ALTERNATE MATERIALS OF CONSTRUCTION FOR GEOTHERMAL APPLICATIONS

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Abstract

A program to develop non-metallic materials for use in geothermal processes is in progress. To date, several high temperature polymer and polymer concrete systems were formulated, laboratory and field tests were performed in brine, flashing brine, and steam at temperatures up to 260°C (500°F), and economic studies were started. Laboratory data for exposure times > 2 years are available. Results are also available from field exposures of up to 24 months in five geothermal environments. Good durability is indicated. Testing at five of these sites is continuing and plans to initiate tests at other sites are being implemented. Work was also started to develop materials for use in high temperature seals for well drilling, logging and energy extraction processes. Work accomplished during the period January-March 1979 is described in the current report.

Summary

The following are the highlights of the January-March 1979 activities performed under the Alternate Materials of Construction for Geothermal Applications Program.

Task 1. An RFP for work to develop sealing materials for use in drill bit seals, packers, logging equipment and blow-out preventors was advertised. Five proposals were received and one or more contracts will be awarded.

Task 1. Polymer concrete (PC) containing organosiloxane polymers has been found to be hydrothermally stable after 60 days in 25% brine at 300°C. The compressive strength of the composite is independent of temperature over the range 25°C to 350°C. Possible applications include protective liners and elastomeric seals. Work to extend the stability to 400°C is in progress.

Task 2. An RFP for the design and fabrication of PC pipe to be tested in direct utilization processes has been advertised. The purpose of the request is to obtain full-size sections for evaluation by potential users and to assist in establishing commercial sources of supply.

Task 3. PC containing 50 wt% St - 35 wt% acrylonitrile - 5 wt% acrylamide - 10 wt% divinyl benzene has exhibited the highest strength and greatest durability of any organic-based PC material to date. After 8 months in brine at 238°C, the strength is 204 MPa at 20°C and 162 MPa at 150°C.

Task 3. PC samples exposed for 2 yr to pH 1 HCl at 90°C have exhibited no deterioration.

Task 4. Samples and lined pipe evaluated after exposure at Raft River for 18 months have exhibited no deterioration or scale accumulation. PC samples without cement as a constituent of the aggregate started to deteriorate after 90 days.

Task 4. A prototype PC-lined steam separator has been in operation at East Mesa for 30 days. No scale build-up on the walls of the vessel has been observed. Similar observations have been made for pipe in test for 408 days.

Task 5. A study on the economic impact of the use of non-metallic materials of construction in direct utilization processes has been completed. Reductions in capital costs which translate into lower energy costs ranging from \$0.06/10⁶ Btu to \$0.30/10⁶ Btu were calculated. Based on the projected direct utilization applications in the Rocky Mountain area by the year 2000, these energy cost savings are equivalent to an annual savings of \$50 x 10⁶ to \$300 x 10⁶.

Alternate Materials of Construction for Geothermal Applications

Progress Report No. 18
January-March 1979

Introduction

The cost and the reliability of geothermal electric power plants and direct utilization processes depend heavily on the availability of suitable construction materials. The chemically active nature of geothermal brine demands the use of materials with high erosion/corrosion resistance. The identification of materials with suitable properties will be a big step toward the development of a stable geothermal industry. If successfully implemented, this use of non-metallic materials such as plastics, polymer concrete and ceramics in geothermal electric generating processes could result in a 10 to 20% cost reduction. Based upon projections of USA direct utilization applications by the year 2000, energy cost savings equivalent to an annual savings of $\$50 \times 10^6$ to $\$300 \times 10^6$ have also been estimated.

Improved sealing materials for use in geothermal well drilling operations, well-logging techniques and energy extraction equipment are also needed. Seals represent an important part in almost every geothermal process component and improving their performance will have a significant impact on cost.

Work on the development of non-metallic construction materials for use in geothermal systems was initiated in April 1974. Since that time, several high-temperature polymer concrete systems have been formulated, laboratory and field tests performed in brine, flashing brine, and steam at temperatures up to 260°C , and economic studies started.

Laboratory data for exposure time > 2 years are available. Results are also available from field exposure of up to 2 years in six geothermal environments. Good durability is indicated. Work at five test sites is currently in progress. The results to date have indicated the potential for the successful use of concrete polymer composites as lining materials for process piping and vessels in geothermal power systems and as durable low thermal conductivity piping for process heat and district heating applications.

Economic studies performed concurrently with the research program have identified several cost-effective uses for the materials in geothermal processes. Large cost reductions as a substitute for stainless steel, titanium, and Hastelloy in acid-handling systems, condensate-piping systems, reinjection lines, and steam separators are indicated. Uses in cooling towers, district heating systems, and in the protection of concrete surfaces also appear cost-effective.

A study has indicated that the use of polymer concrete lining materials as a partial replacement for the corrosion allowance in carbon steel components for a 50 MWe geothermal plant will reduce the cost of power by ~ 6.2 mills per kwh.¹ Results from a study completed during the current report period indicate capital cost reductions up to 13% for a direct utilization (district heating) application.² These data are summarized in Task 5 of this report.

The scope of the BNL program has been broadened in FY 1979 to include investigations of other non-metallic materials such as plastics, ceramics, and refractory cements. Investigations to develop high temperature sealing methods and materials have also been initiated. BNL is performing

in-house research in each of the areas and in conjunction with industrial and university groups will manage a series of contracted efforts aimed at evaluating and developing alternative materials of construction for power and direct utilization processes. Projects for determining: (1) engineering design requirements, (2) failure mode, and (3) properties of materials will be undertaken. Future efforts will include development of prototype equipment and the demonstration of the applications of the new materials. The work will be performed with potential geothermal plant owners in order to establish the groundwork for rapid implementation and to transfer the technology to industry.

In the previous report³ it was stated that polymer concrete (PC) containing organosiloxanes appeared hydrothermally stable in brine at 300°C. The results indicated that the optimum properties for either of the two organosiloxane systems tested (75 wt% &-9208 - 25 wt% styrene or 97 wt% RZ - 3 wt% V47) occurred when an aggregate consisting of < 30 µm silica flour was used in conjunction with Type II or III portland cement in a ratio of 90/10 or 95/5. The feasibility of using the materials for high temperature seals was being determined.

A test to determine the resistance of PC pipe to acid soil conditions was completed. After 1104 days in pH 2.9 soil, concrete specimens were completely disintegrated and severe corrosion was noted on carbon steel pipe. No indication of deterioration was apparent on two PC samples.

Tests of PC pipe in static 5% H₂SO₄ and in flowing 65°C water were being continued. To date no loss of strength has been detected. Comparative sections of reinforced concrete, asbestos cement, and vitrified clay exhibited strength losses.

The fabrication of a PC-lined steam separator and ancillary piping was completed. Testing at East Mesa was scheduled to commence during February 1979.

PC-lined pipe at East Mesa had not deteriorated or exhibited any scale build-up after exposure to 160°C brine for 7651 hr. The test was being continued. Carbon steel pipe had a 5-cm layer of scale after ~ 2000 hr.

Bond strength measurements were made after exposure of PC-lined pipe to flowing 280,000 ppm brine at 235°C. A strength of 8.9 MPa at 200°C was measured. No deterioration of the liner or corrosion of the steel pipe was apparent.

"Requests for Proposals" for work on high temperature seals and for the design and fabrication of PC components were being prepared for release during the second quarter of FY 1979.

Work on a study by the Burns and Roe Industrial Services Company (BRISC) to estimate the impact of the use of non-metallic materials of construction in direct utilization processes was nearing completion. Two processes, sugar beet refining and barley malting, had been evaluated. The preliminary results indicated that the substitution of a PC lining for the carbon steel corrosion allowance could reduce the cost of the brine system in a 4,536 ton/day beet refining plant by 27%. In a 1.4×10^6 lit/yr barley malting plant, the cost was reduced by 37%. Considerably larger reductions appeared feasible if prestressed PC vessels could be used.

Work in all of the above areas continued during the report period January-March 1979. Accomplishments are summarized below.

Task 1. Selection of High Temperature Materials

Work is being performed to develop polymers, polymer concrete composites, ceramics and refractory cements which can be used in geothermal processes. In a separate program,⁴ research is being performed to determine if cementing materials can be formulated for use in well completion systems at temperatures up to 400°C.

During the current report period work was continued on the development of polymer concrete (PC) containing organosiloxane (OS) and cross-linked mixtures of styrene (St), acrylonitrile (ACN), acrylamide (Aa) and methacrylamide (MAa). Studies of the interactions between polymers and inorganic fillers were performed. In-house research was started on high temperature sealing materials and a "Request for Proposal" (RFP) for work on seals was advertised. Each of these topics is discussed below.

Sealing Materials

In-house research to develop elastomeric materials was started. The following properties are required: elongation > 50%, tensile strength 2.34 MPa to 10.34 MPa and hydrolytic stability in the temperature range 200° to 400°C.

Preliminary screening tests performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) identified several aromatic-type polymers that have onset of thermal degradation temperatures (T_2) > 230°C. The materials include phenol formaldehyde-polyamide resin mixtures, styrene-polyphenylene oxide-triallyl cyanurate mixtures and polysulfones. Work to modify the properties of these systems is in progress and tests to measure the tensile strengths and elongations of the polymers and copolymers after 30 day exposures in brine at 240°C have been initiated.

Plans for subcontracted work to develop high temperature sealing materials for use in drill bit seals, packers, logging equipment and blow-out preventors have been implemented. During the report period an RFP was advertised and five proposals received. The review process is in progress and the award of one or more subcontracts will take place during May.

Styrene (St)-Acrylonitrile (ACN)-Acrylamide (Aa) -Divinyl Benzene (DVB) Copolymers

Laboratory testing of PC specimens containing varying amounts of St, ACN, Aa, and DVB in brine is continuing. These data are given in Task 3.

A simplified method for producing PC containing that monomer mixture has been developed. In previous work it was necessary to heat the monomer mixture to 45^o to 50^oC prior to mixing with the inorganic filler in order to dissolve the solid Aa. In an attempt to eliminate the heating requirement, tests were performed in which the Aa was included as a partial constituent of the aggregate. After mixing the aggregate with the other monomer constituents, the formulation was cured by use of an initiator (azobisisobutyronitrile) and heating to 60^oC.

Infrared (IR) and TGA evaluations indicated that both fabrication methods yield copolymers with the same chemical structure.

Compressive strength measurements performed at different temperatures on specimens prepared by each of the methods have also given similar results. The data, given in Figure 1, are for samples containing 11.5 wt% monomer (50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB), 62 wt% silica sand and 26.5 wt% Type III portland cement.

Figure 1. Compressive strength of St, ACN, Aa, and DVB polymer concrete at various temperatures.

Preparation method; Δ, Aa added as a solid to filler.

X, Aa dissolved in other monomers prior to mixing with filler.

Organosiloxane (OS) Polymers

A study to evaluate the effect of the cement filler composition on the properties of PC containing a 97 wt% RZ - 3 wt% V47 organosiloxane mixture has been completed. Samples were exposed to a 25% brine solution at 300°C for 60 days and the test results are summarized in Figures 2-6. The results indicate that the PCs are thermally and hydrolytically stable and that the optimum cement concentration is in the range 15 to 18 wt%. Data given in Figure 7 indicate that over the temperature range 25° to 350°C, the compressive strength of one composite formulation is essentially constant at a value of ~ 72 MPa.

A study has been started to further improve the mechanical properties of PCs containing the RZ-V47 organosiloxane mixture. In this work various additives are being included in the inorganic phase and the effects on hydrothermal stability determined. The data, given in Figure 8 and Table 1, are summarized in terms of a strength factor (α).

$$\alpha = \frac{\partial_1}{\partial_0}$$

where

∂_1 = strength after exposure to brine at 300°C.

∂_0 = initial strength.

The results to date indicate that the inclusion of MgSiO_3 , CaSiO_3 and Fe_2O_3 improves the hydrothermal stability of the composite by significant amounts. This work is being continued.

It is well known that the introduction of polar groups into the molecular chain will increase the thermal stability and the adhesion coefficient of organosiloxane polymers. Tests have been performed on

Figure 2. Compressive strength and absorption of OS PCs after exposure to brine at 300°C. OS composition, 97% RZ - 3% V47. Aggregate composition, 90% sand - 10% cement. I, Type I portland cement; II, Type II portland cement; III, Type III portland cement; V, Type V portland cement.

Figure 3. Compressive strength and absorption of OS PCs after exposure to brine at 300°C. OS composition, 97% RZ - 3% V47. Aggregate composition, 95% sand - 5% cement. I, Type I portland cement, II, Type II portland cement, III, Type III portland cement, V, Type V portland cement.

Figure 4. Compressive strength and absorption of OS PCs after exposure to brine at 300°C. OS composition, 97% RZ - 2% V47. Aggregate composition, 80% sand - 20% cement. I, Type I portland cement; II, Type II portland cement; III, Type III portland cement; V, Type V portland cement.

Figure 5. Compressive strength and absorption of OS PCs after exposure to brine at 300°C. OS composition, 97% RZ - 3% V47. Aggregate composition, 80% sand - 20% cement. I, Type I portland cement; II, Type II portland cement; III, Type III portland cement; V, Type V portland cement.

Figure 6. Compressive strengths of OS PCs, after exposure to brine at 300°C, as a function of cement type and concentration. Summary of results.

Figure 7. Compressive strength of OS PC as a function of temperature. OS composition, 97% RZ - 3% V47. Aggregate composition 90% sand - 10% Type V portland cement.

Figure 8. The effect of additives on the hydrolytic stability of OS PCs after exposure to brine at 300°C for 30 days.

Table 1

Strength Factors for OS PC Containing Additives after Exposure to Brine at 300°C

<u>Additive</u> Concentration, wt%	<u>MgSiO₃</u>			<u>CaSiO₃</u>			<u>Fe₂O₃</u>			<u>Mica</u>			<u>Carbon Black</u>	
	<u>2</u>	<u>4</u>	<u>6</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>2.5</u>	<u>1.0</u>
Strength Factors														
α_1	1.02	0.76	1.17	1.31	0.79	1.06	1.01	0.96	0.54	0.84	0.87	0.55	0.52	1.16
α_2	0.72	--	1.15	0.5	1.11	--	0.61	1.16	0.51	0.70	0.96	0.51	0.37	0.76

 α_1 , after 30 days in brine at 300°C. α_2 , after 60 days in brine at 300°CWithout additives, $\alpha_1 = 0.89$ $\alpha_2 = 0.61$

copolymers containing 97 wt% RZ and 3 wt% ACN. In a nitrogen atmosphere, the copolymer is stable up to a temperature of 400°C. Additional work in this area is planned.

Vinyl-Type Polymers

In the previous report,³ it was described that the addition of tricalcium silicate (abbreviated form C_3S) to vinyl-type PC results in mechanical and physical properties greater than those obtained from PC containing calcium carbonate, calcium hydroxide and silica flour. The results suggested that the presence of C_3S has two significant effects which tend to improve the strength and durability of PC in hot brine. The first is due to the hydration products of C_3S formed during exposure to hydrothermal conditions, and the second is due to a chemical reaction between the C_3S and the polymer.

During the current period, data regarding the effect of the reaction products on the hydrothermal stability have been obtained and a proposed reaction mechanism developed.

Polymethylmethacrylate (PMMA) was selected for use as a binder in this study and reactions between it and C_3S during exposure to brine at 240°C were evaluated. IR, TGA, DTA and mechanical tests were performed.

Results of the IR analysis are shown in Figures 9 and 10. As shown in Figure 9, the IR spectra of anhydrous C_3S is characterized by a wide absorption band occurring around 840 cm^{-1} . IR absorption bands (sample No. b) of C_3S -filled PMMA samples before exposure to brine indicate a symmetric stretching vibration of CH_2 groups at 2940 cm^{-1} , a stretching vibration of $C=O$ groups at 1710 cm^{-1} , an asymmetric and symmetric deformation vibration of CH_3 groups at 1420 cm^{-1} , and at 1130 cm^{-1} a band which

Figure 9. Infrared spectra of anhydrous C₃S and C₃S-filled PMMA: a, anhydrous C₃S grains, b, C₃S-filled PMMA before exposure to brine.

Figure 10. Infrared spectra of hydrated C₃S and C₃S-filled PMMA after exposure to hot air and hot brine: c, C₃S-filled PMMA after heating in dry oven, d, hydrated C₃S after exposure to hot brine, e, C₃S-filled PMMA after exposure to hot brine.

may be due to an asymmetric vibration of the C-O-C group.

In Figure 10, the spectra (sample No. c) for C_3S -filled PMMA samples after exposure for 10 days to hot air at $240^{\circ}C$ was observed to be similar to that of the control sample. This curve seems to demonstrate that an interaction of C_3S with PMMA molecules does not occur when the sample is exposed to hot air. The C_3S pastes were prepared with a water to C_3S ratio of 0.35, and subsequently cured under water for 7 days at $25^{\circ}C$. The IR spectra for the cured C_3S specimen after exposure for 10 days to brine at $240^{\circ}C$ is represented by the curve for sample No. d. This curve has four major absorption bands due to the C_3S hydrate at 3400, 1440, 1195, and 960 cm^{-1} . This spectra also indicates that the hydration products of C_3S can be recognized from the disappearance of the anhydrous C_3S band at 840 cm^{-1} . The IR spectra for C_3S -filled PMMA after exposure to brine (sample No. e) illustrates a very interesting curve; namely, the two new bands at 1540 and 1398 cm^{-1} . These bands represent an asymmetric stretching vibration and a symmetric stretching vibration of the COO^{-} (Ca) group, respectively, which are due to an ionic bond between Ca^{2+} ions and carboxylate anions (COO^{-}) which developed during exposure to the hydrothermal conditions. It is believed that these bonds correspond to the results reported by Leyte et al.⁵ and Crisp et al.⁶ for the IR studies of the interaction between metal oxides and an aqueous solution of polyacrylic acid.

The chemical reaction mechanisms occurring at the interface between PMMA and C_3S grains are believed to be represented by a reaction process as shown in Figure 11. As indicated in the figure, Ca^{2+} ions are released readily by the attack of the hot brine on the anhydrous C_3S grains. These Ca^{2+} ions produced in a aqueous media develop an electrostatic

Figure 11. Reaction mechanisms between C_3S and PMMA during exposure to brine.

interaction with the carbonyl groups ($-C=O^-$) which become more strongly electropositive by the elevated temperature. Thus the carboxylate group can be changed easily to the carboxylate ion ($-COO^-$) by the electrostatic interaction. The chemical effect of Ca^{2+} ions may be presumed to be a cross-linking function which connects two $-COO^-$ groups between PMMA chains and within a single chain.⁷⁻⁹ A partial Ca-PMMA complex is covered with hydration products of C_3S which form under the conditions of high temperature and pressure in the autoclave.

The thermal stability of the Ca-PMMA complex produced by the ionic bonding of Ca^{2+} ions with carboxylate (COO^-) ions was investigated by TGA and DTA analysis.

As shown in Figure 12, the TGA curve of the Ca-PMMA complex indicates that the loss of material begins to occur slowly at approximately $300^\circ C$, exclusive of the weight decrease occurring rapidly in the range 40° to $\sim 150^\circ C$ which is probably due to vaporization of neutral H_2O molecules co-ordinated to Ca^{2+} ions in Ca^{2+} bridges.¹⁰ The temperature at which $\sim 25\%$ weight loss of the complex occurs is about $570^\circ C$. Compared to the onset temperature of thermal decomposition obtained from the TGA curve for the Ca-PMMA complex, the thermal decomposition of C_3S -filled PMMA samples before exposure to brine occurs gradually around $200^\circ C$. This is $\sim 100^\circ C$ lower. This curve also indicates that the weight loss of 25% of product takes place at about $390^\circ C$.

From the DTA thermogram in Figure 12 of the Ca-PMMA complex, it can be seen that a large exothermal peak occurs at about $480^\circ C$ at the same time that the thermal degradation of the unexposed complex shows to be

Figure 12. TGA and DTA thermograms of C_3S -filled PMMA before and after exposure for 10 days to 25% brine at 240°C.

Figure 13. Isothermal degradation of the MMA- C_3S system before and after autoclave exposure.

almost finished. The broad exothermal peak at about 80°C is probably a result of the influence of neutral H_2O molecules co-ordinated to those Ca^{2+} ions in Ca^{2+} bridges, as described in the TGA curve. On the contrary, the thermogram of C_3S -filled PMMA before exposure to brine is characterized by two large exothermal peaks at about 320°C and 390°C . The peak at 390°C seems to represent the end temperature of degradation of PMMA itself.

In order to determine the thermal stability of the Ca-PMMA complex at 200° , 300° , and 350°C , tests were performed using a DuPont TGA operated in the isothermal mode. The results, given in Figure 13, indicate good thermal stability at 300°C after an initial rapid loss of weight, probably due to the neutral co-ordinated H_2O molecules. The curve at 350°C for the complex indicates a gradual weight loss with time, and probably represents the limit of its thermal stability

The curves of C_3S -filled PMMA before exposure to brine indicate a good thermal stability at 200°C , however, at 300° and 350°C there is a rapid degradation of PMMA with time.

From the results of the thermal behavior tests described above it appears that the thermal stability of the Ca-PMMA complex produced by ionic-bonding between the Ca^{2+} cations and the polyanions in a hot aqueous media is far better than that of C_3S -filled PMMA before exposure.

The physical properties of the Ca-PMMA complex were investigated from the results of compressive strength tests of polymer mortar prepared by the addition of 70 wt% silica sand to 12 wt% MMA monomer containing 18 wt% C_3S . Silica flour was also evaluated as a filler and the results compared to those from C_3S . The results given in Table 2, indicate that

Table 2
Compressive Strength of PMMA Polymer Mortar Containing C_3S or Silica Flour

Composition ^a	Compressive strength, ^b psi (MPa)		
	Before exposure	After exposure to hot air at 240°C for 10 days	After exposure to brine at 240°C for 10 days
12% P - 70% S - 18% SiO_2	11,480 (80.4)	371 (2.6)	-- ^c
12% P - 70% S - 18% C_3S	17,530 (122.7)	2,850 (20.0)	7,735 (54.2)

a - P = MMA; S = 50 wt% #16 sand (size, 1.19 mm) - 25 wt% #30 sand (size, 0.595 mm) - 25 wt% #100 sand (size, 0.149 mm); SiO_2 = silica flour; C_3S = tricalcium silicate.

b - Values are averages for two 2.2-cm-diam. x 4.4-cm-long cylinder specimens.

c - Failed (large expansion) and removed from test.

the strength of Ca-PMMA complex polymer mortar formed during the brine exposure is 54.2 MPa. However, the silica flour-filled PMMA polymer mortar specimens failed in the test as a result of the large expansion produced by the thermal decomposition of the polymer.

The strength reduction of PMMA polymer mortar containing 18% C_3S after 10 days in brine and in a dry oven at $240^{\circ}C$ was $\sim 56\%$ and $\sim 84\%$, respectively. It appears from these results that the Ca-PMMA complex formed by the hydrothermal conditions has a greater effect on the thermal stability of PMMA polymer mortar than the effect of only the interaction which occurs between the C_3S and the CH_2 group. Also, the hydration products of C_3S which are formed in the hydrothermal environment contribute significantly to the improved compressive strength of samples after exposure to brine.¹¹ Furthermore, the data suggest that the addition of only 18% C_3S to polymer mortar makes it possible to significantly improve the thermal stability to temperatures near $240^{\circ}C$.

Task 2. Process Technology

Work to develop the technology to produce PC and PC-lined pipe and vessels for use in containing geothermal fluids is continuing.

In order to provide larger quantities of prototype PC pipe for evaluation by potential users and to assist in establishing commercial sources of the material, BNL is in the process of awarding one or more subcontracts for design and fabrication of PC pipe.

During March an RFP was advertised. The RFP solicited proposals for research and development work to obtain test data required for the design and fabrication of PC pipe rated for an operating condition of 793 KPa at $120^{\circ}C$. A PC formulation consisting of a 12 wt% concentration

of a 55 wt% styrene - 36 wt% acrylonitrile - 9 wt% TMPTMA monomer mixture and 88 wt% of an aggregate consisting of 70 wt% silica sand - 30 wt% Type I portland cement was specified.

The second part of the program will include the design and fabrication of eight 1.53-m-lengths of 25.4-cm-i.d. reinforced or non-reinforced PC pipe and two 25.4-cm-i.d. 90° elbows, all hydrostatically tested and rated for service at 793 KPa pressure at 120°C. Joint configurations designed for the operating conditions will be provided on each PC section to permit the joining of the sections and installation into field test facilities.

The submission date for proposals is May 2, 1979. Award of a contract during the next report period is anticipated.

In the previous report³ plans to perform a test to determine the technical feasibility of removing scale from PC-lined pipe by use of cavitation techniques were described. This test was performed in February by Daedalean Associates, Inc. in conjunction with other descaling tests conducted at the San Diego Gas and Electric Company Geothermal Loop Experimental Facility. The results from the test indicated that it was possible to remove an ~ 5-mm-thick layer of scale from the surface of a PC-lined pipe without significant damage to the PC. Changes in the design of the nozzle would lead to further improvements.

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 non-metallic materials are being determined. Several autoclaves operated at conditions simulating geothermal environments in which field tests

are in progress or being planned are utilized in the test program.

The results from compressive strength measurements made on PC specimens containing varying amounts of St, ACN, Aa, and DVB after exposure to a 25% brine solution at 238°C for times up to 8 months are summarized in Table 3. Five compositions were evaluated. A PC containing a 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB monomer mixture in conjunction with a 70 wt% sand - 30 wt% Type III portland cement aggregate exhibited the best durability. Compared to a control strength of 180.8 MPa, the compressive strength increased to 237.6 MPa after brine exposure for 30 days and has gradually decreased to 204.1 MPa after 240 days. Based upon studies on the effects of aggregate composition, the initial increase in strength upon brine exposure was probably due to C_2S and C_3S hydration products. The subsequent decrease is due to degradation of the polymer. This PC formulation has given the highest strength and durability to brine obtained to date with an organic-based PC.

Shrinkage during curing of the St, ACN, Aa, DVB system has been a problem in producing crack-free PC pipe or liners on steel pipe. A method for solving this problem currently under investigation is to substitute polystyrene for a small fraction of the styrene. Tests to date indicate that the shrinkage of samples containing 45 wt% St - 5 wt% PSt - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB is a factor of 10 lower (1% to 0.1%) than that for a formulation containing 50 wt% St. Samples containing the former have not exhibited strength decreases or increases in water absorption after exposure to 238°C brine for 30 days. These tests are continuing.

Table 3

Compressive Strength of PC After Exposure to
25% Brine at 237°C

Monomer composition, wt%				Compressive strength (MPa) after brine exposure, days						
<u>St</u>	<u>ACN</u>	<u>Aa</u>	<u>DVB</u>	<u>Control</u>		<u>30</u>		<u>120</u>		<u>240</u>
52.5	40	5	2.5	191.6 ^a	211.9 ^a	128.2 ^b	160.9 ^a	127.9 ^b	124.7 ^a	95.6 ^b
62.5	30	5	2.5	202.4	227.0	141.9	174.9	136.4	174.2	137.9
50	40	5	5	189.5	196.1	150.9	147.3	136.0	123.8	111.4
50	37.5	5	7.5	176.6	237.1	166.2	177.8	150.4	162.6	151.2
50	35	5	10	180.8	237.6	161.9	231.9	148.3	204.1	161.7

Composite composition, 13 wt% polymer - 87 wt% aggregate

St, styrene

ACN, acrylonitrile

Aa, acrylamide

DVB, divinyl benzene

a, tested at 20°C

b, tested at 150°C

Each value is the average of 2 specimens.

Testing of commercially supplied proprietary organic coating materials which were applied to steel rods by the vendor is continuing. In the previous report³ observations after 60 days in 25% brine at 238°C were given. One sample failed completely after 30 days and blisters were apparent on the remaining three samples after exposure for 60 days. To date after 90 days in test, continued blistering, cracking, and peeling is apparent.

In Report No. 12¹², tests in which PC samples were being exposed to pH 1 hydrochloric acid at 90°C were described. Samples containing the following monomer mixtures were being tested: 60 wt% St - 40 wt% TMPTMA, 55 wt% St - 36 wt% TMPTMA - 9 wt% Hetron 197, and 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA. Figure 14 shows the samples after exposure for 236 days. The concrete control specimen failed (21% weight loss) after 21 days but no attack on the PC was evident as determined by pH and weight change measurements.

During the current report period the test was terminated after a total exposure time of 2 yr. Comparison of the samples as shown in Figures 14 and 15 indicates no appreciable change in appearance. The weight of the specimens and the pH of the acid solution also remained essentially constant.

In Figure 15 a specimen (identified R5) containing 80 wt% St - 12 wt% polyphenylene oxide (PPO) - 8 wt% TMPTMA used in conjunction with a 70 wt% sand - 30 wt% cement filler is also shown. This PC did not deteriorate after 1 yr in test.

Figure 14. PC after exposure to pH 1 hydrochloric acid at 90°C for 236 days. Concrete control failed after 21 days.

No. 544, 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA

No. 549, 55 wt% St - 36 wt% TMPTMA - 9 wt% Hetron 197

No. 434, 60 wt% St - 40 wt% TMPTMA

Figure 15. PC after exposure to pH 1 HCl at 90°C for 2 yr.

No. 549, 55 wt% St - 36 wt% TMPTMA - 9 wt% Hetron 197

No. 544, 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA

No. R-5, 80 wt% St - 12 wt% PPO - 8 wt% TMPTMA

No. 434, 60 wt% St - 40 wt% TMPTMA

Task 4. Field Tests

In previous reports, results from tests performed at The Geysers, Baca Wells, Klamath Falls, Raft River and East Mesa were given. Tests are currently in progress at East Mesa, Coso Hot Springs, Devils Kitchen, San Diego Gas and Electric, and Fenton Hill. The status of each of the on-going tests and results from evaluations performed on samples returned from Raft River during the report period are summarized below.

Raft River

Testing of PC samples in the "Raft River Mobil Corrosion, Deposition and Components Test Laboratory" was started in September 1976. A description of the specimens and the test section was given in Report No. 8.¹³ The test conditions were as follows: temperature 135°C, flow rate 755 lit/min, and pressure 896 KPa.

In Report No. 11¹⁴ data for two PC formulations, 50 wt% St - 33 wt% ACN - 17 wt% TMPTMA, and 60 wt% St - 40 wt% TMPTMA, both containing a 90 wt% sand - 10 wt% flyash aggregate, after 90 days in test were given. Twenty specimens were evaluated. The St-ACN-TMPTMA exhibited small weight increases (~ 1%), increased water absorption from ~ 1.1% to 2.1% and reductions in compressive strength from an average of 109 MPa to 74.6 MPa. Samples containing 60 wt% St - 40 wt% TMPTMA exhibited slight weight losses (~ 0.6%), increased absorption and a decrease in strength from 103 MPa to 69 MPa. Work performed after these tests were initiated indicated that the deterioration can be prevented by the inclusion of portland cement in the aggregate (Task 1).

Data for the above systems after 2 yr in test are now available. These results indicate better durability for the St-ACN-TMPTMA system, but when compared to 90 day results, both materials exhibited further degradation. The compressive strength of samples containing the St-ACN-TMPTMA formulation decreased 7.6% to 68.9 MPa and the water absorption increased ~ 126% to an average of 4.75%. The strength of the St-TMPTMA formulation decreased to 49 MPa (~ 29%) and the absorption increased to 3.25%.

As expected, samples containing portland cement have not exhibited any appreciable deterioration after exposure for 18 months. These data are summarized in Table 4. The results indicate that for the three cement contents investigated, strength increases rather than decreases occurred during the hydrothermal exposure. This has been observed in laboratory tests (see Table 3) and is due to C_2S and C_3S hydration products. The results also support earlier observations that the optimum cement concentration is in the range of 20 to 30 wt%.

A 1.2-m section of 15-cm-diam Sch 40 steel pipe that contained a 2.54-cm-thick PC liner was returned to BNL after exposure for ~ 2 yr. The liner consisted of a monomer mixture of 70 wt% Derakane - 30 wt% triallyl cyanurate and an 80 wt% silica sand - 20 wt% calcium aluminate cement aggregate. Pictures of the section were given in Report No. 12.¹² Visual inspection indicated the surface to be smooth and free of cracks. No scale accumulation or erosion damage was evident. Measurements of the bond strength to the steel and the strength of the PC are being made but the results are not yet available.

Table 4

Properties of PC After Exposure for 18 Months at Raft River

<u>Aggregate</u>		<u>Controls</u>		<u>PC After Exposure</u>		<u>Water</u> <u>absorption, %</u>
<u>sand</u>	<u>cement</u>	<u>Compressive</u> <u>strength, MPa</u>	<u>Water</u> <u>absorption, %</u>	<u>Compressive strength, MPa,</u> <u>at 23°C</u>	<u>at 150°C</u>	
90	10	85.4	0.92	151.7	110.6	1.7
80	20	88.5	1.28	174.8	136.4	1.7
50	50	88.5	1.49	140.7	130.5	3.1

Exposure temperature 135°C.

Composition, 12 wt% monomer - 88 wt% aggregate.

Monomer, 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA.

Each data point represents average of 6 samples.

East Mesa

Testing of two 2.4-m sections of PC-lined carbon steel pipe is being continued at the East Mesa Geothermal Site. The liners are composed of a 60 wt% St - 40 wt% TMPTMA monomer mixture used in conjunction with a 70 wt% sand - 30 wt% Type III portland cement. One section has been exposed to brine flowing from wells 8-1 and 6-2 at a rate of 226-302 lit/min and a temperature of $\sim 160^{\circ}\text{C}$ for ~ 9810 hr. No deterioration or scale accumulation has been detected. An ~ 5 -cm layer of scale accumulated on carbon steel pipe downstream of the PC test section in ~ 2000 hr.

The second section is being exposed to flashing brine. After ~ 7100 hr, no deterioration or scale accumulation is apparent. The condition of the pipe at the time of the last inspection is shown in Figure 16.

The prototype PC-lined carbon steel steam separator and ancillary piping, described in the previous report,³ were installed and the test started in February. The unit is shown in Figure 17. The unit has been operated for 30 days with no apparent scale build-up on the walls of the separator. However, the small diameter brine discharge line and scale build-up in steel pipe downstream has on several occasions restricted the flow to the point that the brine level in the vessel has become excessive, thereby causing shutdown. Plans to increase the size of the line to 15-cm have been made.

U. S. Naval Weapons Center

Sections of PC and PC-lined pipe have been in test since May 1978 at two locations, Devils Kitchen and Coso Hot Springs. Both test sites are shallow steam pockets delivering ~ 135 and 320 kg/hr, respectively, of steam at $\sim 105^{\circ}\text{C}$. Both tests were continued throughout the report period.

Figure 16. PC-lined pipe after exposure for ~ 7100 hr to flashing brine at 160°C . No scale accumulation was observed.

Figure 17. PC-lined steam separator (right) and PC-lined pipe installed at East Mesa.

Small corrosion test coupons (5.1-cm-diam x 6.35-mm thick) have been prepared and shipped to the site for exposure to higher temperature fluids. Start-up of the test has been delayed.

San Diego Gas and Electric Company (SDG&E)

Sections of PC-lined pipe and small cylindrical specimens are currently being tested at the SDG&E Geothermal Loop Experimental Facility at the Salton Sea. One ~ 25-cm-diam pipe section has been installed in the brine reinjection line since August 1978. A PC formulation consisting of 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA and 70 wt% sand - 30 wt% Type III portland cement was used for the liner. In the reinjection line the flow rate is typically 190 lit/min and the temperature ~ 93°C. Results from the first inspection of the section were given in Report No. 16.¹⁵ At that time no signs of abrasion or erosion were apparent. No additional information has been supplied since that time.

A similar section has been installed between the first and second stage steam separators. To date a report on its' performance has not been received.

Cylindrical PC samples installed in the second steam separator in August 1978 have been removed and shipped to BNL. Data from these will be given in the next report.

Los Alamos Scientific Laboratory (LASL)

Testing of PC-lined pipe, elbows and test cylinders was initiated in October 1978 at the LASL Fenton Hill hot rock geothermal site. The test was run without difficulty until late fall when operations were suspended to permit remedial cementing of the well. A date for resumption of the test has not been received.

Task 5. Technology Transfer and Economic Evaluation

Studies to identify areas in geothermal processes where the use of non-metallic materials such as plastics, concrete polymer composites and refractory cements can favorably affect the economics of the processes are continuing.

Work to evaluate direct utilization processes has been performed as a subcontract with the Burns and Roe Industrial Services Corporation (BRISC). A report has been written.² The Executive Summary and Conclusion are given below.

Applied research and development and technical management of the Department of Energy (DOE) national program on development of non-metallic materials of construction for geothermal applications is being performed by BNL. As part of this effort, BRISC was engaged to assess the cost effectiveness of these materials in three processes which were designed for direct utilization of geothermal energy. The results of this assessment indicate that significant cost savings could be achieved by using non-metallic materials in processes utilizing water at temperatures up to about 150°C.

An extensive review of the available literature was conducted by BRISC in order to ascertain those processes for which sufficient design and cost data had been published to permit this economic assessment to be made. Only three such processes could be found as of September 1978. While there are undoubtedly many other applications in which non-metallic materials could be profitably utilized, the published design and cost data for these was not detailed enough to permit a comparative cost estimate to be made.

Coury and Associates, Inc. developed complete process details for the production of 4536 ton/day of crystal sugar from beets and for malting 141 million lit/yr of barley for use in the brewing industry. In both cases, the process has been adapted to use a geothermal fluid as the main process energy source.

LLC Geothermal Consultants performed a conceptual design study for a geothermal district heating system in Klamath Falls, Oregon. Four different piping material (metallic and non-metallic) combinations were considered in their study.

From the results of this investigation it is concluded that the total cost of the vessels and piping in typical geothermal fluid systems could be reduced significantly through the use of non-metallic materials. The estimated savings for the sugar beet plant are indicated below:

	<u>Metallic design w/ corr. allow.</u>	<u>Epoxy lined vessels & PC pipe</u>	<u>PC lined vessels & PC pipe</u>
Cost of Vessels & Piping (delivered)	\$566,030	\$321,720	\$370,430
% Savings	Base	43%	35%

The above capital cost savings translate to a reduction in energy cost of \$.05-\$.06/10⁶ Btu (\$.047-\$.057/10⁹ J), which represents a savings of about 2%. The impact on energy cost appears relatively low because the total cost of the vessels and piping discussed only represents about 5% of the total geothermal plant capital cost.

Similarly, for the barley malting plant, the savings attributable to the use of non-metallic materials are shown below:

	<u>Metallic design w/ corr. allow.</u>	<u>Epoxy lined vessels & PC pipe</u>	<u>PC lined vessels & PC pipe</u>
Cost of Vessels & Piping (delivered)	\$150,590	\$92,600	\$96,620
% Savings	Base	39%	36%

These capital cost savings for the barley malting plant are equivalent to an energy cost savings of \$.05-\$.06/10⁶ Btu (\$.047-\$.057/10⁹ J) which is a savings of 2%.

In the district heating system study, two types of in-ground pipe installation alternatives were discussed. The first was a direct burial approach where the pipe and insulation were enclosed in a protective jacket. The second alternative involved installation of the insulated pipe in a concrete box or trench which had a removable top for access. For each installation alternative, the following tables compare the estimated piping system costs for various metallic and non-metallic piping materials:

Direct Burial

	<u>Steel pipe FRP jacket</u>	<u>FRP pipe FRP jacket</u>	<u>AC pipe AC jacket</u>	<u>PC pipe PC jacket</u>
Cost of Piping & Insulation (installed)	\$956,000	\$969,000	\$726,000	\$698,000
% Savings	Base	-1%	24%	27%

Concrete Trench

Cost of Piping & Insulation (installed)	\$1,364,000	--	--	\$1,183,000
% Savings	Base	--	--	13%

For the direct burial case, the energy cost savings attributable to the use of AC or PC pipe in lieu of steel are $\$0.26/10^6$ Btu ($\$.25/10^9$ J) (12%) and $\$0.30/10^6$ Btu ($\$.28/10^9$ J) (13%), respectively. For the concrete trench case, the energy cost savings obtained by using PC pipe is $\$0.25/10^6$ Btu ($\$.24/10^9$ J) (9%).

Based on the projected direct usage of geothermal energy in the Rocky Mountain area of the USA by the year 2000, the energy cost savings are in the range of $\$50 \times 10^6$ to $\$300 \times 10^6$.

Other conclusions drawn from this study are as follow:

1. The cost of epoxy coating or polymer concrete (PC) linings on carbon steel tanks and pressure vessels is less than the cost of providing adequate corrosion allowances for many geothermal applications.
2. The use of prestressed and reinforced solid PC tanks and vessels may result in a cost savings of 50-70% relative to the cost of carbon steel units with a polymer concrete lining. A more detailed feasibility study of this approach should be performed.
3. Available data indicates that for pipe sizes 50-cm and under, asbestos cement (AC) or solid PC pipe is more economical than carbon steel pipe for geothermal applications, even where corrosion is not a major consideration. The same applies to fiberglass reinforced plastic (FRP) pipe in sizes up to 20-cm. However, further technical development is required before AC, FRP, and PC pipes could be specified commercially for these applications.
4. The use of solid PC pipes may be more economical than PC linings for sizes up to 50-cm in diameter, assuming practical solutions to the technical issues discussed earlier can be found.

5. While the results of this study indicate that large FRP pipe is equivalent in cost to steel pipe, the former may have an advantage in systems handling more corrosive fluids where corrosion allowances would be required on the steel pipe.

6. Further improvements in the tensile strength of PC pipe will further enhance the attractiveness of using it.

Task 6. Administrative

During the current report period, three "Project Status Reports" were submitted to DGE and Progress Report No. 17³ was issued. Two papers "High Temperature Polymer Concretes from Organosiloxane Resins"¹⁶ and "The Effect of Tricalcium Silicate on the Thermal Stability of Condensation-Type Polymer Concretes"¹⁷ have been accepted for publication in The International Journal of Cement Composites. Another paper¹⁸ "Hydrothermal Stability of Vinyl-Type Polymer Concrete Containing Tricalcium Silicate" has been submitted to Cement and Concrete Research.

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