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Concrete^P-Polymer Materials for Geothermal
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Progress Report No. 6,
July-September 1975.

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INFORMAL REPORT

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Concrete-Polymer Materials for Geothermal Applications

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Introduction

Concrete-polymer materials have been under development at Brookhaven National Laboratory for several years. The work has created world-wide interest and commercial applications have emerged in several foreign countries.

The availability of durable and economic materials of construction for handling hot brine and steam is a serious problem in the development of geothermal energy. Hot brine is an aggressive fluid and it chemically attacks most conventional materials of construction. Even in the concept of extracting energy from the low lying hot rock, it is expected that minerals in the rock will be leached by the water which is pumped down to extract the heat. This will cause severe corrosion problems in the well and processing equipment. Since conventional steel materials cannot be used because hot salt solutions chemically attack steel, alloys such as high chrome-nickel steel and more noble metals such as tantalum are being considered for these plants. However, even the exotic metals have limited capability and the investment required becomes prohibitive.

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The standard grouting materials used to cement well casings into the ground are severely attacked by brine and steam at temperatures $>200^{\circ}\text{C}$. Brine extracted from deep wells in the Imperial Valley has an average "down-hole" temperature of 300°C . Shallower wells having temperatures of 200°C are available and they are presently being developed. Materials of construction are required for well cementing materials, piping to transport brine from wells and to reinjection wells, scrubber off-gas lines, and for cooling tower components.

The research program to determine if concrete-polymer composite materials can be utilized in geothermal power systems was initiated in April 1974. Five progress reports titled Polymer Concrete Composites for Energy Related Systems have been issued¹⁻⁵. Work accomplished during the period July 1-September 30, 1975 is described in the current report. The title and format of the report have been changed to reflect the revised program plan for fiscal year 1976.

Task 1. Selection of Lining and Well Cementing Materials

Polymer concrete (PC) systems that can be utilized as protective linings and well cementing materials at temperatures up to 300°C are being developed.

During the current report period, work to increase the thermal stability of the styrene-acrylonitrile (ACN) - trimethylol-propane trimethacrylate (TMPTMA) ^{polymer} system was continued. Results

obtained to date are summarized in Table 1. In these studies the ratio of styrene to ACN concentration was held at ~ 1.5 (the azeotropic composition) and the amount of crosslinking agent (TMPTMA) was varied. The data indicate that the maximum strength after exposure to 238°C air for 30 days occurs at TMPTMA concentrations between 9 and 17%. Based upon these results, specimens with these concentrations were selected for autoclave testing and in field tests at The Geysers and Bacca Wells. This is discussed in Tasks 3 and 4. Experiments to determine the optimum TMPTMA concentration and to determine the effect of other styrene-ACN ratios are in progress.

Testing of a high temperature epoxy system was performed. A 5.6% weight loss and a strength of 4210 psi was measured after the 30 day thermal stability test. Differential thermal analysis (DTA) evaluation of the polymer indicated that the material was not as stable as the styrene-ACN system. Additional testing will be performed in autoclaves to determine its resistance to steam and hot brine.

Task 2. Process Technology

The techniques for placing PC protective linings on steel surfaces are being developed. Currently, the thickness required to produce an impermeable liner is being determined. An electrical resistivity technique⁶ developed by the State

TABLE I

Thermal Stability of Styrene-Acrylonitrile-TMPTMA Polymers

<u>Styrene^a</u> <u>concentration, %</u>	<u>Acrylonitrile^a</u> <u>concentration %</u>	<u>TMPTMA</u> <u>concentration, %</u>	<u>Weight^b</u> <u>loss, %</u>	<u>Compressive^b</u> <u>strength, psi</u>
60	40	0	2.4	2285
57.2	38.1	4.7	1.7	4932
55	36	9	2.3	5525
50	33	17	2.8	5615
42.8	28.5	28.5	4.3	1700

a, Styrene-acrylonitrile ratio ~ 1.5

b, After 30 day exposure to air at 238°C
radiation-induced polymerization

of California for bridge deck applications is being used to measure the permeability. The results to date indicate that a thickness of $\geq 3/8$ in. will be impermeable to static water at 20°C. Tests will be performed at elevated temperature in flow systems.

Task 3. Physical and Chemical Property Measurements

In support of the experimental work being performed in Tasks 1, 2, and 4, the mechanical and chemical resistance properties of concrete polymer materials are being determined.

Preliminary testing of 0.75-in.-diam x 1.5-in.-long PC specimens in autoclaves containing a synthetic Imperial Valley geothermal brine⁷ (25% salt concentration) at temperatures of 177°C and 218°C was continued during the report period. Two monomer systems, 60 wt % styrene - 40 wt % TMPTMA and 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA are being evaluated. The PC formulations consist of 12 wt % of the monomer mixture and 88 wt % sand.

Test results are available for a 207 day exposure at 218°C and the data are given in Figure 1. The experiment was terminated at that time when the last specimens in the series were tested. The data indicate that the compressive strengths of both formulations decreased by $\sim 50\%$ within the first 12 days and then continued to decrease at a much slower

COMPRESSIVE STRENGTH OF PC AFTER EXPOSURE TO 25% BRINE PRELIMINARY LABORATORY TEST

FIGURE I

rate. The styrene-TMPTMA system decreased from 4100 psi after exposure for 12 days to 1800 psi at 207 days. At 104 days (the last previously reported data point) the strength was 3500 psi. At shutdown, the strength was still approximately twice that required for use as a lining material.

The 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA system exhibited only a slight decrease (~ 200 psi) in compressive strength over the last 100 days in test. At shutdown the strength was 800 psi.

Based upon the results from tests performed in steam subsequent to the fabrication of the samples in this series, it appears that the stability of the PC can be improved by the addition of portland cement to the aggregate. This will be investigated in field tests at Bacca Wells and in autoclave experiments.

At 177°C, the decrease in strength is progressing at a much slower rate. After 142 days, the styrene - TMPTMA and styrene-ACN-TMPTMA systems had strengths of 3900 and 6100 psi, respectively. These tests are continuing.

A large number of specimens were placed in test during the current report period. Autoclaves have been designated for operation at each of the environments in which field testing will be performed. Specimens of two sizes, 2-in.-cubes and 1-in.-diam x 2-in.-long cylinders, are being used

in these tests in order to duplicate the requirements of the field test effort. Test variables include polymer composition, aggregate composition and particle size distribution, and method of polymerization.

Six polymer compositions are being tested in wet steam at the temperature conditions (238°C) found at The Geysers. Data are available for 5 systems. To date two compositions show promise. One system composed of 55 wt % styrene - 36 wt % ACN - 9 wt % TMPTMA and "Clear Creek" aggregate, polymerized at 82°C with tert butylazoisobutyronitrile, had a compressive strength of 3400 psi after exposure for 25 days at 238°C.

A 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA monomer mixture, in combination with an aggregate containing 90% sand and 10% portland cement, radiation polymerized, had a compressive strength of 7250 psi after 25 days exposure. Specimens polymerized with tert butyl perbenzoate and by promoter-catalyst techniques had strengths of 2250 and 6550 psi respectively. These data compare reasonably well with data obtained at The Geysers (see Task 4) and those from the thermal stability tests described in Task 1.

Autoclave tests have been started at conditions simulating those expected at Bacca Wells, Imperial Valley, Raft River, and Klamath Falls. Results from these tests are not yet available.

Task 4. Field Tests

Field testing programs are currently in progress at The Geysers and at Bacca Wells in New Mexico. Cooperative programs have been established and plans to initiate testing at Klamath Falls, Oregon; Raft River Valley, Idaho; and the Lawrence Livermore Laboratory site in the Imperial Valley of California are being implemented. Preliminary discussions have been held with the Bureau of Reclamation to establish a test program at their East Mesa, California site. The status of each of these programs is summarized below.

The Geysers

Tests started at The Geysers during the previous progress report were completed. Based upon the favorable results, specimens have been fabricated for a second series of tests which are designed to obtain strength and permeability data for exposure times up to 24 months.

In the first test series, thirty-six 2-in.-cube PC specimens were exposed in a test chamber mounted at the top of a well to dry steam at a temperature of 238°C . The purpose of the test was to determine if the durability and strength characteristics were adequate to make the use of the PC as a well cementing material feasible. For this application low permeability and a compressive strength of ~ 1000 psi are required for the 15 year life expectancy of a well.

Two polymer systems, 60 wt % styrene - 40 wt % TMPTMA and 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA were selected for use in these tests. Three methods of polymerization, radiation, thermal-catalyst, and promoter-catalytic were utilized. The PC formulation consisted of 12 wt % polymer and 88 wt % of an aggregate containing 90% sand and 10% portland cement. Experimental data for the samples were given in Table 1 of Progress Report No. 4.⁴

The first examination of the specimens was performed after a 30 day exposure. At that time 4 samples, each containing 60 wt% styrene - 40 wt% TMPTMA and polymerized by promoter-catalytic techniques, were found to have swelled and cracked. All of the other samples were crack-free.

A second examination of the specimens was performed at the end of 60 days. With the exception of one sample which showed some erosion on one surface, no deterioration was apparent. Compressive strength, water absorption, and permeability measurements were made on samples representing each monomer type and method of polymerization.

The results from the compression tests indicated higher strengths for the styrene-ACN-TMPTMA system (average 4800 psi) than for the styrene-TMPTMA system (average 3425 psi). Little effect due to the method of polymerization was noted. All of the strengths were considerably higher than those of the standard well cementing materials which were used as controls.

Tests to determine the permeability of the samples to air and water were performed by the Union Oil Company. Compared to the controls, the styrene-ACN-TMPTMA samples polymerized with benzoyl peroxide (sample No. 37) and by promoter-catalytic techniques (samples No. 39 and 46) had very low permeability. These materials also exhibited the lowest water absorptions. The other PC formulations had approximately the same permeability as the cement controls.

Based upon these results, the Union Oil Company suggested that a second series of styrene-ACN-TMPTMA specimens, polymerized with benzoyl peroxide and by promoter-catalytic techniques, be prepared for long-term testing. This series is discussed below. All of the remaining specimens from Series No. 1 were placed back into test.

Field testing of Series No. 1 was terminated in late September after a total exposure time of 90 days. A report from Union Oil on the appearance of the samples is being prepared. Permeability tests on two samples will be made at Union Oil. The remaining samples will be returned to BNL for evaluation.

As described above, a second series of tests will be performed. The total of eighty-four 2-in.-cube specimens were prepared. Testing is scheduled to commence in early October.

Examinations will be performed after exposure for 3, 6, 12, and 24 months.

Two monomer systems, 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA and 55 wt % styrene - 36 wt % ACN - 9 wt % TMPTMA, will be evaluated in these tests. The former was selected based upon the results from autoclave tests and field test series No. 1. The second monomer composition has been shown in autoclave experiments to have good stability. Other test variables include aggregate composition and polymerization method.

Bacca Wells

After many delays, testing at Bacca Wells in New Mexico was started in early October. In the first series of tests, twelve 2-in.-cube PC specimens similar to those that were evaluated in Series No. 1 at The Geysers, are being exposed. The test environment is a 2% brine solution at a temperature of $\sim 200^{\circ}\text{C}$. The initial observation will be after 90 days.

Klamath Falls

With the cooperation of Dr. John W. Lund of the Oregon Institute of Technology, arrangements have been made to expose samples in wells in Klamath Falls, Oregon. The test environment will be water containing a few hundred

ppm of salts at a maximum temperature of 125°C.

Although the material problems in Klamath Falls are primarily associated with the "down hole" heat exchangers, it is anticipated that the data from these tests can be used in the development of durable, low cost, low temperature loss piping systems. In addition to durability to the geothermal fluid, resistance to the high sulfate containing soils found in many parts of the west is also needed.

Based upon previous work⁸ which indicated the stability of the 60 wt % styrene - 40 wt % TMPTMA system in distilled water and seawater at 177°C, this system will be evaluated in the Klamath Falls test. PC, polymer-impregnated concrete (PIC), and glass-polymer composite (GPC) will be tested.

A total of forty-eight 1-in.-diam x 2-in.-long cylinders (22 PC, 22 PIC, and 4 GPC) will be sent to Klamath Falls early in October. Samples, contained in 1.5-in.-diam x 24-in.-long stainless steel baskets, will be placed in 6 wells. Half of the specimens will be evaluated after exposure for 6 months, the remainder after a 9 month period. These tests are scheduled to start during the first part of the next report period.

Raft River Valley and Boise

Concrete polymer materials may have application in medium temperature geothermal systems where piping with low-cost, minimum thermal losses, and durability to internal and external environmental conditions is essential. Geothermal fluids meeting this condition (temperature $\sim 150^{\circ}\text{C}$) exist in the Raft River Valley Region of Idaho where, in cooperation with the Aerojet Nuclear Company (ANC), testing of concrete-polymer materials will be started.

Initial testing will be performed in the "Raft River Mobile Corrosion, Deposition, and Components Test Laboratory". A 4-ft section of 4-in. Sch 40 pipe in the facility has been designated by ANC for use by BNL. The anticipated fluid conditions are a maximum temperature of 150°C and a flow rate of ~ 400 gal/min. The chemical analysis of the water is given in Ref. 9.

Specimens of PC and PIC in the form of cylinders and thin discs are currently being fabricated for use in the initial series of tests. Compressive strength, permeability, water absorption, and dimensional stability measurements will be made on the cylindrical samples. The discs will be used in abrasion measurements. Contingent upon the results from the first series of tests, a section

of PC lined pipe may be installed in the facility.

Consideration is being given to the installation of lengths of 12-in.-diam PIC, PC, or GPC pipe in the piping system that will connect the two geothermal wells at the Raft River site. Testing of pipe in the Boise, Idaho geothermal space heating project is also under consideration.

Lawrence Livermore Laboratory (LLL)

Discussions with Dr. A. L. Austin of LLL have indicated his willingness for BNL to test materials in conjunction with LLL experiments in the Imperial Valley of California. The samples will be exposed to a 25% brine solution at a temperature of $\sim 250^{\circ}\text{C}$. LLL is currently constructing a test trailer which will house their experimental equipment. Provisions will be made in the trailer to accommodate the BNL experiments. The plans will be confirmed at a meeting at LLL during November. Testing is tentatively scheduled to start early in 1976.

East Mesa

Preliminary discussions have been held with the Bureau of Reclamation (USBR) in an attempt to start a materials test program at their East Mesa facility. The anticipated test conditions will be a 25% brine concentration at a temperature of $\sim 160^{\circ}\text{C}$. A flow rate of 50 to 80 gal/min and a pressure

of ~ 100 psi is anticipated. Approval of the proposed program has been received from the USBR. A meeting to establish requirements and schedule for the program will be held in November.

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