ALTERNATE MATERIALS OF CONSTRUCTION FOR GEOTHERMAL APPLICATIONS

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M. STEINBERG - Head
L.E. KUKACKA - Project Leader

Contributors:

L.E. Kukacka

J. Fontana

W. Horn

J. Amaro

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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. Laboratory data for exposure times > 1 year are available and 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 July 1 - September 30, 1976 is described in the current report.

Summary

The feasibility of using polymer concrete (PC) to cement well casings has been demonstrated by the successful completion of 2 water wells in Kentucky.

PC pipe capable of withstanding the environmental conditions at Raft River has been produced. Exposure of a prototype section in an autoclave to a 400 ppm brine solution at 150°C (302°F) for 78 days has resulted in no apparent deterioration. Plans are being made to install a test section at Raft River.

Samples of PC have been exposed to pH 1 and 3 hydrochloric acid solutions at temperatures of 20°C (68°F) and 90°C (194°F). No deterioration has been observed after exposure times of up to 300 days. These results indicate that PC may have application in acid handling systems which may be required for the control of silica precipitation.

Field testing continued at The Geysers and Klamath Falls and a test was started at Raft River. The field test scheduled to be performed at Niland was delayed by higher priority LLL experiments.

A private company has acquired the capability of extruding PC pipe up to a diameter of 15 in. When available, sections will be obtained for field testing.

Alternate Materials of Construction
for Geothermal Applications
Progress Report No. 10
July - September 1976

Introduction

A serious problem in the development of geothermal energy is the availability of durable and economic materials of construction for handling hot brine and steam. Hot brine and other aerated geothermal fluids are highly corrosive materials and they chemically attack most conventional materials of construction. 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 performed to date has been published in nine progress reports.²⁻¹⁰ The title of the current report has been changed to reflect the revised program plan for FY 1977. A summary of accomplishments to date in the program is given 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).

Studies to evaluate the effects of various types of aggregate on the durability of the composites were initiated.

Cooperative field-test programs were started at Baca Wells, Klamath Falls, Raft River, The Geysers, and Niland. Testing at Baca Wells has been completed. All other tests are continuing.

Laboratory tests to determine the resistance of polymer concrete (PC) materials to pH 1 and pH 3 hydrochloric acid solutions and to soils containing high sulfate concentrations are continuing. To date excellent durability is indicated.

Work was started to develop the techniques for producing PC pipe and thin impermeable linings on steel surfaces. Testing of these materials at simulated Niland and Raft River 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 transitional quarter, 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. Aggregate consisting of quartz, fly ash, silica sand, and mixtures of silica sand and portland cement have been used. To date, the greatest durability has been obtained when a 90 wt% sand-10 wt% portland cement is used.

During the current report period, tests were initiated to optimize the silica sand to portland cement ratio in the aggregate. Three sand/cement ratios (9, 4, and 1) are being evaluated in conjunction with 3 monomer formulations; 50 wt% styrene-33 wt% acrylonitrile (ACN)-17 wt% trimethylolpropane trimethacrylate (TMPTMA), 55 wt% styrene-36 wt% ACN-9 wt% TMPTMA, and 60 wt% styrene-40 wt% TMPTMA.

The initial thermal stability of the specimens as determined by differential thermal analysis (DTA) was found to be unaffected by changes in the portland cement concentration. Tests to measure the long-term stability to hot air and to 25% brine at 238°C (460°F) are in progress. Evaluation of these specimens will include DTA, compressive strength, weight loss, and water absorption.

Task 2 Process Technology

Work is in progress to develop the technology required to produce PC or PC lined carbon steel pipe for use in transporting geothermal fluids. During the report period sections of 3.5-in.-i.d. x 5.5-in.-o.d. pipe were made for use in durability tests (See Task 3). Pipe sections containing wire mesh reinforcement as a means of reducing the required wall thickness were also produced. The results from the latter tests were inconclusive since inadequate compaction of the PC around the wire mesh

resulted in leakage at a hydrostatic pressure of ~ 200 psi.

During the next report period a prototype section of 4-in.-pipe will be fabricated and subjected to a long-term static test at the conditions that can be expected at Raft River [135°C (275°F) and 130 psi]. Contingent upon the results from this work and materials testing currently in progress at Raft River (See Task 4), a 3 ft section will be prepared for installation at the Raft River facility.

During the previous report period work to determine the feasibility of cementing a geothermal well with PC was described. This work was continued and during July two water wells were successfully cemented at Maxey Flats, Kentucky. The work was performed in conjunction with the Water Resources Division of the Geological Survey and is described in Ref. 12.

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 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 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 approximately 15°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 ~ 600 days. Strength measurements were made after exposure for 417 days. At that time the strengths were the same as those measured after exposure for 63 days. A visual inspection of the samples will be made during the next report period.

Tests in an environment simulating the well-head conditions at the San Diego Gas and Electric Co. facility [25% brine, 238°C (460°F)] are also in progress. Work is being performed to optimize the styrene-ACN-TMPTMA system for these operating conditions. During the report period three monomer systems were evaluated. The PC formulations consisted of 12 wt% of the monomer and 88 wt% of a sand-portland cement aggregate. Figure 1 shows the specimens after removal from the autoclave for visual inspection.

Sample 682 in Figure 1 consists of a monomer mixture containing 50 wt% styrene-33 wt% ACN-17 wt% TMPTMA. The sample has been exposed in 25% brine at 238°C (460°F) for 141 days.

Figure 1. PC specimens after exposure to 25% brine at 238°C.

A sample containing 52 wt% styrene-35 wt% ACN-13 wt% TMPTMA (Sample No. 676) has been exposed for 118 days. Earlier tests indicated a control strength of 16,940 psi and 16,238 psi after exposure for 28 days.

The third specimen shown in Figure 1 (No. 666) consists of 55 wt% styrene-36 wt% ACN-9 wt% TMPTMA. This sample has also been exposed for 118 days. Testing of the 3 samples is continuing.

Autoclave testing of 1 x 6 x 0.5-in. PC specimens containing 60 wt% styrene-40wt% TMPTMA and 50 wt% styrene-33 wt% ACN-17 wt% TMPTMA has been continued. The samples are identical to those that will be tested by Lawrence Livermore Laboratory (LLL) (See Task 4). To accelerate the test, the samples are being exposed to 25% brine at a temperature of 238^oC (460^oF) rather than the anticipated field temperature of 210^oC (410^oF). After 28 days in test, slight bowing of the bars occurred but cracks were not apparent. The specimens were then attached to a rod in the same configuration that will be utilized by LLL and the test was restarted. Visual examination of the bars after 72 days in test indicated the samples to be crack-free and sound. The samples after test are shown in Figure 2.

Flexure tests were performed on 2 of the samples. Compared to the controls, neither sample exhibited a reduction in flexural strength after exposure for 72 days.

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 PC formulations were tested after exposure to a 400 ppm brine solution at 150^oC (302^oF) for 183 days. Visual

Figure 2. PC liners after exposure to 25% brine at 238°C for 72 days.

examination of the specimens indicated that they were free of cracks and had not swollen. Typical samples are shown in Figure 3.

One formulation consisting of a 12 wt% concentration of 60 wt% styrene-40 wt% TMPTMA and 88 wt% of a sand aggregate exhibited a strength reduction from 11,312 psi to 7,825 psi after 183 days. This sample is similar to those being field tested at Klamath Falls.

Samples containing an aggregate consisting of 90% sand-10% portland cement have not exhibited strength reductions after exposure for 183 days. These tests are continuing.

A section of 3.5-in. i.d. PC pipe is being tested at the simulated Raft River Valley conditions in preparation for the installation of test pieces at Raft River and Boise. The pipe has a wall thickness of 1-in. and the burst pressure is 400 psi. A visual inspection of the section was made after exposure for 78 days. No evidence of attack was apparent (See Figure 4). This test is continuing.

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 field work at Lawrence Livermore Laboratory has indicated that a reduction of pH levels over the range of 5.0 to 1.6 resulted in complete elimination of scale over the temperature range 220°C (428°F) to 105°C (221°F).¹³

Figure 3. PC specimens after exposure to 400 ppm brine at 150°C for 183 days.

Figure 4. PC pipe after exposure to 400 ppm brine at 150°C for 78 days.

Tests to measure the resistance of PC to a pH 3 hydrochloric acid solution at 20°C (68°F) were terminated after 300 days. At that time, no evidence of corrosion as determined by weight change and pH measurements had been detected. Compressive strength and absorption measurements will be made but the data are not yet available.

In early July, three PC specimens and a concrete control were placed in a pH 3 hydrochloric acid solution at 90°C (194°F). Evidence of attack on the concrete was immediate. After 40 days, the control exhibited a weight loss of 21%. Slight weight gains (maximum 0.03%) were noted for all of the PC samples.

The 3 PC samples and a new control were then placed in a pH 1 solution at 90°C (194°F). After 21 days, the concrete control had a weight loss of 19%. The weight of the PC samples remained constant. These samples and the remainder of the control are shown in Figure 5. This test is continuing.

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

Figure 5. Control (bottom) and PC specimens after exposure to pH 1 hydrochloric acid solution at 90°C for 21 days.

strength of ~ 1000 psi are required for the life expectancy of the well. Due to the need for improved geothermal well cementing materials, ERDA has started a separate program entitled, "Cementing of Geothermal Wells". To date, two progress reports have been written.¹¹⁻¹²

Exposure of 2-in. cube PC samples in a well-head test chamber to dry steam at a temperature of 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 tested. Aggregate composition and polymerization method are other variables in this test series.

Specimens have been removed for evaluation after exposure for 90 and 180 days. The results to date are in agreement with earlier data. 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.

The next evaluation is scheduled after exposure for one year. This will occur during the next report period (November 1976).

Baca Wells

A 180 day test to determine the durability of PC to flashing brine at a temperature of ~ 160°C (320°F) was completed at Baca Wells during the previous report period. The test results given in Ref. 10 indicate that samples containing styrene-TMPTMA had strengths which were essentially unaffected by the exposure. Samples containing styrene-ACN-TMPTMA polymerized by promoter-catalyst 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.

An attempt to arrange for additional testing at the Union Oil site at Baca Wells is being made. At this time the well utilized for materials testing is not available.

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.

Field testing was started in November 1975. Forty eight 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). In February 1976 after 90 days in test, 24 specimens were removed for evaluation. Twelve additional specimens were removed from test in June 1976 after 180 days in test. These are shown in Figure 6. It is planned to remove the remaining samples during the next report period.

All of the specimens tested have been found to be free of cracks. The results from compressive strength and water absorption tests are summarized in Table 1.

Figure 6. PC and GPC samples after exposure
at Klamath Falls for 180 days.

Table 1

Klamath Falls, Test Series No. 1, Summary of Results

Fluid, hot water

Temperature, as shown below

Specimen size, 1 1/8-in.-diam x 2 1/4-in.-long

Monomer, 60 wt% styrene - 40 wt% TMPTMA

Polymer content, 12 wt%

Thermal-catalytic polymerization using 0.5 wt% α -tert butylazo isobutyronitrile

Sample No.	Sample type	Well temperature, °C	Controls		90 day exposure		180 day exposure	
			Compressive strength, psi	Boiling water absorption, %	Compressive strength, psi	Boiling water absorption, %	Compressive strength, psi	Boiling water absorption, %
408	PC	-	8889	-	-	-	-	-
409	PC	-	8158	-	-	-	-	-
418	PC	27	-	-	9256	1.4	-	-
419	PC	27	-	-	7889	1.7	-	-
420	PC	27	-	-	-	-	6568	1.2
421	PC	27	-	-	-	-	7329	1.8
430	PC	66	-	-	8248	-	-	-
431	PC	66	-	-	7444	-	-	-
422	PC	70	-	-	7821	-	-	-
423	PC	70	-	-	7632	-	-	-

Table 1 (Continued)

Sample No.	Sample type	Well temperature, °C	Controls		90 day exposure		180 day exposure	
			Compressive strength, psi	Boiling water absorption, %	Compressive strength, psi	Boiling water absorption, %	Compressive strength, psi	Boiling water absorption, %
412	PC	70.5	-	-	8034	-	-	-
413	PC	70.5	-	-	5923	-	-	-
410	PC	70.5	-	-	-	-	6416	1.4
411	PC	70.5	-	-	-	-	7929	1.3
416	PC	99	-	-	8120	1.7	-	-
417	PC	99	-	-	9957	1.5	-	-
414	PC	99	-	-	-	-	6357	2.1
415	PC	99	-	-	-	-	8352	1.1
493	PIC	-	14,188	1.5	-	-	-	-
494	PIC	-	10,690	1.9	-	-	-	-
480	PIC	27	-	-	9111	-	-	-
481	PIC	27	-	-	11,282	1.1	-	-
478	PIC	27	-	-	-	-	6526	0.6
479	PIC	27	-	-	-	-	7016	0.6
488	PIC	42	-	-	10,979	1.5	-	-
489	PIC	42	-	-	11,231	1.9	-	-
484	PIC	70	-	-	6363	1.0	-	-
485	PIC	70	-	-	8470	-	-	-
472	PIC	70.5	-	-	9231	-	-	-
473	PIC	70.5	-	-	7872	-	-	-
470	PIC	70.5	-	-	-	-	11226	0.6
471	PIC	70.5	-	-	-	-	9552	0.6

Table 1 (Continued)

Sample No.	Sample type	Well temperature, °C	Controls		90 Day Exposure		180 Day Exposure	
			Compressive strength, psi	Boiling water absorption, %	Compressive strength, psi	Boiling water absorption, %	Compressive strength, psi	Boiling water absorption, %
476	PIC	99	-	-	10,718	1.5	-	-
477	PIC	99	-	-	7376	1.8	-	-
474	PIC	99	-	-	-	-	7523	1.2
475	PIC	99	-	-	-	-	9772	1.0
449	GPC ^a	-	2689	1.8	-	-	-	-
450	GPC ^a	-	2445	1.7	-	-	-	-
437	GPC ^a	66	-	-	1686	6.9	-	-
439	GPC ^a	66	-	-	1294	1.1	-	-
451	GPC ^b	-	3423	3.3	-	-	-	-
452	GPC ^b	-	4150	2.7	-	-	-	-
456	GPC ^b	42	-	-	4245	5.5	-	-
457	GPC ^b	42	-	-	3676	6.2	-	-

PC, polymer concrete

PIC, polymer-impregnated concrete

GPC, glass polymer composite

a, aggregate - No. 4 sieve size

b, aggregate - No. 16 sieve size

Both properties appear independent of the exposure temperature but strength reductions with time are apparent. After 180 days in test, PC specimens exhibited average strength losses from 14 to 18.5%. Larger losses have been measured for the PIC but they can probably be attributed to the omission of silane coupling agents from the monomer formulation. The water absorptions have remained essentially constant throughout the test.

The above results are in agreement with recent laboratory and field data which indicate that the use of an aggregate containing portland cement is essential for durability.¹⁰ The reason for this is not known and is currently being investigated in Task 1. This effect was not known a year ago when the Klamath Falls samples were produced and cement was not included in the aggregate mix.

The Klamath Falls test results have been confirmed in autoclave tests. PC samples which did not contain a portland cement aggregate lost ~ 30% of their initial strength after exposure to a 400 ppm brine solution at 150°C (302°F) for 183 days. Samples containing an aggregate consisting of 90% sand and 10% portland cement exhibited strength increases during the same period. These tests were discussed in Task 3.

During the next report period the remaining samples at Klamath Falls will be evaluated. If approval can be obtained from Dr. Lund, a second series of specimens will be prepared for field testing.

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 exist in the Raft River Valley Region of Idaho where, in cooperation with the Aerojet Nuclear Company, testing of concrete polymer materials has been started.

Tests in which PC specimens are being exposed to the low salinity fluid at a temperature of 135°C (275°F) were started in September 1976. The flow rate is ~ 200 gpm and the pressure 130 psi.¹⁴ A description of the specimens and the test section which is installed in the "Raft River Mobile Corrosion, Deposition, and Components Test Laboratory" was given in Progress Report No. 8.⁹

Current plans are to remove half of the specimens from test after exposure for 3 months (early December). 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 pipe or PC lined pipe. Fabrication of prototype sections has been started (See Task 2) and durability tests at simulated Raft River conditions are in progress (Task 3).

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.

During the previous report period¹⁰ a series of 1 x 6 x 0.5-in. PC bars were sent to LLL for exposure at Niland to flowing brine at a temperature of $\sim 210^{\circ}\text{C}$ (410°F). The work was originally scheduled to start in July but to date the bars have not been placed into test.¹⁵ The revised estimated starting date for the tests is November. Laboratory testing of identical specimens in 25% brine at 238°C (460°F) has been in progress for 72 days. This work is described in Task 3.

Task 5 Technology Transfer and Economic Evaluation

A company named Architectural Research Corporation of Livonia, Michigan has been identified as a potential supplier of PC pipe to the geothermal industry. The company has recently acquired the capability of producing 12 ft lengths of PC pipe up to a diameter of 15-in. When available, sections of pipe will be obtained for use in field demonstrations.

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