control value of 425°C.

Testing of a styrene-TMPTMA PC lined steel pressure vessel was described in the previous progress report. Initial inspection of the vessel was made after exposure to brine at 218°C for 138 hr. Considerable peeling and separation of the PC from the vessel wall occurred. Since the temperature of the

DIFFERENTIAL THERMAL ANALYSIS OF
60 WT.% STYRENE - 40 WT.% TMPTMA

(a) AS PREPARED CONTROL

(b) 12 DAYS AT 218°C IN CONCENTRATED BRINE

SAMPLES, -100 MESH, RUN IN FLOWING ARGON AT 10°C/MIN.

FIGURE 1

externally-heated vessel was controlled by use of a thermocouple which was located in the brine, it is estimated that the steel-PC interface was at a temperature considerably higher than 218°C. A sample of polymer which had been immersed in the brine during the 138 hr test was examined visually and by use of the DTA. The sample was crack-free and the DTA results were in agreement with previous data.

As a result of the unknown temperature history of the liner, a PC lined pipe section was prepared for complete immersion in brine at 218°C. The pipe was 4.5-in.-i.d. and contained a 1-in.-thick PC liner. Testing of the section is in progress. Examination after exposure for 12 days indicated some loss of PC from the annulus. Most of the losses appeared to be from areas that initially had low polymer contents as a result of evaporation or drainage. The top and bottom surfaces which are cut surfaces appeared in good condition. No loss of bond to the steel was apparent.

A series of 2-in. PC cubes identical to those sent to the Union Oil Company are being tested in the autoclaves at 218°C. Two test environments, concentrated brine and wet steam, are being investigated. Data from the tests are not yet available.

Compressive strength measurements were made on 2-in.-cube specimens representative of those being tested in the autoclaves. These data are summarized in Table 3. Specimens

Table 3

Initial Compressive Strengths for Polymer Concrete Prior
to
Exposure to Geothermal Environments

Specimen size, 2 x 2 x 2-in.
Polymer concentration, 12 wt%
Monomer systems and polymerization
conditions listed below

<u>Monomer system</u>	<u>Polymerization method</u>	<u>Compressive strength,^a psi</u>
S-T-A	R	20,745
S-T-A	D	13,925
S-T-A	C	10,637
S-T-A	E	10,212
S-T	R	14,250
S-T	D	10,925
S-T	C	10,175
S-T	B	10,312

S-T, 60 wt% styrene - 40 wt% trimethylolpropane trimethacrylate (TMPTMA)

S-T-A, 50 wt% styrene - 17 wt% TMPTMA - 33 wt% acrylonitrile

R, radiation induced polymerization. Total gamma exposure
 2.5×10^7 rad

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

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

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

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

a, average of 2 specimens tested at 20°C

polymerized by radiation exhibited the highest strengths probably as a result of decreased evaporation and drainage losses during polymerization and the formation of a higher molecular weight polymer. Compressive strengths of 20,745 and 14,250 psi were obtained for the styrene-ACN-TMPTMA and styrene-TMPTMA systems respectively. DTA examination of these materials is in progress.

In conjunction with the above, thermal stability tests are being performed at 238°C in an air-circulating oven. This is the expected temperature of the steam at The Geysers. The samples are weighed daily. To date after 14 days, all of the specimens have exhibited weight losses. The styrene-ACN-TMPTMA system polymerized by radiation is the most stable with a total weight loss of 1.3%. This test will be continued.

Tests are being performed to determine the effect of thermal shock on PC lined steel pipe. During the previous report period a 0.5-in. thick PC liner containing 60 wt % styrene-40 wt % TMPTMA was placed on the inside of an 8-in.-diam steel pipe. The surface of the pipe was sandblasted prior to application of the PC. The specimen was cooled to 0°C and then immersed in boiling water. The test was continued under these conditions for a total of 18 cycles. No deterioration was apparent. A larger temperature differential (-57° to 100°C) was then applied. After 11 cycles, 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.

BNL has performed preliminary experiments which indicate the fly ash, sulfur, glass, paper, and other forms of solid urban waste can be incorporated into composite materials which can be used for construction purposes. Potential applications include highway patching materials, pipe, building block, pilings, and railroad crossties. Fly ash has been used in conjunction with sewage sludge for soil stabilization and pavement sub-bases. In this application it can be used as a replacement for cement which is in short supply.

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. In this manner, waste available from a municipality can be converted into a useful product which can then be utilized by the same municipality.

The cooperative research program between BNL and Teledyne National continued to function during the report period. Emphasis is being placed on the optimization of variables that affect the mold release properties. These variables include monomer-type and composition, inhibitor content, type of release agent, and form surface finish. Numerous 3-in.-diam x 6-in.-long cylinders and several 8-in.-diam pipe sections have been cast and the results indicate that the material exceeds the requirements for extra-strength pipe as specified in ASTM C-14.

Based upon the results from an economic analysis performed by Teledyne National which indicated that 12-in.-diam pipe would have the greatest potential for economic viability, a form has been fabricated to produce 5-ft sections of this size pipe. Studies using this form will be started during the next report period.

IV. Polymer-Impregnated Concrete

The development of the use of polymer-impregnated concrete (PIC) for use in energy related systems was continued.

Field testing of electrically heated PIC panels to determine their suitability as deicing devices on canal lock walls was continued. The test, described in the previous progress report, is being performed in the Soo Canal near Sault Ste. Marie, Michigan. The panels were used successfully to melt ice until late February when the lock was shut down and drained for routine maintenance. No detrimental effects have been noted. Present plans are to remove the panels in late April for examination.¹

Preliminary experiments to determine the effect of polymer impregnation on the properties of prestressed concrete railroad ties have been completed. This work, described in the previous report, was performed in conjunction with the Blakeslee Company. The results from the test indicate a factor of two increase in the load carrying capacity of the tie. A significant improvement in the bond between the prestressing steel and the concrete was noted. Blakeslee is currently evaluating the economics of the process.

¹Verbal communication, L. David Minsk, U. S. Army Cold Regions Research and Engineering Laboratory, March 26, 1975.

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