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DEPARTMENT of APPLIED SCIENCE

Concrete-Polymer Materials for Geothermal
Applications

Progress Report No. 8
January-March 1976

Process Technology Division

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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, field testing initiated at three geothermal sites, and economic studies started. Work accomplished during the period January 1-March 31, 1976 is described in the current report.

Summary

Field testing programs are in progress at The Geysers, Baca Wells, and Klamath Falls. Specimens are available for testing at Raft River and at the San Diego Gas and Electric Co. facility at Niland, California.

Specimens have been evaluated after exposure at The Geysers to dry steam at 238°C (460°F) for 3 months. High strength and low absorptions were noted and the results were in good agreement with earlier data. The next evaluation will be performed in May after exposure for 6 months.

A six month inspection of specimens being exposed at Baca Wells to flashing brine at 160°C (320°F) will be made in April. Specimens being exposed in autoclaves to 25% brine at 177°C (350°F) for 280 days show good durability.

Samples exposed to down-hole conditions at Klamath Falls for 3 months show no deterioration. The next examination is scheduled after 6 months exposure.

Economic studies to identify potential applications for concrete polymer materials have been started. Applications in condensate piping systems, acid handling systems, reinjection lines, cooling towers, district heating systems, and to protect concrete surfaces appear cost effective.

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Introduction

The feasibility of using concrete-polymer composites as a material of construction for handling hot brine was demonstrated in 1972 in work sponsored by the Atomic Energy Commission and the Office of Saline Water.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 determine if the composites were applicable to geothermal systems was initiated in April 1974. Since that time laboratory and field tests have been performed. The results to date have been summarized in seven progress reports.²⁻⁸

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. 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.⁹

General guides to materials selection for oxygen-free geothermal systems have been published by Shannon⁹ and the results are summarized in Table 1. At temperatures of 120°C (250°F) and pH < 6, the use of expensive materials such as

Table I
Candidate Materials for Oxygen-Free Geothermal Systems

120°C (250°F)			120°C-180°C (250°F-350°F)			180°C (>350°F)		
	Material	Problems		Material	Problems		Material	Problems
<u>Dry Steam</u>	Carbon Steel	Corrosion fatigue Erosion High corrosion if steam condenses		Carbon Steel	Corrosion fatigue Erosion Specify corrosion allowance		Cr-Mo steels	Corrosion fatigue Erosion Specify significant corrosion allowance R&D on turbine materials
	Low alloy steels			Low alloy steels			12 Cr steels	
	12 Cr steel			12 Cr steel				
				Titanium			Zirconium	
				Zirconium			Titanium	Lack of data
<u>Water</u>								
pH >8	Carbon steel	Erosion		Carbon steel	Hydrogen embrittlement Erosion Specify corrosion allowance		Alloy steels	Hydrogen embrittlement Erosion Specify corrosion allowance Need R&D for data
				Low alloy steels			(for strength	
pH 6-8	Carbon steel	Erosion		Carbon steel	Erosion Specify corrosion allowance			R&D Required
				Low alloy steels				
	Aluminum	Test for pitting		Aluminum	Test for pitting		Titanium or 56Ni-15Cr-16Mo*	
	Titanium			Titanium	Test for pitting and crevice corrosion (especially in brines)			
pH 4-6	316 SST	<50 ppm Cl ⁻ required		56Ni-15Cr-16Mo				
	Carbon steel	Short life uses only		Aluminum	Pitting Test required			R&D Required Titanium or 56Ni-15Cr-16Mo*
	Aluminum	Test for pitting		Titanium				
	Titanium			Zirconium				
	Zirconium							
	316 SST	<50 ppm Cl ⁻ required		56Ni-16Cr-16Mo*				
pH 4	56Ni-15Cr-16Mo*							
	Titanium	R&D Required		Titanium	R&D Required			R&D Required
	Zirconium			Zirconium				
	56Ni-15Cr-16Mo*							

*Such as Hastalloy C

titanium, zirconium, and Hastalloy C is suggested.

At a temperature of 60°C (140°F) severe corrosion of carbon steel occurs in aerated geothermal fluids. The corrosion rate in aerated systems is reported to be 100 times greater than in oxygen free geothermal fluids.¹⁰ As a result, all condensate and cooling water piping at The Geysers is constructed of stainless steel or plastic-lined material. It is also necessary to coat all concrete surfaces that come in contact with water with coal-tar epoxy compounds or synthetic rubber.¹¹

The corrosion rate of carbon steel is also highly dependent upon the pH of the brine. At the predicted pH of 4.9 for oxygen-free Salton Sea brines and a temperature of 50°C (122°F), a service life of < 15 yr is estimated.⁹ At a pH of 4, the estimated service life is 2 yr.

Electrochemical attack due to high sulfate containing soils present in many parts of the western states may restrict the use of carbon steel pipe in the development of medium temperature geothermal reservoirs. Durable and low-cost piping systems with minimum thermal losses are essential.

Noting the above materials problems, it appears that concrete polymer composites may have application in many parts of geothermal processes. Durability tests under laboratory and field conditions are in progress and economic studies are being made in order to identify cost-effective applications.

Work accomplished during the period January 1-March 31, 1976 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 (572°F) are being developed.

Based upon the strong effect that aggregate composition has on the stability of polymer concrete (PC) to hot brine and steam (see Task 3), work during the current report period was primarily on the selection of aggregate for use in various geothermal environments. Materials such as quartz and silica sand, flyash, and portland cement are being incorporated into PC's. Testing of the various materials is in progress.

Work to select and evaluate potential high temperature polymer systems was continued. None of the materials evaluated during the report period were as stable as the styrene-trimethylolpropane trimethacrylate (TMPTMA) or styrene-acrylonitrile (ACN)-TMPTMA mixtures that are currently being field tested.

Task 2 Process Technology

The use of PC as a well cementing material is under investigation. In addition to determining the durability of PC formulations at the down hole conditions, it is necessary to determine the pumpability and curing times at the anticipated pressure and temperature conditions. Experiments to measure the latter have been started.

The initial work is being performed using the 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA monomer mixture which has shown good durability in field tests at The Geysers. Polymerization rates have been measured at 82°C (180°F) at pressures up to 900 psig. This work will be extended to higher temperatures and pressures. Methods for reducing the polymerization rates in order to allow adequate time for placement will then be developed.

Work to develop techniques for installing thin PC liners on steel pipe is in progress. Tests have indicated that liners 3/8-in. thick are impermeable. Autoclave tests are in progress to determine if long-term exposure to hot brine will reduce the permeability and bond strength.

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 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 232°C (450°F), and is ~ 15°C (27°F) higher than the temperature at which specimens are being 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 375 days. Measurements made after exposure for 280 days indicated strengths essentially the same as those measured after 63 days.⁸ The next series of strength measurements will be made at 420 days.

Tests in an environment simulating the vapor phase in the second steam separator at SDG & E are also in progress. Data are available for exposures up to 100 days. To date, three monomer mixtures; 60 wt % styrene - 40 wt % TMPTMA, 60 wt % styrene - 5 wt % ACN - 35 wt % TMPTMA, and 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA, have given the best results. The monomers are mixed with a sand-cement or sand-flyash aggregate. Strengths after exposure for 100 days are in the order 3000 to 4000 psi. Samples containing other types of aggregate have failed.

Similar effects have been noted in 25% brine at 232°C (450°F) (well-head conditions at SDG & E) and in steam at 238°C (460°F) (The Geysers). Additional tests with sand-cement aggregate are in progress.

Evaluation of specimens at conditions simulating those anticipated at Raft River and more severe than those at Klamath Falls was started during the previous report period. Three monomer-sand-portland cement formulations have been exposed to a 400 ppm brine solution at 150°C (302°F) for 87 days. This exposure time was selected to coincide with the first observation of Klamath Falls samples (see Task 4). Visual examination of the autoclave specimens indicated that the cylinders were free of cracks. The specimens have been placed back into test.

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 Laboratory¹³ has indicated that it may be possible to stabilize silica in geothermal brines by acidification with hydrochloric acid. It has also been reported by Berman¹⁴ 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.

Expensive materials of construction such as titanium, zirconium, and Hastalloy are recommended for use with pH 4 solutions at 120°C (250°F) (see Table 1). A possible alternative may be to place PC liners on carbon steel pipe and vessels.

Tests to measure the resistance of PC to pH 3 hydrochloric acid solutions at 20°C (68°F) have been in progress for 90 days. To date, no corrosion as determined by weight and pH measurements is evident. Control specimens of concrete and carbon steel have shown slight amounts of attack during the same period. Testing in pH 1 solutions at 20°C (68°F) and pH 3 solutions at 90°C (194°F) will be started during the next report period.

Materials for piping systems which are resistant to the acid soil conditions found in the western part of the U.S. are needed for the development of medium temperature geothermal reservoirs. Concrete polymer materials may also have application in these systems.

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 60 days. To date, changes in weight, absorption, or electrical resistivity have not been detected.

Task 4 Field Tests

Field testing programs are currently in progress at The Geysers, Baca Wells, and Klamath Falls. Specimens have

been prepared for testing at the San Diego Gas and Electric Company site at Niland, California and by Aerojet Nuclear at Raft River, Idaho. The test section for the latter has been shipped but testing has not been started. 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.

Test Series No. 1 was completed during September 1975 and the data were given in the previous progress report.⁸ The results indicated that a formulation consisting of 12 wt % of a monomer mixture containing 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA and 88 wt % of a 90% sand - 10% portland cement aggregate exhibited high strength (4500 psi) and low permeability (< 1 milli Darcy). Measurements made after exposure for 90 days gave results essentially the same as those made after 60 days. Lower strengths (3800 psi) were exhibited by a formulation containing styrene, TMPTMA, sand, and portland cement.

As a result of the encouraging results, a second series was placed into test during November 1975. 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. Other

test variables include aggregate composition and polymerization method.

The first examination of the specimens was made during February 1976 after exposure to dry steam at 238°C (460°F) for 3 months. Other examinations will be made after 6, 12, and 24 months.

Four of the samples which were identical to those which gave the best results in Series No. 1 (12 wt % of the 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA monomer mixture and 88 wt % of a 90% sand - 10% portland cement aggregate) exhibited compressive strengths (5000 psi) and water absorptions (3.7%) which were in good agreement with earlier results.

All specimens which contained aggregate other than the sand-cement mixture cracked during the 3 month exposure. This was not unexpected since similar results were recently obtained from autoclave tests which were run concurrently with the field tests. DTA analyses of the specimens are being made to determine if reactions between the polymer and various types of aggregate occurred. Samples of the 55 wt % styrene - 36 wt % ACN - 9 wt % TMPTMA with sand-cement aggregate are currently in test in the autoclaves but results are not yet available.

The 6 month examination of samples at The Geysers will occur during May.

Baca Wells

In cooperation with the Union Oil Company, testing of a series of PC specimens in flashing brine at a temperature

of $\sim 160^{\circ}\text{C}$ (320°F) is continuing at Baca Wells in New Mexico. Materials with compositions identical to those that were evaluated in Series No. 1 at The Geysers are being tested. The test has been in progress since October 7, 1975. Initial plans were to inspect the samples after a 100 day exposure. Subsequent changes by Union Oil to the operating schedule for the well have resulted in extending the first exposure period to 180 days. The samples are currently scheduled for examination on April 6.

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 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.

Forty-eight cylindrical specimens of PC, polymer-impregnated concrete (PIC) and glass-polymer composite (GPC) were placed in test on November 29. Based upon earlier work, a 60 wt % styrene - 40 wt % TMPTMA monomer mixture was selected for evaluation. The water temperature in the 6 wells being

utilized ranges between 27°C (81°F) and 99°C (210°F). Half of the samples were removed from test in late February after exposure for 3 months. The remainder were placed back into test. The next examination is scheduled for late May.

Visual examination of the specimens after the 3 month exposure indicated that all of the samples were free of cracks and sound. Compressive strength and water absorption tests were performed. The PC specimens had an average compressive strength of 8030 psi which was essentially equal to that of the controls. The water absorption (average 1.5%) was also unchanged. Over the range of test conditions, the strength and absorption were independent of temperature.

Similar effects were noted for the PIC. Average values of 9300 psi and 1.5% were measured for the compressive strength and water absorption, respectively.

Two aggregate size distributions were used in the GPC specimens. Samples containing aggregate that passed through a No. 16 sieve were not affected by the 3 month exposure. Specimens containing larger aggregate (- No. 4) lost ~ 50% of their initial strength. This is being investigated.

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 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 (302°F) and a flow rate of ~ 400 gal/min. The chemical analysis of the water is given in Ref. 12.

During the current report period 24 PC specimens were fabricated and shipped to ANC for use in the first series of tests in this facility. Two monomer mixtures, 60 wt % styrene - 40 wt % TMPTMA and 50 wt % styrene - 33 wt % ACN - 17 wt % TMPTMA were used in the preparation of the samples. The monomers containing 1.5 wt % benzoyl peroxide initiator were mixed with a sand and flyash aggregate and polymerized at 85°C (185°F). The monomer concentration in the mix was 12 wt %. Tests performed on control samples indicated compressive strengths $> 12,000$ psi and water absorptions of $< 1\%$. Typical samples, their containment basket, and the 4-ft long materials test section are shown in Figure 1.

Half of the samples will be removed after exposure for 3 months. Additional samples will be added at that time.

Fig. 1

It is planned to remove all of the samples after 6 months. Contingent upon the results, the test section will then be replaced with a section of PC lined pipe.

It is anticipated that the first series of tests will be started in late April.

Lawrence Livermore Laboratory/San Diego Gas and Electric Company

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 program and in the performance of the tests. BNL will produce the samples and LLL will design the holding fixtures and install the specimens. Current plans are to expose specimens for periods up to 18 months to brine at the well head, the inlet to the second steam separator, and in the reinjection line. Depending upon the flow rate and pressure, the maximum brine temperature anticipated is $\sim 232^{\circ}\text{C}$ (450°F).

Twenty 1 x 6 x 0.5-in. PC bars will be placed at each of the three test positions listed above. Measurements to be performed after exposure will include weight loss, scale build-up, abrasion, permeability, and flexural strength.

During the current report period specimens were fabricated for the field tests and strength measurements were performed. The samples will be shipped to LLL when

start-up of the SDG & E plant is imminent. Laboratory testing of similar specimens in 25% brine and wet steam at 238°C (460°F) is currently in progress. This work was described in Task 3.

Task 5 Economic Evaluation

Economic studies were initiated during the current report period to identify cost effective uses for concrete polymer materials in geothermal processes. Preliminary results, summarized in Table 2, indicate that large cost benefits can be accrued by use of PC-lined carbon steel components as replacements for stainless steel, tantalum, and Hastalloy in condensate piping systems, reinjection lines, and steam separators. Uses of PC or PIC in cooling towers, district heating systems, and to protect concrete surfaces also appear cost effective. These studies are being continued.

Table 2

**Cost Comparison for Use of Concrete Polymer Materials
for Geothermal Applications**

<u>Use</u> <u>The Geysers</u>	<u>Current</u> <u>material</u>	<u>Estimated</u> <u>cost, \$/unit</u>	<u>Type of concrete</u> <u>polymer material</u>	<u>Estimated</u> <u>cost, \$/unit</u>	<u>Benefit,</u> <u>\$/unit</u>
Condensate and cooling water pipe	stainless steel	120/ft ^a	carbon steel with PC liner	30/ft ^a	90/ft
Cooling towers (all wetted parts)	stainless steel or aluminum	1.15/lb ^b 1.15/lb ^b	PC PC on carbon steel	0.10/lb 0.30/lb ^b	1.05/lb .85/lb
Protective liners on concrete	coal tar epoxies	1.20/lb	PC	0.10/lb	1.10/lb
<u>Imperial Valley brines</u>					
Steam separators	stainless steel Hastalloy tantalum	1.25/lb ^c 8.56/lb ^c 120/lb ^c	PC on carbon steel " "	0.40/lb ^c 0.40/lb ^c 0.40/lb ^c	.85/lb 8.16/lb 119/lb
reinjection lines acid handling system	stainless steel stainless steel	120/ft ^a 26/ft ^e	carbon steel with PC liner	30/ft ^a 5.50/ft ^e	90/ft 20/ft
<u>Raft River and Boise</u>					
Distribution piping	Transite Carbon steel with external coating	8.60/ft ^{a,d} 25/ft ^a	PC or PIC PC or PIC	5/ft ^a 5/ft ^a	3.60/ft 20/ft

a, assume 12-in. pipe
b. assume 0.25 in. plate
c, assume 0.5 in. plate

d, pressure rating, 200 psi
e, assume 4-in. pipe

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