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Concrete-Polymer Materials for Geothermal
Applications.

Progress Report No. 7,
October-December 1975.

Radiation Division

MASTER

**BROOKHAVEN NATIONAL LABORATORY
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Concrete-Polymer Materials for Geothermal
Applications

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October-December 1975

Radiation Division

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Concrete-Polymer Materials for Geothermal
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Introduction

The availability of durable-low cost materials of construction is a serious problem in the development of geothermal energy. The high temperature hypersaline brines in the Salton Sea area of California appear to represent the largest potentially exploitable part of the USA geothermal energy base. Before this resource can be developed, economically acceptable solutions to the problems associated with this brine, corrosion and scaling, must be found.

The standard grouting materials used to cement well casings into rock are severely attacked by brine and steam at temperatures $> 200^{\circ}\text{C}$. Brine extracted from deep wells in the Salton Sea area 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 also required for steam separators, piping to transport brine from wells and to reinjection wells, scrubber off-gas lines, and for cooling tower components.

Materials problems also exist in plants which utilize dry steam geothermal reservoirs. At The Geysers in northern California, carbon steel is used for the main steam lines and ancillary-equipment. However, after the steam condenses and is exposed to air in the condenser and cooling towers, some of the hydrogen sulfide is oxidized to sulfate, which in combination with other compounds in the condensate, becomes highly corrosive. As a result, all condensate and cooling water piping must be constructed of stainless steel or plastic-lined material. Concrete surfaces in contact with water are coated with coal-tar epoxy compounds or synthetic rubber.¹

The development of medium temperature geothermal reservoirs such as those at Boise, Idaho and in the Raft River Valley region of that state requires the use of piping systems which have low-cost and minimum thermal losses. Durability to high sulfate containing soils present in many parts of the West is also essential. It has been reported that steel pipe sections installed in the Boise geothermal heating district have developed leaks due to external attack after only 2 months in service.

Based upon the results from AEC and OSW sponsored research that indicated the long term stability of concrete-polymer materials in seawater at 177°C and in acid solutions,² a research program to determine if the composites can be utilized in geothermal systems

was initiated in April 1974. Since that time laboratory and field tests have been started. The results obtained to date have been reported in six progress reports.³⁻⁸ Work accomplished during the period October 1-December 31, 1975 is described in the current report.

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)-trimethylolpropane trimethacrylate (TMPTMA) system was continued. Previous data⁸ indicated that the maximum strength after exposure to air at 238°C for 30 days occurred at TMPTMA concentrations between 9 and 17%. Specimens containing 13% TMPTMA are currently being tested in the oven and in brine. Results from these tests are not yet available.

Attempts to improve the workability of PC materials containing styrene-ACN-TMPTMA mixtures are being made since drainage of the low viscosity mixture from the aggregate has been found to be a problem in the casting of thin ($\sim 3/16$ in.) impermeable liners. The results to date indicate that considerable improvement can be obtained by the

addition of ~ 10% Hetron 197, a high-temperature polyester, to the styrene. PC specimens with compressive strengths of ~ 11,500 psi have been produced. This monomer formulation has been used previously in the partial impregnation of a concrete liner on a vertical tube evaporator at Freeport, Texas.²

During the next report period work to determine the thermal stability of methyl methacrylate-acrylonitrile-acrylamid mixtures will be started.

Task 2 Process Technology

Work to develop the techniques for placing PC protective linings on steel surfaces is continuing. Permeability and water absorption measurements have been made on 8 x 8-in. slabs. The monomer formulations currently being field tested at The Geysers, Baca Wells, and Klamath Falls have been used in the preparation of the slabs. If the viscosity of the monomers is increased by replacing 10% of the styrene with polystyrene, impermeable liners 3/16 in. thick can be produced. Small slabs are currently being exposed in autoclaves to simulated Raft River Valley geothermal conditions. If the materials maintain their strength and impermeability, a 24 in. long section of lined pipe will be prepared for field testing at Raft River. Sections of PC pipe designed to withstand the pressure and temperature conditions at Raft River and Boise will also be produced.

As a result of the favorable results obtained in the first series of field tests at The Geysers, interest in the possible use of PC as a well cementing material has increased. In addition to determining the durability of PC formulations at the "down hole" conditions, the pumpability and curing times at the pressure and temperature conditions representative of those in geothermal wells must be determined. Work to investigate the latter has been started. To date all of the high pressure equipment has been assembled. Experimental work will commence during the next report period.

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. The tests are being performed in autoclaves (see Figure 1) at conditions simulating environments in which field tests are in progress or being planned. The facility consists of 10 autoclaves which are designed for continuous operation with brine and steam at a temperature of 220°C and 2 other pressure vessels rated at 280°C.

Preliminary testing of PC specimens in an autoclave containing a synthetic Imperial Valley geothermal brine⁹ (25% salt concentration) at a temperature of 177°C was continued

Figure 1

during the report period. The temperature condition for this test is $\sim 15^{\circ}\text{C}$ higher than the temperature expected in field tests at Baca Wells and East Mesa. 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 280 day exposure and the data are given in Table 1. The experiment was terminated at that time when the last specimens in the series were tested. The data indicate that the compressive strength of the styrene-ACN-TMPTMA formulation decreased by 36% to 7000 psi during the first 63 days and then was essentially constant for the remainder of the test. A similar trend was obtained for the PC containing 60% styrene - 40% TMPTMA. Compared to an initial strength of 9600 psi, the strength leveled off after 63 days at a value of ~ 4200 pi.

Results from tests in which the two monomer formulations described above were exposed at 200°C to a 10% brine solution for 100 days are also available. The samples used in this test are similar to those currently being field tested at Baca Wells. This field test is described in Task 4. The aggregate used in these samples consisted of 90% sand and 10% portland cement. After exposure for 100 days, three samples containing

Table 1

Compressive Strength of PC After Exposure to a
25% Synthetic Geothermal Brine at 177°C

PC Material ^{a,b}	Compressive strength, psi ^c				
	Exposure time, days	0	63	142	280
60 wt % styrene - 40 wt % TMPTMA		9600	4450	3900	4352
50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA		10,900	7000	6100	7567

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

b, thermal-catalytic polymerization

c, tested at room temperature

styrene-TMPTMA had an average strength of 8175 psi. The strength of the styrene-ACN-TMPTMA specimens was 7625 psi. Both values are higher than those obtained for non-portland cement containing samples after exposure to 25% brine at 177°C for 100 days (see Figure 1 in Progress Report No. 6).

As an initial attempt to simulate the environment in the first steam separator at the San Diego Gas and Electric Company project at the Salton Sea, specimens are being exposed in the vapor phase above a 25% brine solution at 218°C. Four monomer compositions have been tested and the results are given in Table 2. To date the strengths are similar to those obtained after exposure to brine. These tests are continuing.

Five PC formulations are being exposed to the vapor above a 25% brine solution at 238°C. Data are available for exposure times up to 25 days. To date specimens containing 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA have shown the best resistance to the environment. Compressive strengths of ~ 7000 psi have been measured.

The operating conditions for the autoclaves are being modified in order to closer approximate conditions in which field tests will be performed. It is planned to use geothermal brines from the field sites in these tests. The following conditions are being established:

Table 2

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

PC Material ^a	Compressive strength, psi ^b				
	Exposure time, days	42	86	100	126
60 wt % styrene - 40 wt % TMPTMA		7000	7200	--	--
57 wt % styrene - 38 wt % ACN - 5 wt % TMPTMA		13760	--	--	5800
55 wt % styrene - 36 wt % ACN - 9 wt % TMPTMA		--	--	8400	--
50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA		7700	--	--	--

a, specimen size 2-in. cubes

b, tested at room temperature

<u>Simulated test site</u>	<u>Temperature, °C</u>	<u>Fluid</u>
Southern California Edison	238	25% brine
The Geysers	238	steam
San Diego Gas and Electric	204	steam
San Diego Gas and Electric	204	25% brine
Baca Wells and East Mesa	163	10% brine
Raft River, Klamath Falls, Boise	150	200 ppm brine

A serious problem associated with the conversion of the energy content of hypersaline geothermal systems to electric power is precipitation of amorphous silica and other phases that can ultimately cause scaling of the power plant equipment. The rate of polymerization of monomeric silica is dependent upon pH, temperature, salinity, silica concentration, and the presence of solids. Recent work at Lawrence Livermore Laboratory¹⁰ has indicated that it may be possible to stabilize silica in geothermal brines by acidification with hydrochloric acid. It has also been reported by Berman¹¹ that scale formation can be minimized by the avoidance of any material that reacts with acid at pH 3 in the well or surface equipment.

Tests to determine the resistance of PC materials to attack by pH 3 hydrochloric acid solutions at 20°C have been initiated. To date, after 14 days in test, no corrosion is evident and the

pH of the solution has remained constant. Under the same condition a concrete control specimen started to deteriorate after 4 days. Previous work has shown the resistance of polymer impregnated concrete to 15% hydrochloric acid solutions.¹² Contingent upon the results from these tests, experiments will be started using stronger acid solutions at elevated temperatures.

Task 4 Field Tests

Field testing programs are currently in progress at The Geysers, Baca Wells, and Klamath Falls. Cooperative programs have been established and plans to initiate testing at Raft River, Bosie, San Diego Gas and Electric, and East Mesa are being implemented. The status of each of these programs is summarized below.

The Geysers

Test series No. 1 at The Geysers was completed during the previous report period.⁸ In this test, 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, polymerized by three methods; radiation, thermal-catalyst, and promoter-catalytic, were evaluated. Compression, absorption, and permeability tests were performed after exposure for 60 and 90 days and the results are given in Table 3.

The results from compression tests indicated higher strengths for the styrene-ACN-TMPTMA system (average 4500 psi) than for the styrene-TMPTMA system (average 3826 psi). After exposure for 90 days, the strengths of both formulations were essentially the same as those after 60 days. The strengths are 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 by promoter-catalyst had very low permeabilities. After 60 days in test, values of < 1 milli Darcy were measured for 2 samples (average of three, 10 milli Darcy's). Similar results were obtained after 90 days. These materials also exhibited the lowest water absorptions. Six specimens after removal from their shipping tray at the completion of the 90 day exposure are shown in Figure 2.

Table 3

The Geysers, Test Series No. 1, Summary of Results
Test Environment, Dry Steam at 460°F

Monomer system	Polymerization method	Controls		60 day exposure			90 day exposure		
		Compressive strength, psi ^a	Boiling water absorption, %	Compressive strength, psi	Boiling water absorption, %	Permeability milli Darcy's	Compressive strength, psi	Boiling water absorption, %	Permeability, milli Darcy's
50% styrene-33% ACN-17% TMPTMA	R	20745	0.6	4838	7.3	109 ^b	4682 ^d	6.4 ^d	126 ^c
	thp	10600	2.1	—	9.2	330 ^e	2925 ^b	8.7 ^d	187 ^b
	Bzp/DMA/DMT	10200	2.6	4163	6.9	10 ^c	4835 ^d	3.4	2 ^d
	Bzp	10500	2.3	5400	6.4	180 ^b	4025 ^c	7.1 ^d	64 ^c
60% styrene-40% TMPTMA	R	14250	1.8	3325	7.8	64 ^c	2613 ^d	4.9	72 ^d
	thp	10175	2.5	3275	8.4	189 ^b	4177 ^c	7.9 ^d	295 ^c
	Bzp	10300	3.7	3675	7.1	82 ^b	4692 ^c	6.3 ^d	173 ^c

a, one sample tested unless otherwise noted

b, average of 4 samples

c, average of 3 samples

d, average of 2 samples

e, average of 5 samples

R, radiation-induced polymerization

thp, 1 wt % tert butyl perbenzoate

Bzp/DMA/DMT, 2 wt % benzoyl peroxide/1 wt % dimethyl aniline/0.5 wt % dimethyl toluidine

Bzp, 1.5 wt % benzoyl peroxide

Figure 2

As a result of the encouraging results, a second series of specimens was prepared for testing at The Geysers. Eight-four samples (described in Ref. 8) were prepared, and the test was started on November 17. The first examination of the samples is scheduled for mid February. Other examinations will be performed after exposure for 6, 12, and 24 months.

Baca Wells

Testing of a series of PC specimens in flashing brine at $\sim 160^{\circ}\text{C}$ was started at Baca Wells in New Mexico on October 7. The samples are similar to those that were evaluated in Series No. 1 at The Geysers. The first observation of the specimens will be made after 100 days.

Klamath Falls

With the cooperation of Dr. John W. Lund of the Oregon Institute of Technology, samples of concrete-polymer materials are being exposed in 6 geothermal wells in Klamath Falls, Oregon. Although the material problems in Klamath Falls are primarily associated with the "down hole" heat exchangers, it is anticipated that the data from these 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.

During the current report period forty-eight cylindrical specimens were fabricated and sent to Klamath Falls. Testing was started on November 29. One cold water well, 3 hot water open wells, and 2 closed wells are being utilized. Water analyses and temperature profile measurements have been supplied to BNL by Dr. Lund. Half of the specimens will be evaluated after exposure for 3 months (late Feb.), the remainder after a 6 month 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. 13.

Twenty specimens of polymer impregnated concrete have been prepared and sent to ANC for use in abrasion measurements. These tests will be performed in conjunction with ANC material evaluations.

A sample holder which will fit into the Raft River test facility has been designed, materials procured, and fabrication started. The assembly will consist of a 24-in. section of 6-in. Sch 40 pipe, concentric reducers, and couplings to mate with the 4-in. Sch 40 pipe used in the ANC facility.

A series of cylindrical-shaped specimens will be exposed in the initial test which is scheduled to start during the next report period. Contingent upon the results and work being performed in Task 2, a 24-in. length of PC lined pipe will be installed in the facility.

Plans are being made to install lengths of 12-in.-diam PIC, PC, or GPC pipe in the piping system that connects the two geothermal wells at the Raft River site. Pipe will also be tested in the Boise, Idaho geothermal space heating project. This work will be performed in fiscal year 1977.

Lawrence Livermore Laboratory/San Diego Gas and Electric Co.

Meetings were held with representatives of the Lawrence Livermore Laboratory (LLL) and the San Diego Gas and Electric Co. (SDG & E). A program has been established in which BNL will test materials at the SDG & E site in the Salton Sea as part of the ERDA-SDG & E Geothermal Utilization Project. LLL will cooperate with BNL by coordinating the program and in the performance of the tests. BNL will produce the samples and LLL will design the holding fixtures and install the specimens. Samples will be exposed in the brine and vapor environment existing in at least the first separator and effluent flowing through the reinjection pipeline. The tests will probably commence during the last quarter of fiscal year 1976.

Discussions at LLL indicated that it was impractical to test concrete-polymer materials in the LLL experiments scheduled for January-March 1976 at the Sinclair No. 4 test site. The LLL test program during that period will be to determine if scaling can be reduced by control of the pH. Material evaluations will be performed in subsequent tests. BNL participation in the latter may be possible.

East Mesa

Meetings to establish a materials test program were held with the Bureau of Reclamation (USBR) at the East Mesa

test site and at Boulder City, Nevada. Preliminary approval by the USBR of the proposed program was obtained. In the tests, samples will be exposed to low salinity brines (2 to 3%) and vapor at a temperature of $\sim 160^{\circ}\text{C}$. The work cannot be initiated until the ERDA test facility at the site is completed and approval of the ERDA/USBR operating committee is obtained. It does not appear that tests can be started prior to July 1976.

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