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POLYMER CONCRETE PIPE FOR HIGH-TEMPERATURE CORROSIVE ENVIRONMENTS

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ABSTRACT

Polymer concrete is a composite material which has strength and durability characteristics greatly superior to those of portland cement concrete and better durability than steel. Polymer concrete has been successfully tested in brine, flashing brine and steam at temperatures up to 260°C. Exposures were as long as 960 days. Glass filament wound polymer concrete pipe was developed with excellent strength, low weight, and a cost comparable to or less than schedule 40 steel. Connections can be made with slip joints for low pressure applications and flanged joints for high pressure applications.

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.

General guides to materials selection for oxygen-free geothermal systems have been published by Shannon.¹ At temperatures of 120°C and pH <6, the use of expensive materials such as titanium, zirconium, and Hastalloy C is suggested.

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At a temperature of 60°C, severe corrosion of carbon steel occurs in aerated geothermal fluids. The corrosion rate in aerated systems is reported to be 100 times greater than in oxygen free geothermal fluids.² As a result, all condensate and cooling water piping at The Geysers is constructed of stainless steel or plastic-lined material. It is also necessary to coat all concrete surfaces that come in contact with water with coal-tar epoxy compounds or synthetic rubber.³

The corrosion rate of carbon steel is also highly dependent upon the pH of the brine. At the predicted pH of 4.9 for oxygen-free Salton Sea brines and a temperature of 50°C, a service life of <15 yr is estimated.¹ At a pH of 4, the estimated service life is 2 yr.

Electrochemical attack due to high sulfate containing soils present in many parts of the western states may restrict the use of carbon steel pipe in the development of medium temperature geothermal reservoirs. Durable and low-cost piping systems with minimum thermal losses are essential.

The feasibility of using polymer concrete composites as a material of construction for handling hot brine was demonstrated in 1972 in work sponsored by the Atomic Energy Commission and the Office of Saline Water.⁴ The results from these tests indicated that the composites had long-term stability in seawater at 177°C and in acid solutions. Based upon these results, a research program to determine if the composites were applicable to geothermal systems was initiated in April 1974. Since that time, 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. 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 currently in progress. The results to date have indicated the potential for the successful use of polymer concrete 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.

A summary of polymer concrete test results is given in Table 1. Figure 1 shows the effect of pH 1 hydrochloric acid on polymer concrete samples at 90°C. Figure 2 shows the effects of 150°C brine on a sample of polymer concrete pipe. Figure 3 is a view of the Battelle Northwest Laboratory (BNWL) test facility at East Mesa.

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 production 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.⁶ Results from a study indicate capital cost reductions up to 13% for a direct utilization (district heating) application.⁷

The Burns and Roe Industrial Services Company (BRISC) estimated the impact of the use of non-metallic materials of construction in direct utilization processes.⁶⁻⁷ Two processes, sugar beet refining and barley malting, were evaluated. The results indicated that the substitution of a polymer concrete lining for the carbon steel corrosion allowance could reduce the cost of the brine systems in a 9×10^6 kg/day beet refining plant by 27%. In a 1.4×10^6 lit/yr barley malting plant, the cost was reduced by 37%. Considerably larger reductions appeared feasible if prestressed polymer concrete vessels could be used (see Table 2).

Experimental and Results

Polymer concrete consists of an aggregate mixed with a monomer, which is subsequently polymerized in place. The techniques used for mixing and placement are similar to those used for portland cement concrete, and after curing a high strength durable material is produced. The most important process variables are monomer and aggregate composition and the aggregate particle size distribution. Specimens can be produced with compressive strengths of 200 MPa. Full strength is attained immediately after the polymerization reaction is completed. Polymerization can be accomplished using polymerization initiators in conjunction with heat or at ambient temperature using initiators and promoters. Depending upon the temperature and the concentrations of the promoter and the initiator, the cure time can be varied from a few minutes to four hours.

Several polymer systems that can be used in high temperature polymer concrete formulations have been developed. For components designed to operate at 120°C, a monomer mixture consisting of 55 wt% styrene, 36 wt% acrylonitrile and 9 wt% trimethylolpropane trimethacrylate (TMPTMA) to which a 1% by weight of total monomer concentration of a silane coupling agent has been added, has produced good results. Curing of the monomer mixture for high temperature applications is accomplished using a two-step polymerization process. The first stage of polymerization is performed at ambient temperature by the use of benzoyl peroxide-98 as an initiator and dimethyl aniline as a promoter. The second stage involves the use of azobisisobutyronitrile (AIBN) or di-tert-butyl peroxide (DTBP) and subsequent heating at 150°C for 4 hours.

The durability of polymer concrete to geothermal fluids is highly dependent upon the composition of the aggregate. Materials such as quartz, silica, flyash and portland cement have been investigated. Above 218°C, only polymer concrete materials containing aggregate consisting of silica sand-portland cement mixtures have been durable. An aggregate consisting of 70 wt% silica sand and 30 wt% Type I portland cement has given the best results.

After the required amounts of initiators and promoters are dissolved in the monomer, the material is mixed conventionally with the sand-cement aggregate using explosion-proof equipment. It is then placed in forms which are coated with a silicone release agent. External vibration is used to compact the polymer concrete. Dependant upon the initiator and promoter concentrations, size of the batch, form mass etc., curing can generally be controlled to occur in 1 to 2 hr. After removal from the form, the polymer concrete is subjected to additional heating to insure that the polymerization reaction is complete. Typical values of the compression and splitting tensile strength of the polymer concrete described above, measured at elevated temperatures, are given in Figures 4 and 5.

The polymer concrete formulation, described above, has a great adhesion to most materials. The choice of mold materials is very limited. Polished steel works fairly well, but becomes scratched fairly easily. No mold release has been found that is completely satisfactory. Another drawback to casting polymer concrete pipe is shrinkage of the pipe onto the inner form. The inner form can be coated with silicone rubber but silicone rubber is expensive and has a limited life, when in contact with uncured polymer concrete.

Producing glass filament reinforced pipe is a solution to the molding problem. Glass filament wound pipe technology can be adapted for use with the high temperature polymer concrete formulation described above. Filament wound pipe can be made thinner, and therefore lighter, it is less fragile and losses less strength at high temperatures. Even though glass cloth and glass roving is expensive, the total cost per foot of pipe is comparable to that of schedule 40 steel pipe.

The polymer concrete used in making filament wound pipe was a modification of the polymer concrete used for casting pipe. The amount of cement was kept the same at 30%, by weight, but all of the aggregates larger than 50 microns were removed. This slurry was carried onto the mandrel with the glass roving. Coarse aggregates were sprinkled onto the wet mandrel and densified with a roller. Glass cloth layers were applied to give the pipe strength in the axial direction. Each combination of glass roving, slurry, coarse aggregate and glass cloth produces a layer 3.7 mm thick. Multiple layers can be applied to produce a pipe of any desired thickness. After four hours at room temperature the pipe can be removed from the mandrel and oven cured.

Two types of pipe joints have been evaluated with filament wound polymer concrete pipe. Slip joints can be made by forming the bell while winding the pipe; the spigot is formed by surface grinding the opposite end after removal from the mandrel. Flanges have been cast onto the ends of the pipe using the polymer concrete batch containing coarse aggregate.

Filament wound polymer concrete pipe sections have been joined by both methods and successfully tested to 862 kPa at 100°C. Pipe sections 7.6 mm thick have been hydrostatically tested to 4.14 MPa at ambient temperatures. Pipe sections 7.6 mm thick, 15.24 cm I.D. and 25.4 cm long have a crushing strength of 36.7 Kg/cm. Sections 12.7 mm thick, 15.24 cm I.D. and 25.4 cm long have a crushing strength of 136 Kg/cm.

These strength values are equal to or greater than those for cast polymer concrete pipe. The cost of a 1 cm thick filament wound pipe is nearly the same as a cast piece 1.9 cm thick (see Table 3), but the weight per unit length is approximately one-half that of cast pipe. The cost of filament wound polymer concrete pipe is approximately 15% greater than schedule 40 steel pipe at 15 cm I.D. but is 22% less expensive than 30 cm diameter pipe.

Figure 6 shows a filament wound polymer concrete pipe with a cast-on polymer concrete flange. Figure 7 shows a 25 cm section of filament wound polymer concrete pipe.

CONCLUSIONS

Polymer concrete is a composite material which has strength and durability characteristics greatly superior to those of portland cement concrete and better durability than steel. Laboratory and field tests show the material able to withstand the rigors of exposure to geothermal fluids. Polymer concrete systems have been successfully tested in brine, flashing brine and steam at temperatures up to 260°C. Exposures were as long as 960 days. Field tests have been conducted at The Geysers, U.S. Bureau of Mines Corrosion Facility, Raft River and the East Mesa Geothermal Facility.

Glass filament wound pipe is being developed incorporating the durable polymer concrete. Connections can be made using slip joints for lower pressure applications and cast-on flange joints for higher pressure applications. Pipe sections 1.0 mm thick can withstand a hydrostatic pressure of more than 4140 kPa. Sections 1.5 mm thick have a crushing strength of 1250 Kg/m.

Cost estimates show that 15 cm I.D. glass filament wound pipe would be approximately 15% more expensive than schedule 40 steel pipe. Thirty cm I.D. filament wound pipe would be approximately 22% less expensive. In addition, the glass filament wound pipe weighs only 30% as much as the comparable schedule 40 steel pipe and is more durable in harsh environments.

REFERENCES

1. Shannon, D.W., Economic Impact of Corrosion and Scaling Problems in Geothermal Energy Systems, BNWL-1866 UC-4, January, 1975.
2. Tolivia, E., "Corrosion Measurements in a Geothermal Environment", United Nations Symposium, Pisa, Italy, Geothermics Special Issue 2, Vol. 2, pp. 1596-1601, 1970.
3. Kruger, P., and Otte, C., Geothermal Energy; Resources, Production, Stimulation, Stanford University Press, Stanford, CA, 1973, pp. 157-8.
4. De Puy, G.W., et. al., Concrete-Polymer Materials Fifth Topical Report, BNL 50390 and USBR REC-ERC-73-12, Dec. 1973.

5. Kukacka, L.E., et. al., Progress Reports No. 13 and 14, ERDA Contract EY-76-C-02-0016, BNL 50751, Brookhaven National Laboratory, Upton, L.I., N.Y.
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.
7. Cabibbo, S.V., et. al., Economic Assessment of Using Nonmetallic Materials in the Direct Utilization of Geothermal Energy, Burns and Roe Industrial Services Corp., BNL 51112, February, 1979.

Table 1

POLYMER CONCRETE TESTING IN GEOTHERMAL FLUIDS

Location	Conditions	Duration	Results
Laboratory	25° brine, 238°C	325 days	Slight Corrosion, Corners
Laboratory	25° brine, 177°C	960 days	No Deterioration
Laboratory	pH 1, HCl, 90°C	441 days	No Deterioration
Laboratory	pH 1, HCl, 200°C	170 days	No Deterioration
Geysers	steam, 238°C	18 months	No Deterioration
Baca	flashed brine, 160°C	180 days	No Deterioration
Raft River	fluid, 135°C	90 days	No Deterioration
Raft River	fluid, 150°C	132 days	No Deterioration
Raft River	500 ppm brine, 204°C	in progress	
East Mesa	brine, 160°C	60 days	No Deterioration
Niland	brine, 220°C	in progress	

Source, Ref. 5

Table 2

SAVINGS WITH POLYMER CONCRETE⁶

Heber Plant

	<u>ORIGINAL METAL</u>	<u>POLYMER CONCRETE</u>	<u>SAVINGS</u>	<u>% REDUCTION OR SAVINGS</u>
<u>Battery Limits</u>				
Equipment				
Flash Tanks	\$561,610	\$90,548	\$471,062	83.9
Ejectors and Condensers	18,634	20,206	-1,572	-8.4
Vent Scrubber	11,019	5,784	5,235	47.5
Sub total	\$ 591,263	\$ 116,538	\$474,725	80.3
Lines	<u>1,408,112</u>	<u>1,001,763</u>	<u>406,349</u>	<u>28.9</u>
Total B.L.	\$1,999,375	1,118,301	881,074	44.1
<u>Outside Battery Limits</u>				
Brine Supply Lines	\$1,090,080	\$ 713,028	\$ 377,052	34.6
Brine Reinjection Lines	<u>6,134,860</u>	<u>3,654,187</u>	<u>2,480,673</u>	<u>40.4</u>
Total O.B.L.	7,224,940	4,367,215	2,857,725	39.6
<u>Grand Total</u>	\$9,224,315	\$5,485,516	\$3,738,799	40.4

NILAND PLANT

<u>Battery Limits</u>	<u>Original Metallic</u>	<u>Polymer Concrete</u>	<u>Savings</u>	<u>% Reduction or Savings</u>
Equipment	\$ 698,915	\$ 381,027	\$317,888	45.5
Lines	<u>905,919</u>	<u>670,666</u>	<u>235,853</u>	<u>26.0</u>
	\$1,604,834	\$1,051,093	\$553,741	34.5

Table 3

COST AND WEIGHT OF CAST AND FILAMENT WOUND PIPE

	15.24 cm I.D. x 1 cm thick	30.5 cm I.D. x 1 cm thick
Cost of FWPC pipe (material and labor)	\$19.55/m	\$35.20/m
Weight of FWPC pipe	12.45 Kg/m	24.14 Kg/m
	15.24 cm I.D.x1.9 cm thick	30.5 cm I.D.x1.9 cm thick
Cost of Cast Pipe (material and labor)	\$20.43/m	\$36.42/m
Weight of Cast Pipe	24.66 Kg/m	46.56 Kg/m
	15.24 cm I.D.x.98 cm thick	30.5 cm I.D.x.98 cm thick
Cost of Sch 40 Pipe	\$17.13/m	\$48.29/m

LIST OF FIGURES

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

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

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

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

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

Figure 2. PC pipe after exposure to 400 ppm brine at 150°C for 252 days.
No deterioration is apparent.

Figure 3. BNWL test facility at East Mesa. The PC specimens are positioned in the insulated pipe in the left foreground of the figure.

Figure 4. Compressive strength vs. temperature for polymer concrete cylinders.

Figure 5. Splitting tensile strength vs. temperature for polymer concrete cylinders.

Figure 6. Filament wound polymer concrete pipe with cast-on polymer concrete flange.

Figure 7. Section of 25 cm I.D. filament wound polymer concrete pipe.

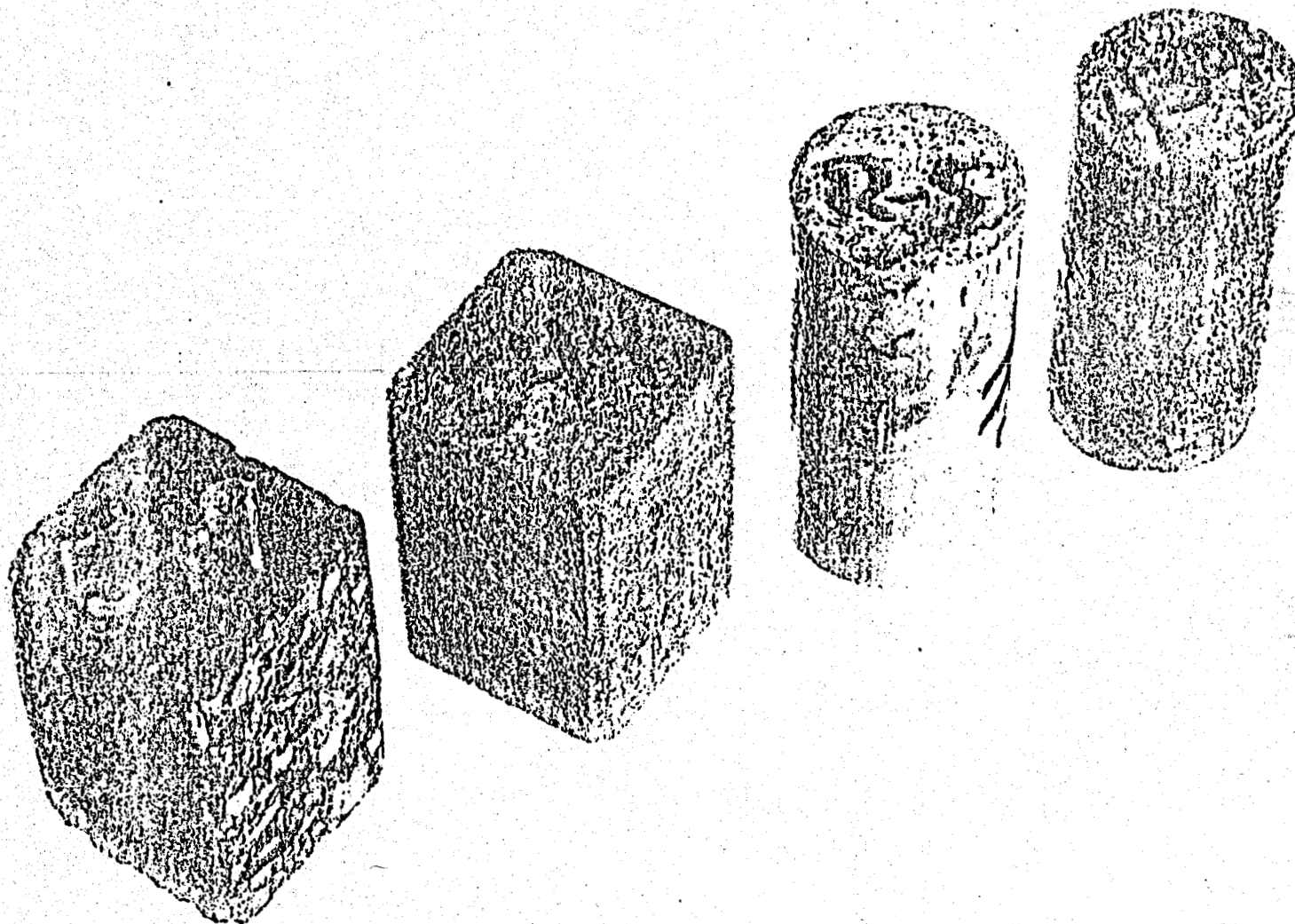


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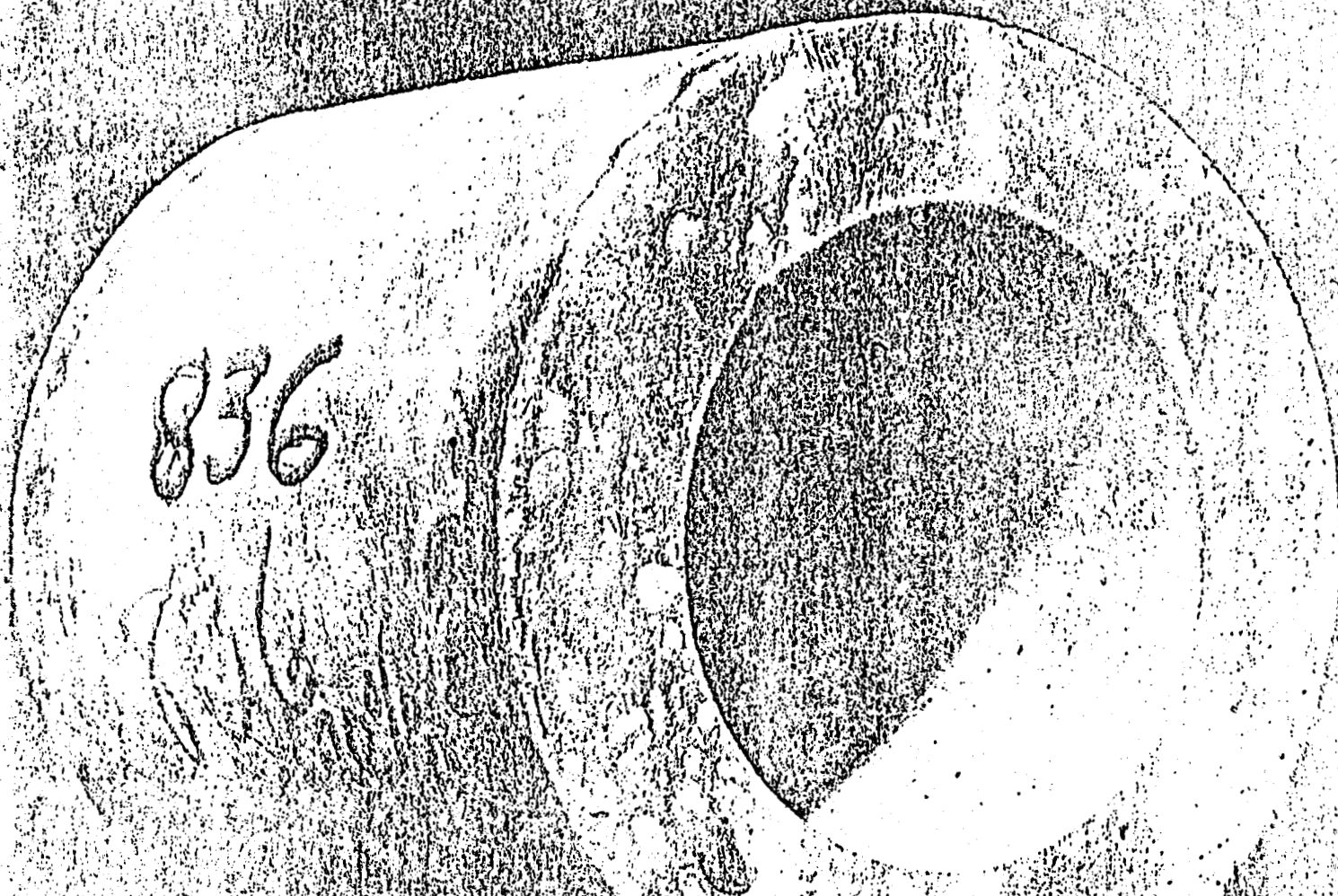


Figure 2. PC pipe after exposure to 400 ppm brine at 150°C for 252 days.
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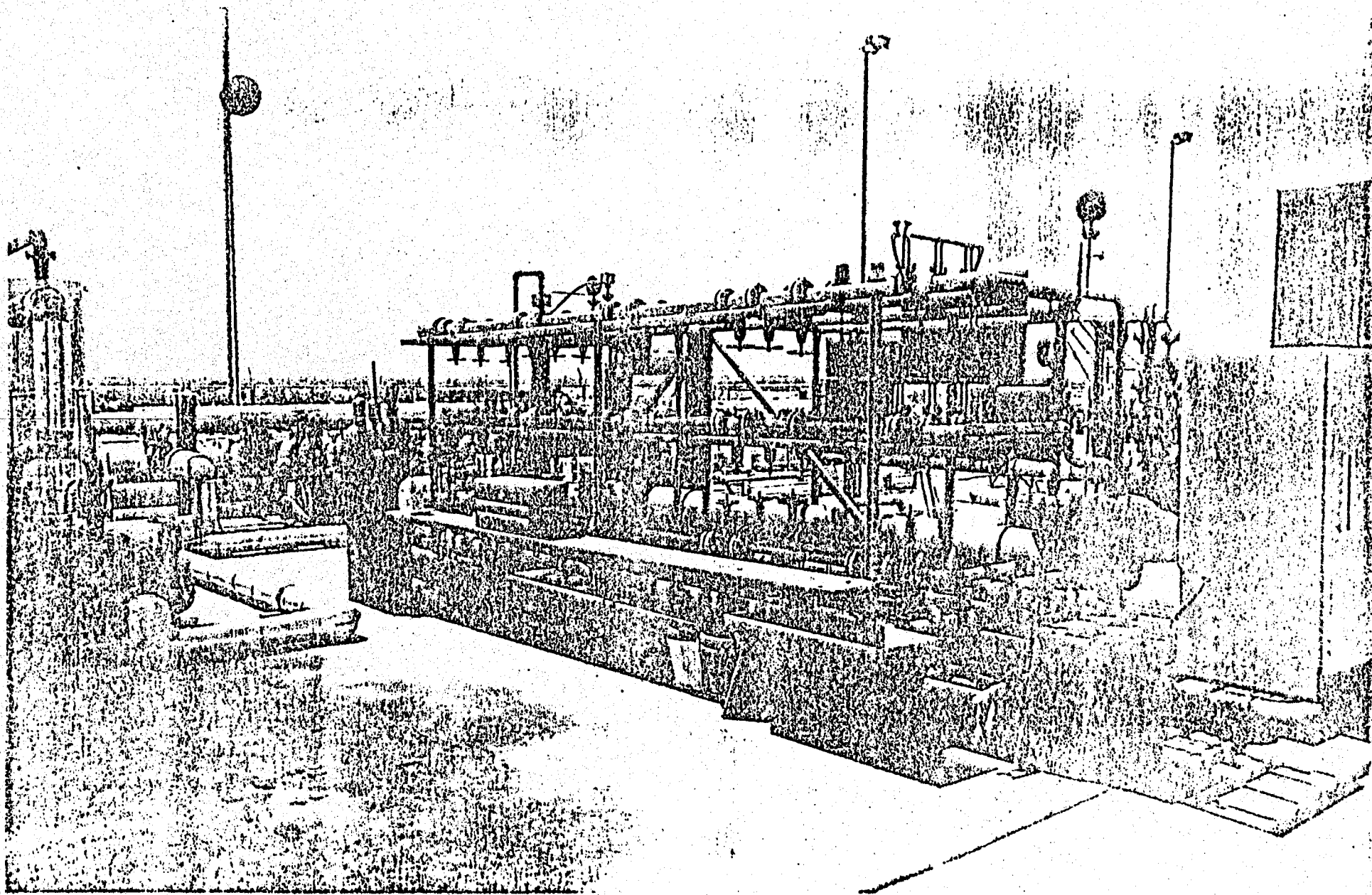


Figure 3. BNWL test facility at East Mesa. The PC specimens are positioned in the insulated pipe in the left foreground of the figure.

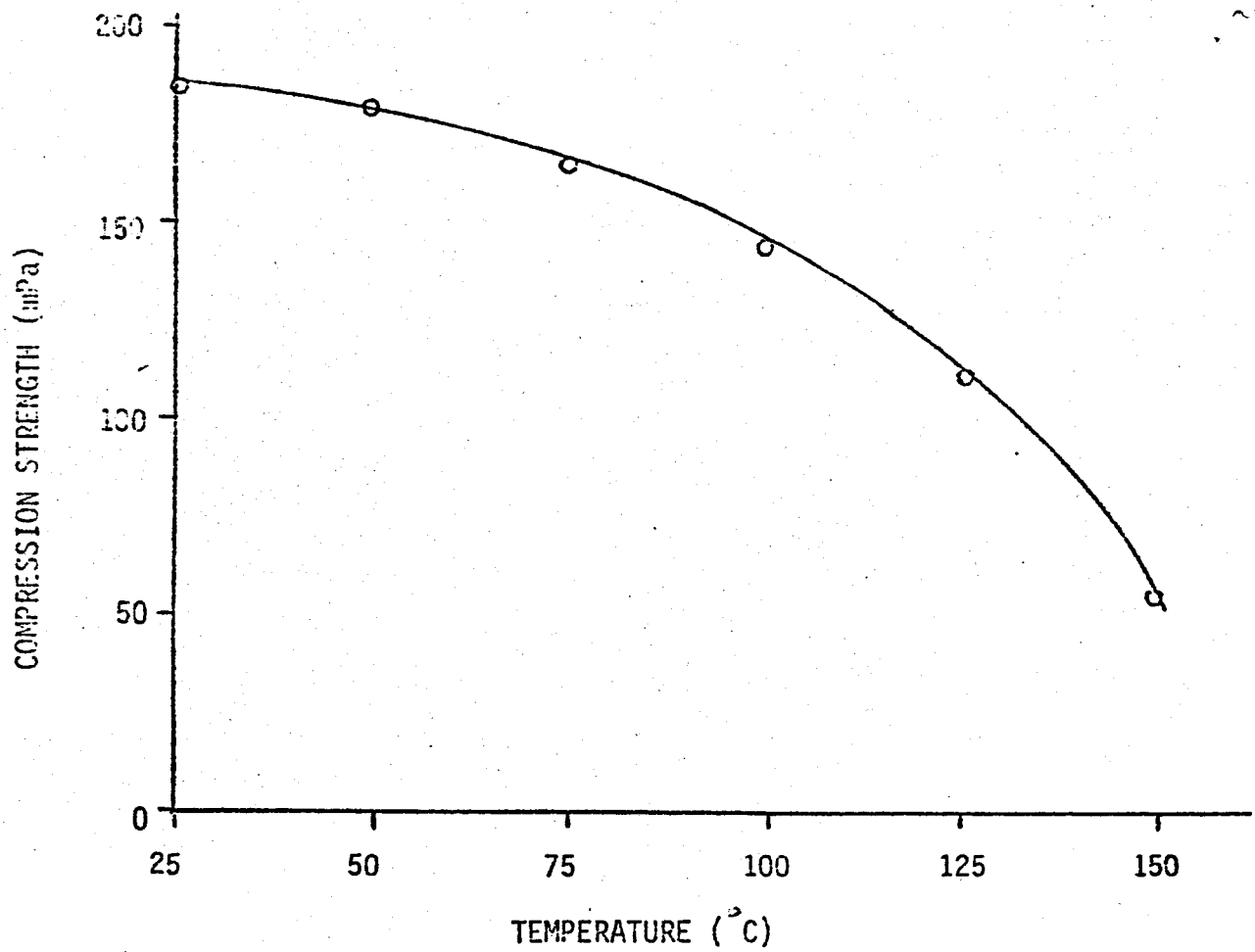


Figure 4. Compressive strength vs. temperature for polymer concrete cylinders.

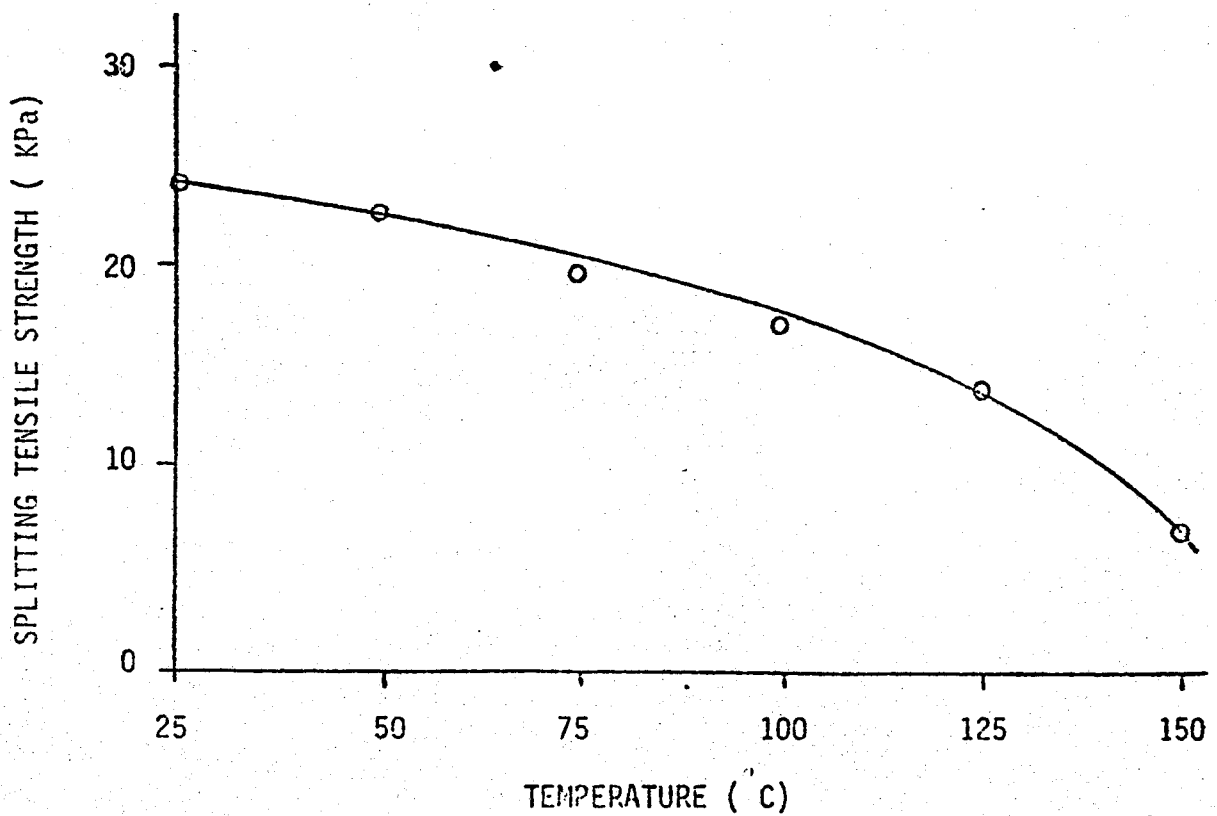


Figure 5. Splitting tensile strength vs. temperature for polymer concrete cylinders.

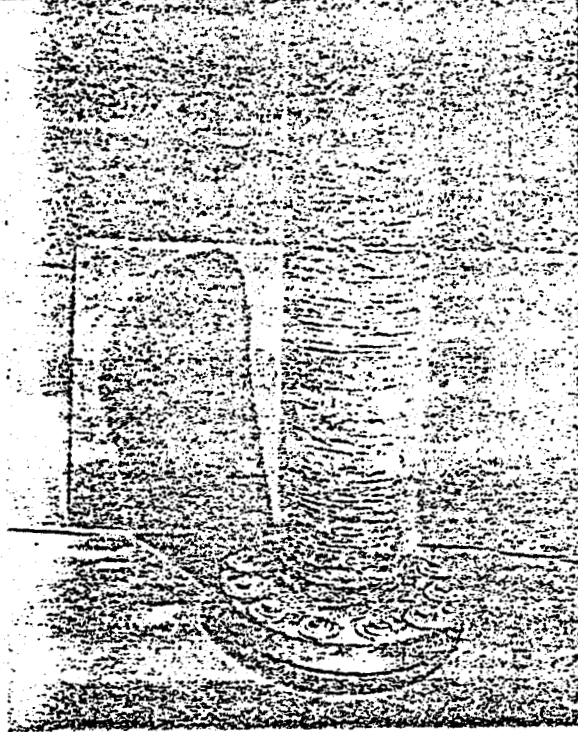


Figure 6. Filament wound polymer concrete pipe with cast-on polymer concrete flange.

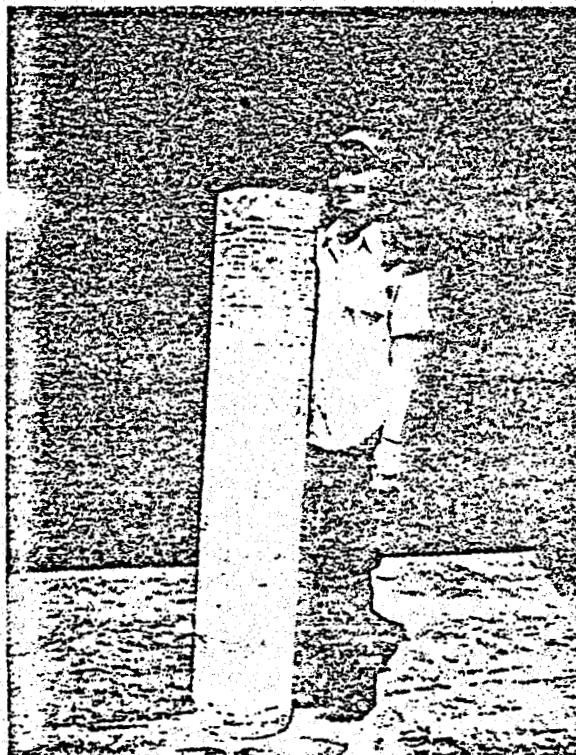


Figure 7. Section of 25 cm I.D. filament wound polymer concrete pipe.