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ALTERNATE MATERIALS OF CONSTRUCTION FOR GEOTHERMAL APPLICATIONS

PROGRESS REPORT NO. 15
OCTOBER 1977 - MARCH 1978

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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 four of these sites is continuing and plans to initiate tests at other sites are being implemented. Work accomplished during the period October 1977 - March 1978 is described in the current report.

Summary

Test results indicate that polymer concrete (PC) containing mixtures of styrene-acrylonitrile-acrylamide or methacrylamide produce composites with the best high temperature and chemical resistance obtained to date. The results show that the use of a 12 wt% concentration of a 55 wt% styrene-35 wt% acrylonitrile-5 wt% acrylamide-5 wt% TMPTMA monomer mixture in conjunction with 88 wt% of a 70 wt% silica sand-30 wt% portland cement aggregate produces a composite with a compressive strength at 20°C (68°F) in the range 25,000 to 30,000 psi. The PC is thermally stable to ~ 240°C (464°F).

Work to determine the effect of calcium oxide compounds of anhydrous cement on the durability of PC is continuing. The results indicate that the $3\ CaO \cdot SiO_2$ component of cement has the greatest effect on the thermal stability of vinyl-type polymers.

Work to determine the descaling characteristics of PC has been started. Scale has been used successfully as aggregate in PC. Specimens with compressive strengths up to 8,000 psi were produced. Durability tests are in progress. If successful, the technique may yield an environmentally and economically acceptable method for the disposal of scale.

Laboratory testing of specimens in simulated geothermal environments is continuing. Samples tested after exposure to a 25% brine solution at 177°C (350°F) for 960 days had strengths essentially the same as those measured after 63 days.

Field testing is in progress at The Geysers, Raft River, East Mesa, and Niland. Samples have been shipped to the U.S. Naval Weapons Center for installation at Coso Hot Springs. Plans have been made to install

pipe specimens at the Los Alamos Scientific Laboratory Fenton Hill site and in the San Diego Gas and Electric Company Geothermal Loop Experimental Facility.

Work to determine the economic impact of the use of non-metallic materials of construction in direct utilization processes has been started.

Alternate Materials of Construction for Geothermal Applications

Progress Report No. 15
October 1977 - March 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 purpose of the current Brookhaven National Laboratory (BNL) program is to identify areas in geothermal processes where non-metallic materials such as concrete polymer composites, plastics, and refractory cements may be utilized in a cost-effective manner and to develop and test these materials under laboratory and field conditions.

The feasibility of using concrete polymer composites as materials of construction for handling hot brine and steam was demonstrated in 1972.[1] As part of this work the concrete liner on a vertical tube evaporator at the Office of Saline Water Desalting Facility in Freeport, Texas was partially impregnated to a depth of ~0.25 in. The results from these tests indicated that the composites have long-term stability in seawater at 177°C (350°F) and in acid solutions. Based upon these results, a research program to develop the composites for use in geothermal systems was started in April 1974. To date, high temperature polymer concrete (PC) systems have been formulated, and laboratory and field tests performed in brine, flashing brine, and steam at temperatures up to 260°C (500°F). Results from field test exposures of up to 24 months are available. To date, good durability is indicated. Tests are currently in progress at four field sites (The Geysers, Raft River, East Mesa and Niland) and work at three others (LASL, Coso Hot Springs and SDG&E) is scheduled to commence in the near future. Work performed during the period October 1977 - March 1978 is described in the current report. Future reports will be issued on a quarterly basis.

Summary of Previous Report[2]

Experiments to determine the effect of aggregate composition on the durability of PC to high temperature brine were being performed. The results indicated that the presence of portland cement in the aggregate greatly enhanced the durability. The evidence also indicated that CaO reacts chemically with $-CH_2$ groups in the vinyl monomers. However, there was no evidence whether the reaction is caused by free CaO or the calcium ion.

Field testing of a 6-in.-diam section of lined pipe was in progress at Raft River and sections of pipe were being prepared for installation at East Mesa, Niland, and the U.S. Naval Weapons Center.

Laboratory testing of specimens in simulated geothermal environments was continued. Samples exposed to 25% brine solutions at 177°C (350°F) for 900 days had not deteriorated. Similar results were obtained with pipe specimens exposed to a 400 ppm solution at 150°C (302°F) for 312 days.

Samples exposed to a pH 1 hydrochloric acid solution at 90°C (194°F) for 441 days did not deteriorate. Samples containing silica sand-portland cement aggregate yielded similar results after 170 days in pH 1 hydrochloric acid at 200°C (392°F).

Field testing of specimens at Raft River and The Geysers was continuing. Samples removed from The Geysers and East Mesa were evaluated. Good durability was indicated after exposure to 238°C (460°F) steam at The Geysers for 18 months. Similar observations were noted for samples exposed for 60 days to 160°C (320°F) flowing brine at East Mesa.

Plans were made to initiate two tests at Niland and to start additional work at The Geysers and East Mesa during the next report period.

Task 1. Selection of Lining Materials

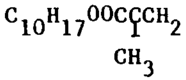
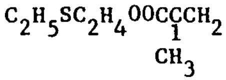
Work is being performed to develop polymer formulations and PC composites which can be used as materials of construction at temperatures up to 260°C (500°F). In a separate program,[3] research is being performed to determine if materials can be formulated for use as well cementing materials at temperatures up to 400°C (750°F).

To date two monomer formulations, 60 wt% styrene - 40 wt% trimethylolpropane trimethacrylate (TMPTMA) and 50 wt% styrene - 33 wt% acrylonitrile - 17 wt% TMPTMA, have been shown to be durable to geothermal fluids. Both systems can be polymerized using chemical initiators and heat or by chemical initiators and promoters. The latter monomer system appears suitable for temperatures up to $\sim$ 240°C (464°F).

During the current report period several monomer systems have been evaluated. These are listed in Table 1.

TABLE 1

Properties of Monomer Systems for High Temperature PC Applications

Monomer	Structure	Molecular weight	Melting point, °C	Boiling point, °C	Flash point, °C	Condition
styrene (St)	$C_6H_5CHCH_2$	104.14	-31	146	31.1	liquid
acrylonitrile (ACN)	CH_2CHCN	53.06	-82	77.3	1.1	liquid
acrylamide (Aa)	$CH_2CHCONH_2$	71.08	84.5	125	——	solid
methacrylamide (MAa)	$CH_2CHCONHCH_3$	85.1	111	——	——	solid
isobornyl methacrylate (IBOMA)	 $C_{10}H_{17}OOC\underset{CH_3}{\underset{\mid}{C}}CH_2$	222	——	——	127.7	liquid
ethylthioethyl methacrylate (ETEMA)	 $C_2H_5SC_2H_4OOC\underset{CH_3}{\underset{\mid}{C}}CH_2$	174	——	102	79.4	liquid
methyl methacrylate (MMA)	$CH_3CCHCOOCH_3$	100.1	-50	101	0	liquid

Sample Preparation

Earlier work[1] has indicated that a silica sand mixture consisting of 50 parts by weight of sieve size No. 16, 25 parts of No. 30, and 25 parts of No. 100 has the proper particle size distribution to produce a high quality PC with a minimum polymer content. For high temperature applications, Type III portland cement is added to this mixture to enhance the durability to brine and steam. Possible explanations for this effect were discussed in the previous report.[4]

The monomers are mixed in a glass beaker and polymerization initiator is added and dissolved. If acrylamide or methacrylamide are included in the monomer mixture, the mixture is heated to 150°C (302°F) prior to the addition of initiator to dissolve the solid monomer. The formulation is mixed with the sand-cement aggregate and placed in a glass tube which is coated with a release agent. Vibration is used to compact the PC. The samples are cured in an oven at 60°C (140°F) for 16 hr and for 2 hr at 85°C (185°F). After cooling, the samples are removed from the form. Prior to testing, they are cut to a length to diameter ratio of 2, and dried for 18 hr at 105°C (220°F).

Copolymer Systems

Several monomer mixtures have been used to produce high temperature PC formulations. The properties of these materials are summarized in Tables 2 and 3. It can be seen from the tables that formulations containing styrene (St) - acrylonitrile (ACN) - acrylamide (Aa) and St - ACN - methacrylamide (MAa) produce PC with properties superior to those containing isobornyl methacrylate (IBOMA), ethylthioethyl methacrylate (ETEMA) and methyl methacrylate (MMA). As a result, emphasis has been

TABLE 2

Polymer Concrete Properties

Monomer system	Monomer ratio	Polymer weight loss after 30 days at 460°F	Boiling Water absorption, %, after			Compressive strength, psi, after			
			prep.	32 days in oven at 460°F	autoclave	prep.	boiling water absorp.	32 days in oven at 460°F	autoclave
St-ACN-Aa	57.5-40-2.5	18.0	2.27	5.09	1.71	20542	10542	3111	10942
	60-35-5.0	25.6	1.37	6.66	2.0	24375	19750	2013	12030
	55-40-5.0	18.8	0.98	4.73	1.84	19750	20167	7128	13547
	55-37.5-7.5	28.5	0.96	10.03	1.38	20917	21083	752	5812
St-ACN-MAa	57.5-40-2.5	25.5	2.74	6.80	3.59	15333	13000	1812	5919
	60-35-5	18.4	1.88	4.84	2.64	17042	13458	3111	10855
	55-40-5	15.8	1.49	5.43	1.30	19000	19167	5396	7222
	55-37.5-7.5	9.6	0.94	2.57	1.55	22250	14833	5496	8889

1. monomer loading - 12 wt%
2. sand-cement ratio, 80-20
3. initiator, azobisisobutironitrile (AIBN)

TABLE 3

Polymer Concrete Properties

Monomer system	Monomer ratio	Catalyst		Boiling water absorption, %,	Boiling water absorption, %, after oven at 460°F	Weight loss after oven at 460°F	Compressive strength, psi,after			Boiling water absorp. after autoclave %
		name	wt%				prep.	Boiling water absorp.	autoclave	
IBOMA-MMA 12% monomer loading	95-5	BPO	2.0	0.16	22.70[1]	7.98[1]	10442	13009	4008	3.51
	90-10	AIBN	0.75	0.34	15.47	8.79	12279	13208	6723	3.71
	85-15	AIBN	0.75	0.38	17.83	8.76	11504	11482	5824	4.45
	80-20	BPO	2.0	0.16	17.98	8.51	15443	15730	7513	2.70
	70-30	AIBN	0.75	0.50	13.84	8.02	14049	13363	7644	3.64
	60-40	AIBN	0.75	0.57	14.32	8.31	14226	11062	10235	3.38
	50-50	BPO	2.0	0.37	15.46	7.71	20957	19956	13135	1.66
IBOMA-MMA -ETEMA 13% monomer loading	94-5-1	AIBN	0.75	0.54	19.33[2]	8.59[2]	10363	9615	6899	5.22
	84-15-1	AIBN	0.75	0.64	19.75	7.78	13184	11880	5025	5.28
	69-30-1	AIBN	0.75	1.05	—	7.37	13931	10748	7000	3.92
	59-40-1	AIBN	0.75	1.19	20.55	7.72	14744	7927	6798	3.69
	49-50-1	AIBN	0.75	1.48	18.09	7.76	15214	9103	6378	4.68
	90-5-5	AIBN	0.75	0.56	25.39	8.41	12799	8953	5168	5.10
	80-15-5	AIBN	0.75	0.85	18.81	7.49	14385	10855	4748	5.85
	70-25-5	AIBN	0.75	1.20	18.89	6.21	9145	8718	4983	5.69
	70-20-10	AIBN	0.75	0.64	19.11	6.73	14359	12222	6143	4.53
	60-30-10	AIBN	0.75	1.12	16.64	6.49	16047	12777	6487	4.52
	50-40-10	AIBN	0.75	0.78	18.95	6.73	17308	16803	9211	3.47

1, after 1 day exposure at 460°F

2, after 4 day exposure at 460°F

placed on the development of the first two systems.

Experiments were performed to determine if copolymers or mixtures of homopolymers of St, ACN, Aa or MAa were formed during the polymerization process. The formation of copolymers was confirmed by solubility tests. It was determined that the copolymerization products do not dissolve in solvents for polyacrylonitrile such as dimethylformamide or in acetone, a solvent for polystyrene. This indicates the absence of homopolymers. It was also noted that homogeneous transparent films without signs of inclusions were produced when the copolymers were press-molded. This also is evidence of the formation of true copolymers.

An IR spectroscopy investigation of the molecular structure of the copolymerization products (Figure 1) showed that all absorption bands characteristics of polystyrene, polyacrylonitrile, and polyacrylamide (3400-3500, 3040, 2930, 2220, 1600, 1500 and 1450 cm^{-1}) are present in the spectra.

Tests have been performed to optimize the monomer composition with respect to the properties of the PC. The concentrations of each monomer constituent in the formulations were selected based upon the reactivity of each monomer. PC samples were made containing 12 wt% of the monomer formulations and 88 wt% of filler composed of an 80-20 silica sand - Type III portland cement mixture. The results from property evaluations performed on these specimens are given in Table 2. These data indicate that the boiling water absorption after exposure of the specimens in an oven at 238°C (460°F) for 32 days increases as the concentration of Aa is increased and decreases with increased MAa content. These data are plotted in Figure 2. The compressive strength increases with increased MAa and decreases as the Aa concentration is increased (Figure 3).

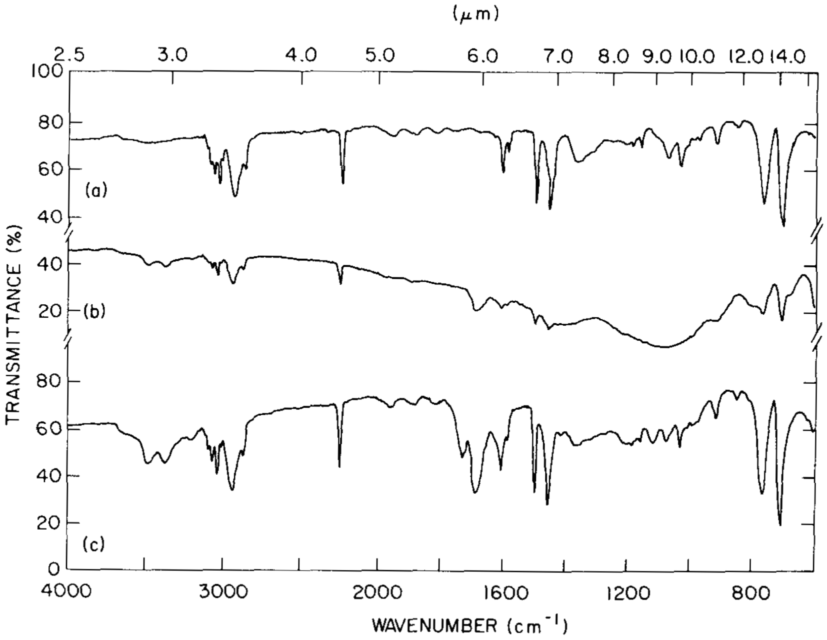


Figure 1. Infra-red structure of St-ACN-Aa copolymer.

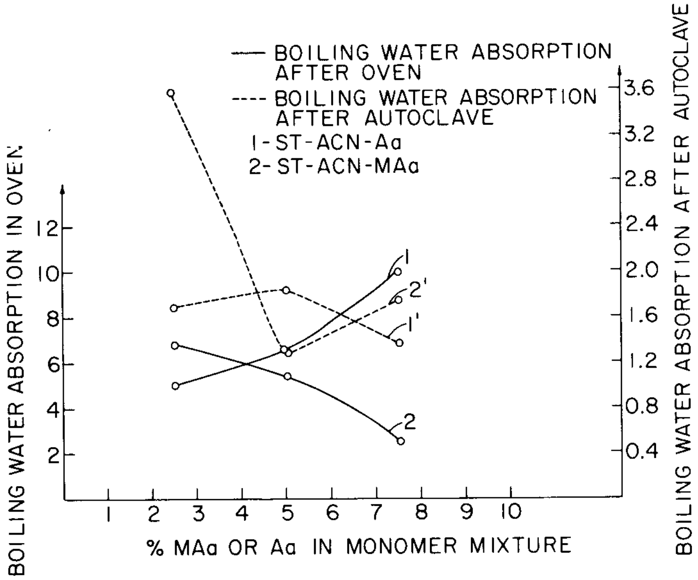


Figure 2. The effect of monomer composition on the boiling water absorption of PC.

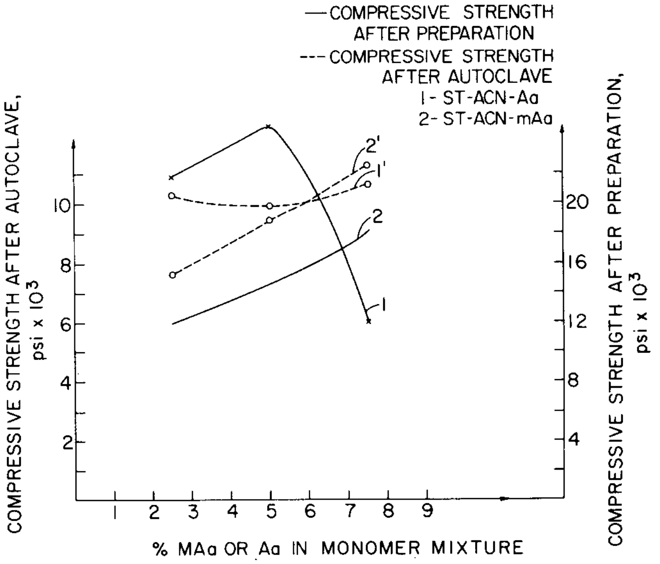


Figure 3. The effect of monomer composition on the compressive strength of PC.

1, 1^1, St - ACN - Aa

2, 2^1, St - ACN - MAa

The addition of cross-linking agents to the monomer mixtures improves the thermal and chemical stability of the copolymers. Two cross-linking materials, trimethylolpropane trimethacrylate (TMPTMA) and divinyl benzene (DVB), are being studied. Data from these studies are given in Tables 4 and 5 and Figures 4-6. These results indicate that the optimum TMPTMA concentration as determined by compressive strength (Figure 4), boiling water absorption (Figure 5), and weight loss tests is between 5 and 7 wt%.

Studies to determine the effect of the ratio of ACN to St in formulations containing St - ACN - Aa and a crosslinking agent (TMPTMA or DVB) were also performed. Data plotted in Figure 7 indicate that for a TMPTMA concentration of 5 wt%, the compressive strengths of PC samples after exposure to air at 238°C (460°F) and to brine at 238°C (460°F) are essentially the same. The strength is maximum in the ACN/St range of 0.4 to 0.5 and then decreases. This is in good agreement with copolymerization theory.

The effect of DVB concentration on the properties of PC containing St - ACN - Aa was determined. The data indicate that the optimum concentration is in the range 1 to 8 wt%. In this range, the PC has the highest compressive strength (Figure 8), lowest water absorption (Figure 9), and lowest weight loss after exposure to hot air (Figure 6). Increasing ACN/St ratios in the range 0.45 to 0.8 in PC samples containing 1 wt% DVB (Figure 10) increases the initial compressive strength from ~12,000 to 17,000 psi.

Additional work is in progress to determine which of the two cross-linking agents is superior. At this time samples containing DVB appear

TABLE 4

Concentration of TMPTMA as a Function of Properties of Polymer Concrete

Concentration TMPTMA, wt%	ACN/St ratio	Compressive strength, psi., after				Polymer weight loss after 30 days in oven at 460°F, %	Boiling water absorption after	
		prep.	boiling water absorption	oven, 30 days at 460°F	autoclave 460°F		autoclave, %	oven, %
0	0.73	19750	20167	7128	13547	18.8	2.00	6.66
	0.60	24375	19750	2013	12030	25.6	1.71	5.09
2.5	0.64	22832	23009	9217	15420	10.0	0.83	1.71
5.0	0.80	26842	25000	11200	12435	5.96	0.71	0.65
	0.64	25817	26754	17409	16000	5.94	0.70	0.52
	0.50	27895	26316	20348	20348	5.96	0.68	0.61
	0.38	26053	23421	20522	19304	7.96	0.71	0.85
7.5	0.82	27982	27193	22000	8000	5.06	0.59	0.35
	0.66	23333	21491	21739	8087	5.03	0.71	0.46
	0.52	20965	16404	22696	5044	5.41	0.51	0.50
	0.40	29737	17895	24087	12870	6.19	0.53	0.63
10	0.88	28597	27281	12226	5130	7.09	0.69	0.64
	0.69	28158	26053	16696	11304	5.16	0.63	0.40
	0.55	26930	23509	25478	11913	5.89	0.62	0.64
	0.42	26404	18333	25130	13148	5.44	0.43	0.48

Acrylamide concentration, 5 wt%

TABLE 5

Concentration of DVB as a Function of Properties of Polymer Concrete

Concentration DVB, wt%	ACN St ratio	Compressive strength, psi., after				Weight loss of polymer after 30 days in oven at 460°F, %	Boiling water absorption after	
		prep.	boiling water absorption	oven, 30 days at 460°F	autoclave 460°F		autoclave, %	oven, %
				Concentration Aa, 5 wt%				
0	0.73	19750	20167	7128	13547	18.8	2.00	6.66
	0.76	24375	19750	2013	12030	25.6	1.71	5.09
1.00	0.74	24825	25263	16870	18435	6.12	1.03	0.71
	0.59	25263	22632	16609	16696	5.86	0.78	0.61
	0.47	21754	18947	11652	21913	7.19	0.63	0.88
2.5	0.85	28070	26930	18365	13826	5.48	0.73	0.56
		26496	25043	19159	22393			
	0.76	24211	23622	17878	22348	5.62	0.60	0.60
	0.60	24737	22895	16783	13304	5.54	0.64	0.53
	0.48	25351	22018	21670	22609	5.44	0.69	0.67
5.0	0.80	25128	23675	16965	27607	6.76	0.69	1.14
7.5	0.75	22906	23504	14310	29915	8.30	0.58	1.61
10	0.70	21966	23162	7761	27778	12.89	0.52	2.76
				Concetration MAa, 5 wt%				
2.5	0.85	26552	26000	17148	20128	4.83	0.65	0.58
5.0	0.80	25130	24000	18383	16068	4.84	0.48	0.69
7.5	0.75	22348	23913	14835	8761	4.44	0.59	0.51
10.0	0.70	18522	18957	19300	17992	14.13	4.13	0.60

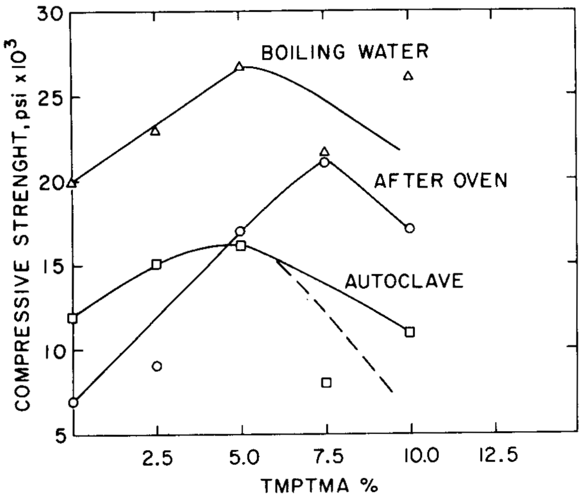


Figure 4. Compressive strength as a function of cross-linking agent concentration.

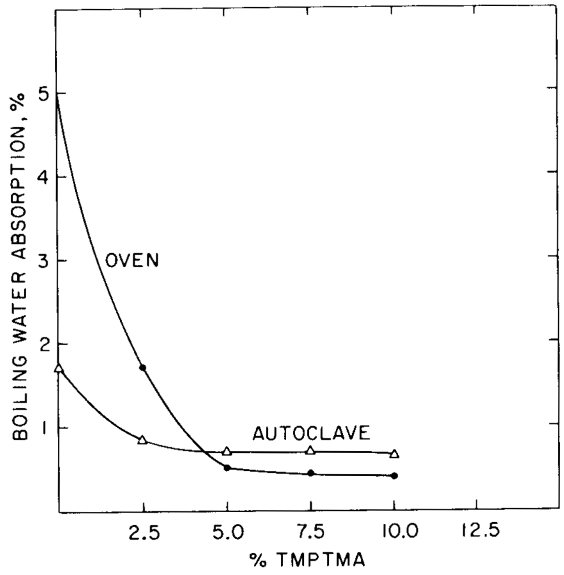


Figure 5. The boiling water absorption of PC as a function of TMPTMA concentration.

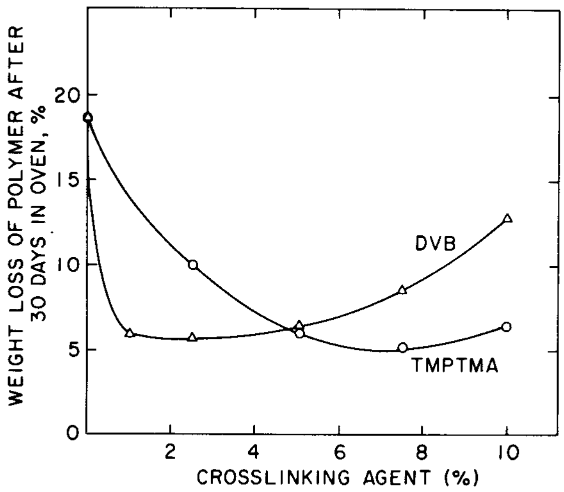


Figure 6. Polymer weight loss as a function of cross-linking agent concentration.

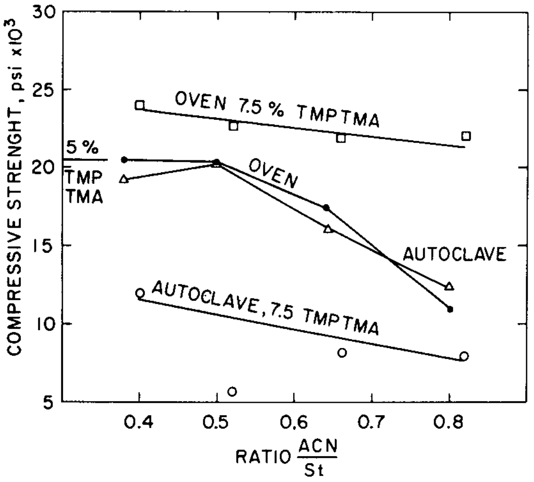


Figure 7. The compressive strength of PC containing TMPTMA as a function of ACN/St ratio.

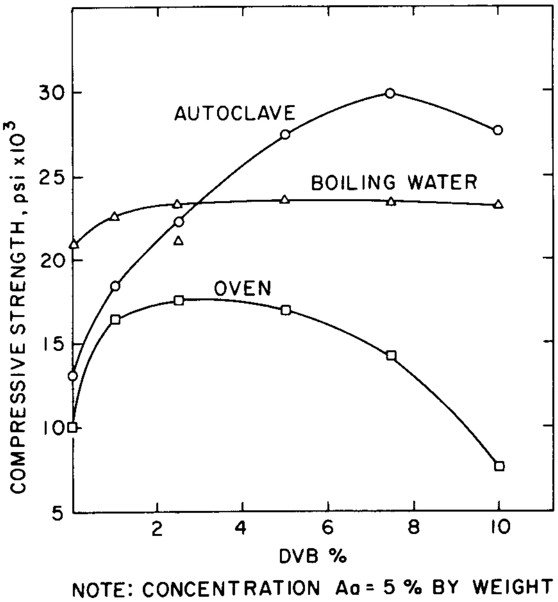


Figure 8. The compressive strength of PC as a function of DVB concentration.

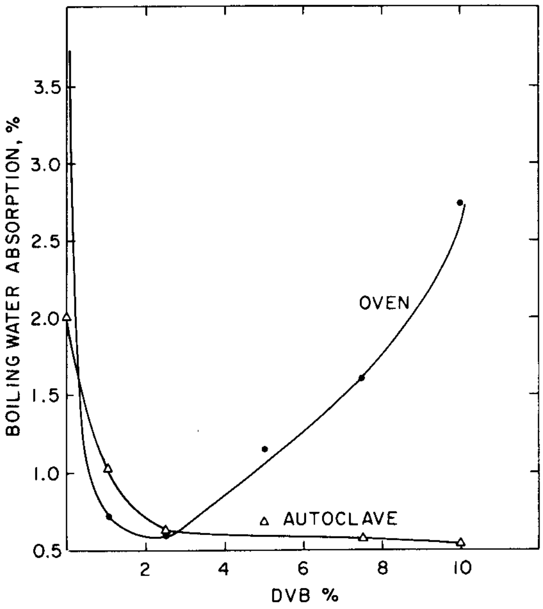


Figure 9. The boiling water absorption of PC as a function of DVB concentration.

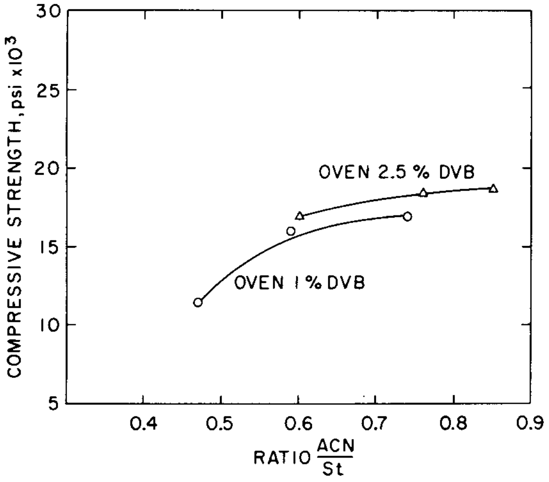


Figure 10. The compressive strength of PC containing DVB as a function of ACN/St ratio.

more stable to hot brine than samples containing TMPTMA. In hot air, the opposite trend has been observed.

Another important parameter in the preparation of PC is the effect of polymer content on the properties of the composite. To obtain information on this variable, a series of PC samples containing a monomer mixture of 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA in conjunction with a 70 wt% silica sand - 30 wt% Type III portland cement aggregate were tested. The polymer loading was varied between 12 and 20 wt%. These results, summarized in Table 6 and Figure 11, indicate that the compressive strengths decreased with increasing polymer loading.

If a PC containing 12 wt% polymer can be assumed to be a homogeneous system, further increases in polymer content result in the formation of heterogeneous sections of polymer. These impede the filling of the capillaries, therefore reducing the cohesive force between polymer and aggregate. Electron microscopic studies support this assumption. Figures 12-13 show fractured surfaces of PC samples containing 12 and 20% polymer loadings, respectively. The composite containing 12 wt% polymer (Figure 12) has a more uniform surface than the sample containing 20 wt% (Figure 13). The polymer appears to be evenly filling the pore space between the sand grains and cement and a continuous three-dimensional polymeric network is formed.

Studies are also in progress to determine the optimum ratio of sand to cement in the aggregate used to produce PC. The results from these studies are summarized in Table 7 and Figure 14. It was observed that increases in cement content from 10 to 30% resulted in increases in compressive strength from 20,000 to 27,000 psi. The water absorption

TABLE 6

Summary of Test Results for Polymer Concrete Systems Containing
55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA and 70 wt% - 30 wt% Sand-Cement Aggregate

	Monomer loading, wt%			
Property	12.0	15.0	17.5	20.0
Compressive strength (psi) after				
a. preparation[1]	28319	25421	24737	17457
b. boiling water	25841	23333	22193	21053
c. oven (30 days, 460°F)	17537	12649	14297	11955
d. autoclave (10 days, hot brine)	17743	16052	15704	——
Boiling Water absorption (%) after				
a. preparation[1]	0.33	0.26	0.26	0.24
b. oven (30 days, 460°F)	0.90	1.10	1.27	1.47
c. (10 days, hot brine)	0.64	0.64	0.59	——

[1] average of 4 specimens

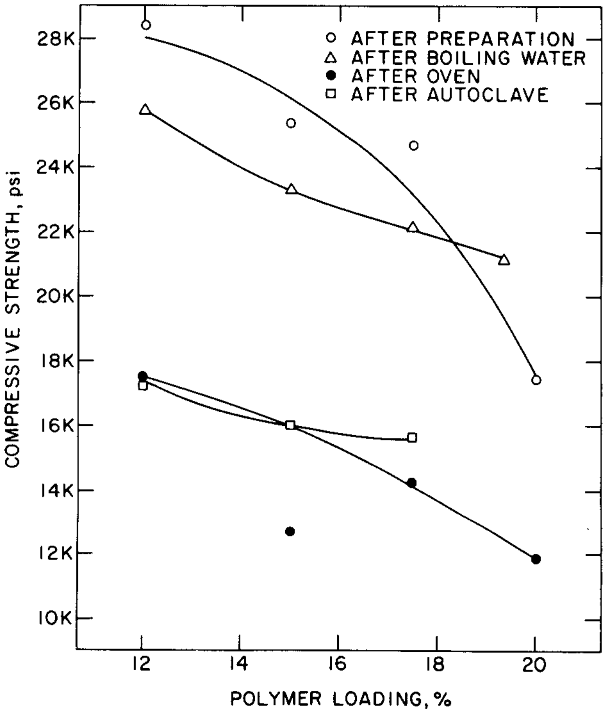


Figure 11. The effect of polymer loading on the compressive strength of PC.

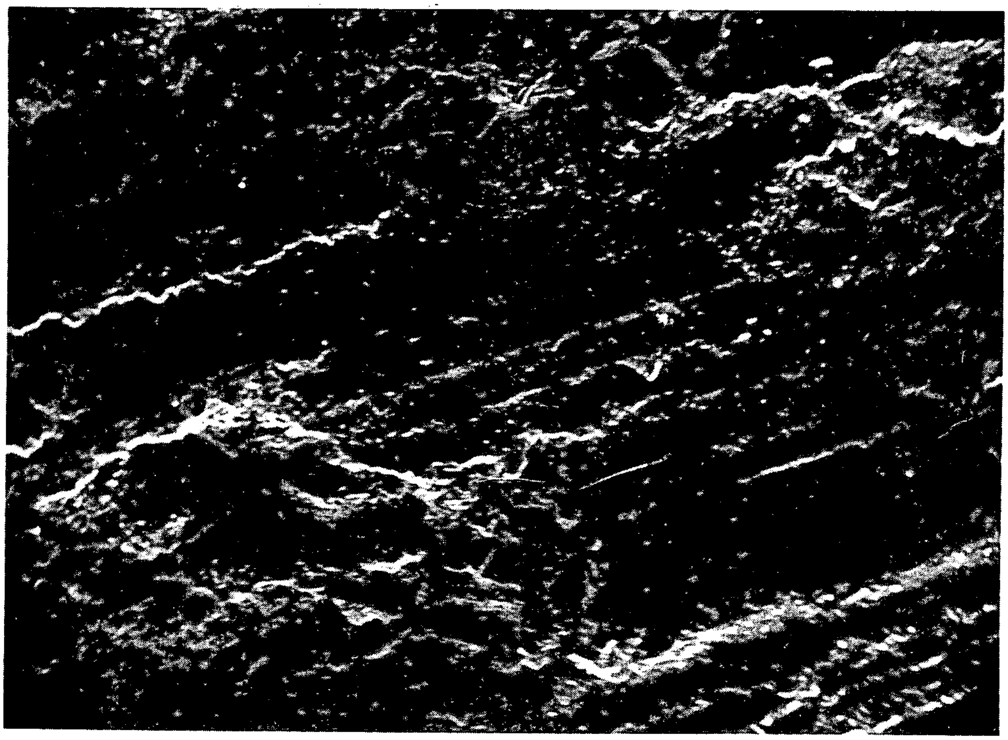


Figure 12. Scanning electron microscope picture of fractured surface of PC sample containing a 12% polymer loading.

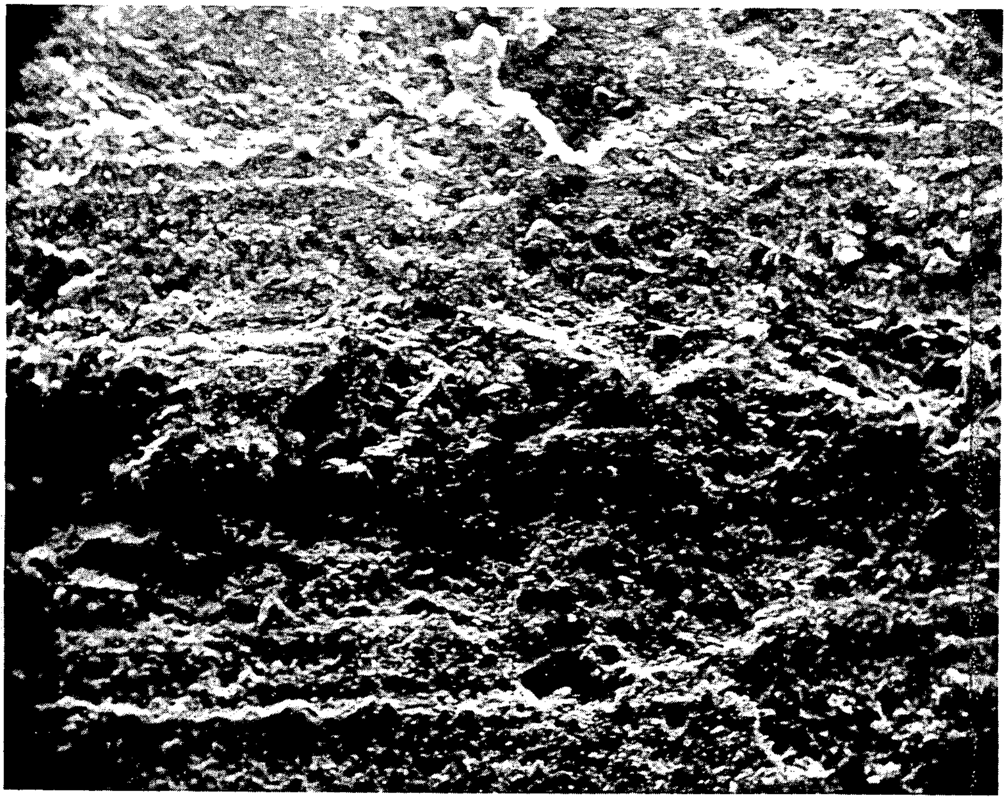


Figure 13. Scanning electron microscope picture of fractured surface of PC sample containing a 20% polymer loading.

TABLE 7

Properties of Polymer Concrete as a Function of Sand-Cement Composition

Aggregate composition, sand-cement, wt%	90-10	80-20	70-30	60-40	50-50
Monomer composition	55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA				
Boiling water absorption (%) after:					
a. preparation	0.78	0.62	0.85	0.38	0.42
b. oven (30 days, 460°F)	0.90	1.02	0.87	1.18	2.69
Compressive strength (psi) after:					
a. preparation	22212	24248	28319	20620	26549
b. boiling water	20266	——	27841	22920	23028
c. oven (30 days, 460°F)	18926	15537	17547	19174	16694
Monomer composition,	55 wt% St - 37.5 wt% ACN - 7.5 wt% MAa				
Boiling water absorption (%) after:					
a. preparation	2.05	1.25	1.41	2.33	2.63
b. oven (30 days, 460°F)	5.57	3.82	4.06	7.21	7.42
Compressive strength (psi) after:					
a. preparation	14655	15080	18620	13327	7168
b. boiling water	10779	19097	15027	6478	5699
c. oven (30 days, 460°F)	3652	4300	2209	1565	973

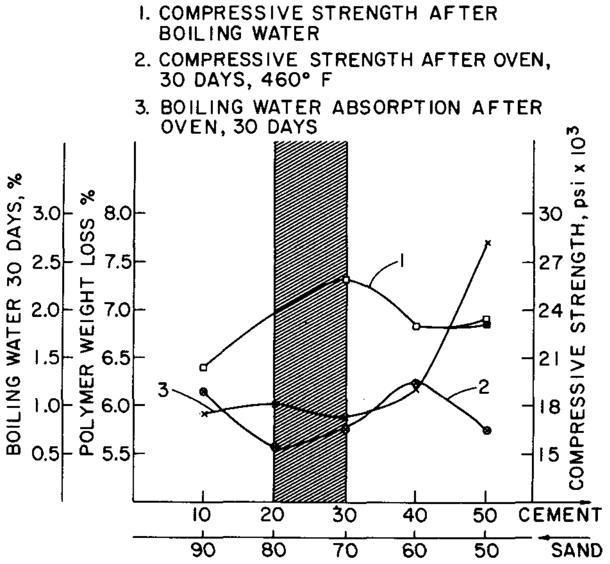


Figure 14. The effect of sand-cement in aggregate on the properties of PC.

remained essentially constant over this range. Further increase in cement content reduces the strength and increases the water absorption. This may be explained by the reduced porosity resulting from the added cement fines. This reduces the cohesive forces between the polymer and the filler. As discussed above, increases in the polymer content of the mix beyond 12 wt% results in further reductions in properties.

Based upon the results to date, the optimum filler composition for use with the St - ACN - Aa - TMPTMA system is in the range 70 to 80 wt% silica sand and 20 to 30 wt% cement.

During the next report period the following work will be performed.

1. The thermal properties of the systems as a function of ACN concentration will be determined.

2. Long-term laboratory and field tests to determine the durability will be continued.

3. Experiments using siloxane as a high temperature binder for PC will be initiated.

Studies to determine the effect of aggregate composition on the durability of high temperature PC materials are also continuing. In the previous report[5] it was stated that the increased thermal stability of PC formulations of vinyl-type monomers and aggregate containing portland cement was not due to free CaO but to CaO compounds of cement.

During the current report period work to determine the effect of CaO compounds of anhydrous cement such as tricalcium silicate ($3\ CaO \cdot SiO_2$), dicalcium silicate ($2\ CaO \cdot SiO_2$) and tricalcium aluminate ($3\ CaO \cdot Al_2O_3$) on the thermal stability was performed.

Differential scanning calorimeter (DSC) and infra-red (IR) analysis studies are being performed on PC samples containing each of the above compounds in conjunction with polymethyl methacrylate (PMMA). The results from the DSC thermograms indicated that 3 $CaO \cdot SiO_2$ derived from the chemical reaction between $CaCO_3$ and SiO_2 had a significant effect on the thermal stability of PMMA.

The thermograms of PMMA containing 3 $CaO \cdot SiO_2$ did not exhibit a noticeable endothermic peak in the range 160°-200°C (320°F to 392°F) compared with that of a PMMA-$CaCO_3$-SiO_2 system. Generally, the first endothermic peak of PMMA itself is characterized by the double peaks at 180°C (356°F) and 193°C (383°F). The first broad peak actually represents the change from the crystalline solid to a liquid crystal state. The thermal decomposition of PMMA, therefore, is considered to occur in the temperature range of 150°C-210°C (302°F-410°F).

The endothermic peak near 200°C (392°F) of PMMA samples combined with CaO-SiO_2 systems has a tendency to disappear with increasing CaO contents. If the onset temperature of endothermal effect is not considered, the thermograms of PMMA-3 $CaO \cdot SiO_2$ systems indicate that the first endothermic peak for PMMA is increased from 180°C to 303°C (356°F to 580°F) due to the addition of 66 wt% 3 $CaO \cdot SiO_2$.

As an attempt to better understand the effect of CaO in CaO-SiO_2 systems on the thermal stability of vinyl-type polymers, the heat of fusion of the first peak in the region of 180°C-210°C (356°F-410°F) for these samples was obtained by using the equation $\Delta H = KRA/WS$ where: ΔH = Heat of fusion in calories/gram; K = Calibrated instrument constant; R = Range sensitivity in mcal/sec.-in.; A = Peak area in square inches; W = Sample weight in milligrams; S = Recorder chart speed in in./sec.

The heat of fusion of PMMA itself and PMMA samples containing $CaO \cdot SiO_2$, $3\ CaO \cdot 2\ SiO_2$, $2\ CaO \cdot SiO_2$, $3\ CaO \cdot SiO_2$ and type III portland cement, were 34.93 cal/g, 4.99 cal/g, 3.07 cal/g, 1.74 cal/g, 0.00 cal/g and 1.23 cal/g, respectively. The heat of fusion of PMMA containing 66 wt% type III portland cement was 1.23 cal/g. These data indicate that the $3\ CaO \cdot SiO_2$ component of cement has the greatest effect on thermal stability of vinyl-type polymers.

From IR spectras it has been noted that the absorption band of the $-CH_2-$ group for the region 3000-2900 cm^{-1} of PMMA becomes smaller with increased CaO content in $CaO-SiO_2$ systems. Also, the IR spectras of PMMA containing $3\ CaO \cdot SiO_2$ and type III portland cement were observed to have very similar absorption bands which contained smaller bands at 3020 cm^{-1} and 2970 cm^{-1} than those of PMMA.

To obtain further information about the interaction between the $3\ CaO \cdot SiO_2$ and the $-CH_2-$ group, a quantitative analysis was performed by using the IR absorbance ratio obtained by dividing the absorbance of the $-CH_2-$ group at 2970 cm^{-1} by the absorbance of the $-C=O$ group at 1730 cm^{-1}. These results indicate that the absorbance ratio of PMMA containing $3\ CaO \cdot SiO_2$ is almost the same (0.23 vs 0.25) as that of PMMA containing type III portland cement.

The results from the IR study indicate that the interaction between the $-CH_2-$ group of the vinyl-type polymer and the CaO of $CaO \cdot SiO_2$ systems takes place as described in the previous report.[5]

At present, the mechanical evaluation, DSC study and IR analysis after exposure for 30 days to 25% brine at 238°C (460°F) of PMMA and polystyrene combined with each of the $CaO-SiO_2$ systems, $CaO-Al_2O_3$ systems and $CaO-Al_2O_3-Fe_2O_3$ systems are in progress.

Task 2. Process Technology

Work to develop the technology required to produce PC and PC - lined pipe and vessels for use in containing geothermal fluids is continuing. During the report period sections of PC pipe and lined pipe were fabricated for testing at Coso Hot Springs. Sections of PC lined pipe are currently being fabricated for installation at East Mesa, Fenton Hill and in the San Diego Gas and Electric Company Facility at the Salton Sea. This work is described in Task 4.

Previous work has focused on the application of PC liners to straight sections of steel pipe. During the current report period techniques for lining elbows and reducers have been developed. Components of this type (see Figure 15) will be exposed to flowing geothermal fluid during the next report period.

To date, PC-lined pipe has been joined to adjacent pipe using flanged connections. The feasibility of welding using techniques similar to those used in connecting cement-lined pipe has recently been demonstrated.

Work to determine the descaling characteristics of PC surfaces is in progress. Preliminary data from one field test at East Mesa indicate that the small amount of scale that was deposited could be easily brushed off. In a second test, scale accumulation was not apparent.

In an attempt to obtain quantitative data on the descaling characteristics, a subcontract has been awarded to Daedalean Associates, Inc. of Woodbine, Maryland. BNL will provide 25 rectangular samples (6x6x0.75 -in) of PC to Daedalean for use in tests in which the PC will be exposed

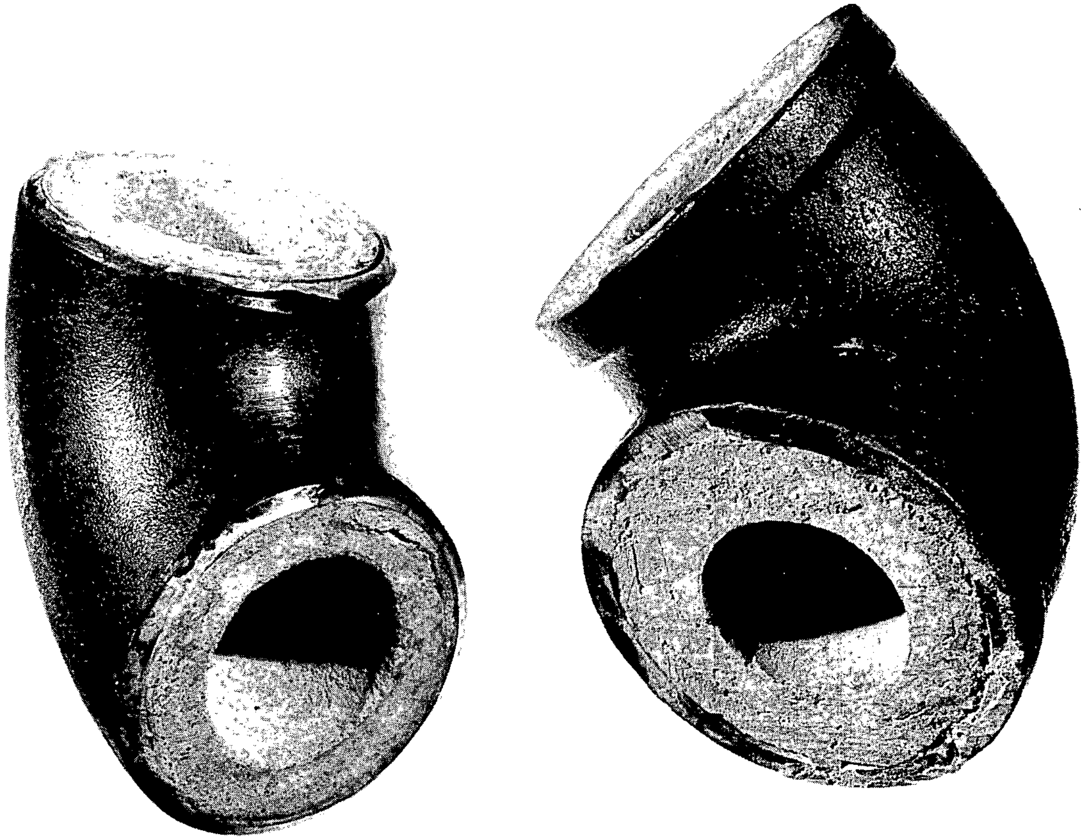


Figure 15. PC-lined pipe elbows.

to high pressure cavitating water jets. The threshold intensity of erosion for polymer concrete will be measured and it will be compared with that of steel. Experimental work on this effort will start during the next report period.

Samples of geothermal scale received from Daedalean have been successfully used as aggregate in PC. Specimens with compressive strengths up to 8,000 psi were produced. Durability tests will be started. If successful, the technique may yield an environmentally and economically acceptable method for the disposal of scale.

Task 3. Physical and Chemical Property Measurements

In support of the experimental work being performed in Tasks 1, 2 and 4, the mechanical and chemical resistance properties of concrete polymer materials are being determined. The tests are being performed in autoclaves at conditions simulating environments in which field tests are in progress or being planned.

Preliminary testing of PC specimens in an autoclave containing a 25% concentration of synthetic Imperial Valley geothermal brine at a temperature of 177°C (350°F) was completed during the report period. Two PC formulations, 60 wt% St - 40 wt% TMPTMA and 50 wt% St - 33 wt% ACN - 17 wt% TMPTMA were tested. The PC mixes which were selected prior to the performance of the aggregate optimization tests described in Task 1, consisted of 12 wt% of the monomer mixture and 88 wt% of a 90 wt% silica sand-10 wt% portland cement aggregate. Polymerization was initiated using 2% benzoyl peroxide by weight of monomer and heating to 80°C (176°F).

The results of compressive strength measurements made on the specimens as a function of time are given in Table 8. As noted, both

Table 8

Compressive Strength of PC After Exposure to 25% Brine at 177°C (350°F)

Exposure time, days	PC No. 1	PC No. 2
	Compressive strength, psi	
0	9600	10900
63	4450	7000
142	3900	6100
280	4352	7567
466	4355	7511
960	4880	7310

PC No. 1, 60 wt% styrene-40 wt% TMPTMA.

PC No. 2, 50 wt% styrene-33 wt% acrylonitrile-17 wt% TMPTMA.

Aggregate, 90 wt% sand-10 wt% portland cement.

Specimen size, 0.75-in.-diam x 1.5-in.-long.

Strengths measured at 20°C (68°F).

series exhibited initial reductions in strength, probably due to the decomposition of low molecular weight fractions of the polymer or an insufficient amount of portland cement in the aggregate. Strengths measured after 960 days were essentially the same as those measured after 63 days. Visual inspections made throughout the test indicated no cracking or other signs of deterioration.

Testing of several PC formulations in a 400 ppm brine solution at 150°C (302°F) was terminated after exposure for 490 days. Two monomer systems, 50 wt% St - 33 wt% ACN - 17 wt% TMPTMA and 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA used with calcium aluminate, alumdum and type III portland cements were tested. These results are summarized in Table 9.

Work to determine the feasibility of using PC materials in high temperature-low pH environments is continuing. Two tests are currently in progress.

In one test 3 PC samples are being exposed to a pH 1 HCl solution at 90°C (194°F). To date, the samples have been in test for 620 days. No evidence of corrosion as determined by pH and weight change has been detected.

A test in pH 1 HCl at 200°C (392°F) is also in progress. Three monomer formulations 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA, 50 wt% St - 33 wt% ACN - 17 wt% TMPTMA and 60 wt% St - 40 wt% TMPTMA used in conjunction with aggregate containing 90 wt% sand - 10 wt% portland cement were being evaluated. No deterioration was apparent after ~ 170 days. Unfortunately after 240 days, failure of the temperature control on the autoclave resulted in a temperature excursion to an undetermined value. Inspection of the samples indicated complete disintegration of the

Table 9

Compressive Strength of PC After a 490 Day Exposure to 400 ppm Brine at 150°C (302°F)

Monomer	Aggregate	Compressive strength, psi[a]	
		Control	Exposure
50% St - 33% ACN - 17% TMPTMA	50% sand-50% calcium aluminate cement	24,640	24,135
	80% sand-20% calcium aluminate cement	23,474	15,278
	80% sand-20% alumdum cement	19,915	3,785
	80% sand-20% Type III cement	25,217	16,945
	50% sand-50% alumdum cement	17,197	8,638
55% St - 36% ACN - 9% TMPTMA	80% sand-20% calcium aluminate cement	23,580	18,288

a, average of 2 specimens tested at 20°C (68°F)

St, styrene

ACN, acrylonitrile

TMPTMA, trimethylolpropane trimethacrylate formulation containing 55 wt% St. Surface deterioration of the sample containing 50 wt% St was apparent but essentially no attack was apparent on the PC containing 60 wt% St - 40 wt% TMPTMA. Testing of this material is continuing.

Task 4. Field Tests

To date, tests have been completed at The Geysers, Baca Wells, Klamath Falls, Raft River and East Mesa. Tests are currently in progress at The Geysers, Raft River, East Mesa and Niland. Samples of pipe have been shipped to the U.S. Naval Weapons Center for installation at Coso Hot Springs. Plans to install pipe at the Los Alamos Scientific Laboratory Fenton Hill site and in the San Diego Gas and Electric Company loop at Niland have been made and the materials have been ordered.

The Geysers

Testing of PC materials in flowing dry steam at a temperature of 238°C (460°F) has been in progress at the Geysers since May 1975. To date 90 day and 2 yr tests have been completed and a third test of at least a 6 month duration is in progress. During the current report period the evaluation of samples exposed for up to 2 yr was completed. These samples, shown in Figure 16, had compressive strengths ranging between 2278 psi (sample X-10) and 335 psi (X-8). The average strength and water absorption was 1570 psi and 8.5% respectively. Earlier samples evaluated after exposure for 180 days had values of 2350 psi and 8.7%.

Test series No. 3 consisting of 48 cylinders was placed into test in November 1977. Four monomer systems; 80 wt% St - 12 wt% polyphenylene oxide - 8 wt% TMPTMA, 30 wt% St - 60 wt% triallyl cyanurate - 10 wt%

GEYSERS
AFTER 2 YEARS

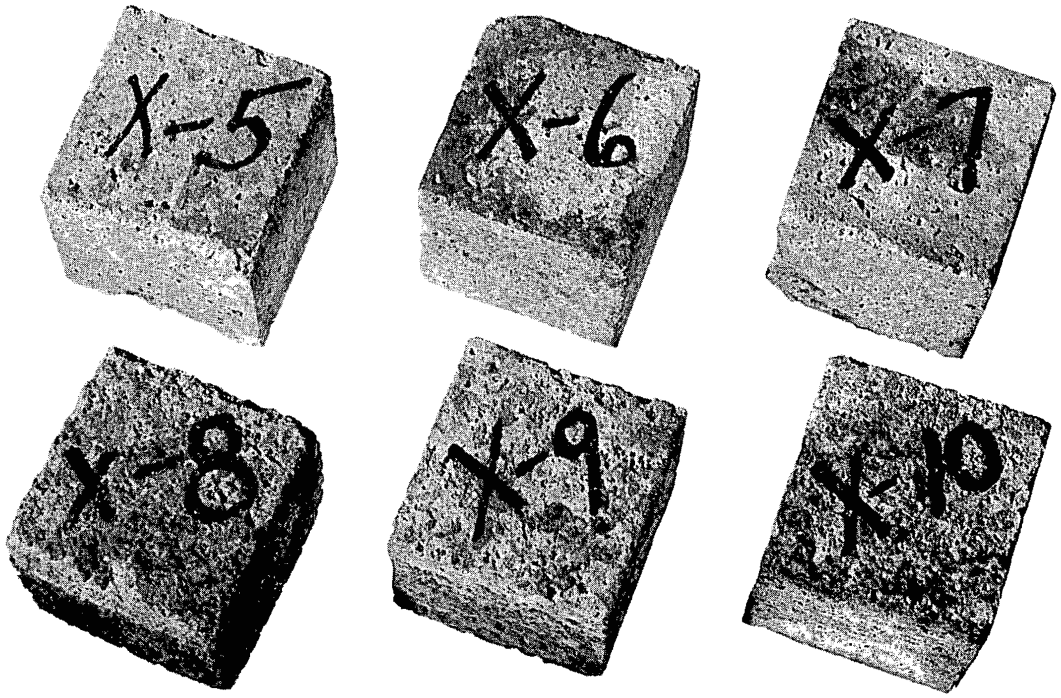


Figure 16. PC specimens after exposure for 2 years to dry steam at 238°C (460°F).

polyphenylene oxide, 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 sand-cement aggregate are being evaluated. Results are not yet available, but based upon earlier laboratory work, these systems are expected to yield improvements over the results obtained in Series No. 1 and 2.

Raft River

One test has been completed at Raft River and two others are in progress. The tests currently in progress are being performed at a temperature of 135°C (275°F) and flow rate of ~ 200 gpm utilizing the "Raft River Mobile Corrosion, Deposition and Component Test Laboratory."

In one test a series of 2-in. cubes has been exposed for ~ 480 days. An evaluation performed after exposure for 90 days indicated good durability.

A 4-ft. section of PC-lined pipe has been exposed to the fluid for ~ 300 days. A date for the first visual inspection has not yet been established.

East Mesa

During the previous report period[5] 48 hollow cylinders of PC (7/8-in.-o.d.x3/16-in.-wall x 2 3/8-in.-long) were removed after exposure to flowing brine at ~ 160°C (320°F) for 60 days. The samples consisted of two monomer mixtures, 50 wt% St - 33 wt% ACN - 17 wt% TMPTMA and 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA, in conjunction with 4/1 and 1/1 ratios of sand and portland cement aggregate. It was reported that the inner surfaces of the hollow cylinders were free of scale and the scale on the outer surfaces was easily brushed off. No decrease in crushing strength as a result of the 60 day exposure was observed. Additional evaluation of the samples is in progress.

An 8-ft section of PC-lined 3-in. Sch 40 carbon steel pipe was installed at East Mesa on December 6, 1977. The pipe (shown in Figure 17) is being exposed to ~ 160°C (320°F) brine flowing from Well 6-1 at a rate of 60-80 gal/min. The salt content is ~ 26,000 ppm.

The first inspection of the pipe was made after exposure for ~ 60 days. No deterioration of the PC or scale accumulation was apparent. Scaling of the connecting steel pipe was observed. This test is continuing. Plans are being made to install similar sections in lines containing two phase flow. Fabrication of the pieces is in progress and installation during the next report period is anticipated.

Arrangements are being made to test several sections of polymer-impregnated concrete and asbestos cement pipe that were prepared and installed by the Bureau of Reclamation at East Mesa ~ 2 yr ago, but never exposed to brine. The pipe (see Figure 18) is impregnated with 60 wt% St - 40 wt% TMPTMA and has been given to BNL. Plans to connect it to the test manifolds are being made.

Niland

Two experiments are currently in progress utilizing the Bureau of Mines facility at Niland. These experiments were started during January 1978 and to date test results are not available.

In one test, PC cylinders containing 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA are being exposed to 6 environments. These are in the 220°C (428°F) brine at the inlet to the first steam separator, the brine and

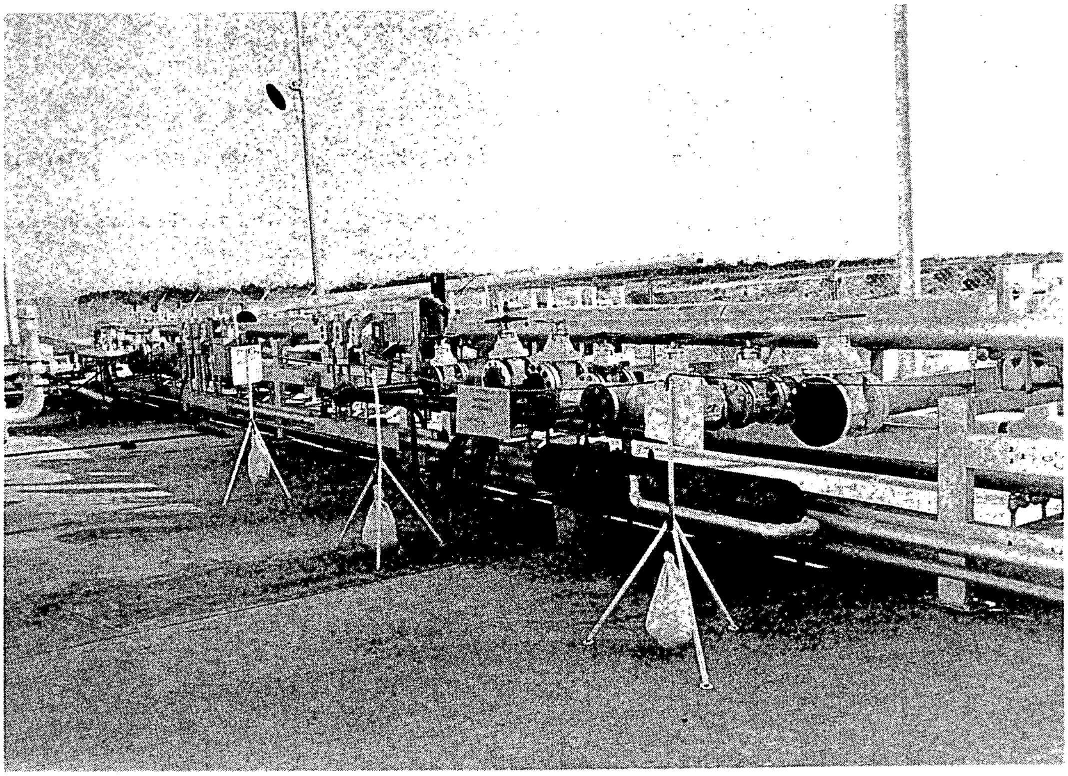


Figure 17. PC-lined pipe in test at East Mesa.

Figure 18. Polymer impregnated concrete and asbestos cement pipe installed at East Mesa but not as yet connected to brine system.

steam effluents from the first and second steam separators, and at the steam/brine interface in the second separator.

The second test is of a 4-ft section of lined pipe (see Figure 19) which was installed during December 1977. The section was designed for service in a 25% brine solution at 260°C (500°F) and 350 psi pressure. A date for the first inspection of the unit has not been set.

U.S. Naval Weapons Center

Twelve sections of PC and PC-lined pipe (see Figure 20) have been fabricated and shipped during March for testing at Coso Hot Springs.

The PC-lined pipe consists of 4-ft lengths of 3-in.- Sch 40 pipe lined with a 0.5-in. thick PC. A total of 7 lengths were fabricated. The PC pipe is 3.5-in.-o.d.x0.75-in.-wall. Three monomer formulations; 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA, 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA and 80 wt% St - 12 wt% polyphenylene oxide - 8 wt% TMPTMA were used in conjunction with a 70 wt% silica sand - 30 wt% type III portland cement aggregate. The pipe will be installed by Naval Weapons Center personnel and testing should commence during the next report period. Tests in low temperature aerated and non-aerated geothermal fluids will be performed. The former will be accomplished by the introduction of air into the fluid through holes drilled into the PC pipe.

Los Alamos Scientific Laboratory (LASL)

Arrangements have been completed to test PC-lined pipe and fittings at the LASL Fenton Hill hot rock geothermal site. This test will represent the first exposure of PC-lined elbows to flowing geothermal fluids. Fabrication of the test configuration, shown in Figure 21, is in progress.

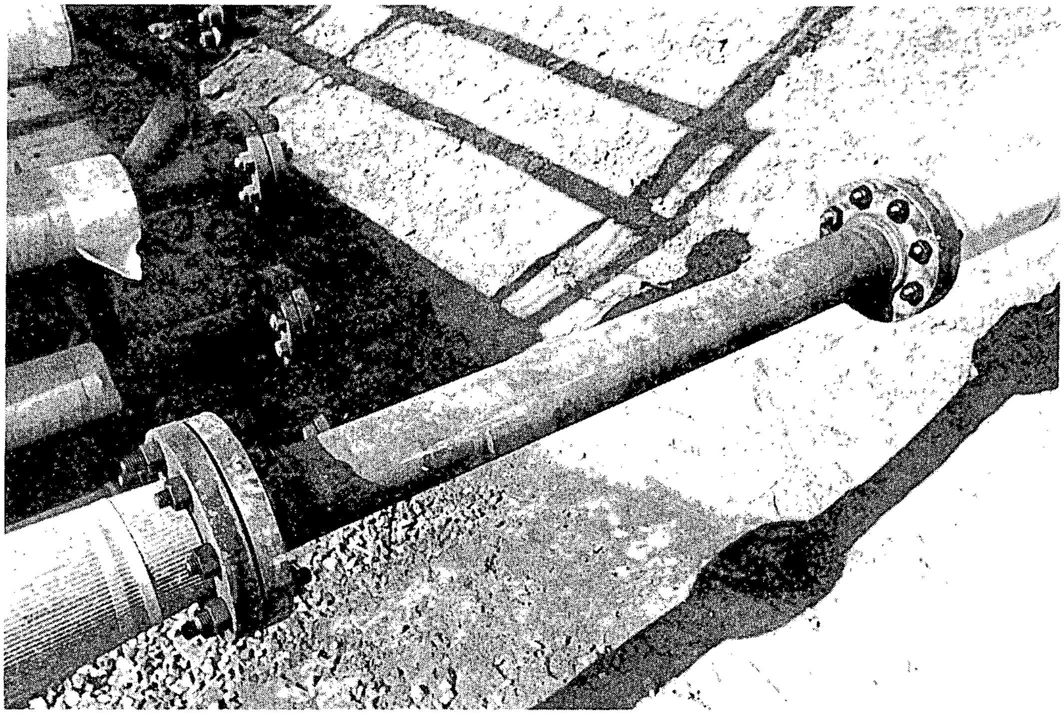
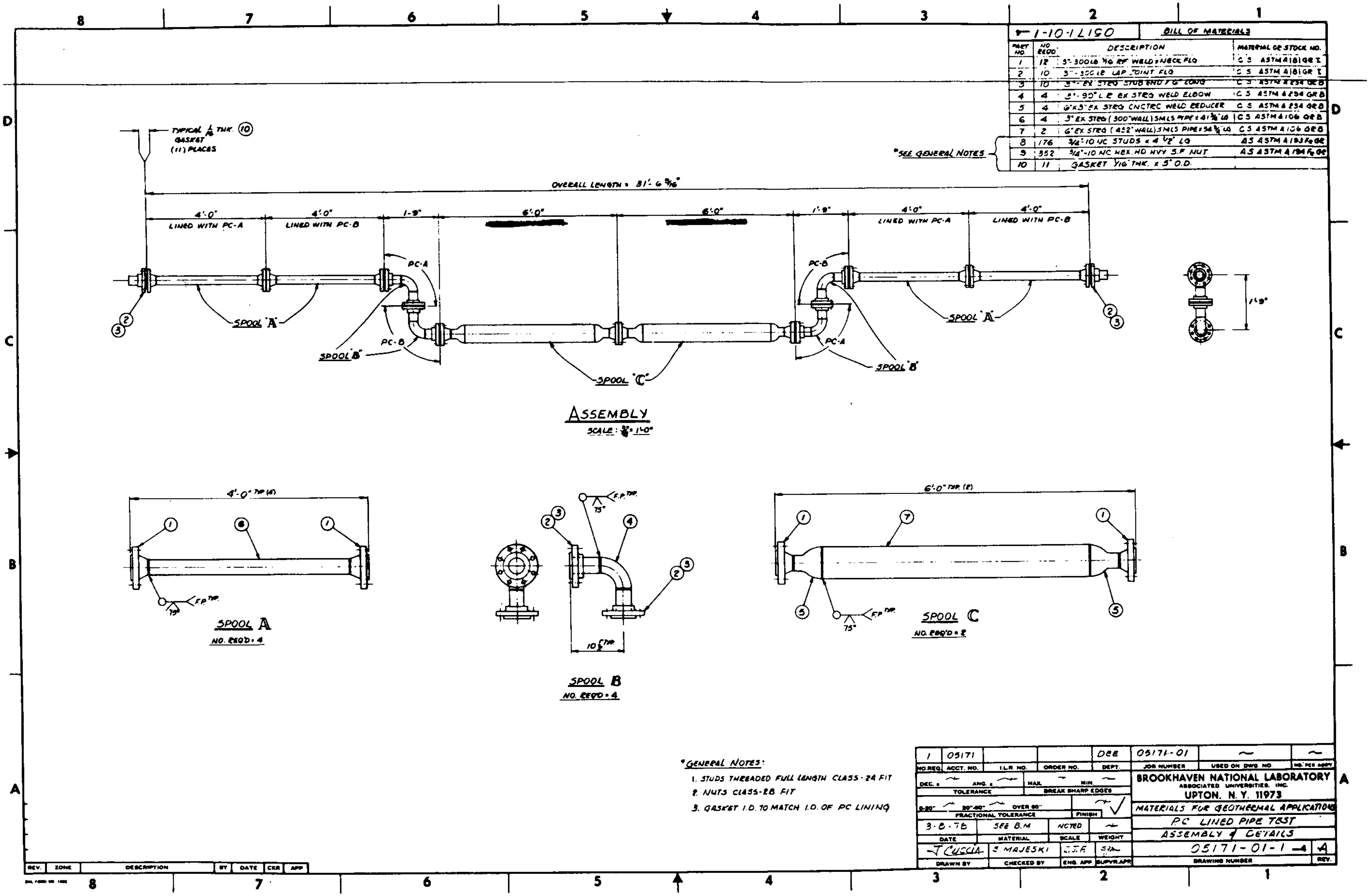


Figure 19. PC-lined pipe in test at USBM facility at Niland.

Figure 20. PC pipe to be tested at Coso Hot Springs.



1-10-1L150 **BILL OF MATERIALS**

PART NO.	NO REQ'D	DESCRIPTION	MATERIAL OR STOCK NO.
1	12	3"-300LB 1/16 RF WELD NECK FLG	C.S. ASTM A181 GR I
2	10	3"-300LB LAP JOINT FLG	C.S. ASTM A181 GR I
3	10	3"-EX STRG STUB END × 6" LONG	C.S. ASTM A234 GR B
4	4	3"-90° L.R. EX STRG WELD ELBOW	C.S. ASTM A234 GR B
5	4	6"×3" EX STRG CNCTRC WELD REDUCER	C.S. ASTM A234 GR B
6	4	3" EX STRG (.300" WALL) SMLS PIPE × 41 3/8" LG	C.S. ASTM A106 GR B
7	2	6" EX STRG (.432" WALL) SMLS PIPE × 54 3/4" LG	C.S. ASTM A106 GR B
8	176	3/4"-10 NC STUDS × 4 1/2" LG	A.S. ASTM A193 Gr B7
9	352	3/4"-10 NC HEX. HD HVY S.F NUT	A.S. ASTM A194 Gr 2H
10	11	GASKET 1/16" THK. × 5" O.D.	

*SEE GENERAL NOTES (parts 8–10)

*GENERAL NOTES:

1. STUDS THREADED FULL LENGTH CLASS-2A FIT
2. NUTS CLASS-2B FIT
3. GASKET I.D. TO MATCH I.D. OF PC LINING

NO. REQ. 1	ACCT. NO. 05171	I.L.R. NO.	ORDER NO.	DEPT. DEE	JOB NUMBER 05171-01	USED ON DWG. NO. ~	NO. PER ASSY ~

TOLERANCE: DEC. ± ~ ANG. ± ~
BREAK SHARP EDGES: MAX. ~ MIN. ~
FRACTIONAL TOLERANCE: 0-20" ~ 20"-60" ~ OVER 60"
FINISH: √
DATE: 3-8-76
MATERIAL: SEE B.M
SCALE: NOTED
WEIGHT: ~
DRAWN BY: J Cuccia
CHECKED BY: S. MAJESKI
ENG. APP: J.J.F.
SUPVR. APP: S.M.

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
UPTON, N.Y. 11973

MATERIALS FOR GEOTHERMAL APPLICATIONS
PC LINED PIPE TEST
ASSEMBLY & DETAILS

DRAWING NUMBER: 05171-01-1-4
REV.: A

Figure 21. PC test configuration to be installed at Fenton Hill.

Start-up of the test during the latter part of the next report period is planned. The anticipated test conditions are temperature 185°C (365°F), pressure 250 psi and flow rate 150 gpm.

San Diego Gas and Electric Company (SDG&E)

The SDG&E has requested that 3 sections of PC-lined pipe be provided for test at their Geothermal Loop Experimental Facility (GLEF). Two 6-ft-long sections of 10-in.-diam pipe and a 8-in.-diam x ~ 4-ft-long section will be fabricated.

Two of the pipes will be installed in the brine injection line. The injection flow rate is typically 50 gpm, and the brine is at ~ 93°C (200°F) and 100 psi. The 8-in.-diam section will be installed between the first and second stage flash drums and will carry about 150 gpm of brine at 150 psig and 182°C (360°F). Installation of the sections during April is anticipated.

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.

During the previous report period a study to evaluate electric generating processes was completed. This report has been issued.[6]

Work to evaluate direct utilization processes has been initiated. In this work, the Burns and Roe Industrial Services Corporation, under contract to BNL, will review 3 conceptual designs for direct utilization processes and determine if savings in capital and operating costs can be accrued by the use of non-metallic materials in applicable portions of the processes. A report summarizing the results from this study will be issued in late FY 1978.

Task 6. Administrative

During the current report period, 6 "Monthly Administrative Letters" were submitted to DGE and Quarterly Progress Report No. 14[2] was issued. A paper entitled "Polymer Concrete Materials for Use in Geothermal Energy Processes" was prepared for presentation at the "Second International Symposium on Polymers in Concrete" which will be held in Austin, Texas October 25-27, 1978.

Two invited papers on the use of polymer concrete to repair concrete structures were presented at the "World of Concrete" symposium in Pheonix, January 10-13, 1978.

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3. Cementing of Geothermal Wells, Progress Report No. 7, October-December 1977, BNL 50808.

4. Cementing of Geothermal Wells, Progress Report No. 6, July-September 1977, BNL 50738.

5. Alternate Materials of Construction for Geothermal Applications, Progress Report No. 14, July-September 1977, BNL 50751.

6. Economic Assessment of Polymer Concrete Usage in Geothermal Power Plants, Burns and Roe Industrial Services Corporation, Brookhaven National Laboratory Report BNL 50777, November 1977.

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