Concrete-Polymer Materials for Geothermal
Applications

Progress Report No. 9

April - June 1976

Process Technology Division

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Abstract

A program to determine if concrete polymer materials can be utilized as materials of construction in geothermal processes has been in progress since April 1974. Since that time high temperature polymer concrete formulations have been developed, laboratory tests performed in simulated geothermal environments, field testing initiated at four geothermal sites, and economic studies started. To date, field test results have been obtained for 180 day exposures to dry steam, flashing brine, and hot water. Good durability is indicated. Work accomplished during the period April 1 - June 30, 1976 is described in the current report.

Summary

Preliminary tests to determine the feasibility of using polymer concrete (PC) to cement a well casing into place have been performed. A bond strength of ~ 5 psi was measured at the PC-sand interface. The bond required for geothermal and oil wells is estimated to be between 3 and 10 psi. A 20 ft casing will be cemented with a high temperature PC during July.

PC pipe capable of withstanding the shut-in pressure of the Raft River Well RRGE-1 has been produced. Plans will be made to install test sections at Raft River and at Boise.

Specimens have been exposed in an autoclave to 25% brine at 177°C (350°F) for 417 days. No deterioration is apparent. Samples exposed to simulated San Diego Gas and Electric, Raft River, and Klamath Falls conditions have shown good durability.

Field tests are in progress at The Geysers and Klamath Falls and a 180 day test at Baca Wells has been completed. Samples examined after 180 days at Baca Wells and The Geysers show good durability. Samples were also removed from 3 wells at Klamath Falls but the results are not yet available.

Field tests at Niland and Raft River are scheduled to start during the next report period.

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Introduction

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 and other aerated geothermal fluids are highly corrosive materials and they chemically attack most conventional materials of construction. To date, corrosion and scale incrustations have been encountered in all geothermal plants, and to various degrees, adversely affected plant life times and power output.

The feasibility of using concrete polymer composites as materials of construction for handling hot brine was demonstrated in 1972.¹ The results from these tests indicated that the composites had long-term stability in seawater at 177°C (350°F) and in acid solutions. Based upon these results, a research program to develop the composites for use in geothermal systems was started in April 1974. Since that time laboratory and field tests have been performed.

Work accomplished to date has been published in eight progress reports²⁻⁹ and is summarized below.

Preliminary tests to determine the stability of styrene, trimethylolpropane trimethacrylate (TMPTMA), and acrylonitrile (ACN) terpolymers were completed. Durability testing in brine and steam is being performed in autoclave-type experiments at temperatures up to 238°C (460°F).

Based upon the favorable results that were obtained from the initial experiments, cooperative field-test programs were started at The Geysers, Baca Wells, Klamath Falls and Raft River. Data from field exposures of up to 180 days have been obtained. These tests are continuing.

Laboratory tests were started to determine the resistance of polymer concrete (PC) materials to pH 3 hydrochloric acid solutions and to soils containing high sulfate concentrations. Excellent durability is indicated.

Work was started to develop the techniques for producing thin impermeable PC linings on steel surfaces. Impermeable liners 3/16-in. thick were produced and repeated cycling between -57° and 150°C (-71° and 302°F) did not result in apparent loss of bond. Testing of these materials at simulated Raft River Valley geothermal conditions was started.

Cost-benefit analyses were started and several cost effective uses for the materials were identified. Applications in condensate piping systems, cooling water systems, cooling towers, steam separators, and acid handling systems, appear to have potential.

During the last quarter of Fiscal Year 1976, work was continued in each of the program tasks. The work is described in the current report.

Task 1 Selection of Lining and Well Cementing Systems

PC systems that can be utilized as protective linings and well cementing materials at temperatures up to 300°C (572°F) are being developed.

Experiments to identify the type of aggregate that

should be used in various geothermal environments were continued. Materials such as quartz, silica, flyash, and portland cement are being investigated. To date, only PC materials containing an aggregate consisting of 90 wt % silica sand and 10 wt % portland cement have been durable to brine and steam at temperatures $> 218^{\circ}\text{C}$ (425°F). Below this temperature, specimens containing quartz, flyash, and silica sand have shown good durability. Experiments to determine the reason for these effects are planned, but the start has been delayed due to laboratory renovations and a lack of manpower.

Work to continue the development of new high temperature PC formulations has also been delayed.

Task 2 Process Technology

The use of PC as a well cementing material is under investigation. For this application, the ability to pump and cure the material down-hole is essential.

During the current report period preliminary experiments were performed to determine the feasibility of cementing a well with PC. In this work, 6-in. diameter x 5-ft long sections of simulated well casing were inserted into holes in the ground and cemented into place. A PC consisting of a 25% concentration of 95 wt % methyl methacrylate - 5 wt % TMPTMA and 75 wt % of a fine silica sand aggregate was used in these tests. After curing using 1.5% benzoyl peroxide as the initiator and a promoter consisting of 1% dimethyl aniline and 0.5% dimethyl toluidine, the force required to pull the casing from the ground was determined (see Figure 1). The measured bond

Figure 1

strength (~5 psi) is in the range reportedly needed (3 to 10 psi) for geothermal wells.

In all cases failure occurred at the PC-sand interface. Sections of the casing after removal are shown in Figure 2. Good bonding of the PC to the pipe and evidence of monomer migration into the sides of the hole are apparent.

During a recent visit to BNL, representatives of the Water Resources Division, Geological Survey (USGS) became aware of the well cementing effort and they decided to use PC in several water wells that will be drilled at the Maxey Flates, Kentucky radioactive waste burial site this summer. The cementing work will be performed by the drilling contractor with BNL providing technical assistance.

A PC containing a 60 wt % styrene - 40 wt % TMPTMA monomer will be used in the cementing operation. Tests have indicated that this system will polymerize in water and good durability has been noted after 180 day exposures at The Geysers and Baca Wells (see Task 4).

The first well will be cemented to a depth of ~ 20 ft and drilled open hole below this depth. The contractor will place the PC by pressure grouting from inside the 6-in. I.D. casing, using a cement plug at the end of the drill stem.

The USGS also plans to cement a 6-in. casing in a 9-in. drillhole to a depth of ~ 20 ft for experimental purposes. An excavation about 15 ft deep will then be made around the casing, and the casing cement cut off. Portions of the cement and interface seals will be examined,

Figure 2

and possibly tested for hydraulic conductivity. If the PC is found to be satisfactory, several wells to be drilled later in the summer will be cemented with the material. The first well cementing is scheduled for early July. To aid in technology transfer, representatives of the well cementing service companies have been invited by USGS to witness the test.

Work is also being performed to develop the technology required to produce PC or PC lined carbon steel pipe for use in transporting geothermal fluids. Sections of 6-in. I.D. pipe have been cast from PC containing 60 wt % styrene - 40 wt % TMPTMA. A typical section is shown in Figure 3. The wall thickness was varied from 0.75 to 1.25 in. Hydrostatic tests have been performed on the specimens and burst pressures varying between 100 and > 350 psig were measured. The latter test was terminated before failure due to a leaking gasket. The results indicate that non-reinforced PC would be adequate to contain the 180 psig shut-in pressure of the Raft River Well RRGE-1.¹⁰

Pipe sections containing wire mesh reinforcement are presently being fabricated in an attempt to reduce the required wall thickness.

Sections of PC lined carbon steel pipe have been fabricated using a centrifugal casting process. It is planned to install a 3-ft long section of the material into the "Raft River Mobile Corrosion, Deposition, and Components Test Laboratory".

Task 3 Physical and Chemical Property Measurements

In support of the experimental work being performed

Figure 3

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 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 (428°F) and 2 other pressure vessels rated at 280°C (536°F).

Preliminary testing of PC specimens in an autoclave containing a 25% concentration of a synthetic Imperial Valley geothermal brine at a temperature of 177°C (350°F) was continued during the report period. The temperature condition for this test is approximately the same as that expected at the inlet to the second steam separator at the San Diego Gas and Electric Company (SDG & E) facility when the well-head temperature is at 238°C (460°F), and is $\sim 15^{\circ}\text{C}$ (27°F) higher than the temperature at which specimens were exposed at Baca Wells. 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 % of a sand-portland cement aggregate.

The test has been in progress for 417 days. Visual examination made at that time indicated the specimens to be crack-free and dimensionally stable. Three samples were tested in compression and the results indicated a strength of 7,500 psi for the styrene - ACN - TMPTMA composite and 4,355 psi for the styrene - TMPTMA. The strengths were the same as those measured after exposure

for 63 days (see Progress Report No. 5).⁶ This test is continuing.

Tests in an environment simulating the well-head conditions [25% brine, 238°C (460°F)] at the SDG & E Facility are also in progress. Three monomer systems and 2 aggregate mixtures are being evaluated. Visual examination after exposures varying between 28 and 80 days indicated the specimens to be crack-free and sound. The compressive strengths ranged from 16,238 psi for a sample containing 52 wt % styrene - 35 wt % ACN - 13 wt % TMPTMA that had been exposed for 28 days to 3,660 psi for a 60 wt % styrene - 40 % TMPTMA sample exposed for 80 days. The strength of 16,238 psi was the highest that has been observed to date after exposure at these conditions. Additional work in Task 1 to optimize the styrene-ACN-TMPTMA system will be performed.

Autoclave testing of 1 x 6 x 0.5-in. PC specimens identical to those that will be tested by Lawrence Livermore Laboratory (LLL) (see Task 4) has been started. To accelerate the test, the samples are being exposed to 25% brine at a temperature of 238°C (460°F) rather than the anticipated field temperature of 210°C (410°F). After 28 days in test, slight bowing of the bars has occurred but cracks are not apparent. The specimens have been attached to a rod in the same configuration that will be utilized by LLL and the test has been restarted.

An evaluation of specimens at conditions simulating those at Raft River and more severe than those at Klamath Falls was continued throughout the report period. Three

monomer-sand-portland cement formulations were tested after exposure to a 400 ppm brine solution at 150°C (302°F) for 183 days. Visual examination of the specimens indicated that they were free of cracks and had not swollen. Testing of a duplicate set of samples has been started.

Tests to measure the resistance of PC to a pH 3 hydrochloric acid solution at 20°C (68°F) have been in progress for 180 days. To date, no evidence of corrosion as determined by weight change and pH measurements has been found. Control specimens of concrete and carbon steel continue to show slight amounts of attack during the same period. The start of testing in pH 1 solutions at 20°C (68°F) and pH 3 solutions at 90°C (194°F) was delayed due to laboratory renovations. The tests will commence during the next report period.

In preparation for tests which will be performed at Raft River and Boise, Idaho, samples of PC have been buried in soil which is saturated with a 10 % (2N) sulfuric acid solution. The test has been in progress for 150 days. To date, changes in weight, absorption, or electrical resistivity have not been detected. Control specimens of concrete and carbon steel show signs of deterioration.

Task 4 Field Tests

Field testing programs are currently in progress at The Geysers, Klamath Falls and Raft River. A test has been completed at Baca Wells and specimens have been shipped to Niland, California for testing by Lawrence Livermore Laboratory (LLL). The status of each of these programs is summarized below.

The Geysers

Tests are in progress to determine if the strength and durability characteristics of PC are adequate to make its use as a well cementing material feasible. For this application, low permeability, good bonding, and a compressive strength of ~ 1000 psi are required for the life expectancy of the well.

Exposure of 2-in. cube PC samples in Test Series No. 2 to dry steam at a temperature 238°C (460°F) has been continued. Two monomer systems, 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA and 55 wt % styrene - 36 wt % ACN - 9 wt % TMPTMA are being evaluated. Aggregate composition and polymerization method are other variables in this test series.

During the current report period 21 samples were removed from test after exposure for 180 days. The results are in agreement with those obtained earlier. All samples containing an aggregate consisting of 90% sand and 10% portland cement have shown good durability. Composites containing other types of aggregate have failed. This has also been observed in autoclave tests.

Baca Wells

In cooperation with the Union Oil Company, a test to determine the durability of PC to flashing brine at a temperature of $\sim 160^{\circ}\text{C}$ (320°F) was performed at Baca Wells, New Mexico. The test was started on October 7, 1975 and terminated on April 6, 1976. The total exposure time was 180 days.

Materials with compositions identical to those that

were evaluated in Series No. 1 at The Geysers were tested. The series consisted of two monomer mixtures, 60 wt % styrene - 40 wt % TMPTMA and 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA, mixed with an aggregate consisting of 90% sand and 10% portland cement. Mix data for the series were given in Progress Report No. 4.⁵ Three polymerization methods; radiation, thermal-catalytic, and promoter-catalyst, were utilized.

The specimens were found to be in good condition after the 180 day test. Two samples (No. 5 and No. 29) which contained the 60 wt % styrene - 40 wt % TMPTMA mixture polymerized using benzoyl peroxide and dimethyl aniline, were slightly cracked. This system produced similar results after a 30 day exposure at The Geysers.⁶ All of the other materials were crack free. The samples after the 180 day exposure are shown in Figure 4.

Tests performed on the samples included dimensional stability, weight change, water absorption, and compressive strength. Little if any changes in the dimensions and weight were detected. The results from compressive strength and water absorption tests are summarized in Table 1. Compared to the controls, all of the samples containing styrene-TMPTMA (including the 2 cracked cubes) had strengths which were essentially unaffected by the exposure. The samples containing styrene-ACN-TMPTMA polymerized by promoter-catalyst (No 6 and No. 27) were also unaffected. The other samples exhibited strength reductions and increases in absorption. These strengths are in the same order as those obtained after 180 day exposures at The Geysers.

Figure 4

Table 1
Baca Wells Test Specimens

Summary of Results

Fluid, flashing brine
Temperature, 160°C (320°F)
Specimen size, 2 - in. cubes
Aggregate, 90% sand - 10% portland cement
Polymer content, 12 wt %

<u>Monomer systems</u>	<u>Sample No.</u>	<u>Polymerization method</u>	<u>Exposure time, days</u>	<u>Boiling water absorption, %</u>	<u>Compressive strength, psi</u>
50% styrene - 33% ACN - 17% TMPTMA	a	R	0	0.6	20,745
	28	R	180	2.3	12,938
	a	tbp	0	2.1	10,600
	4	tbp	180	3.8	4,037
	a	BPO/DMA/DMT	0	2.6	10,200
	6	BPO/DMA/DMT	180	2.1	13,187
	27	BPO/DMA/DMT	180	2.2	11,450
	a	BPO	0	2.3	10,500
	2	BPO	180	7.3	5,875
	a	R	0	1.8	14,250
	1	R	180	1.1	13,812
	25	R	180	1.5	9,938
60% styrene - 40% TMPTMA	a	tbp	0	2.5	10,175
	26	tbp	180	3.4	8,250
	a	BPO/DMA	0	-	10,925
	5 ^b	BPO/DMA	180	1.1	13,475
	29 ^b	BPO/DMA	180	1.1	13,913
	a	BPO	0	3.7	10,300
	3	BPO	180	1.0	10,825
	30	BPO	180	0.9	12,613

a, controls, average of 2 specimens

b, specimens cracked prior to strength testing

R, radiation-induced polymerization

tbp, 1 wt % tert butyl perbenzoate

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

BPO, 1.5 wt % benzoyl peroxide

BPO/DMA, 1.5 wt % benzoyl peroxide/ 1 wt % dimethyl aniline

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 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 tests can be used in the development of durable, 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.

On November 29, 1975, 48 cylindrical specimens of PC, polymer-impregnated concrete (PIC) and glass polymer composite (GPC) were placed into wells at temperatures ranging between 27°C (81°F) and 99°C (210°F). Half of the specimens were removed in late February 1976 after exposure for 3 months. All of those specimens were found to be free of cracks and of high strength.⁹ The compressive strength and water absorption were independent of the exposure temperature.

Twelve additional specimens were removed from test on June 7 after exposure for 6 months. These samples have not yet been returned to BNL for evaluation. Based upon autoclave tests being performed at simulated Klamath Falls and Raft River conditions (see Task 3), deterioration is not anticipated.

Exposure of the remaining 12 specimens is continuing.

Depending upon other commitments for the wells, the samples will remain in test at least through the summer and possibly for another 6 months.

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 $\sim 150^{\circ}\text{C}$ (302°F)] exist in the Raft River Valley Region of Idaho where, in cooperation with the Aerojet Nuclear Company (ANC), testing of concrete-polymer materials has been 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 (302°F) and a flow rate of ~ 400 gal/min.

A 4-ft long materials test section containing 24 PC specimens was shipped to ANC during the previous report period. A description of the unit and the specimens was given in Progress Report No. 8.⁹ Testing has not yet been started. Hopefully this will occur during July.¹¹ It is planned to remove half of the samples after exposure for 3 months. Additional samples will be added at that time. All of the samples will be removed after 6 months. Contingent upon the results, the test section will be replaced with a section of PC lined pipe. Work to develop the

process technology required to make this section has been started (see Task 2).

Twenty 2-in.-diameter x 0.25-in. thick discs of cement impregnated with 60 wt % styrene - 40 wt % TMPTMA were sent to ANC during November 1975 for use in abrasion tests.⁸ Typical samples are shown in Figure 5. The tests have been completed¹¹ but the results have not yet been received.

Lawrence Livermore Laboratory/San Diego Gas and Electric Co.

A program has been established in which BNL will test materials at the San Diego Gas and Electric Co. (SDG & E) site at Niland, California as part of the ERDA-SDG & E Geothermal Utilization Project. Lawrence Livermore Laboratory (LLL) will cooperate with BNL by coordinating the project and in the performance of the tests. BNL will produce the samples and LLL will design the holding fixtures and install the specimens.

The start of a test in which PC samples will be exposed for periods of up to 18 months to brine at the well head, the inlet to the second steam separator, and in the reinjection line, has been delayed by higher priority work which is in progress at Niland.¹² Until this test can be started, short-term exposures will be made in conjunction with material evaluations being performed by Dr. Lyman Lorensen of LLL. In this work, 1 x 6 x 0.5-in. PC bars will be attached to a rod and inserted into a 3-in. I.D. pipe where they will be subjected to flowing brine (velocity ~ 180 ft/sec) at a temperature of ~ 210°C (410°F). In initial tests, 3 bars containing 60 wt % styrene - 40

Figure 5

GEO THERMAL SAMPLES
RAFT RIVER

wt % TMPTMA and 3 containing 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA will be evaluated. Other monomer formulations will be exposed as space in the facility becomes available.

The specimens have been shipped to LLL and it is anticipated that the test will start during July.

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