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ALTERNATE MATERIALS OF CONSTRUCTION FOR GEOTHERMAL APPLICATIONS

PROGRESS REPORT NO. 17
OCTOBER - DECEMBER 1978

PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
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Abstract

A program to determine if non-metallic materials such as polymers, concrete polymer composites, and refractory cements can be utilized as materials of construction in geothermal processes is in progress. To date, 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 (500°F), and economic studies started. Laboratory data for exposure times > 2 years are available. Results are also available from field exposures of up to 24 months in four geothermal environments. Good durability is indicated. Work at five of these sites is continuing and plans to initiate other tests are being implemented. Work accomplished during the period October - December 1978 is described in the current report.

Summary

Polymer concrete (PC) containing organosiloxanes appears hydrothermally stable in brine at 300°C. The results to date indicate that the optimum properties for either of the two organosiloxane systems tested (75 wt% Y-9208 - 25 wt% styrene or 97 wt% RZ - 3 wt% V47) occur when an aggregate consisting of < 30µm silica flour is 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 is being determined.

The thermal stability of high temperature vinyl-type polymers can be further increased by the use of tricalcium silicate as a filler material. With condensation-type polymers such as phenol formaldehyde (PFR), epoxy and furan, only the PFR appears to react with C_3S although the reaction mechanism is different.

A test to determine the resistance of PC pipe to acid soil conditions has been 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 flowing 65°C water and 5% H_2SO_4 are in progress. To date no loss of strength has been detected. Comparative sections of reinforced concrete, asbestos cement and vitrified clay have exhibited strength losses.

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

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

Bond strength measurements have been 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 are being prepared for release during the second quarter of FY 1979.

A partial draft of a Burns and Roe Industrial Services Company report on the impact of the use of non-metallic materials of construction in direct utilization processes has been received. To date, two processes, sugar beet refining and barley malting, have been evaluated. The results indicate that the substitution of a PC lining for the carbon steel corrosion allowance can reduce the cost of the brine system in a 5,000 ton/day beet refining plant by 27%. In a 4×10^6 bushel/yr barley malting plant, the cost is reduced by 37%. Considerably larger reductions are feasible if prestressed PC vessels can be used.

Alternate Materials of Construction for Geothermal Applications

Progress Report No. 17
October - December 1978

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 expensive materials such as Type 316 stainless steel and titanium base alloys may be required to insure long-term operation.

The identification of materials with suitable properties will be a big step toward the development of a stable geothermal industry. If successfully implemented, this program could result in a reduction of 10 to 20% in the cost of geothermal power. Considerable cost benefits in direct utilization processes are also anticipated.

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 at Brookhaven National Laboratory (BNL)

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 > 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 five test sites is in progress. These results 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 Reductions in the capital cost of direct utilization processes are also expected.

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 on the development of sealing

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.

Work performed in the program during the period October-December 1978 is described in the current report.

Summary of the Previous Report²

Polymer concrete(PC) containing organosiloxanes or a cross-linked mixture of styrene, acrylonitrile and acrylamide appeared to have excellent thermal and chemical resistance. Samples containing these materials exhibited essentially no change in strength after exposure to brine at 238°C for 120 days. Other monomer systems exhibited initial reductions followed by a leveling off in strength. Organosiloxane PC also has excellent high temperature strength. At 350°C, the compressive strength was ~ 35 MPa.

A test to determine the feasibility of using a cavitating system to remove scale from PC surfaces was performed. The results indicated that the threshold intensity of erosion for the PC was considerably lower than that of geothermal scale. This is a disadvantage which probably

can be overcome by the development of a nozzle with an immediate reduction in the effective range of intensity. This would allow removal of the scale without damage to the PC liner.

Field testing of small test samples and prototype sections of PC-lined pipe was in progress at Coso Hot Springs, Devils Kitchen, East Mesa, and the San Diego Gas and Electric Company facility at the Salton Sea. Visual inspections of the materials indicated good durability.

Test samples had been returned to BNL after testing in steam at The Geysers and high salinity brine at the Bureau of Mines facility at the Salton Sea. Evaluation of the materials was in progress.

A test configuration was installed at the Los Alamos Scientific Laboratory Fenton Hill site. Start-up of the test in October was anticipated.

Based upon the good durability and scale-free service exhibited by PC-lined pipe after an eight month test at East Mesa, a lined steam separator was being fabricated. It was anticipated that the unit would be installed during the next report period.

Studies to determine the economic impact of the use of non-metallic materials in direct utilization processes were in progress. Two processes, barley malting and sugar beet refining, were being evaluated. The performance of a similar analysis on a district heating application was scheduled.

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,³ 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 PC containing organosiloxane (OS) and crosslinked mixtures of styrene (St), acrylonitrile (ACN), acrylamide (Aa), and methacrylamide (MAa). Recent data for the latter system are given in Task 3, Physical and Chemical Property Measurements. Work to study interactions between polymers and inorganic fillers was also continued. Previous work indicated that significant improvements in properties could be obtained by the use of reactive filler materials.

Organosiloxanes are chemically resistant and can be made hydrothermally stable by crosslinking. Both properties are very important for geothermal applications.

In the previous report² initial studies to determine the thermal and hydrolytic stability and strength of PC specimens containing organosiloxanes were described. Two organosiloxanes, Union Carbide Y-9208 and Rhodia Corporation RZ, were used in these tests. Based upon the encouraging results obtained, work to optimize the monomer and aggregate systems was started. The work performed to date is summarized below.

Sand Particle Size

The particle size of the silica sand used in PC containing organosiloxanes has an effect on the properties of the composite and is dependent upon the viscosity of the monomer. The best results for the organic binders with viscosities close to the viscosity of water, were obtained when a mixture of sand sizes was used. In this case, the low viscosity monomer could easily be mixed with the filler to wet the particles and

to fill the voids in the aggregate. When the viscosity of the monomer mixture is increased, the percentage of filler that the monomer wets decreases. The result, therefore, is nonuniform polymer loading which decreases the durability and strength. The effect of sand particle size on the compressive strength of the organosiloxane PC is illustrated in Table 1.

For a 75 wt% organosiloxane - 25 wt% styrene mixture, decreasing the particle size from 600 μ m to < 30 μ m resulted in an increase in strength from 4.7 to 41.6 MPa. The addition of portland cement to the aggregate results in further strength improvement. When 10 wt% Type III portland cement was added to the filler, the compressive strength increased to 85.2 MPa.

Type of Cement

As was indicated above, the addition of cement significantly improves the strength and durability of siloxane PC composites. A study to determine the influence of various types of cement on the properties of PC is in progress. Four different commercially available types of cement which were included as a partial constituent of the aggregate were tested. Compound composition of these materials is given in Table 2.

The properties of PC as a function of cement type are summarized in Table 3 for a 75 wt% Y-9208-25 wt% styrene monomer system and in Table 4 for a 97 wt% RZ-3 wt% V47 system. PC samples containing Type I and II cements in conjunction with the Y-9208-styrene monomer system had high strengths (Figure 1). Type II cement used with the RZ-V47 system also yielded high strength (Figure 2). The sand-cement ratios were 90

Table 1

Compressive Strength of Organosiloxane as
a Function of Sand Particle Size

Monomer composition, wt%		Aggregate composition		Compressive strength, MPa
OS	St	wt%	Sieve opening, μm	
75	25	100	< 30	41.6
75	25	100	150	12.5
75	25	100	600	4.7
75	25	90	< 30	85.2
		10 Type III cement		
75	25	90	150	31.6
		10 Type III cement		
75	25	90	600	21.8
		10 Type III cement		
75	25	36*	1180	40.3
		17	600	
		17	150	
		30 Type III cement		

OS, Organosiloxane

St, Styrene

* Aggregate composition, used for organic systems.

Composite composition, 35 wt% monomer - 65 wt% aggregate.

Table 2

Compound Composition of Portland Cements

Type of Cement	Compound composition, %							
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaSO ₄	Free CaO	MgO	Ignition loss
I	49	25	12	8	2.9	0.8	2.4	1.2
II	46	29	6	12	2.8	0.6	3.0	1.0
III	56	15	12	8	3.9	1.3	2.6	1.9
V	43	36	4	12	2.7	0.4	1.6	1.0

Table 3

Properties of Siloxane PC as a Function of Cement Type

Aggregate composition, wt%		Cement type	Boiling H ₂ O absorption, %	Compressive strength, MPa	Modulus of elasticity, MPa
Sand ^a	Cement				
90	10	I	0.075	111.8	6500
		II	0.072	46.6	4301
		III	0.03	119.3	5175
		V	0.02	100.7	4825
80	20	I	0.12	66.2	--
		II	0.05	63.8	--
		III	0.06	42.5	--
		V	0.07	95.1	--
70	30	I	0.09	60	--
		II	0.08	105.3	--
		III	0.12	73.8	--
		V	0.05	104.2	--

Monomer composition, 75 wt% Y-9208 - 25 wt% styrene.

Curing agent, 1.0 wt% di-tert-butyl peroxide.

Curing condition, 110°C - 18 hr, 165°C - 4 hr.

a, particle size, sieve opening < 30 µm.

Composite composition, 35 wt% monomer - 65 wt% aggregate.

Table 4

Properties of Siloxane PC as a Function of Cement Type

Aggregate composition, wt%		Cement type	Boiling H ₂ O absorption, %	Compressive strength, MPa	Modulus of elasticity, MPa
Sand ^a	Cement				
95	5	I	0.06	81	--
		II	0.09	111.2	--
		III	0.1	70.5	--
		V	0.09	49.1	--
90	10	I	0.07	106.9	6826
		II	0.08	101.6	--
		III	0.05	52.9	6791
		V	0.11	74.39	7526
85	15	I	0.11	86.1	--
		II	0.08	102.9	--
		III	0.08	72.2	--
		V	0.13	70.85	--
80	20	I	0.22	47.5	--
		II	0.12	71.6	--
		III	0.19	72.7	--
		V	0.14	68.2	--

a, particle size, sieve opening < 30 μ m.

Monomer composition, 97 wt% RZ - 3.0 wt% V47.

Curing agent, 1.0 wt% di-tert-butyl peroxide.

Curing condition, 110°C - 18 hr, 135°C - 3 hr, 170°C - 2 hr.

Composite composition, 35 wt% monomer - 65 wt% aggregate.

Figure 1. Compressive strength and boiling water absorption as a function of cement type. Monomer composition, 75 wt% Y-9208 - 25 wt% St. Sand-cement ratio, 1-90:10, 2-80:20, and 3-70:30.

Figure 2. Compressive strength and boiling water absorption as a function of cement type. Monomer composition, 97 wt% RZ - 3 wt% V47. Sand-cement ratio, 1-95:5, 2-90:10, and 3-85:15.

to 10 and 95 to 5, respectively. The amount of water absorbed was lowest for samples containing Type III and V cement (Figures 1 and 2). Stress-strain curves (Figures 3 and 4) indicate that PC samples containing Type I and II cement are more brittle than PC containing the other cements. This brittleness can be reduced slightly using Type III cement. Greater reductions can be obtained using Type V cement. The reasons for this effect is probably due to the differences in the chemical composition of the cements.

Additional work is being performed to determine if the elasticity of the composite can be altered to the extent that the material will have elastomeric properties at high temperature. If so, applications as sealing materials are feasible.

Sand-Cement Ratio

Studies are also in progress to determine the optimum ratio of sand to cement that should be used in the composites. The results from compressive strength tests made before and after exposure of samples in autoclaves to brine at temperatures of 275°C and 300°C are summarized in Table 5. The data indicate that PC samples containing cement up to a concentration of 15% are stable after exposure to brine at 275°C. Only the composites containing sand and cement in ratios of 95 to 5 and 90 to 10 showed stability at 300°C. Figure 5 shows several samples after exposure for 30 days in an autoclave at 300°C.

Infrared spectroscopy analyses (see Figure 6) and scanning electron microscopy studies of the structure of the PC before and after exposure to brine at 300°C did not indicate changes in structure and composition. The electron microscope indicated fragments of resin adhering to the

Figure 3. Compressive stress-strain curves for siloxane PC after preparation as a function of cement type. Monomer composition, 75 wt% Y-9208 - 25 wt% styrene. Aggregate composition, 90 wt% flour sand - 10 wt% cement. 1-Type I cement, 2-Type II cement, 3-Type III cement, and 4-Type V cement.

Figure 4. Compressive stress-strain curves for siloxane PC after preparation as a function of cement type. Monomer composition, 97 wt% RZ - 3 wt% V47. Aggregate composition, 90 wt% flour sand - 10 wt% cement. 1-Type I cement, 2-Type II cement, 3-Type III cement, and 4-Type V cement.

Table 5

Sand-Cement Ratio for System RZ-V47 (Ratio 97:3)

Aggregate ratio, wt%		Boiling water absorption, wt%	Compressive strength, MPa, after			Modulus of elasticity, MPa After exposure to hot brine for 30 days at 300°C
Sand ^a	Cement ^b		Boiling water	30 days in autoclave at 275°C	30 days in autoclave at 300°C	
100	0	0.02	49.9	48.3	--	--
95	5	0.08	74.2	55.9	79.6	8845
90	10	0.07	90.2	69.7	57.1	7963
85	15	0.04	36.2	40.6	--	--
80	20	0.54	15.2	weak	--	--
70	30	0.69	34.2	weak	--	--
95 ^c	5	0.09	89.1	48.5	60.9	9100
90 ^c	10	0.12	46.4	107.2	62.8	5460

Initiator, 1/2 wt% DTBP, 1/2 wt% Silane A-174.

Curing condition, 125°C - 16 hr

150°C - 3 hr

180°C - 3 hr

a, particle size, sieve opening < 30 µm.

b, portland cement Type III.

c, These samples were made by using wetting agent.

Composite composition, 35 wt% monomer - 65 wt% aggregate.

Figure 5. PC samples after exposure to brine at 300°C.

Figure 6. Infrared absorption spectra of siloxane PC samples before (A) and after (B) exposure to brine at 300°C.

filler surfaces. These observations support the possibility of chemical bonding between the resin and the calcium silicate compounds of portland cement.

The results to date indicate that the optimum properties for either of the two organosiloxane systems tested (75 wt% Y-9208 - 25 wt% styrene or 97 wt% RZ-3 wt% V47) occur when an aggregate consisting of $< 30\mu\text{m}$ silica flour is used in conjunction with Type II or III portland cement in a ratio of 90/10 or 95/5.

In previous progress reports and a recent publication,⁴ work to determine the effects of CaO -containing compounds of anhydrous cement on the thermal and chemical stability of PC containing vinyl-type monomers (styrene, methyl methacrylate etc.) was described. The work indicated that the $3\text{CaO}\cdot\text{SiO}_2$ (C_3S) component of cement has the greatest effect on the durability and that the probable cause is an interaction between the $-\text{CH}_2-$ group of the polymer and the CaO in $\text{CaO}\cdot\text{SiO}_2$ compounds.

During the current report period, work in which a mixture of vinyl-type polymers (55 wt% St - 36 wt% acrylonitrile (ACN) - 9 wt% trimethylolpropane trimethacrylate (TMPTMA)) and condensation-type polymers (epoxy, phenol formaldehyde and furan) were used in conjunction with the filler materials was performed. The results to date are summarized below.

Vinyl-Type Polymers

1. The addition of C_3S to PC containing a mixture of vinyl-type polymers resulted in compressive strengths greater than those obtained using other C-S system compounds and significantly higher than these from calcium carbonate, calcium hydroxide and silica-containing materials.

2. Reductions in compressive, tensile and flexural strengths of < 10% were obtained when PC samples containing 17 wt% C_3S were exposed to 25% brine at $240^{\circ}C$ for 10 days. Specimens containing equal concentrations of silica flour and calcium carbonate had reductions > 40%.

3. Although the maximum strain decreased, the modulus of elasticity of C_3S filled PC after exposure to hot brine was observed to be almost the same value as that before exposure. This suggests a conversion toward a more brittle material caused by the hydration products of C_3S and a transformation among polymer molecules.

4. The addition of C_3S to a polymer having carboxylate groups in the molecule results in ionic bonding between Ca^{2+} of the C_3S and $-COO^{\ominus}$ of the polymer during exposure to hot brine at $240^{\circ}C$. The reaction products may prevent the thermal decomposition of polymer itself caused by the crosslinking function of Ca^{2+} which connects to $-COO^{\ominus}$.

5. $C_3SH_{1.5}$ and $\alpha-C_2SH$ formed by the hydration of C_3S during exposure to the hydrothermal environment also limits the strength reduction of PC containing C_3S . A similar effect on absorption was also detected.

Condensation-Type Polymers

1. The C_3S constituent of anhydrous cement has a significant effect on the thermal stability of PC containing phenol formaldehyde resin (PFR). This is possibly due to a reaction occurring between the C_3S and the highly polar hydroxyl group in the PFR molecule.

2. Silica flour does not affect the thermal stability of PRF PC.

3. The thermal stability of epoxy and furan resins, condensation-type polymers that do not have a highly polar group, was not improved by the addition of C_3S .

4. $C_3SH_{1.5}$ and $\alpha-C_2SH$ formed by the hydration of C_3S during exposure to hydrothermal environments reduces the water absorption of PFR PC containing C_3S .

5. The addition of 15 wt% Type III portland cement to PFR PC increased the compressive strength 87% compared to control specimens.

6. After exposure to brine at $240^{\circ}C$ for 30 days, samples containing 15 wt% Type III portland cement exhibited strength reductions of $\sim 12\%$. Samples containing silica flour instead of the cement had strength reductions of 44%.

7. The condensation-type polymerization of PFR results in the formation of a porous material owing to the by-products released during the curing process. When PFR is mixed with anhydrous cement to produce a PC which is subsequently exposed to hot water, only a part of this pore structure is filled by the hydration products. Therefore, before the composite can be used as a protective liner in high pressure hydrothermal process, additional work to reduce the permeability is required.

Work to develop high temperature sealing materials for use in drill bit seals, packers, logging equipment and blow-out preventors has been started. Plans for in-house research and subcontracted efforts have been formulated. A "Request for Proposal" has been prepared for release during the next report period. Depending upon the technical content of the proposals and the funding requirements, one or more subcontracts will be awarded.

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.

During the current report period a prototype 61 cm-diam x 183-cm-long PC-lined steam separator and ancillary piping were fabricated and shipped to the East Mesa Geothermal Site for testing. The techniques used to install ~ 13 mm thick liners on 10-m of pipe, 6 elbows, the vessel shell and baffle plates were the same as those described in previous reports. The assembled unit and a view of the interior of the separator are shown in Figures 7 and 8, respectively.

Several PC formulations were utilized for the liners in order to minimize shrinkage in critical locations such as the baffles and end plates and to obtain comparative data on their durability in liquid and vapor environments. The formulations and the components lined with each are summarized below. Each formulation contained 11.5 wt% monomer.

<u>Component</u>	<u>Monomer</u>	<u>Aggregate</u>
Shell	55 wt% St - 36 wt% ACN - 9 wt% TMPTMA	70 wt% sand - 30 wt% Type III cement
Baffles and end plates	60 wt% St - 40 wt% TMPTMA	90 wt% sand - 10 wt% Type III cement
Pipe	60 wt% St - 40 wt% TMPTMA	70 wt% sand - 30 wt% Type III cement
	55 wt% St - 36 wt% ACN - 9 wt% TMPTMA	70 wt% sand - 30 wt% Type III cement
Elbows	60 wt% St - 40 wt% TMPTMA	70 wt% sand - 30 wt% Type III cement
	55 wt% St - 36 wt% ACN - 9 wt% TMPTMA	70 wt% sand - 30 wt% Type III Cement
	50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB	70 wt% sand - 30 wt% Type III cement

Figure 7. External view of PC-lined steam separator and ancillary piping prior to installation at East Mesa Geothermal Site.

Figure 8. PC liner on steam separator prior to installation at East Mesa Geothermal Site.

In the previous report² initial studies to determine the descaling characteristics of PC surfaces using cavitation techniques were described. Plans have been made to continue this work by the performance of a test to remove an ~ 5-mm-thick layer of scale that accumulated on the surface of a PC pipe after exposure at Niland for 90 days to an ~ 280,000 ppm brine at 235°C.

The test will be performed in the field during February 1979 by Daedalean Associates, Inc. Contingent upon the results, additional tests may be conducted on pipe presently installed at the San Diego Gas and Electric Company, Geothermal Loop Experimental Facility.

In order to provide larger quantities of prototype pipe for evaluation by potential users and to assist in establishing commercial sources of the material, BNL is planning to award one or more subcontracts for design and fabrication of PC components. The scope of work will include engineering design requirements, property measurements, failure mode and component fabrication. The RFP will be prepared during the next report period and contracts will be awarded during the third quarter of FY 1979.

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.

In the previous report² test data were given for St-ACN-Aa-DVB systems after exposure for 120 days to 25% brine at 238°C. One system containing 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% divinyl benzene (DVB) exhibited essentially no change in strength during the test. After 120 days a compressive strength of 232 MPa was measured. This test is continuing but no further measurements were made during the report period.

Specimens similar to those above except that TMPTMA was used as a crosslinking agent instead of DVB are being tested under the same conditions. Results for two formulations, 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA and 50 wt% St - 40 wt% ACN - 5 wt% MAa - 5 wt% TMPTMA, are given in Figure 9. Both formulations exhibited substantial losses in strength during the first 60 to 90 days in test. Beyond that time no further deterioration is evident. These tests are continuing. Similar results have been obtained in field tests described in Task 4. Based upon these and earlier results, DVB appears to be a more effective crosslinking agent for St-ACN-Aa/MAa systems than TMPTMA.

Testing of four commercially supplied proprietary organic coating materials which were applied to steel rods by the vendor has been in progress for 60 days in 25% brine at 238°C. Observations after 30 days exposure indicated complete deterioration of one material, slight blistering of a second and discoloration of the third. The remaining sample appeared to be sound.

Observations made after 60 days indicated the formation of blisters on all of the coating materials. The test is continuing but complete failure of the specimens within a short time is probable.

Figure 9. Compressive strength of PC specimens after long-term exposure to brine at 238°C. a, 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA; b, 50 wt% St - 40 wt% ACN - 5 wt% MAa - 5 wt% TMPTMA.

To evaluate the corrosion resistance of PC to acid soil conditions of the type that might be encountered in district heating applications in the Northwest, samples of PC, concrete and black iron pipe were placed in soil containing 10% H_2SO_4 . The pH of the soil was 2.9. The test was started on January 16, 1976, and observations made after exposure for 480 days were given in Progress Report No. 13.⁵

After 1104 days in test (January 25, 1979), the samples were removed and examined. Complete deterioration of the concrete and severe corrosion of the black iron was apparent. The two PC formulations, 60 wt% St - 40 wt% TMPTMA and 50 wt% St - 33 wt% ACN - 17 wt% TMPTMA, in conjunction with 90 wt% sand - 10 wt% portland cement, showed no attack. During the exposure, the samples exhibited weight gains of 2.2 and 0.7%, respectively. These are probably due to absorption of moisture from the soil.

Evaluation of PC pipe containing glass aggregate as a possible material for use in direct utilization processes is in progress. Tests are being conducted in flowing water at 65°C and in 5% H_2SO_4 . For comparative purposes sections of reinforced concrete, asbestos cement and vitrified clay pipe are also being tested.

Testing of PC pipe in hot water has been in progress for 130 days. To date, no loss of three-edge bearing strength is indicated. Similar results were obtained after exposure for 40 days to a 5% H_2SO_4 solution.

Data from vitrified clay, reinforced concrete, and asbestos cement samples exposed to water for up to 217 days show considerable scatter. All samples tested have yielded strengths less than the unexposed controls but no trend with time is apparent.

Severe degradation upon exposure to 5% H_2SO_4 is indicated. Samples of vitrified clay pipe and reinforced concrete had strength reductions of 52% and 37%, respectively, after exposure for 37 days. The asbestos cement samples lost 35% after 42 days. All of these tests are continuing.

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 additional evaluations performed on samples returned during the previous quarter from The Geysers and the Bureau of Mines site at Niland, are summarized below.

The Geysers

Testing of PC materials in flowing dry steam at $238^{\circ}C$ was started in May 1975. Tests of 3, 24, and 9 mo duration were performed. Evaluation of the third series was performed during the report period.

Two monomer formulations, 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA and 50 wt% St - 40 wt% ACN - 5 wt% MAa - 5 wt% TMPTMA in conjunction with a 70 wt% sand - 30 wt% cement aggregate, were evaluated. The test was started in November 1977 and concluded in August 1978. Visual inspection of the samples after exposure indicated cracks in some of the specimens while other samples containing the same formulation appeared sound.

The results from compressive strength measurements made as a function of test temperature on the MAa-containing PC after exposure for 270 days at The Geysers are given in Figure 10. Compared to a control strength of

Figure 10. Compressive strength of PC containing 50 wt% St - 40 wt% ACN - 5 wt% MAa - 5 wt% TMPTMA as a function of test temperature after exposure to dry steam at 238°C for 270 days.

124 MPa at a test temperature of 25°C, a strength of 90 MPa was measured. This compares well with laboratory data obtained after exposure in 238°C brine for up to 150 days (see Figure 9).

PC specimens containing Aa also produced similar results. After exposure at The Geysers, a strength of 82 MPa at 25°C was measured. This is considerably lower than the control value of 196 MPa but in good agreement with values predicted from laboratory data (Figure 9).

Niland

During the previous report period a 122-cm-long section of 10.2-cm diam pipe that contained a 13-mm PC liner was examined after test at the Bureau of Mines Materials Testing Facility. The pipe had been lined with a monomer formulation of 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA mixed with a 70 wt% silica sand - 30 wt% Type III portland cement. Visual inspection of the unit after exposure to the 280,000 ppm flowing brine at 235°C for 90 days indicated an ~ 5-mm thick layer of a uniformly deposited lead sulfite scale. The amount of scale was estimated to be similar to that expected for steel surfaces. No deterioration of the PC or loss of bond to the steel was apparent.²

Sections of the pipe have recently been tested to measure the bond strength of the PC to the steel after the brine exposure. At 25°C the bond strength was 10.3 MPa. Measurements made at 100°C and 200°C indicated values of 10.4 and 8.9 MPa, respectively. A section of the pipe after the bond test is shown in Figure 11. The ability of the PC liner to withstand the high force required to disbond it from the steel and the absence of salts or corrosion products on the steel are indications of the strength and impermeability of the liner. Tests to determine the

Figure 11. PC-lined pipe after exposure to 235°C brine and measurement of bond strength. Left, steel pipe, right, PC liner after disbondment from steel.

depth of salt penetration into the liner are planned.

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 7651 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 4951 hr, no deterioration or scale accumulation is apparent.

A prototype PC-lined carbon steel steam separator and ancillary piping were fabricated and shipped to East Mesa for test. This is described in Task 2. Start-up of the unit during February 1979 is anticipated.

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. No apparent deterioration has been reported.

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. Data obtained to date were given in the previous progress report.² The tests were continued throughout the report period but additional inspections were not made.

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. Resumption of the test during the next report period is expected.

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 is being performed as a subcontract with the Burns and Roe Industrial Services Corporation. A partial draft of a report on the impact of the use of non-metallic materials of construction in direct utilization processes has been received. To date, two processes, sugar beet refining and barley malting, have been evaluated. The results indicate that the substitution of a PC lining for the carbon steel corrosion allowance can reduce the cost of the brine system in a 5,000 ton/day beet refining plant by 27%. In a 4×10^6 bushel/yr barley malting plant, the cost is reduced by 37%. Considerably

larger reductions are feasible if prestressed PC vessels can be used.

These studies and one on a district heating system for Klamath Falls will be completed during the next report period.

Task 6. Administrative

During the current report period, three "Project Status Reports" were submitted to DGE and Progress Report No. 16² was issued. A paper entitled, "Polymer Concrete Materials for Use in Geothermal Energy Processes", was presented at the Second International Symposium on Polymers in Concrete.⁶ A paper entitled, "The Effect of Dicalcium Silicate and Tricalcium Silicate on the Thermal Stability of Vinyl-Type Polymer Concrete", was published in Cement and Concrete Research.⁴ Another paper,⁷ "The Influence of the Curing Agent Concentration and Curing Temperatures on the Thermostability of Styrene-Acrylonitrile-Acrylamide-Trimethylolpropane Trimethacrylate Copolymer Systems", has been accepted for publication in the Journal of Applied Polymer Science. Two others, "High Temperature Polymer Concretes from Organosiloxane Resins"⁸ and "The Effect of Tricalcium Silicate on the Thermal Stability of Condensation-Type Polymer Concretes"⁹ have been submitted for publication in The International Journal of Cement Composites.

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