PRESENT STATUS OF THE POLYMERIC-MATERIALS SCREENING PROGRAM FOR THE LLL GEOTHERMAL PROJECT

Lyman E. Lorensen

C. M. Walkup

E. T. Mones

July 9, 1975

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

MASTER
DISTRIBUTION OF THIS DOCUMENT UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$ ___*; Microfiche \$2.25

<u>* Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

LAWRENCE LIVERMORE LABORATORY
University of California/Livermore, California/94550

UCRL-51843
**PRESENT STATUS OF THE
POLYMERIC-MATERIALS SCREENING
PROGRAM FOR THE LLL GEOTHERMAL PROJECT**

Lyman E. Lorensen

C. M. Walkup

E. T. Mones

MS. date: June 12, 1975

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Contents

Abstract	1
Introduction	1
Interim Results	2
Hot-Brine Tests in Stainless Steel Pressure Vessels	6
Tests at 300°C	6
Tests at 250°C	10
Materials Tests at Geothermal Wells	11
Test Results on Nozzles	12
Test Results on Wear Plates	15
Equipment	15
Part Fabrication	16
Future Work	16
Acknowledgments	16
References	18
Appendix	19
Detailed Test Results on Nozzles	19
Detailed Test Results on Wear Plates	26
References	26

PRESENT STATUS OF THE POLYMERIC-MATERIALS SCREENING PROGRAM FOR THE LLL GEOTHERMAL PROJECT

Abstract

Progress is reported on the continuing experimental program aimed at finding high-performance polymeric materials for use in the Lawrence Livermore Laboratory "Total Flow" process for producing electricity by the use of geothermal brines. Out of a total of 29 polymeric materials which have been screened in a 300°C static brine-test, 7 types of polymers have withstood tests up to 555 hr with less than 10% weight loss. Also, 5 polymeric materials were tested at 250°C for possible service in the less demanding plant components. Polymer structures containing either substantial aromaticity, fluorine, carbonized structure, or aliphatic unsaturation which as been crosslinked,

show considerable stability. The presence of water-sensitive groups such as imide, amide, or ester is detrimental even in very thermally stable polymers. Eight nozzles and two wear plates were tested in the field. While plugging of nozzle throats by well debris made interpretation of results difficult, both the nozzles and a wear plate of Teflon PFA showed minimal scale deposition and erosion after more than 100 hours of operation. Teflon TFE, and to a much lesser extent Teflon PFA, developed surface fibrils while subjected to well flow. Equipment corrosion problems, acquisitions, part fabrication, critical-path planning and future-work plans are discussed.

Introduction

Lawrence Livermore Laboratory (LLL) has initiated a program aimed at economic generation of electrical energy from hot geothermal brine. In this scheme (called the "Total Flow" process¹), hot, pressurized geothermal brine is piped to the surface of the ground, directed through special nozzles against turbine blades, and then condensed for reinjection via deep wells. Because of the difficult environmental problems associated with handling hot, high-pressure brine, LLL has

been conducting a special program aimed at selecting and screening materials for the down-hole brine delivery pipe, nozzles, turbines, condenser parts and brine reinjection pipes. In addition to mechanical strength, desirable properties of these materials include thermal stability, resistance to corrosion and chemical attack, erosion resistance, and anti-scaling characteristics. This program, as described in Ref. 2, has been under way for some time and has been supplemented

in a number of specific respects. Among these are:

1. Information available in the literature and from vendors has made it unnecessary to conduct oven and thermogravimetric analysis (TGA) thermal stability tests for characterizing materials.

2. Hot-brine-flow-erosion tests are being conducted at wells rather than in the laboratory.

3. Our tests now include polymer-lined metal pipe as well as filament-wound pipe.

4. The LLL Geothermal Test Facility will include salt-free two-phase "clean steam" tests of nozzles and wear plates. A flowchart of events in the complete testing and evaluation program is shown in Fig. 1. The steps in this sequence are shown in a format corresponding to the Critical Path method as prepared by an LLL computer code.

5. Present turbine designs require use of specialized protective coatings. Plans for selecting and evaluating such coatings are now under way.

6. Nozzle designs have been enlarged to minimize debris entrapment.

7. In order to better simulate turbine geometry, a black-type wear plate is being exposed to edge-on flow testing.

INTERIM RESULTS

Out of a total of 29 materials which have been screened in the 300°C static

brine test, 7 types or families of polymers have withstood longer term tests (up to 555 hr) with less than 10% weight loss. Five materials tested at 250°C for possible service in less demanding components show reduced but unpredictable weight losses. Polymer structures containing either substantial aromaticity, fluorine, carbonized structures, or aliphatic unsaturation which has been crosslinked show considerable stability. The presence of water-sensitive groups such as imide, amide, or ester is detrimental even in very thermally stable polymers. Eight nozzles and two wear plates have been exposed to flow from a geothermal well. While plugging by well debris made interpretation of nozzle results difficult, both nozzles and a wear plate of Teflon PFA* showed minimal scale deposition and erosion after more than 100 hours of operation. Nozzle designs have been enlarged to minimize debris entrapment. Also, a blade-type wear plate is being exposed to edge-on-flow testing in order to better simulate turbine geometry. Present turbine designs will require some protective coatings and plans for selecting and evaluating such coatings are now under way.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

Fig. 1A. Critical-path chart for the materials-screening program (part 1)

Fig. 1B. Critical-path chart for the materials-screening program (part 2)

Fig. 1C. Critical-path chart for the materials-screening program (part 3)

Hot-Brine Tests in Stainless Steel Pressure Vessels

TESTS AT 300°C

Since the start of the testing and evaluation program a total of 29 materials has been examined. The results of those tests are listed in Table 1, for materials which lost more than 10% weight after 72 hours at 300°C, and Table 2 for those which lost less than 10% weight after 72 hours at 300°C. The percent weight changes with heating time for the better materials are plotted in Figs. 2A and 2B. As indicated in these figures, several samples showed a rather rapid initial weight loss, probably from loss of monomer, other low molecular weight fragments, or water.

Stabilization then followed. Six materials, a carbon/graphite cloth heat-shield-type composite, two DuPont Teflons, Hercules H-resins, Whittaker Imidite polybenzimidazole, polyphenylquinoxaline/Modmor II carbon fiber and a Ferro phenolic, all show very good stability far beyond 72 hours. A seventh material type, Firestone Dienite, shows some promise in certain versions. This is especially encouraging in view of the low cost of 1,2-polybutadiene.

It should be noted that some of the materials listed in Tables 2 and 3 contained nonpolymeric additives such as fillers which function to improve

Table 1.

Materials showing more than 10 wt% loss after 72 hr in 300°C synthetic brine

Material class or type	Supplier and/or trade name	Filler	Weight loss (%)
Polyphenylene Sulfide (PPS)	Phillips-Ryton	40% glass fiber	Flowed ^a
Polyphenylene Sulfide (PPS)	Phillips-Ryton	40% glass fiber	Flowed ^a
Polyimide	Meldin		31
Epoxy/Thornel 50 S Carbon fiber		Estimated 60% carbon fiber	43(100) ^b
Aromatic Polyester	Carborundum-Ekonol 900		69
Carborane	Olin-Dexsil-201		82
Polyimide	DuPont-NR150B		100
Polyimide	DuPont-NR150B		100
Polyimide	DuPont Vespel		100
Polyimide	Monsanto-Skybond 700		100
Polyamide	DuPont-KS Polyamide		100

^a PPS flowed during the test, breaking into smaller pieces some of which could not be recovered. It was not felt that the polymer was necessarily degraded, however.

^b Predicted loss if the sample had been 100% polymer.

Table 2.

Materials showing less than 10 wt% loss after 72 hr in 300°C synthetic brine

Material class or type	Supplier and/or trade name	Filler	Weight change (%)
Polybenzimidazole (PBI) foam			+79 ^a
Polyimide/carbon fiber Kermid 601/Thornel 400		Estimated 60% carbon fiber	+35 ^b
Polyaromatic	Hercules H-Resin-HA-54	40 wt% Al ₂ O ₃	+6
Carbon/carbon fiber composite			+4
Polytetrafluoro- ethylene	DuPont Teflon TFE		+1
Fluorinated (perfluoroalkoxy) copolymer	DuPont Teflon PFA		0
Polyaromatic	Hercules H-104 Resin		0
Polyaromatic	Hercules H-124,	50 wt% graphite	0
Polyphenylquinoxaline/ carbon fiber		Estimated 60% carbon fiber	0
Polyaromatic	Hercules HA-54 Resin Stabilized	40 wt% Al ₂ O ₃	-1(1.7) ^c
Poly-1,2-butadiene	Firestone Dienite X-644	10% chopped glass	-2(2.2) ^c
Phenolic/fiberglass	Ferro Corp.	Estimated 70% fiberglass	-3(10) ^c
Poly-1,2-butadiene	Firestone Dienite X-644	10% chopped glass	-5(5.6) ^c
Poly-1,2-butadiene	Firestone Dienite X-556		-5
Polybenzimidazole	Whittaker Imidite 2803		-5
Polybenzimidazole	Whittaker Imidite 2803		-5
Poly-1,2-butadiene	Firestone Dienite X-643	20% chopped glass	-8(10) ^c
Poly-1,2-butadiene	Firestone Dienite X-555		-9
Poly-1,2-butadiene	Firestone Dienite X-555		-9

^aThe PBI foam showed gains of 79 wt% at 144 hr and 82 wt% at 240 hr, indicating that the foam had filled with salts from the 25 wt% salt-content brine. These salts could not be washed out readily and remained after drying the sample to constant weight.

^bThe polymer was undoubtedly removed by the hot brine, leaving a porous fiber matt to collect salts.

^cPredicted loss if the sample had been 100% polymer.

Fig. 2A. Weight loss vs time in 300°C brine (part 1)

Fig. 2B. Weight loss vs time in 300°C brine (part 2)

certain performance factors. In Tables 1 and 2, both observed losses and losses normalized to 100% polymer are given since we do not always know filler contents exactly nor whether the filler remains unattacked in hot brine. Because further study needs to be done to determine the mechanism of weight loss, the most reliable comparisons are among materials which are 100% polymer.

It was hoped that polyimides would perform better than was actually observed. Reference 3 notes that the polyimide film, Kapton, remains flexible after 1 year in boiling water. Other references are not so optimistic, stating that resistance to superheated steam is low, etc.⁴ Thermal stability of the polyimides in at least some samples should be quite adequate, particularly for those formed by the condensation process. Other desirable properties of the polyimides include strength, oxidative stability, ease of fabrication (including filament winding), and availability at a reasonable cost.

However representative materials failed (by foaming or dissolving) in as short a time as 21 hours. See Table 3. Seven addition types of polyimides are currently available as well as at least two condensation types (Vespel or Kapton, and Skygard). See Ref. 5.

TESTS AT 250°C

Materials which fail the 300°C brine test may still be useful for the lower temperature application in nozzles (240°C), turbine parts (60°C) and condenser parts (50°C). A further incentive for conducting tests at lower temperatures is that the less thermally stable candidates are often economically very attractive. Results of initial tests of such materials are given in Table 4. As expected, the observed weight losses are higher at 300°C than at 250°C. Differences between the observed and calculated 300°C values result from the fact that the calculated values were extrapolated from the observed

Table 3.
Effect of 300°C brine on polyimides

Material	Results after indicated heating time	
	21 hours	72 hours
Meldin		-31%(brittle, porous residue) ^a
DuPont NR150B		-100% ^a
Kerimid 601/Thornel 400		+35%(carbon fibers trapped salts) ^a
Skybond 700	Foamed residue	
DuPont NR150B	-100% ^a	
Vespel	Charred residue	

^aPercent weight change

Table 4.
Weight loss vs time in 250°C artificial brine

Material	Weight loss after 72 hours			Weight loss after 202 hours		
	250°C (%)	300°C (calculated ^a) (%)	300°C (observed) (%)	250°C (%)	300°C (calculated) (%)	300°C (observed) (%)
Dienite X-555	-0.11%	- 3.5	-8.9	-1.7	- 54	-15
Dienite X-644	-1.9	- 61	-3.6	-2.3	- 74	- 7
Hercules H-104	-0.4	- 12.8	-0.6	- .9	- 29	- 0.2
Hercules HA-54	-0.2	- 6.4	-1	0	-	-
Imidite 2803	-3.9	-100	-5	-4.9	-100	- 6

^a Assuming that weight loss is proportional to reaction rate, and that reaction rate follows the Arrhenius approximation of doubling with each 10°C rise in temperature.

250°C values. The latter, however, are an uncertain basis for such calculations due to the likely contribution of non-degradative processes (monomer or water loss) to the relatively small total losses involved at 250°C. Particularly encouraging is the improved performance of the inexpensive 1,2-polybutadiene "Dienites" at 250°C.

Some generalizations regarding the ability of various materials to survive hot brine can now be made. Hydrolyzable linkages within molecules are undesirable, as evidenced by the poor performance of polyimide, the aromatic polyester, the carborane and the polyamide. Some of the

crosslinking phenomena involved in the cure of epoxy resin are also reversible at high temperatures in the presence of water. In contrast to these sources of instability, a high degree of aromaticity combined with water-insensitive linkages (such as are found in PBI, H-resins, PPQ and phenolic) confers stability. The high-melting fluorocarbons, Teflon TFE and PFA, as well as the highly crosslinked 1,2-polybutadienes also successfully withstand the 300°C brine. There is some evidence that the presence of stabilizers (termed "Antioxidants/Antidegradants" by Firestone) is helpful in the case of the butadiene polymers.

Materials Tests at Geothermal Wells

Following limited initial static tests in a deep well², nozzles and wear plates were prepared for dynamic tests on the stream from a flowing well. These tests were designed to show differences in

erosion resistance of materials under the hot corrosive well conditions. Results with wear plates would offer guidance for selecting materials for turbine blades. The nozzle design is shown in Fig. 3.

Fig. 3. Nozzle design for materials tests

The wear plates were flat specimens approximately $7.6 \times 10.2 \times 0.64$ cm which were clamped on the exit side of the nozzle at such an angle that the expanded stream impinged on the central area.

Four nozzles and their wear plates were mounted on a manifold inside a large chamber. Brine from the well entered on one side, passed through the manifold and four test nozzles, struck the wear plates, then exited at the opposite end (Figs. 4 and 5).

TEST RESULTS ON NOZZLES

Seven nozzles made from five different materials were tested, each for from 110 to 130 hours. Brief comments on each follow. Detailed comments and photographs of these nozzles are found in the Appendix, Figures A1 through A15.

Nozzle N-1. Carbon Fiber or Felt Impregnated With Carbon Via the Carbon Vapor Deposition (CVD) Process.

After testing, this nozzle (Fig. A-1) and several others were partially blocked with pieces of scale debris, probably from upstream valves or pipe. These pieces were simply too large to pass the small throats of the nozzles. The resulting choking off of flow allowed evaporation to deposit scale. The scaling pattern with N-1 was unusual in that the heavy internal deposition terminated suddenly, well before reaching the exit rim.

Nozzle N-3. Teflon PFA (Perfluoroalkoxy).

Partial throat blockage allowed some scale buildup (Fig. A-2). Deposits could be flaked off more readily than with Teflon TFE.

Fig. 4. Rear view of chamber for field testing nozzles and wear plates.

Nozzle N-4. Teflon PFA (Perfluoroalkoxy).

No throat blockage occurred, and a very thin scale coating resulted in the cleanest nozzle in the group (Figs. A-3, A-4 and A-5). In the throat end, two small areas of thick filamentary growth could be seen. Magnification showed them to be similar to flat leaves in contrast to the fine hairs found beneath the scale with Teflon TFE (see description of nozzle N-15).

Nozzles N-5 and N-6. DuPont KS Resin (Polyamide)

One sample had debris partially blocking flow, but in the other the throat

area was badly eroded, leaving essentially a straight tube (Fig. A-6).

Nozzle N-13. Polyphenylquinoxaline.

Plugging had taken place, and very heavy scale buildup was present (Fig. A-7). Some very thin scale on the outside of the barrel could be flaked off very readily.

Nozzle N-15. Teflon TFE (Polytetrafluoroethylene, PTFE).

Some scale buildup was evident and was estimated to be more than with the Teflon PFA in N-4. When the scale at the exit end was broken away, very fine hairs could

Fig. 5. Front view of test chamber for field testing nozzles and wear plates.

be seen at the Teflon surface (Figs A-8 through A-11). Scanning Electron Microscopy indicated that these hairs were non-conducting and thus were most probably Teflon TFE. PTFE has some unusual characteristics which might account for such behavior. For example, when a second polymer is molded against PTFE, fluorine is found on the new surface, showing that transfer of PTFE has occurred. (See Ref. A1 of Appendix.) Material transfer is also thought to be involved in friction-reduction properties of PTFE. The highly crystalline nature of PTFE may encourage formation of fibrils, a process analogous

to the yielding of thin plates in the case of highly structurally organized graphite and mica. Such PTFE fiber formation is in fact, taken advantage of in a new product (Teflon K) which yields a very fine "hairnet" dust reducing structure when mixed or ground with various powders.^{A2} The abrasive action of the high-speed expanding stream in the nozzle exit area could induce this fibril formation. Such fibers, if not immediately removed, could initiate scale formation, either by trapping preformed particles capable of further growth, or by acting as nucleating sites for crystal growth as suggested by Fig. A-11.

TEST RESULTS ON WEAR PLATES

Wear Plate WP-2. Teflon TFE, (Polytetrafluoroethylene).

This wear plate was moderately warped, with a distinct valley eroded into the surface where the stream from the nozzle had impinged upon it (Figs. A-12 and A-13). The valley had begun to fill with scale. The surfaces struck by the stream were covered by grooves and sharp cuts contain-

ing scale particles. Tiny hairs or fibrils were present on these surfaces.

Wear Plate WP-4. Teflon PFA (perfluoroalkoxy).

Very little erosion took place and little scale deposition was observed except at the sides of the impact area (Figs. A-14 and A-15). The surface was no longer smooth, but covered with tiny bumps which might have been softened at some point since they lacked sharp edges or fractures.

Equipment

Equipment for testing material samples included two 300 cc stainless steel pressure bombs², and two 100 cc bombs. Tantalum bomb liners and sample supports were used in place of the quartz liners and supports that had been employed in earlier tests. Type 316 stainless steel

thermocouple shields withstood immersion in brine for several hundred hours in contrast to type 347 stainless steel which corroded through in a few hours. The following additional equipment was used in the preparation of test specimens:

Equipment type	Size (cm)	Max Pressure (MPa)	Max Temp (°C)
Buehler specimen press	Cylinder: 3.12 diam x 3.81	68.9	427
Cylindrical mold	Cylinder: 7.62 diam x 10.2	310	427
Flat-disc mold	Cylinder: 15.2 diam x 3.12	>68.9	427
Frame mold	10.2 x 10.2 x 0.64	6.89	427
Bar mold	2.54 x 0.64 x 15.2	6.89	427
Cylindrical mold	3.12 diam x 10.2	517	427

Part Fabrication

Using procedures recommended by the manufacturers, we fabricated parts from Ryton polyphenylene sulfide, Eckonol 900 polyester, NR150B polyimide, Kerimid 601/Thornel 400 composite, and phenolic/

fiberglass. Other samples were received from manufacturers as machinable stock shapes. Some 39 companies have been contacted with regard to supplying materials and parts.

Future Work

We will continue looking for new materials, as well as fabricating and testing them in the form of polymers, composites and coatings. Screening will include: (a) static hot brine tests, (b) testing at the LLL geothermal test facility (now being completed) to study erosion and temperature-resistance, (c) mechanical testing of exposed specimens, and (d) several types of field tests. A series of field tests was concluded in May, 1975 and results will be reported

shortly. Field tests are extremely important for measuring scaling resistance, a critical factor in successful operation of a nozzle/turbine system. The rapid rate of scale buildup is illustrated in Figure 6, where an 11.4 cm o.d. epoxy/fiberglass pipe with walls 0.64 cm thick collected 1 cm of scale during 5 to 6 days as a post-expansion drain line. Material hardness and surface finish as well as surface chemical type will be examined for scaling resistance.

Acknowledgments

The field testing of nozzle- and wear-plate specimens by J. M. Johnson and D. B. Clifton is gratefully acknowledged, as is the Scanning Electron Microscopy

work of J. Steele. Credit is also due the numerous companies who provided samples of materials for testing.

Fig. 6. Epoxy/fiberglass pipe containing scale.

References

1. A. L. Austin, G. H. Higgins and J. H. Howard, The Total Flow Concept for Recovery of Energy from Geothermal Hot Brine Deposits, Lawrence Livermore Laboratory, Rept. UCRL-51366 (1973).
2. L. E. Lorensen, Materials Screening Program for the LLL Geothermal Project, Lawrence Livermore Laboratory, Rept. UCID-16513 (1974).
3. G. R. Berbeco, E. O. Hook, E. L. Lowdermilk, "The Structure and Properties of Polyimides", Proc. Conf. Am. Chem. Soc., 160th, Chicago, 1970 (American Chemical Society, Washington, 1970) pp 169-174.
4. N. Adrova, M. E. Bessonov, L. A. Laius, A. P. Rudakov, Polyimides, A New Class of Heat-Resistant Polymers (IPST Press, Jerusalem, 1969).
5. L. E. Lorensen, SAMPE Q 6, 2 (Jan. 1975), pp 1-13.

Appendix

DETAILED TEST RESULTS ON NOZZLES

Nozzle N-1. Carbon Fiber or Felt Impregnated with Carbon Via the Carbon Vapor Deposition (CVD) Process.

Several large pieces of scale were embedded in the pre-throat entry section. Black deposits were covered with a thin layer of easily removed orange deposit. The nozzle was stuck in its steel holder. Considerable black scale was stuck to the outside of the barrel and was difficult to remove. The exit end was clean 2 to 4 mm down, with no sign of erosion (Fig. A-1). Heavy deposits began at that point, reducing the throat to 3-4 mm.

These forward surfaces had fine white salt deposits on them.

Nozzle N-3. Teflon PFA (Perfluoroalkoxy).

This nozzle had not expanded and was easily removed from its holder. The flat face of the entry end was clean. The pre-throat areas had thin black, glassy coatings covered with an orange film and scale broke away fairly cleanly. The throat was about half blocked with pieces of scale which had come down the pipe. The outside of the barrel was quite clean. The exit end was lined with approximately 1 mm of black scale, beneath which was an orange deposit at the interface (Fig. A-2).

Fig. A-1. Carbon/carbon fiber nozzle N-1, exit end.

Fig. A-2. Teflon PFA nozzle N-3, exit end.

These deposits could be flaked off relatively easily, perhaps more readily than with Teflon TFE. With magnification, few if any fine surface hairs could be seen, in contrast to the hair "growth" on Teflon TFE (see the report on nozzle N-4, below).

Nozzle N-4. Teflon PFA (Perfluoroalkoxy).

Although a duplicate of N-3, N-4 did not become clogged with debris. Some very thin deposits were present in the pre-throat area. In two small areas, deposits were absent, and under magnification bush-like flexible matts of polymer could be seen. At 500 X, leaves or flaps of polymer (nonconducting in SEM) appeared, with small particles of debris present. The nozzle outer surfaces were clean, and the exit-end inner surfaces were covered with

a very thin black coating. No erosion was noted. See Figs. A-3, A-4 and A-5.

Nozzle N-5. DuPont KS Resin (Polyamide).

This nozzle was wedged in the steel retaining plate. Outer surfaces were quite clean (Fig. A-6). The throat restriction had been entirely eroded away, leaving essentially a straight tube with little deposit present.

Nozzle N-6. DuPont KS Resin (Polyamide).

The pre-throat or entry area looked somewhat eroded, but with compensating scale present. It was almost half blocked with debris and well scaled. The throat had eroded little, and the exit-end surfaces were covered with only a very light scale, colored black with some white surface coating over part of the area. No erosion was visible at the exit end.

Fig. A-3. Teflox PFA nozzle N-4, exit end.

Fig. A-4. Teflon PFA nozzle N-4, bush growth in entry end (20 X).

Fig. A-5. Teflon PFA nozzle N-4, bush in entry end (500 X).

Nozzle N-13. Polyphenylquinoxaline.

This nozzle (Fig. A-7) was stuck in its holder. The entry end was apparently completely blocked with pieces of debris "welded" together with scale deposit. The outside of the barrel was covered with very thin (less than a few tenths of a millimeter), spotty yellow deposit which could be flaked off very easily. The exit end had an "extruded" scale buildup, 2 to 3 mm beyond the rim, with a 6- to 7-mm hole remaining.

Nozzle N-15. Teflon TFE (Polytetrafluoroethylene, PTFE).

The nozzle could be rotated, but not removed from the holder, indicating that some expansion due to plastic flow had taken place. (Figs. A-8 through A-11).

The inside of the entry end was coated with a two-layer black deposit a few tenths of a millimeter thick. The layers were brittle, separable and did not adhere strongly. The black color changed to white in the restricted throat area which was closed down to a diam of 6 to 7 mm. The outside of the barrel was about half covered with patches of orange and brown deposit which readily flaked off. At the exit end, there was about 1 mm of "extrusion" deposit extending beyond the rim. This was black "warty" material covered with orange powder. When it was broken away from the rim, a large number of very fine hairs could be seen (even at 40 X magnification) in the area where the deposit had been. In Fig. A-11 (magnification 1500 X) crystal growth appears to be nucleated on the hairs.

Fig. A-6. Polyamide KS resin nozzle N-5, exit end.

Fig. A-7. Ployphenylquinoxaline nozzle N-13, exit end.

Fig. A-8. Teflon TFE nozzle N-15, exit end.

Fig. A-9. Teflon TFE nozzle N-15, showing scale-resin interface at exit end (25 X).

Fig. A-10. Teflon TFE nozzle N-15, showing fibers at scale-resin interface (650 X).

Fig. A-11. Teflon TFE nozzle N-15, showing fibers with probable scale growth (1500 X).

DETAILED TEST RESULTS ON THE WEAR PLATES

Wear Plate WP-2. Teflon TFE (Polytetrafluoroethylene).

This plate (Figs A-12 and A-13) was tested for 108 hours. At completion of the test, the plate was moderately warped. The stream from the nozzle had worn a depression about 1.6 cm wide, 4.4 cm long and at least 0.32 cm deep in the plate. The depression had partially filled with scale at the far end. On removing a few small chips of this scale, it was found that the polymer surface had been markedly roughened by grooves, cuts, and sharp, angular flaps or projections. Almost all cuts had black deposit in the bottom. The surface was also covered with a very fine, delicate web or network of flexible hairs or fibers. This web held many smaller

particles of scale suspended from the surface.

Wear Plate WP-4. Teflon PFA (Perfluoroalkoxy).

After 132 hr exposure a definite darker impact area could be seen, but little if any erosion had occurred (Figs. A-14 and A-15). The surface was roughened by the presence of small bumps, smoothed somewhat by possibly having once been molten or softened. Some small black particles were buried, either by impact penetration or localized flow. Light brown debris particulate was present on the surface. A thin, glassy brittle film of transparent material on the surface made it look quite shiny. This could have been a salt film left behind by evaporation of fluid remaining after the test was completed.

References

- A1. R. G. Azrak, Chemtech (Nov. 1974), pp 683-689.
- A2. R. F. Welch, Jr., J. Teflon **16**, 1 (1975), p 6.

IMM/grw

Fig. A-12. Teflon TFE wear plate WP-2, showing erosion. (1 div = 1 mm).

Fig. A-13. Teflon TFE wear plate WP-2, showing surface features (30 X).

Fig. A-14. Teflon PFA wear plate WP-4 (1 div = 1 mm).

Fig. A-15. Teflon PFA wear plate WP-4, showing surface features (30 X).