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ALTERNATE MATERIALS OF CONSTRUCTION FOR GEOTHERMAL APPLICATIONS

PROGRESS REPORT NO. 19
APRIL-JUNE 1979

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Abstract

A program to develop nonmetallic 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 two of these sites is continuing and plans to initiate tests at other sites are being implemented. Construction of full-scale pipe sections by a commercial firm has started. Work has also been started to develop materials for use in high temperature seals for well drilling, logging and energy extraction processes. Work accomplished during the period April-June 1979 is described in the current report.

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Summary

The following are the highlights of the April-June 1979 activities under the Alternate Materials of Construction for Geothermal Applications Program.

Task 1. L'Garde, Inc. work has resulted in the development of high temperature ($\sim 260^{\circ}\text{C}$) elastomers for casing packer seals. The data indicate that the compounds are superior to commercially available materials. As a result, a contract has been awarded to L'Garde to assist in transferring the technology to industry.

Task 2. The technical feasibility of scale removal from polymer concrete pipe by use of cavitation techniques has been demonstrated.

Task 3. Laboratory testing of styrene-acrylonitrile-acrylamide-divinyl benzene polymer concrete indicates no deterioration after one year in 25% brine at 238°C .

Task 4. Visual inspection of polymer concrete pipe sections in test at the U. S. Naval Weapons Center for ~ 14 mo indicated the pipe to be in relatively good condition. The inside of the pipes were unattacked but the external surfaces were mildly etched from H_2S .

Test cylinders exposed to 182°C brine in a steam separator at the SDG&E facility for 1379 hr did not deteriorate.

Task 5. A study to determine the potential cost impact of the use of nonmetallic materials in shallow wells utilized in direct utilization and ground water-coupled heat pump applications has been started. The work is being performed by the National Water Well Association.

Alternate Materials of Construction for
Geothermal Applications
Progress Report No. 19
April-June 1979

Introduction

A serious problem in the development of geothermal energy is the availability of durable and economic materials of construction for handling hot brine and steam. Hot brine and other aerated geothermal fluids are highly corrosive materials and they chemically attack most conventional materials of construction. Corrosion and scale incrustations have been encountered in all geothermal plants, and to various degrees, adversely affected plant lifetimes and power output. To date, carbon steel has been the primary material of construction but the use of more expensive materials may be required to insure long-term operation.

The availability of low-cost materials with suitable properties will be a big step toward the development of a stable geothermal industry. As a result, a program to develop nonmetallic construction materials was started. Calculations indicate that if successfully implemented, the use of 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 nonmetallic 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 times of ~ 2 years are available. Results are also available from field exposures of up to 2 years in six geothermal environments. Good durability is indicated. Work at two 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 another study indicate that capital cost reductions up to 13% can be attained in a district heating application.²

The scope of the BNL program has been broadened in FY 1979 to include investigations of other nonmetallic 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 is managing 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 are being undertaken. The efforts include development of prototype equipment and the demonstration of the applications of the new materials. The work is being performed with potential geothermal plant owners in order to establish the groundwork for rapid implementation and to transfer the technology to industry.

Highlights of the previous progress report³ are summarized below.

Polymer concrete (PC) containing organosiloxane polymers was 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° to 350°C. Possible applications include protective liners and elastomeric seals. Work to extend the stability to 400°C was in progress.

PC containing 50 wt% styrene - 35 wt% acrylonitrile - 5 wt% acrylamide - 10 wt% divinyl benzene 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 was 204 MPa at 20°C and 162 MPa at 150°C.

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

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

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

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

A study on the economic impact of the use of nonmetallic materials of construction in direct utilization processes was completed. Reductions in capital costs which translate into lower energy costs ranging from \$0.06/10⁶ Btu to \$0.30/10⁶ Btu were calculated.

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

Task 1. Selection of High Temperature Materials

Work is being performed to develop polymers, 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 crosslinked mixtures of styrene (St), acrylonitrile (ACN), acrylamide (Aa) and

methacrylamide (MAa). Studies of the interactions between polymers and inorganic fillers and on high temperature sealing materials were also continued.

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

Earlier results⁵ have indicated that PC containing mixtures of St, ACN, and Aa have excellent high temperature and chemical stability. Further improvements can be obtained by the inclusion of a crosslinking agent such as DVB.

The results from long-term testing of several formulations in brine at 238°C are given in Task 3. It was observed that the strength increases during exposure to brine. This is due primarily to a reaction between the brine and the dicalcium and tricalcium silicate components (C₂S and C₃S) in the portland cement filler to form thermodynamically stable needle-type tobermorite crystals.

Experiments to optimize the formulations have been performed. It was observed that increasing the DVB concentration from 2.5 wt% to 10 wt% increased the compressive strength after brine exposure by 30%. The volume expansion after exposure also decreased with increasing amounts of DVB. Water absorption decreased with increasing strength.

A monomer mixture consisting of 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB was used in experiments to optimize the monomer loading with respect to the PC properties. The samples contained from 13.0 to 27.5 parts of the monomer formulation to 100 parts of the aggregate. The latter consisted of 70 wt% sand and 30 wt% Type III portland cement. The results from this work, shown in Figure 1, indicate that in the range of 13 to 20

parts of the monomer mixture (concentration range 11.5 to 16.7 wt%), the compressive strength ranges from 152 MPa to 142 MPa. Beyond that concentration range the strength decreases markedly. The same effect was observed for the water absorption.

Figure 2 shows the effect on strength of changing the sand to cement ratio in the filler. The results indicate that the highest strength PC with the lowest water absorption is produced when 65 to 90 parts of sand are used with 35 to 10 parts of cement.

Organosiloxane (OS) Polymers

Based upon the favorable results obtained in earlier experiments,³ long-term tests on several formulations have been started. The tests are being performed in a 25% brine solution at 300°C. The first results from these tests will be available during the next report period.

Sealing Materials

Work at L'Garde, Inc. performed under a DOE/DGE contract has resulted in the development of high temperature ($\sim 260^{\circ}\text{C}$) elastomers for casing packer seals. L'Garde data and corroborating results from Sandia Laboratories indicate that the compounds are superior to those that are commercially available for the geothermal environment. For the test conditions, L'Garde's EPDM looks the best for the packer seal, but the current best Viton, EPDM/Viton, and AFLAS compounds, all sealed successfully as well. A report describing this work is being prepared.⁶

BNL has awarded a contract to L'Garde to continue the development of these materials and to assist companies in assimilating the technology. This is discussed in Task 5.

Figure 1. Compressive strength of St-ACN-Aa-DVB PC as a function of monomer content.

Figure 2. Compressive strength of St-ACN-Aa-DVB PC as a function of the sand and cement ratio in the filler.

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 an earlier report⁷, plans 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 1979 by Daedalean Associates, Inc. in conjunction with other descaling tests conducted at the San Diego Gas and Electric Company Geothermal Loop Experimental Facility. During the current period, a written report on the work was received.⁸

A cleaning head with a four nozzle configuration was used in the test. The standoff distance from the nozzle to the scale was about 38 mm and the path width on the scale surface for each nozzle was 19 mm.

The test was begun at a supply pressure of 6.89 MPa and increased at 6.89 MPa increments up to the scale removal threshold. When this point was attained, the cleaning operation began and the time to remove the scale from 2/3 of the pipe length (24 cm) was measured.

The scale removal threshold pressure was achieved at 48.3 MPa. At this pressure the scale could be removed without damaging the PC coating. It required 9 min to remove the ~ 5-mm thick layer of scale from the test section. Multiple passes were made with the hand operated cleaning lance until the scale was removed. A crude centering device was used to keep the cleaning head centered in the pipe, thereby equalizing the erosion intensities seen by the inner pipe surfaces and preventing any erosion of the PC material.

Although the operating parameters were by no means at optimum values for this test, the results obtained look encouraging. The scale was

removed from the PC without erosion damage to the liner. With additional work, it is expected that the descaling time could be reduced substantially.

In order to provide larger quantities of PC pipe for evaluation by potential users, and to assist in establishing commercial sources of supply, BNL has awarded a contract to the Lindsey Manufacturing Company of Azusa, California. The work involves the design and testing of joint configurations for service at 793 KPa at 120°C and the fabrication of 25.4-cm-i.d. pipe and elbows. It is anticipated that components will be available in the Spring of 1980 for testing in direct utilization processes.

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 nonmetallic 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.

Long-term testing of PC specimens containing varied amounts of St, ACN, Aa, and DVB in a 25% brine solution at 238°C has been completed. Data for exposure times up to 1 yr are given in Table 1. The samples are shown in Figure 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 gradually decreased to 204.1 MPa after 240 days. After one year the strength was 214.8 MPa. During the exposure the boiling water absorption increased from 0.2 to 0.9%.

Table 1

Compressive Strength of PC After Exposure to
25% Brine at 238°C

Monomer composition, wt%					Compressive strength (MPa) after brine exposure, days							
St	ACN	Aa	DVB	Control	30		120		240		360	
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	133.5 ^a	99.5 ^b
62.5	30	5	2.5	202.4	227.0	141.9	174.9	136.4	174.2	137.9	132.4	115.8
50	40	5	5	189.5	196.1	150.9	147.3	136.0	123.8	111.4	123.9	113.6
50	37.5	5	7.5	176.6	237.1	166.2	177.8	150.4	162.6	151.2	134.1	115.0
50	35	5	10	180.8	237.6	161.9	231.9	148.3	204.1	161.7	214.8	146.4

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.

Figure 3. PC samples after 360 days exposure in 25%
simulated brine solution at 238°C.

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 9.5% decrease is due to degradation of the polymer. A similar reduction in strength was exhibited for samples tested at 150°C. 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 40 wt% St - 10 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 above monomer/polymer mixture used in conjunction with a 70 wt% SiO_2 - 30 wt% portland cement filler have been exposed in an autoclave to brine at 238°C for 120 days. Compared to a control value of 88.5 MPa, the average strength has gradually increased to a value of 121.8 MPa at 120 days. The strength increase is probably due to C_2S and C_3S hydration products. The water absorption has increased from 0.97 to 1.73% over the same period. The lower strengths of these samples compared with those given in Table 1 for samples without polystyrene are probably due to the polystyrene acting as a plasticizer.

Task 4. Field Tests

In previous reports, results from tests performed at The Geysers, Baca Wells, Niland, Klamath Falls, Raft River, and East Mesa were given. Tests are currently in progress at East Mesa and at the San Diego Gas and

Electric Company Geothermal Loop Experimental Facility at the Salton Sea. Start-up of tests at Fenton Hill is expected in the near future. The status of each of the on-going tests and results from visual inspections performed on pipe samples currently being returned from the U. S. Naval Weapons Center are summarized below.

Raft River

In the previous progress report,³ data were given for samples that had been exposed to 135°C brine in the "Raft River Mobile Corrosion, Deposition and Components Test Laboratory" for 18 and 24 months. The results indicated that the strengths of C₂S and C₃S-containing PC increased during exposure from 60 to 97%. Samples without the reactive fillers exhibited strength reductions ranging between 37 and 52%. Figure 4 shows the samples after removal from test.

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 ~ 160°C for ~ 12,000 hr. At the time of the last visual inspection (~ 9800 hr), no deterioration or scale accumulation was detected. An ~ 5-cm layer of scale accumulated on carbon steel pipe downstream of the PC test section in ~ 2000 hr.

The second section has been exposed to flashing brine for ~ 9500 hr. After ~ 7100 hr, no deterioration or scale accumulation was apparent.

Figure 4. PC samples after exposure for 18 months to 135°C flowing brine at Raft River. Samples No. 568 and 583 contain SiO_2 -flyash fillers, all others contain SiO_2 -Type III cement.

Figure 5. Scale accumulation on the lower side of a steam separator being tested at East Mesa.

The prototype PC-lined carbon steel steam separator and ancillary piping, described in an earlier progress report,⁵ were installed and the test started in February. The unit has been operated for ~ 120 days. During that period scale has accumulated in the brine discharge line and on the wall of the vessel. This has resulted in the brine level in the vessel becoming excessive thereby causing shutdown. Figure 5 shows the scale accumulation in the vessel after one shutdown. The rate of build-up appeared less than that for a similarly-sized steel vessel and the scale does not appear to adhere as well to the surface. Operation of the vessel is continuing.

U. S. Naval Weapons Center

Exposure of sections of PC and PC-lined pipe at Coso Hot Springs and Devil's Kitchen was terminated on June 25, 1979 and the samples have been shipped to BNL.

The test at Coso Hot Springs was initiated on April 5, 1978. In this test, each pipe section was exposed to 98°C steam at a flow of 27 kg/hr. This equates to a velocity of 7.9 m/sec.

At Devil's Kitchen, the temperature, flow and velocity conditions were 98°C, 13.6 kg/hr and 3.3 m/sec, respectively.

Visual inspection⁹ indicated the samples to be in relatively good condition. The casting marks from the mandrel were still discernible on the internal surfaces. The external surfaces on the PC pipe were mildly etched from the H₂S environment and the identification numbers faded considerably.

Upon receipt at BNL, the mechanical properties of the sections will be determined.

San Diego Gas and Electric Company (SDG&E)¹⁰

Sections of PC-lined pipe are being tested at the SDG&E Geothermal Loop Experimental Facility at the Salton Sea. One ~ 25-cm-diam pipe has been installed in the injection line since May 1978 and has undergone daily pigging.

Another 25-cm-diam section was originally installed in a non-pigged bypass loop in the injection line. However, in this location it scaled badly and in December 1978 it was reinstalled in one of the production lines. Operation of both sections is continuing.

Evaluation of cylindrical PC specimens that were exposed in the second steam separator to brine at 182°C and a pressure of 813 KPa for 1379 hr, was completed. Visual inspection indicated the samples to be crack-free and relatively free of scale. The cylinders after exposure are shown in Figure 6.

Six PC formulations were tested and the results are summarized in Table 2. With the exception of specimens containing polyphenylene oxide (Samples No. 5 and 6), all of the materials increased in strength during the exposure. The results for samples containing St-ACN-Aa-DVB were in excellent agreement with laboratory data (see Table 1).

Plans are being made to fabricate two additional sections of 25-cm-diam PC-lined pipe which will be installed in a new injection pipeline where it will be exposed to a clarified, non-scaling brine and will not be pigged. The operating temperature will be ~ 100°C. Fabrication of the sections during the next report period is expected.

Figure 6. PE samples after exposure in steam separator brine at 182°C. Sample formulations given in Table 2.

Table 2

PC Samples Tested at SDG&E - Summary of Results

Sample No. ^a	Monomer composition, wt%	Aggregate composition, wt%		Boiling water absorption, %		Compressive strength, MPa		
		SiO ₂	Type III cement	Before	After	Before ^b	After ^{b,c}	
1	55 St - 36 ACN - 9 TMPTMA	80	20	--	0.77	127.1	148	--
2	55 St - 35 ACN - 5 Aa - 5 TMPTMA	70	30	0.28	0.54	174.3	223	154
3	50 St - 40 ACN - 5 Aa - 5 DVB	70	30	0.27	0.52	189	217	156
4	75 St - 25 Y-9208	90	10	0.06	0.07	40.2	66	44
5	80 St - 12 PPO - 8 TMPTMA	70	30	0.10	0.58	131.2	105.8	29.9
6	80 St - 12 PPO - 8 DVB	70	30	0.11	0.26	146.6	86.6	17.7

St, styrene
 ACN, acrylonitrile
 TMPTMA, trimethylolpropane trimethacrylate
 Aa, acrylamide
 DVB, divinyl benzene
 Y-9208, organosiloxane
 PPO, polyphenylene oxide

Exposure time in brine, 1379 hr
 Brine temperature, 182°C
 Brine pressure, 813 KPa

a, refers to numbers in Figure 6
 b, measured at 25°C
 c, measured at 182°C

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

As part of the effort to transfer the technology developed in the R&D phases of the program, two contracts have been awarded. The contracts will provide larger quantities of materials for testing and to establish commercial sources of supply for the geothermal industry.

As discussed in Task 2, the Lindsey Manufacturing Company of Azusa, California is designing and will produce 25.4-cm-diam PC pipe rated for service at 793 KPa at 120°C. With this background, they will be able to commercially produce PC components for direct and electric generation processes.

Technology transfer on high temperature elastomers is also progressing. In an earlier DGE project entitled, "Geothermal Elastomeric Materials Program" (GEM), L'Garde, Inc. of Newport Beach, California, developed compounds which are superior to those that are commercially available for the geothermal environment. Under a new contract, L'Garde will assist companies in assimilating the GEM technology and continue development of high temperature materials.

Economic studies are continuing. In earlier studies,^{1,2} the potential impact of the use of alternate materials in electric generation and direct utilization processes was determined. During the current report period a

contract was awarded to the National Water Well Association for a study to determine the impact on the cost of shallow wells utilized in direct utilization and ground water-coupled heat pump applications. The work started on June 1, 1979.

Task 6. Administrative

During the current report period, three "Project Status Reports" were submitted to DGE and Progress Report No. 18³ was issued. Papers entitled, "Hydrothermal Stability of Vinyl-Type Polymer Concrete Containing Tricalcium Silicate"¹¹ and "Development of Cement for Geothermal Wells"¹² have been published. Another paper¹³ "Interaction Mechanisms Between Polymethylmethacrylate and Tricalcium Silicate" has been accepted for publication in the Journal of Applied Polymer Science.

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