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MATERIALS SCREENING PROGRAM FOR THE LLL GEOTHERMAL PROJECT

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MATERIALS SCREENING PROGRAM FOR THE LLL GEOTHERMAL PROJECT

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In order to assist in the development of the Lawrence Livermore Laboratory's "Total Flow Concept" for the utilization of hot geothermal brine, a materials selection and screening program has been started. Polymers and composites resistant to the high temperatures, hot brine, and erosive conditions present in a flowing well are being sought. Ultimately fabrication into pipes, turbine nozzles, and turbine blades will be required. Test specimens and test equipment are being obtained. The program outline is presented and a few limited test results reported.

INTRODUCTION

The Lawrence Livermore Laboratory has proposed a new method for using hot geothermal brine to produce electrical energy.* Geothermal steam has been used for many years in a modest way for energy production since it is relatively easy to harness. Only recently has geothermal brine been utilized, and then in an inefficient manner, e.g. by passing it through heat exchangers, or by using only the steam which will flash from the hot brine. The large geothermal brine deposits available, for example in the Salton Sea area, offer considerable incentive to develop highly efficient, economically favorable schemes to recover this energy.

The LLL proposal is inovative (and inherently more difficult than current technology) in at least two ways. First, it is proposed that hot brine with high (25%) salt content be used since it is far more available than the very low salt content brine now being used. Secondly, it is proposed that this brine be passed through the turbine system directly as a two phase stream instead of employing only the flashed steam or a heat exchange fluid as is now done. It is estimated that this will allow 60% more power to be produced by the new method than by either of the current methods.

The decision to attempt to harness the hot, high salt content brine with a direct or total flow turbine arrangement is not without difficulties. Beyond those associated with engineering design are those of material choices, which are the subject of this report.

DISCUSSION AND RESULTS

Program Development

The materials required to implement the total flow concept must withstand somewhat different conditions depending upon location in the system, as indicated in Table 1. (Table 1 on following page). The various adverse conditions inherent in such a flowing system were considered along with ways of handling the resulting problems. A program designed to allow selection of suitable materials was then outlined. These steps are presented below:

A. Conditions to be encountered by materials in well and plant.

1. Three temperature zones, 300, 225, and 60°C.

   The fact that the different temperatures are associated with different kinds of hardware (piping, nozzles, turbine blades, and condenser) means that different materials may be used and that fabrication methods must be considered.

2. The presence of chemicals.

   Downhole pH values of 2 to 3 have been reported for some wells. Carbon dioxide is known to be present in some cases. Oxygen is believed to be absent. As many as 20 elements have been identified in some brines; whether these are catalytically important for organic composite decomposition (as some are for metal corrosion, etc.) is unknown.

3. Erosion from high flow rates.

   The presence of liquid as well as gas intensifies the problem. Solids are not normally expected to be present. A low friction factor is desirable to improve flow rates; it would probably be affected by excessive erosion.

*UCRL-51366, "The Total Flow Concept for Recovery of Energy from Geothermal Hot Brine Deposites" by A. L. Austin, G. H. Higgins, J. H. Howard, April 3, 1973.

Work performed under the auspices of the U.S. Atomic Energy Commission.

4. Scale deposition.

In some flow tests, massive scale deposition inside metal pipes has been observed. This is regarded as a potential deterent to long term, economic system lifetime. The scale is complex, but oxides of Fe, Mn and Si are reported to be present. The mechanism of formation, adhesion, and the influence of surface characteristics and composition are not clear.

5. Physical stresses.

Downhole pressure at 5100 feet is about 2200 psia. Whether the pipe must withstand such pressures or not depends upon the installation method used. Moderate tensile strengths, perhaps several thousand psi, must be present to allow relatively long strings of pipe to be emplaced. Moderate compression and flexural strengths would seem important. Erosion resistance, particularly in the nozzle, is very important, although replaceablity of nozzles and turbine blades could be envisioned in contrast to the relative permanance of the downhole pipe.

B. Plan for materials evaluation.

Since the downhole pipe, nozzles, and turbine blades in addition to being distinctly different physically will function at different temperatures (300, 250 and 60°C), it seemed reasonable to have a separate development program for each. Three subprograms were outlined, each with the assumption that laboratory and field testing would proceed in parallel (Figure 1, 2 and 3). The latter was deemed necessary because little is known about composite performance in hot brine wells. Laboratory tests offer advantages of speed, accurate control of conditions, and easier assessment of results. Correlation of results between the two types of testing would be a goal.

C. Hardware manufacturing processes.

It was further recognized that eventual hardware manufacturing processes for pipe, nozzles and turbine blades would need some laboratory development work, for example should filament winding of pipe with high temperature resin and fiber be required.

No specific provisions were made for providing hardware for the condenser part of the system because of the low temperature, pressure and flow rates involved. It was felt that better present day glass/epoxy or furane composites could be used here, or that selections could be made among candidates tested as outlined above.

The objective, then, in carrying out the above program would be to determine to what extent high temperature polymeric materials or composites can solve the materials problems associated with the total flow concept within the framework of competitive economics.

WORK ACCOMPLISHED TO DATE

Although the program is starting at a low level of effort, some of the initial phases have already been completed, and it

	Well Bottom**	Well Head	Nozzle Exit/ Turbine	Condenser
T, °C	300	225	225/60	50
Pr., psia	2213	360	1.7	ambient
Flow, $lbs./sec/ft^2$	500	500	500	
Velocity, fps	100-200	130	2205/965	

**well depth, 5100 ft.

Table 1. Operating conditions vs. location in system.

FIGURE 1. 300°C DOWN-HOLE TUBING

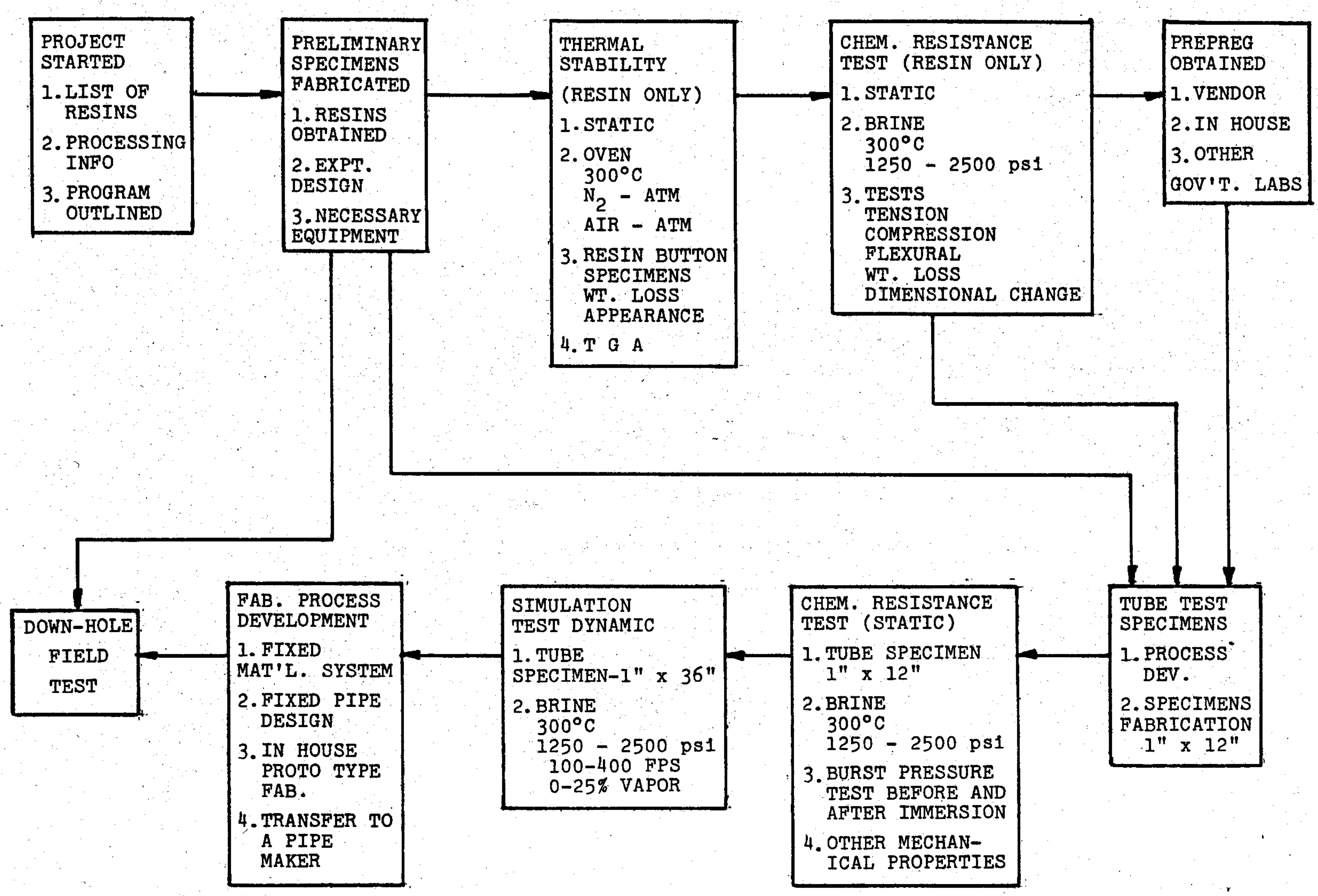


FIGURE 2. 250°C NOZZLE

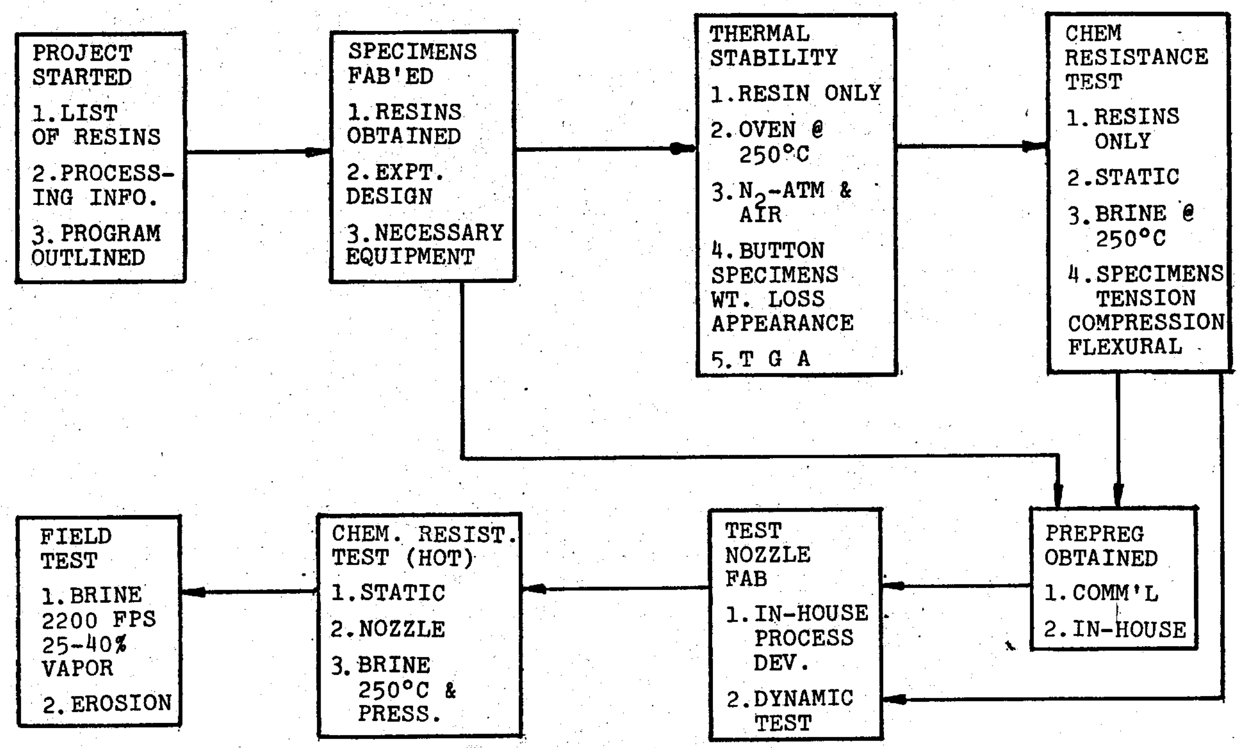
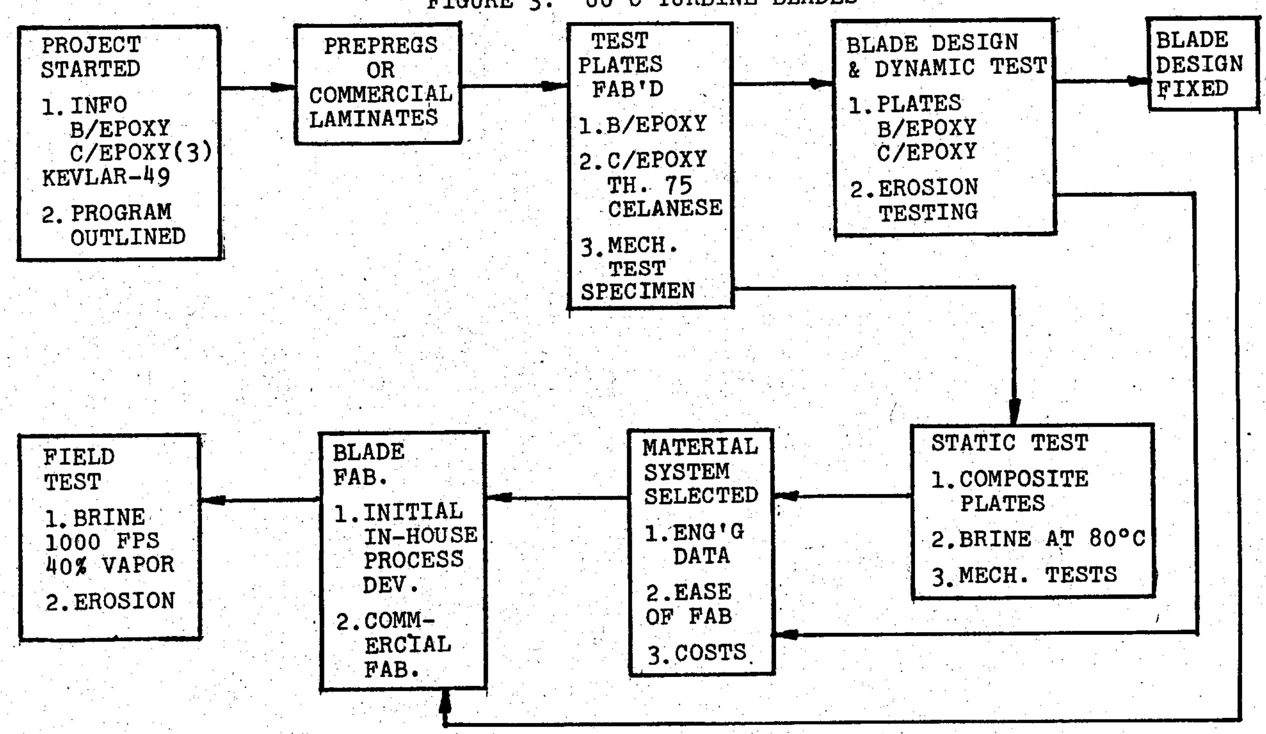


FIGURE 3. 60°C TURBINE BLADES



was felt useful to make a report to stimulate discussion and suggestions for more candidate materials. Figure 1, 2 and 3 will be used as a framework for discussion, although changes in these flow charts are inevitable.

A. Selection of candidate materials.

The initial task, that of listing resin candidates is reasonably complete. A formal literature search has not been done; this would generate a near unmanageable number of references.

MATERIAL CLASS, TRADENAMES	Supplier	Max. Use Temp.	Hydrolytic Resistance	Erosion Resistance	Friction	Tensile psi	Elongation %	Modulus of Elast.	Compr. Strength	Flex. Modulus
CARBON/GRAPHITE	Various	>500°C	E			(3.5K)			(17K)	
CARBORANES										
Dexsil	Olin	500	F			100-600	50-300			
EPOXY										
DEN 438/Thornel			F			>10K				
FLUOROCARBONS										
Teflon-PFA	DuPont	260	E		Low	4.6K	300			100K
Teflon-TFE	DuPont	288	E		Low	2-4K	300	0.6×10^6	1.7K	
H-RESIN	Hercules	215	E	G						10^6
PHENOLIC										
Glass/phenolic	Ferro	300	G							
PHOS-PHONITRILICS	Various	260	G			7K			44K	
POLY-BENZIMIDAZOLES										
Imidite	Narmco	316								
POLYBUTADIENES	Firestone	>250	G			7.5K				
POLYESTERS										
Hetron	Durez	177	F	G		(50K)				
Hetron FA	Durez	302	G	G		(10-17K)	(2)		(10-15K)	(7×10^5)
Ekonol	Carbo-	300								
Ekkcel	rundum	300	G	G	Low	10K	7-9		20K	450K
POLYIMIDES										
Amide-imide	Amoco	260				(56K)	(1.8)	(3×10^6)		(3×10^6)
Skygard 700	Monsanto	370				(57K)	(1.9)	(3×10^6)		
Vespel	DuPont	250	G(H+)			13.5K	6-8	450K	24.4K	450K
NR-150B	DuPont	350				13K	2			
P13N	TRW									(3.6×10^6)
Kinel 5502	Rhodia	250				2.6K			9.65K	610K
Kerimid	Rhodia	250								
Meldin	Dixon									
PHEN. POLY-QUINOXALINE	NOL	300+	G			50-100K				
PYRRONES	NASA	400		G		23K		(5×10^6)	12K	($.7 \times 10^6$)
SILICONES	Dow, GE	300								

Table 2. Candidate materials for geothermal program.
(Entries in parentheses are approximate, or for reinforced samples)

Instead, a search has been made for high temperature or corrosion resistant resins which are, or could become commercially available at reasonable cost in a reasonable time. Very exotic or difficult to work with materials have been excluded. Sources have been personal files, "space age" materials research reports, and personal contacts with people associated with government research centers, airframe manufacturers and commercial polymer manufacturers. Two things have become clear as a result of this survey. First, of the many dozens, or perhaps hundreds of high temperature resins described in the literature, relatively few have become available. Second, despite this, research effort continues and results in real advances periodically, for example in a new generation of polyimides, and aromatic polyesters. New fibers made of carbon, graphite and aromatic polyamides are being successfully used for reinforcement. The list of reasonable candidate materials appears as Table 2. Many of the desired properties are not available, either in the assembled descriptive brochures or research reports partly because some of our requirements are of little interest in most applications. This table will be expanded as we become aware of other possibilities.

B. Acquiring test specimens.

Another task is that of acquiring test specimens. Some have been provided by manufacturers, others have been made in house using purchased materials. That several types of sample shapes are required can be seen by examining Table 3 which was condensed from the flow charts.

Initially, we have concentrated on providing 1-1/4"D x 1/4" discs for use in the static tests, 3" x 4" x 1/8" plates for erosion tests, and nozzles for forthcoming flow tests. The nozzles are cylindrical, approximately 1"D x 1-3/16", with a typical restricted throat design.

C. Equipment needs.
The equipment required to make test specimens from the high temperature polymers, and to carry out the necessary testing is described below:

1. Discs and cylinders have been made using the piston mold from a Buehler Specimen Press. The extra heating capability required was obtained by surrounding the mold with clamshell heaters, insulated with sheet asbestos and Transite board. This unit was placed in a 40,000 lb. press to allow application of pressure to the piston.

2. For making flat plates for erosion tests, a typical 4 x 4" picture frame mold has been acquired. It will be heated in the 40,000 lb. press using platens modified to give the high cure temperatures required.

		In the laboratory
Static:	1)	Thermal stability in N_2 and air (TGA, oven).
	2)	Chemical resistance, in brine at temp. and pressure in closed bombs (check tensile, compressive, flexural, wt. loss and dimensional changes for solid samples, burst pressure for tubes).
Dynamic:		Use special test unit to simulate field by circulating hot brine under pressure.
	1)	Check effect on tubes (burst pressure, etc.).
	2)	Check effect on nozzles (dimensional, wt. changes).
	3)	Check effect on erosion plates (wt. loss).
		In the field
Static:		Downhole in non-flowing well.
Dynamic:		Nozzles, erosion plates and pipes in stream at well head.

Table 3. Specific materials tests.

3. Fiber reinforced plates have been made by filament winding using a flat mandrel 4"x 3.75" x 3/4".

4. Test pieces have been cured in a heavy duty furnace (0-2000°F) or an oven (0-1000°F).

5. Static test in hot brine are being carried out in stainless, high pressure bombs. A rather close fitting quartz vessel (1-3/4"D x 10", 200 ml vol.) is used as a liner to minimize contact between hot brine and metal. The samples are spaced in the brine present within the quartz vessel by means of a stand. The stand was made by fusing five 1" quartz discs inside three vertically held 9" quartz rods at approximately 2" intervals; samples rest on each disc.

6. Filament wound nozzles have been made on the NOL machine by winding on a split spool, the external contour of which duplicates the internal dimensions of the test nozzle.

7. A preliminary design for a hot brine flow test apparatus has been completed (Appendix). High temperature pumps could not be located, so a pressure driven stream must be used. This results in a cyclic flow, but this is deemed acceptable. In principle with such a test usit we can test pipe, nozzles, and turbine blade materials by placing our flat erosion plates in the path of the stream coming from the nozzle.

   Other equipment which will be needed includes a high temperature vacuum oven, and filament winding apparatus for making pipe. The remaining apparatus or capability required for the program as outlined is available at the laboratory.

D. Fabrication of test specimens at LLL.

The fabrication of test specimens has proceeded using some of the materials listed in Table 2 and the equipment described above:

Polyimide, NR 150 A and B (DuPont)

This is a new type of polyimide system in which chain extension takes place with no crosslinking. Products are essentially thermoplastic which allows production of parts with very low void content. Very high glass transition temperatures and good thermal stability permit use at high temperatures.

For the preparation of solid discs, the N-methylpyrrolidone solvent was removed in a vacuum oven at 60°C and the residue densified in the cylindrical piston mold. Several experiments led to adoption of the following cure cycle as being satisfactory for NR 150A: Heat mold and contents to 175°C for 1 hour, raise to 200° for 1 hour, 250° for 1 hour, at 300°, 200 psi was applied, after 1 hour raise to 316° for another hour. Allow to cool under pressure. Densities of 1.41 and 1.36 for 150A and 150 B were obtained, compared to published values of 1.42 and 1.40.

Flate plates of NR 150 A and NR 150 B reinforced unidirectionally with Thornel 400 graphite yarn were made using the filament winder. Seven to 10 layers of fiber were laid down on the flat molds, which were then cured in a press with the following schedule: for NR 150A: Heat to 175°C for 40 min., apply platen weight to the part. Heat at 200° for 40 min., 250° for 40 min., apply 2500 psi and heat at 300° for 1.5 hr., then at 316° for 3 hrs. Allow to cool under pressure.

Microscopic examination of a cross section cut through a cured sample showed a very low void content. A number of flat laminates were prepared in this manner for stacking and curing under pressure to form an erosion test plate.

Several other laminates were cut into 1-1/4" discs; machining was necessary. The surfaces of the discs were coated with fresh binder solution which was allowed to air dry. They were then stacked in the piston mold with the reinforcement alternating at 90°, and cured under pressure to form a cylinder. The cylinder was machined and ground into a test nozzle.

Other test nozzles were made by winding Thornel 400 on the split nozzle mandrel, followed by the usual cure and finish machining. Nozzle erosion tests using these two types of nozzles will give an indication of the importance of fiber orientation.

Ekonol 900 aromatic polyester (Carborundum)

Ekonol is a new high temperature polyester which can be molded. Several trial runs led to the following as a suitable cure schedule in the piston mold: Preheat mold and resin to 316°C, apply 200 psi, increase pressure in increments of 200 psi every 30 sec. to 2000 psi, hold for 5 min., heat turned off, and allow mold to cool before removing the part. Densities of 1.41 were readily achieved, compared to the published value of 1.43. Test cylinders were made as well as discs. Use of the pellets as received gave as good results as more finely ground product.

The cylinders could be machined into test nozzles with no difficulty; dimensions and finish were quite good.

E. Test results.

Test results have been obtained with a few samples. An opportunity to place samples in a deep brine well in the Salton Sea area became available. A sample of PPQ resin, PPQ resin reinforced with carbon fibers, and polyimide (Meldin) were mounted on a holder within a perforated pipe. A number of other materials were present also. The pipe was lowered to approximately 5000 ft. in a well, and allowed to remain for three months. No flow was allowed. Upon removal it was found that the PPQ, while abraded in appearance, was intact. The fiber reinforced PPQ had delaminated, and the polyimide had become granulated. Test temperature was unknown, as was the possible effect of breakdown products from other samples within the test pipe.

FUTURE WORK

Additional candidate materials are being sought, and fabrication into test parts with these as well as with resins on hand will be continued as indicated in the flow diagrams. Testing will be continued as outlined in Table 3.

Candidates are now being screened in bombs filled with hot brine; this will continue. The inclusion of dynamic testing relatively soon is important. The matter of scale deposition and its prevention must receive some attention also.

ACKNOWLEDGEMENTS

The advice and assistance of T. T. Chiao and J. K. Lepper in getting this program underway is gratefully acknowledged, as is the effort of E. T. Mones in preparing and testing samples and J. Mahler in designing a flow test apparatus.

APPENDIX

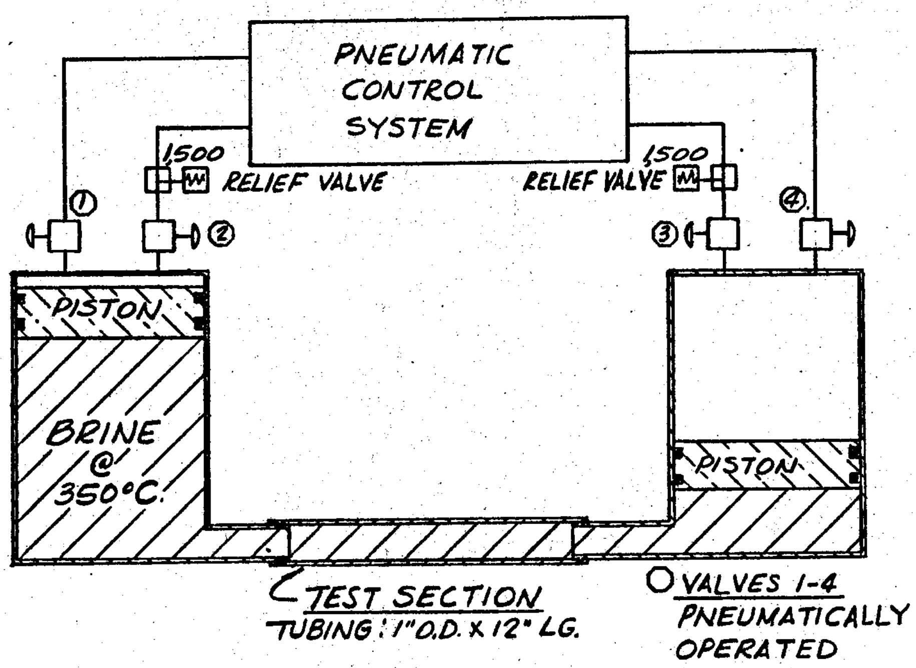
GEOTHERMAL PIPE, NOZZLE AND TURBINE BLADE MATERIAL TESTER

A preliminary design study was conducted to develop a flowing system for evaluating the performance of materials for geothermal applications. The design criteria were that the system would have to pump a geothermal brine thru a 1" diameter x 12" long tube at pressures from 1250 psi to 2500 psi with fluid velocities from 100 to 400 fps and at a temperature of 300°C. These requirements simulate the actual flow conditions found in geothermal wells located in the Salton Sea region of California.

The system designed uses a pneumatically controlled piston arrangement for pumping a geothermal brine thru a 1" D test section. The basic System (see sketch) consists of two heated cylindrical tanks containing brine which are connected together by the 1" D tube being evaluated. In each tank a pneumatically controlled piston applies pressure to the brine. A bias pressure of approximately 1500 psi is maintained in the brine at all times to prevent it from flashing. Flow thru the test section occurs when the pneumatic control system establishes a fixed pressure difference between tanks. This pressure difference provides the driving force that causes the brine to flow thru the test section at a given velocity. Preliminary calculations indicate that a pressure difference of approximately 150 psi @ 1500 psi bias pressure would be required to achieve a steady state flow velocity of 100 fps in the 1" diameter test section.

This system can be designed so that the flow thru the test section can be either uni-directional or bi-directional. The only drawback with this system is that instead of exposing the test section to a continuous flow of brine it subjects it to a pulsating type flow. Therefore, the test section would really be exposed to a more severe environment than it would see in the actual well. Nozzles followed by erosion wear plates (turbine blades) can be installed downstream from the pipe section.

The main advantage of this design is that it is simple and cheap, the tanks can be fabricated out of standard stainless steel tubing and can easily be replaced when damaged. The pneumatic control system is completely isolated from the brine so there should be no problem with corrosion or erosion in this area.



GEOTHERMAL MATERIAL TESTER

Distribution:

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