

# ALTERNATE MATERIALS OF CONSTRUCTION FOR GEOTHERMAL APPLICATIONS

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PROCESS TECHNOLOGY DIVISION

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

Contributors:

L.E. Kukacka                      W. Horn  
J. Fontana                        J. Amaro  
T. Sugama

Work performed for the  
DIVISION OF GEOTHERMAL ENERGY  
UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION  
WASHINGTON, D.C. 20545

DEPARTMENT OF APPLIED SCIENCE

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## Abstract

A program to determine if concrete polymer materials can be utilized as materials of construction in geothermal processes is in progress. To date several high temperature polymer concrete formulations have been identified, laboratory tests performed in simulated geothermal environments, field testing initiated at four geothermal sites, and economic studies started. Laboratory data for exposure times >1.5 years are available. Field test results have been obtained for 180 day exposures to flashing brine and hot water and a 1 year exposure to dry steam. Good durability is indicated. Work accomplished during the period October 1-December 31, 1976 is described in the current report.

## Summary

Significant improvements in the thermal stability of polymer cement lining materials have been made by the use of chemical additives and by increasing the amount of portland cement in the aggregate. An optimum aggregate composition of 50% sand - 50% cement has been determined.

Laboratory testing of specimens at simulated geothermal environments was continued. Samples were examined after exposure to 25% brine at 177°C (350°F) for 601 days, 25% brine at 238°C (460°F) for ~200 days, and 400 ppm brine at 150°C (302°F) for 247 days. Good durability is indicated. Polymer concrete exposed to pH 1 hydrochloric acid at 90°C (194°F) for 110 days has not deteriorated. The concrete control failed after 21 days.

Initial field tests have been completed at Baca Wells, The Geysers, Klamath Falls, and Raft River. Second test series are in progress at The Geysers and Raft River.

Samples evaluated after exposure at The Geysers to dry steam at 238°C (460°F) for one year showed good durability. The strengths were essentially the same as those measured after a 90 day exposure.

Examination of specimens exposed for 70 days at Raft River indicated that polymer-impregnated concrete has good abrasion resistance. Polymer concrete samples exposed in the "Raft River Corrosion, Deposition, and Components Test Laboratory" for 90 days showed strength reductions of ~30%. The use of portland cement in the aggregate can correct this condition.

Samples were removed from 3 wells at Klamath Falls after exposure for 1 year. Test results are not yet available.

Alternate Materials of Construction  
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Introduction

The feasibility of using concrete-polymer composites as materials of construction for handling hot brine was demonstrated in 1972 in work sponsored by the Atomic Energy Commission and the Office of Saline Water.<sup>1</sup> 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 published in ten progress reports<sup>2-11</sup> and are summarized below.

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.<sup>12</sup>

General guides to materials selection for oxygen-free geothermal systems have been published by Shannon.<sup>12</sup> At temperatures of 120°C (250°F) and pH < 6, the use of expensive materials such as 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.<sup>13</sup> 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.<sup>14</sup>

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.<sup>12</sup> 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.

#### Summary of Earlier Work

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 and The Geysers. Initial tests at Baca Wells and Klamath Falls have been completed. Testing at the other sites is 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 first quarter of FY 1977, work was continued in each of the program tasks. This work is described in the current report.

#### Task 1 Selection of Lining Materials

Work is being performed to develop polymer formulations and polymer concrete composites which can be used as materials of construction at temperatures up to 260<sup>o</sup>C (500<sup>o</sup>F). Research is also being performed to determine if materials can be formulated for use as well as cementing materials at temperatures up to 400<sup>o</sup>C (750<sup>o</sup>F). This work is described in a separate program entitled "Cementing of Geothermal Wells".<sup>15</sup>



Figure 1. PC samples after exposure at The Geysers to dry steam at 238°C for 1 year. Samples 275-278 contain aggregate consisting of 90% sand - 10% cement. All others contain only sand.

Experiments to identify the types of aggregate that should be used in various geothermal environments were continued. Materials such as silica sand, portland cement, gypsum (calcium sulfate), aluminum oxide, aluminum hydroxide, and lumnite cement are being investigated.

Based upon earlier observations that PC containing a mixture of silica sand and portland cement aggregate had greater durability in brine and steam than specimens without cement (see Figure 1), a study to optimize the cement content has been performed. In this study, mixtures of sand and portland cement in ratios varying from 9/1 to 1/4 were used in conjunction with three styrene-ACN-TMPTMA mixtures. The thermal stability and strength of the samples after exposure at 238°C (460°F) was measured.

Increased thermal stability with increasing portland cement concentration up to a maximum of 50% was noted. When a 50% sand-50% cement mixture was used in conjunction with a monomer mixture consisting of 55 wt% styrene - 36 wt% ACN - 9 wt% TMPTMA, essentially no change in strength occurred after a 30 day exposure at 238°C (460°F). Testing in a 25% brine solution at 260°C (500°F) is in progress.

Studies to identify other monomer systems which can be used to produce high temperature composites are in progress.

The melting point of a pure polymer can be predicted from the following equation:

$$T_m = \frac{\Delta H_u}{\Delta S_u}$$

where  $T_m$  is the thermodynamic melting point of the polymer  
 $\Delta H_u$  is the enthalpy increase per mole of repeating chain units, and  
 $\Delta S_u$  is the entropy increase per mole of repeating chain units.

The equation predicts that polymers containing groups in their molecular structure with low free rotational energy ( $\Delta S_u$ ) will have the highest melting points and therefore be heat resistant materials.

Polymides and polyphenylene oxides are two classes of high temperature polymers being considered. Initially polyimides produced from pyromellitic dianhydride and the following will be evaluated; 4 4'-diaminodiphenyl ether, m-phenylenediamine, and p-phenylenediamine. Studies to determine if the reactions can be initiated in the presence of sand and cement and the effects of hydrolysis on the composites will also be performed.

The incorporation of a ring-structured material such as n-phenyl meleimide into a polymer will also increase the thermal stability. When a concentration of 10% of n-phenyl meleimide by weight of monomer was added to a mixture containing 55 wt% styrene - 36 wt% ACN - 9 wt% TMPTMA, the weight loss of the composite after 15 days at 238°C (460°F) was reduced by a factor of 6 compared to the controls.

The use of triallyl cyanurate (TAC) as a crosslinking agent for polyester resins is also under investigation. TAC combines the functionality of three allylic groups with the triazine nucleus. The latter is one of the most thermally and chemically stable structures known.

Difficulty in curing polyester containing TAC was encountered initially. This problem has now been resolved using 2% benzoyl peroxide and tricresyl phosphate as the initiator. Specimens have been prepared for use in thermal stability tests which are currently in progress. If the system has adequate thermal resistance, the relatively high viscosity of the polyester should be advantageous in producing thin liners for process piping and vessels.

Copolymers of acrylamide with acrylonitrile and acrylamide with styrene are also being studied. Samples of the bulk copolymers and PC samples have been produced. Testing is in progress.

## 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. Field testing of prototypes will be performed at Raft River and possibly at Boise, Idaho. This is discussed in Task 4.

During the current report period a 3-ft length of 4-in.-i.d. x 6.375-in.-o.d. PC pipe was fabricated. The pipe, a prototype of the section that will be tested at Raft River, was composed of a monomer mixture consisting of 50 wt% styrene - 33 wt% ACN - 17 wt% TMPTMA and an aggregate containing 90% sand - 10% portland cement. After removal from the form, the pipe was cut into three 1-ft sections which are being used in strength and durability tests.

The result from a crushing test indicated an initial three-edge bearing strength of 16,300 lb/ft.

A second test section was emersed in a 400 ppm brine solution at 150°C (302°F) and 80 psi for 30 days. A three-edge bearing strength of 12,000 lb/ft, ~25% less than the control, was measured. Tests to determine if the difference in strength was caused by the exposure to hot brine or non-uniformities in the pipe as a result of poor compaction are underway.

A hydrostatic test at (200 psi and 150°C (302°F) is presently being performed. After 30 days at this condition, the crushing strength will be measured. Contingent upon the results from this test, a 4-ft section will be installed at Raft River.

Work is in progress to develop a durable-low thermal conductivity pipe for use in geothermal space heating applications, such as at Klamath Falls, Boise, and Raft River. A pipe consisting of a lightweight (~0.31 g/cc) core of insulating-type concrete with a thin inner and outer shell of PC to provide strength and durability is envisioned. The lightweight concrete is made by incorporating polystyrene waste as part of the aggregate and subsequent high pressure

steam curing. The thermal conductivity of the resultant material is  $\sim 0.05$  BTU/hr ft<sup>2</sup> °F, only 2.5 times that of fiberglass insulation. Strength and durability tests will be performed on the composite pipe.

### 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  $238^{\circ}\text{C}$  ( $460^{\circ}\text{F}$ ), and is approximately  $80^{\circ}\text{C}$  ( $144^{\circ}\text{F}$ ) 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 90% sand-10% portland cement aggregate.

The test has been in progress for 631 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 made after 631 days indicated no cracking or other signs of deterioration. This test is continuing.

Tests in an environment simulating the anticipated well-head conditions at the San Diego Gas and Electric Co. facility (25% brine,  $238^{\circ}\text{C}$  ( $460^{\circ}\text{F}$ )) are continuing. Three PC formulations containing a 12 wt% concentration of styrene-ACN-TMPTMA mixtures and 88 wt% of a 90% sand-10% portland cement aggregate are being evaluated. Figure 2 shows the specimens after removal from the autoclave for visual

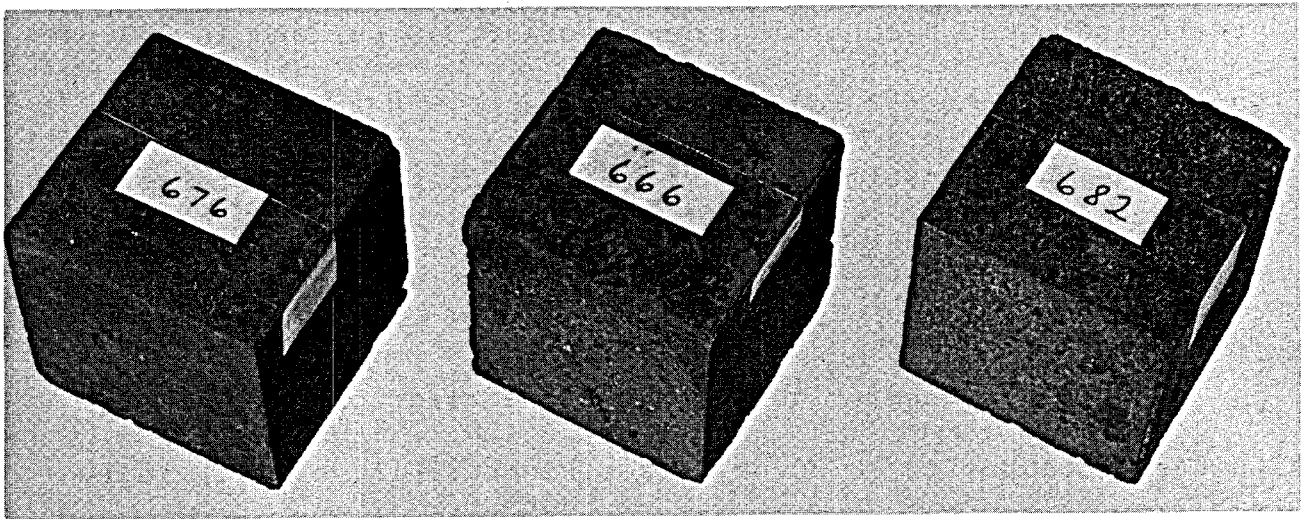


Figure 2. PC specimens after exposure to 25% brine at 238°C.

inspection.

Sample 682 in Figure 2 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<sup>o</sup>C (460<sup>o</sup>F) for 203 days.

A sample containing 52 wt% styrene-35 wt% ACN-13 wt% TMPTMA (Sample No. 676) has been exposed for 180 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 2 (No. 666) consists of 55 wt% styrene-36 wt% ACN-9 wt% TMPTMA. This sample has also been exposed for 180 days.

A comparison of Figure 2 with an earlier photograph made after exposure for ~ 130 days (see Figure 1 in Ref. 11) indicates no apparent changes in the specimens. This test is being continued.

Testing of prototype PC liners has been continued. Two monomer mixtures, 60 wt% styrene-40 wt% TMPTMA and 50 wt% styrene-33 wt% ACN-17 wt% TMPTMA are being evaluated. The samples are identical to those that will be tested by Lawrence Livermore Laboratory (LLL) (See Task 4). To accelerate the test, the samples were exposed to 25% brine at a temperature

of 238<sup>o</sup>C (460<sup>o</sup>F) rather than the anticipated field temperature of 210<sup>o</sup>C (410<sup>o</sup>F). 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 (see Figure 2 in Ref. 11). Flexure tests performed at that time on 2 samples indicated that compared to the controls, neither sample exhibited a reduction in strength.

During the current report period 2 specimens were examined after exposure for 131 days. These samples are shown in Figure 3. The sample containing 60 wt% styrene-40 wt% TMPTMA had a crack completely through the section at the point where the piece was bolted to the support rod. Erosion and scaling of the PC was also apparent.

The sample consisting of 50 wt% styrene-33 wt% ACN-17 wt% TMPTMA was crack free but some erosion of the top surface had occurred. The flexure strength of the piece is being determined but to date the result is not available.

Based upon the good results obtained when 2-in.-cube specimens were exposed for longer times at the same brine

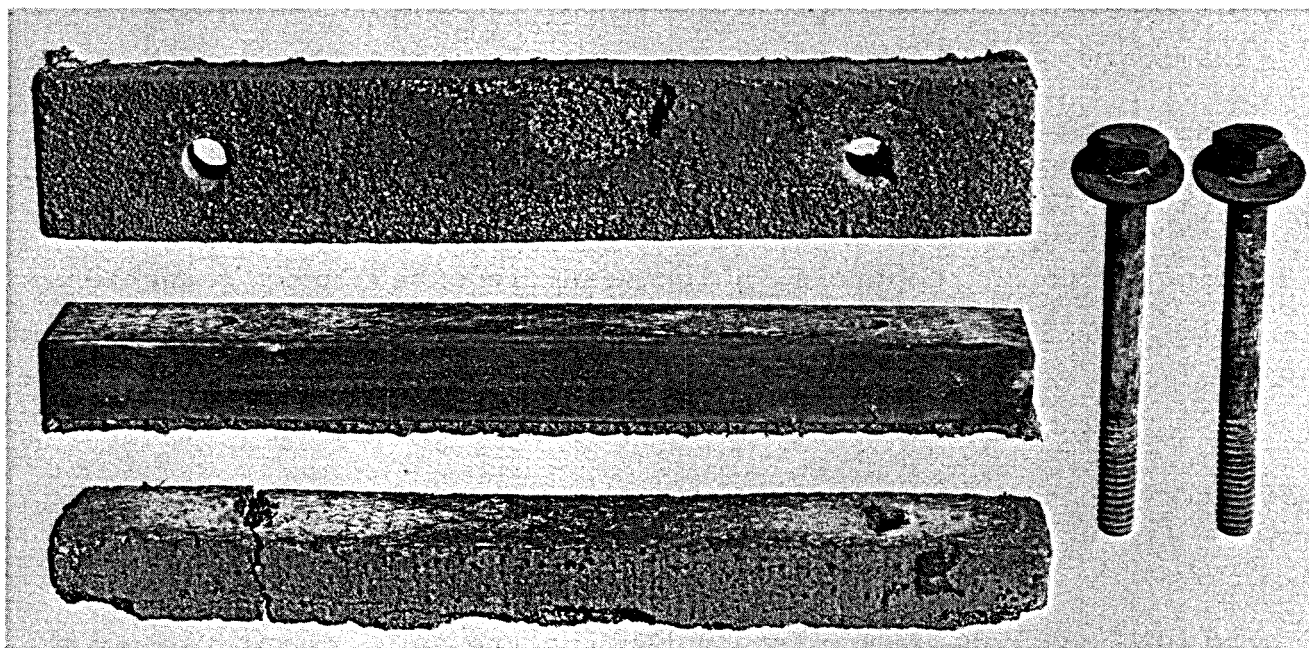


Figure 3. PC liners after exposure to 25% brine at 238°C for 131 days. Top, 50 wt% styrene-33 wt% ACN-17 wt% TMPTMA Bottom, 60 wt% styrene-40 wt% TMPTMA.

conditions (see Figure 2), the deterioration of the bars was unexpected. Stresses resulting from the method of attaching the samples to the support rod or to variations in the concentration of polymer in the samples, therefore producing a non-uniform coefficient of expansion, are possible causes. These tests will be repeated.

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 visually examined after exposure to a 400 ppm brine solution at 150°C (302°F) for 247 days. All of the samples were free of cracks and had not swollen. These samples are shown in Figure 4. Changes in appearance since the previous examination were not apparent.<sup>11</sup> These tests are being continued.

The testing of a 3.5-in.-i.d. x 1-in.- wall PC pipe which is a prototype of sections to be installed at Raft River and Boise was continued. The burst pressure of the pipe is ~ 400 psi. No evidence of attack was apparent after exposure for 140 days to a 400 ppm brine solution at 150°C (302°F). The pipe section is shown in Figure 5.

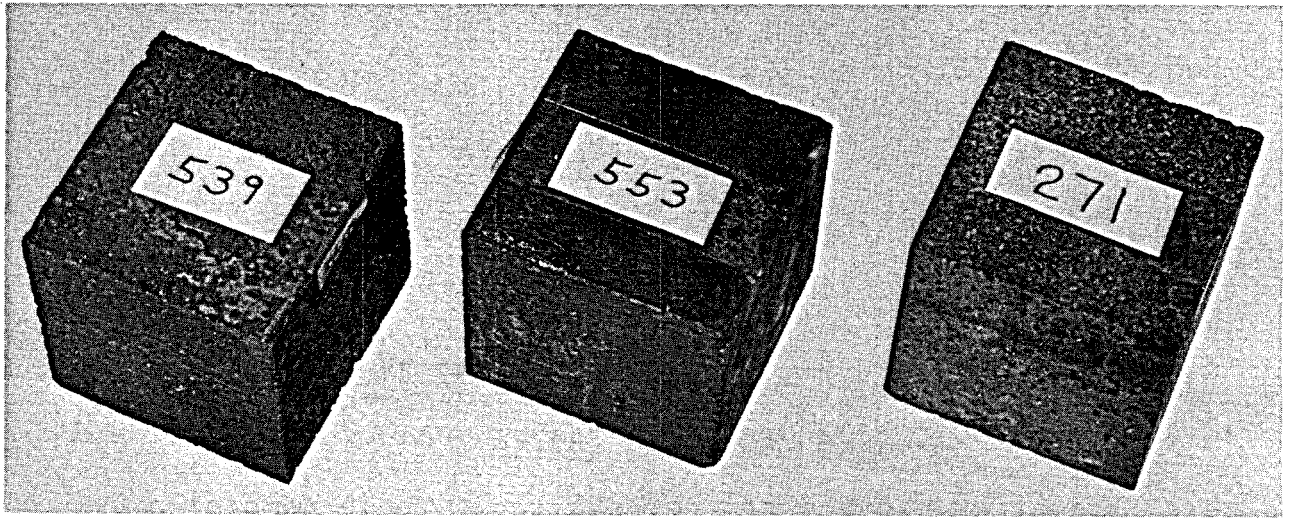


Figure 4. PC specimens after exposure to 400 ppm brine at 150°C for 247 days.



Figure 5. PC pipe after exposure to 400 ppm brine at 150°C for 140 days.

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).<sup>16</sup>

In the previous progress report<sup>11</sup>, results from tests to determine the resistance of PC materials to pH 3 hydrochloric acid solutions at 20°C (68°F) and 90°C (194°F) were presented. No evidence of corrosion was noted after exposure for 300 days at 20°C (68°F). The test at 90°C (194°F) was terminated after 40 days when the concrete control failed. No attack on the PC was evident.

Testing in a pH 1 solution at 90°C (194°F) has been in progress for 110 days. After 21 days, the concrete control had a weight loss of 19%. To date, no evidence of corrosion

as determined by weight change and pH measurements has been detected.

#### Task 4 Field Tests

To date, test series have been completed at Baca Wells, The Geysers, Klamath Falls, and Raft River. Second series are in progress at The Geysers and Raft River. Specimens have been shipped to Lawrence Livermore Laboratory (LLL) for exposure at Niland, California and arrangements are being made to initiate tests at East Mesa. The status of each of these programs is summarized below.

##### The Geysers

Tests are in progress to determine the durability of PC when exposed in a well-head chamber to dry steam at a temperature of  $238^{\circ}\text{C}$  ( $460^{\circ}\text{F}$ ). A preliminary test series was completed in September 1975. The results from this test<sup>8</sup> indicated that the samples had high strength and low permeability after exposure for 90 days.

Based upon these data, a second series was placed in 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 tested. Aggregate composition and polymerization

method are other variables in the test series.

During the current report period samples were evaluated after exposure for 365 days (see Figure 1). The test results were in agreement with earlier data. All samples containing an aggregate consisting of 90% sand-10% portland cement showed good durability. Composites containing other types of aggregate failed. The average compressive strength of specimens exposed to the test conditions for 1 year was 4200 psi, approximately 50% of the control value but in agreement with a value of 4900 psi that was measured after a 90 day exposure.

The next evaluation of specimens is scheduled after exposure for 18 months (May 1977).

#### Baca Wells

A 180 day test to determine the durability of PC to flashing brine at a temperature of  $\sim 160^{\circ}\text{C}$  ( $320^{\circ}\text{F}$ ) has been completed and the data given in Ref. 10. The results indicated that samples containing styrene-TMPTMA were essentially unaffected by the exposure. Samples containing styrene-ACN-TMPTMA polymerized by promoters and initiators were also unaffected. The other samples exhibited strength reductions and increases in absorption. These values were in the same

order as those obtained after 180 day exposures at The Geysers.

#### Klamath Falls

The Oregon Institute of Technology has provided assistance to BNL in exposing samples to geothermal fluids in Klamath Falls, Oregon. To date samples have been evaluated after test periods of 90 and 180 days. These results are summarized in Ref. 11.

During the current report period the last series of specimens was removed from the test wells. The samples have not yet been shipped to BNL.

#### 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 testing of concrete polymer materials has been started. To date, one test series has been completed and a second is in progress.

In the first experiment, twenty 2-in.-diam. x 0.25-in.-thick cement discs, impregnated with 60 wt% styrene-40 wt%

TMPTMA, were subjected to the Raft River fluid in an attempt to measure the abrasion resistance.

A verbal report from Dr. R. L. Miller indicated that after 70 days in test, no deterioration of the polymer-impregnated specimens was apparent. Severe attack was noted on several metallic samples. Dr. Miller is preparing a report on this work.

Testing of PC samples in the "Raft River Mobile Corrosion, Deposition, and Components Test Laboratory" was started in September 1976. A description of the specimens and the test section was given in Progress Report No. 8<sup>9</sup>. The test conditions are as follows: temperature 135°C (275°F), flow 200 gpm, and pressure 130 psi.

During the current report period 20 specimens were removed from test after exposure for 90 days. These samples are shown in Figure 6. Visual inspection indicated the samples to be crack-free.

Samples containing a 50 wt% styrene-33 wt% ACN-17 wt% TMPTMA monomer mixture and a sand-flyash aggregate exhibited a small weight increase (~ 1%) and an increase in water absorption from ~ 1.1% to 2.1%. A reduction in compressive strength from an average of 15,763 psi to 10,821 psi was also noted.



Figure 6. PC specimens after exposure for 90 days to Raft River geothermal fluid at 135°C.

Specimens containing a 60 wt% styrene-40 wt% TMPTMA monomer mixture and the sand-flyash aggregate exhibited slight weight losses ( $\sim 0.6\%$ ) during the test. The average compressive strength decreased from 14,960 psi to 10,000 psi and the water absorption increased.

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.<sup>10</sup> 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 Raft River samples were produced and cement was not included in the aggregate mix.

Testing at Raft River is continuing. Four samples identical to those discussed above will be removed after exposure for 180 days. Forty-six new samples were also placed into test. These samples include the 2 formulations described above modified by the replacement of the flyash with portland cement. A third formulation consisting of 55 wt% styrene-36 wt% ACN-9 wt% TMPTMA and sand-cement aggregate is also being tested. Sand/cement ratios varying from 9/1 to 1/1 will be evaluated with this monomer system.

Plans are being made to install a section of 4-in.-diam. PC pipe in the Raft River test facility. Additional space in the facility will be provided so that the 2 tests can be run concurrently.

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

In June 1976 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  $\sim 210^{\circ}\text{C}$  ( $410^{\circ}\text{F}$ ). The work was originally scheduled to start in July but to date the bars have not been placed into test.<sup>17</sup> The revised estimated starting date for the tests is February.

Task 5 Technology Transfer and Economic Evaluation

As part of the technology transfer effort, a meeting was held with producers of cement-lined pipe. Severe corrosion problems exist when this material is used to transport

60°C (140°F) oil-field water containing high concentrations of H<sub>2</sub>S. As a result of the meeting, at least 2 of the producers are planning experiments with polymer cement-lined pipe and with polymer-impregnated pipe. If successful, this technology will be applicable to process lines in geothermal processes and at least 2 suppliers will be identified.

Task 6 Administrative

During the current report period 3 Monthly Administrative Letters have been submitted to DGE and Quarterly Report No. 10 was issued. An abstract of a paper entitled "The Applicability of Concrete Polymer Materials For Use in Geothermal Environments" was submitted to the Society of Petroleum Engineers (SPE) for presentation at the "1977 SPE Symposium on Oilfield and Geothermal Chemistry".

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Joseph M. Hendrie  
William Horn  
Lawrence Kukacka  
Bernard Manowitz  
David Schweller (ERDA)  
Meyer Steinberg  
Warren E. Winsche  
Arkady Zeldin