PREPRINT UCRL-81019

CONF-780611--2

Lawrence Livermore Laboratory

POLYMERIC AND COMPOSITE MATERIALS FOR USE IN SYSTEMS UTILIZING HOT, FLOWING GEOTHERMAL BRINE. II

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14 APRIL 1978

THIS PAPER WAS PREPARED FOR SUBMISSION TO:
AICHE MEETING IN PHILADELPHIA, PA.
JUNE, 1978

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POLYMERIC AND COMPOSITE MATERIALS FOR USE IN SYSTEMS UTILIZING HOT, FLOWING GEOTHERMAL BRINE

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Abstract

Further progress is reported on a continuing experimental program designed to select high-performance polymeric materials for use in geothermal power plants. In field tests 12 nozzles, 27 wear plates and 2 types of polymer lined pipe were tested. Nozzles made of Teflons TFE and PFA, Tefzel, Ryton PPS and H-Resin/carbon cloth were little changed except for some scaling. The fluorocarbons scaled least rapidly. All blade type wear plates eroded, those based on Tefzel, PPQ and PPS the least. Fluorocarbon lined pipes were little affected by exposure.

In laboratory tests samples were heated at 250 and 300°C in brine. Several materials including fluorocarbon and unhydrolyzable aromatic or cross-linked aliphatic, thermally stable polymers survived for periods up to 1300 h. In erosion tests, coatings based on epoxy resins and a fluorocarbon were most resistant; good adhesion was required.

Introduction

In recognition of the growing energy shortage many relatively undeveloped but potentially important sources of energy are being examined. Among these is geothermal energy.

Geothermal resources are classified as vapor dominated if they produce dry steam, as liquid dominated if hot water prevails, and as dry heat dominated if they consist of dry hot rock strata close to magma extrusions.

"Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48."

Liquid dominated resources are many times more prevalent than the other two. They have recieved little attention until recent years because of recognized problems of corrosion and scaling. These problems are particularly acute in superheated liquid deposits, which are the most attractive from an energy point of view.

To help exploit hot liquid deposits, the Lawrence Livermore Laboratory proposed a "Total Flow" system for extracting energy from the hot brine present in certain areas deep underground. In the Salton Sea area of Southern California for example there are brine wells several thousand feet deep in which the water is at 300°C, and contains roughly 25% dissolved solids. By allowing a slight pressure drop, self-sustained well flow takes place.

In the "Total Flow" system this flow will be expanded through nozzles into a special turbine, accomplishing the critical energy conversion. The cooled brine will then be passed through a condenser system and reinjected into the ground.[1] This system could have a considerably higher efficiency than other systems currently being used or tested.

Concurrent with the "Total Flow" system studies, the Laboratory is participating in an industrial support type program. We are working with the San Diego Gas and Electric Company to develop chemistry and materials technology for conversion systems based on brine flashing.

Regardless of the type of energy extraction process used, all plants in a given geothermal field will be subjected to the same conditions of high temperatures and pressures, corrosive fluid, erosive flow, and scaling. While there may be some variation in severity depending upon specific plant design

the materials problems in all designs have much in common. Materials will be required for parts such as pipes, nozzles, turbines, heat exchangers, separators, tanks, valves, etc. or for coatings for such parts which can withstand the severe geothermal environment. Selected organic polymers and composites are being examined for service under these conditions of thermal, physical and chemical stress. This report discusses progress on a continuing program of laboratory and field testing in which this is being done.[2,3]

In the field test prototype nozzles, wear blades (simulating turbine parts), polymer lined pipes, and special test coupons were exposed to actual geothermal well flow. In the laboratory tests, screening of candidate materials was continued at different temperatures in the presence of brine, and some initial evaluation of polymer coatings was done in the Geothermal Test Facility.

Results and Discussion

The April-May, 1975 Field Test

This was the third test in which materials have been exposed to hot brine in the geothermal field south of the Salton Sea in California. In the first test, three samples of polymeric materials were placed in State No. 1 well at depth of 1500 m and allowed to soak for three months.[2] In the second test a drum-like test chamber was fitted so that well flow passed through four nozzles onto wear plates.[3] The second and third tests were done at the Sinclair 4 well. Brine characteristics were similar in the two wells.

The test equipment and conditions were somewhat different for this third test. Instead of a single chamber three independent test stations were used, each capable of testing a nozzle and wear plate simulating the edge of a turbine bucket. The stream from the nozzle expanded into a large open pipe,

approximating ambient conditions. Pipes could also be attached to the system for test.

During operation of this test facility, the flexibility provided by independent control of each station was very useful. Changing samples was cumbersome however, partly due to the need to descale holders and other parts each time. Since pressures changed as other experiments were added or removed, coordination of test schedules was required.

Objectives of the Field Test

Testing was planned with the following objectives in mind. We hoped to verify earlier results, extend laboratory conclusions, screen new materials, and check the effect of changes in operating variables inherent in a field test of a natural energy source.

Results from Nozzle Exposures

Nozzles are a critical part of the Total Flow System insofar as they control the conversion of thermal to kinetic energy. At this stage of nozzle development geometry was not fixed. For this test nozzle length and throat diameter were doubled, the latter to reduce the plugging by well or pipe debris which took place in the second test.

The materials used for nozzle fabrication had either passed the static laboratory hot brine screening test or were judged capable of doing so with fair certainty. No effort was made to make surfaces extra smooth; standard machining practices recommended for the materials were followed.

Nozzle field performance was based on changes in weight, dimensions and appearance as a function of exposure.

Eighteen nozzles were tested. Well brine was delivered to the test stations at about 240°C at pressures between 2.59 and 2.93 MPa. It was expanded through the nozzles directly onto the blade type wear plates. We experienced premature breakage of six nozzles due to excessive pressure on the mounting flange coupled with vibration from well pulsing. A new nozzle holder incorporating barrel support solved the problem.

Twelve nozzles were tested without breaking. Five failed from excessive erosion (three types of Ekkcels* (aromatic polyesters), an impact resistant polyethylene, and Kynar (polyvinylidene fluoride). Six nozzles survived successfully, Teflons TFE (in duplicate) and PFA, Tefzel (ethylene/ tetrafluoroethylene), Ryton (polyphenylene sulfide), and a Haveg rocket nozzle material based on H-Resin.

All six nozzles which completed the test successfully acquired some scale, primarily in the exit end. Nozzle throats were not eroded but picked up traces of scale (0.13 to 0.76 mm thick). The rate of acquisition is shown in Fig. 1. There is little evidence for a diminishing rate of scale buildup with time despite a continually decreasing expansion ratio (ratio of exit end area to throat area) due to scale accumulation. Rough estimates of the scale buildup rates are about 0.7 g/10 h for the three fluorinated polymers (TFE, PFA and Tefzel), and about 1 g/10 h for Ryton PPS and the Havig composite.

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

Miscroscopic examination of the scaled nozzles was done after potting the bores, sectioning and polishing. They were examined carefully as to the physical characteristics of the scale and its rate of laydown as a function of location in the nozzle, and for changes in the polymeric material. The scale was very rough, particularly in the exit end where it was heaviest. Differences in roughness and thickness were noted, but could not be unequivocally related to nozzle composition, test duration, or well flow variation.

In the fiber reinforced Haveg nozzle, erosion of fibers perpendicular to the surface was less than with those parallel to the surface, as can be seen in Fig. 2. This is in agreement with friction and wear studies reported by Sung and Suh.[4]

In the Tefzel nozzle an internal blister or void appeared in the material forming the entry end of the nozzle (Fig. 3). It probably developed as a result of the high pressure present here; some red deposit could be seen within the blister. It was later shown to contain Al-Si-I and Fe-Zn salts.

In the previous geothermal test series it was shown that the surface of Teflon TFE beneath scale at the exit end of a nozzle was fibrous in nature and the fibers appeared to have nodules on their surfaces.[3] The analogous Teflon surface resulting from exposure in this test was also examined with very similar rods and hairs being present (Fig. 4). They appeared to be Teflon (i.e. insulators in SEM), and analyses of the nodules on the fibers and of the scale surface from the same interface by energy dispersive spectroscopy gave similar results (Table 1). The reduced amount of silicon on the fibers over that present in the adjacent scale could be related to the observation that Teflon does scale

less readily, and silica is thought to be a binder in the inorganic scale matrix.

In the second field test a Teflon PFA nozzle and wear plate had collected considerably less scale than did corresponding parts formed from Teflon TFE. In the third test, not only did both types of nozzles scale faster, but the same degree of difference failed to result here. Comparative data for the development of scale on the two materials in the two tests is shown in Table 2. While the Teflon TFE scaled about three times as fast as did Teflon PFA in the second test, here it scaled only one and one half times as fast as PFA.

Several factors could have contributed to this difference. The nozzles in the third test were twice as long as those used in the second, giving more time to deposit scale. However, more than length was involved for a comparison of scale thicknesses at points equidistant from the respective throats showed a greater scale thickness in the longer nozzle. The expansion ratio (exit area: throat area) was almost twice as great in the second test nozzles as in the third. This resulted in a faster moving stagnant layer next to the walls in the second test nozzles which could have swept away scale precursors. Finally, the faster moving exit stream in the second test nozzles would have allowed fewer of the high solids cooling droplets to approach the nozzle exit end walls, making scale deposition less.

Several additional tests on fluorocarbon nozzles have been carried out. Eight to 1 expansion ratios were used. Acidification has been found to be a useful way to control scaling, but since it causes corrosion in many metals,

a Teflon PFA nozzle was tested, being inert to acids. In nozzle expansion tests, after 20 h with pH 3 brine, no scaling was observed and the nozzle throat had increased only 0.28mm. Whether this was due to resin flow, nozzle expansion to fill the holder, or erosion could not be determined. Metal nozzles still collected thin layers of scale at these lower pH levels.

At the natural brine pH of 5.6, both PFA and titanium alloy nozzles became scaled to about the same extent, with the scale on the PFA nozzle being less adherent.[5] Titanium alloy nozzles coated with a Teflon FEP based primer and with Fluorad FC-721, a fluorinated polymer also became scaled.

The conclusion at this point with regard to material scale resistance is that fluorocarbons, and in particular Teflon PFA may collect scale at a slower rate than other materials, or even remain free of scale under certain conditions. The addition of brine modification agents in combination with fluorocarbon surfaces may be required.

Results from Wear Plate Exposures

Various parts of energy conversion plants will be subjected to severe erosion. Examples are turbine blades in a system such as the Total Flow scheme, tank walls opposite entry ports, and bends or elbows in pipes. Candidate materials for erosion tests were chosen because of demonstrated brine tolerance or published statements regarding toughness.

Test specimens were in the form of a wear blade, made by machining a 30° edge on bars 7.62 x 2.54 x 0.64 cm.

Exposure of wear blades was done at each of the three test stations in the field. The expanding brine stream from the nozzles was allowed to impinge

directly upon blade edges, the blades being held parallel to center stream flow. The decrease in blade height was measured as a function of time.

The influence of measurable if not controllable test variables was determined so that observed differences could be assigned with confidence to material characteristics alone.

Twenty-seven wear blades made of ten different materials were tested, with the erosion results plotted in Fig. 5. The results from those runs which were made in replicate were sufficiently close to suggest that a listing in order of decreasing erosion resistance might be done despite the fact that with 4 materials only single points were available. Such a listing is shown in Table 3, along with measured Shore D and Barcol hardness values. Assuming that this ordering of materials is approximately correct, neither of these different hardness measurements was able to predict erosion resistance in the field.

The nozzle to blade edge distance was difficult to keep constant because of hardware considerations. It ranged between 1.3 and 2.5 cm. To test the effect of this variable, spacing was varied between 0.25 and 5.1 cm as shown in Fig. 6. A single material, Ryton R-4 was used. Also shown is data taken at different times, with slightly thicker samples (0.85 vs 0.64 cm) and at a lower pressure (2.07 MPa instead of the usual 2.76 MPa).

The conclusions are as follows: 1) There would be essentially no effect of spacing in the spacing range of 1.3 to 2.5 cm where we normally worked,

2) Wear rate or erosion depth is not a linear function of time, showing it to be a complex phenomenon. 3) The data suggest that wear rate is greater at the lower pressure. This could be the result of less flaring or spreading of particulate present in the center of the stream at lower pressure. 4) The effect of sample thickness is small. Other data from tests with the softer Teflon TFE and PFA support these conclusions.

Results from Exposing Polymer Lined Pipe

Pipe is needed which will be suitable for bringing hot brine from depth to the plant, for transporting brine within the plant, and for returning spent brine to depth via reinjection wells. All of the five geothermal "stresses" i.e. heat, pressure, corrosion, erosion and scaling, will not be present to the same degree in all locations, so selections will be possible.

Two types of pipe were selected for test, steel spools lined with Teflon TFE, and with Teflon PFA. Our intention was to test both pipes on both the high pressure side as well as the low pressure side of a 1.27 cm orifice. The orifice would simulate a nozzle, providing a pressure and temperature drop, and increased scaling tendencies on the downstream side.

The two pipes were connected in series on the well side of the orifice with flow maintained for 20.5 h at 240°C, 2.86 MPa. The Teflon TFE was unchanged. The lining reported to be Teflon PFA had partially collapsed during cooling due to plugging of the vent system. Analysis showed that the Teflon PFA had inadvertently been mixed with a lower melting polymer during extrusion, which explains the unexpected result. The pipe lined with Teflon TFE was exposed for another 21.3 h on the high pressure side, then for 33.7 h at 150°C and

0.34 MPa on the low pressure side to look for scaling. Only a very thin incomplete lining of black scale was present. Because of these promising results, we hope to continue testing these fluorocarbon lined pipes.

Laboratory Tests

Laboratory activities are an essential part of the program designed to select optimum materials for use in various geothermal applications. New candidate materials were either fabricated using manufacturer's suggestions where available, or obtained directly from commerical sources.

Static Hot Brine Tests in Stainless Steel Pressure Vessels

Candidate materials are screened by immersing in synthetic brine at 300°C for extended periods with weight loss and physical appearance being monitored. In Fig. 7 are shown results from recent tests along with some gathered during the extension of tests reported earlier.[3] Not unexpectedly carbon holds up well, although porosity allows weight gain due to deposition of salts. Fluorocarbons are resistant although Teflon PFA became distorted as did the high molecular weight polyethylene. The high temperature materials polyphenylquinoxaline, polybenzimidazole, and "H-Resin" in differerent forms stood up very well. The ceramoplastic Mykroys reacted quite differently, the 750 made with natural mica being unstable while the 1100 made with "man made" mica was stable. To this list of satisfactory materials should be added phenolic and Teflon TFE reported previously.

Some tests were also carried out at 250°C as shown in Fig. 8. The Dienites, Stilan and Ryton which had done poorly at 300°C were performing much better here.

While in these initial screening tests samples were not stressed, useful information beyond simple weight loss could be obtained. Weight gain or swelling pointed to undesirable porosity, and slumping indicated loss of strength at test temperature. Weight losses as high as 4% did not signal failure. A test duration of at least 500 h appears to be necessary. Field tests thus far have verified the value of such laboratory tests.

Material Tests in the Livermore Geothermal Test Facility

In order to carry out parametric studies of nozzle and turbine designs our engineers set up a small pilot plant type facility using a steam boiler. This was able to generate a two phase flow with the same characteristics as actual flow in the field expect that no salts or permanent gases were present.

A small chamber for studying material erosion was made as shown in Fig. 9 and 10 which is a close up of a nozzle and wear plate in place.

A short run was made using a Ryton nozzle and wear blade. Blade edge erosion was 1.7 mm which was estimated to be slightly less than that observed in the field. The test method therefore appeared to be valid.

Since the coating of metal parts offers a way to combine the most desirable characteristics of polymers and metals with economic advantage, a series of tests with coated metal wear blades was carried out. Since the flow rate from the nozzle approached 550 m/s, the test was severe, allowing test periods of 10 minutes or less.

Coatings tested included epoxy, epoxy/phenolic, epoxy/phenolic/silicone, urethane, Parylene, polyimide, Teflon, phosphonitrilic chloride, polyphenylquinoxaline, anodized aluminum and nickel coated aluminum as controls. The anodized coating was stripped off, while the nickel remained intact. Of the polymeric coatings, Teflon Xylan 1010, an epoxy/phenolic/silicone, and an epoxy/phenolic formulated with 50% silica remained intact except for slight wear on the knife edges.

Poor adhesion to the aluminum wear blade undoubtedly was responsible for stripping in some cases. At the blade edge where kinetic energy is converted to thermal energy upon impact, temperatures could reach 200°C, sufficient to soften or degrade some coatings.

Future Work

Work is continuing both in the laboratory and in the field in order to identify suitable polymeric based materials for use in the evolving designs for geothermal power plants. Coating materials will receive special attention.

Acknowledgements

Recognition should be given to George Tardiff, Terry Alger and Lawrence Owen of the Livermore Geothermal Group for helpful discussions. Technical personnel representing a number of companies must also be given credit for their cooperation in generously supplying materials for test.

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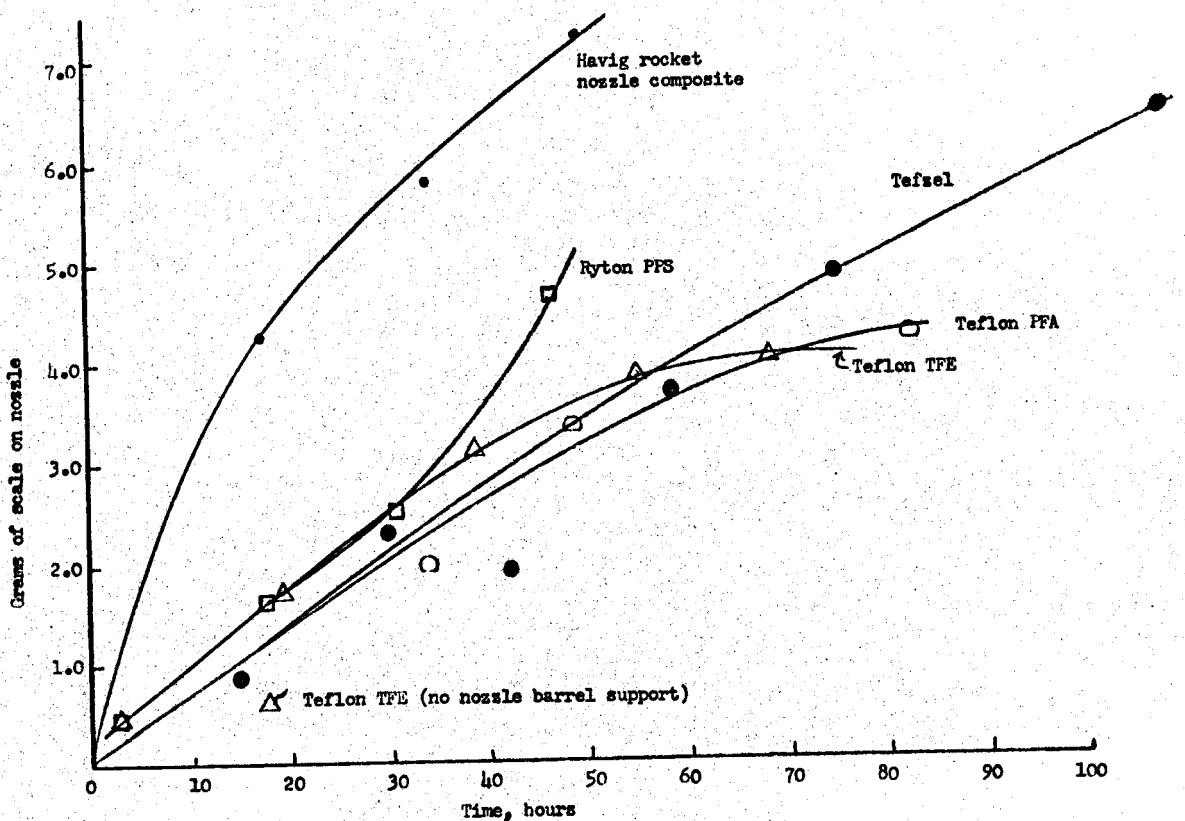

Fig. 1. Rate of nozzle scale acquisition, mainly in exit end.

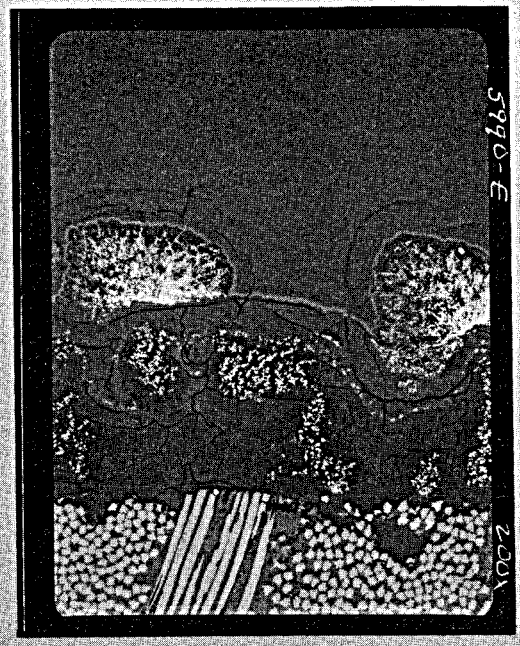

Fig. 2. Reduced erosion of reinforcing fibers perpendicular to composite surface (now covered with scale).

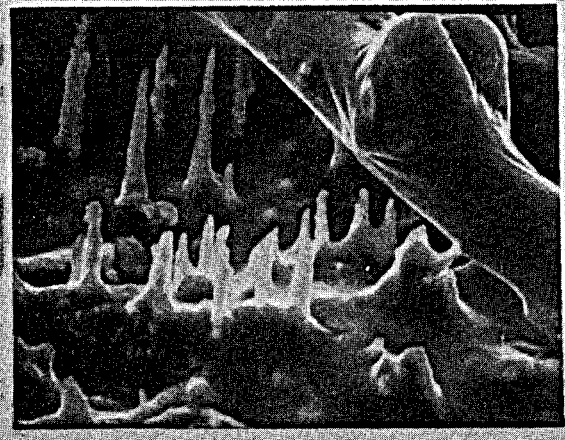

Fig. 4. Rods with scale deposits on Teflon TFE nozzle surface (S.E.M. Image, 3000X).

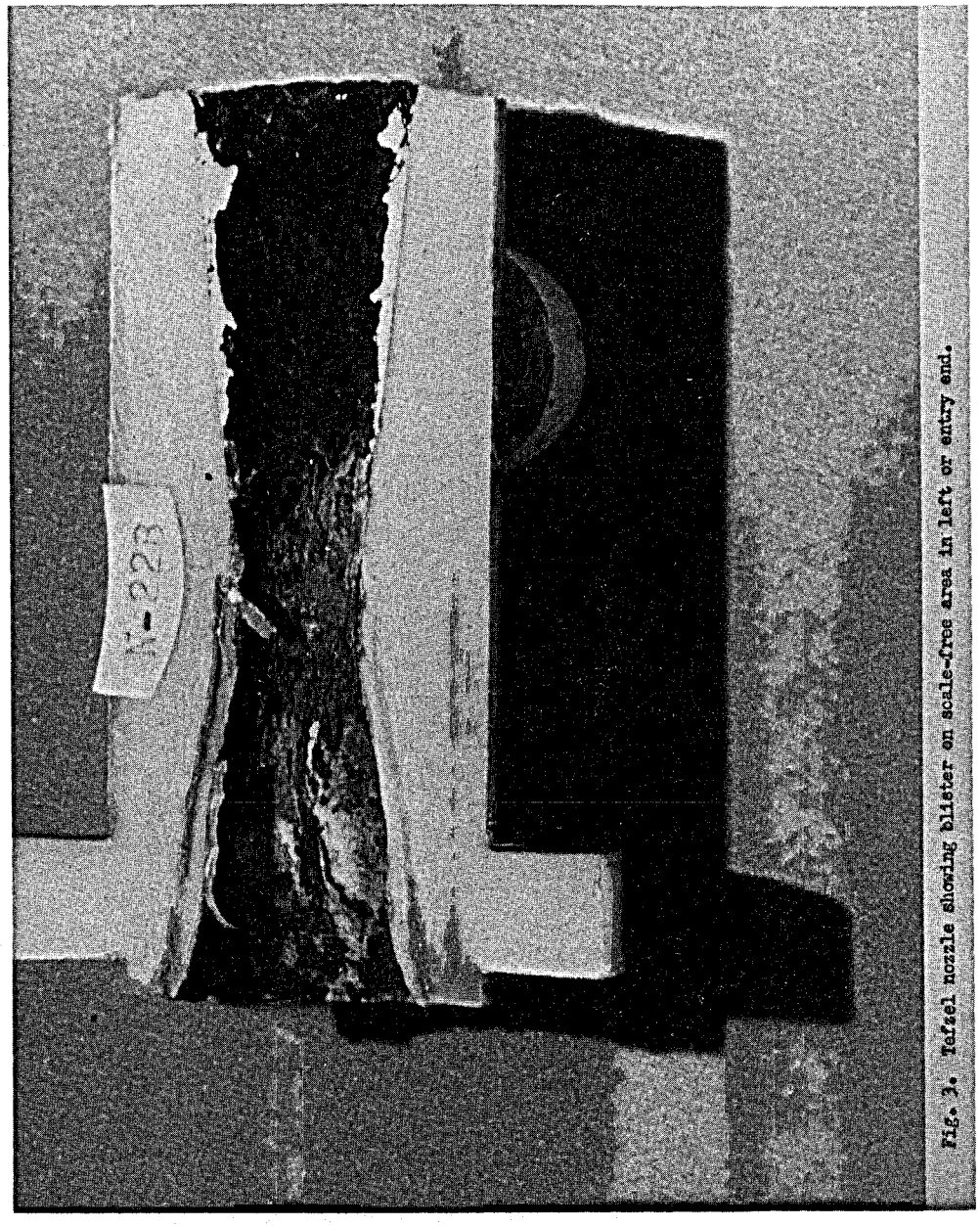

Fig. 3. Tefzel nozzle showing blister on scale-free area in left or entry end.

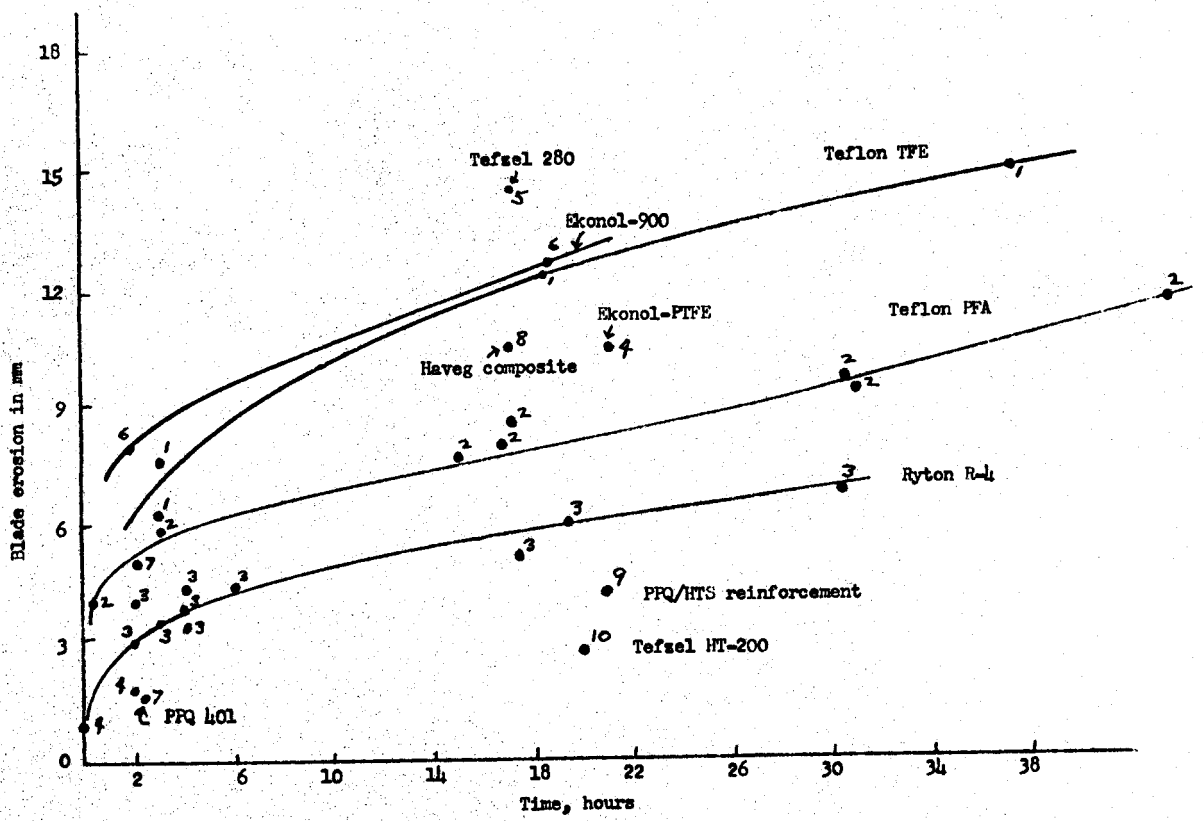

Fig. 5. Wear plate erosion vs time.

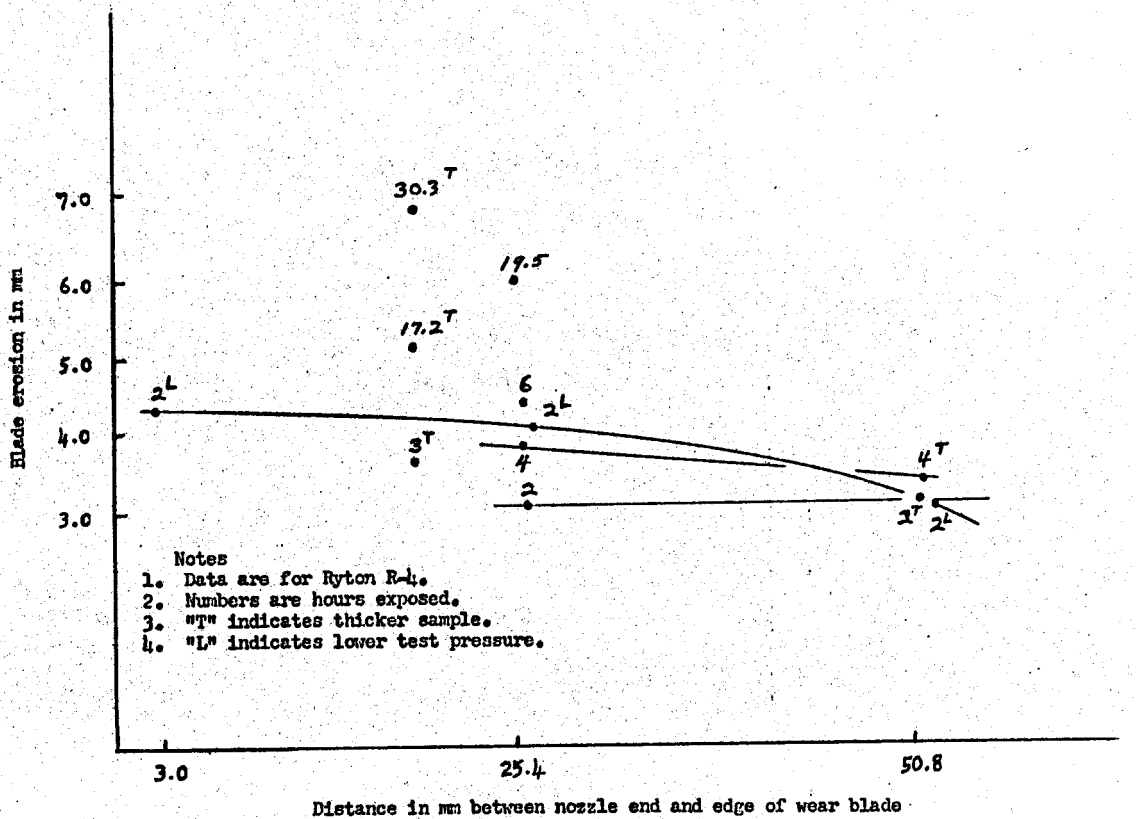

Fig. 6. Effect of changing wear blade edge to nozzle spacing.

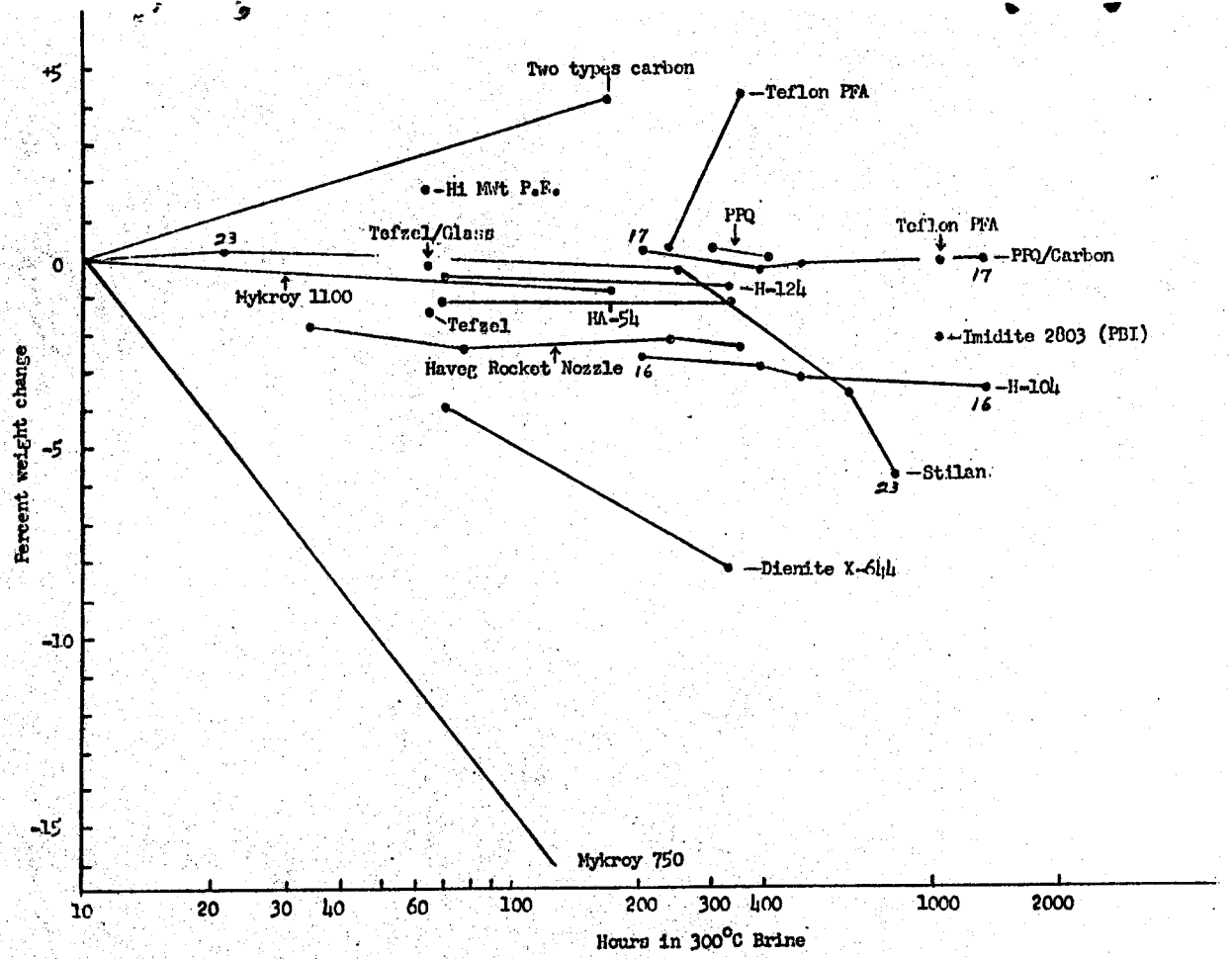

Fig. 7. Weight change vs time in 300°C artificial brine - autoclave tests.

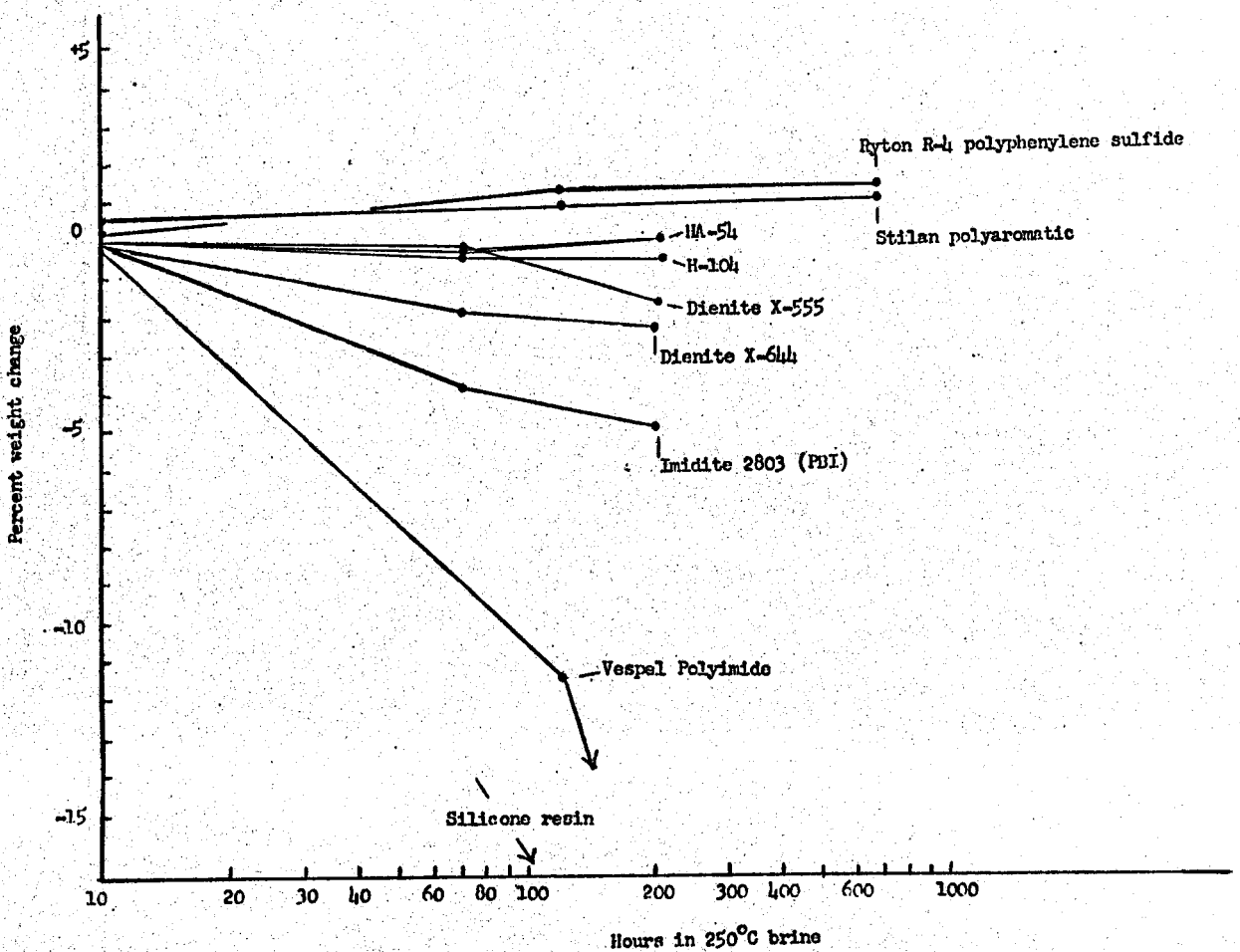

Fig. 8. Weight change vs time in 250°C artificial brine - autoclave tests.

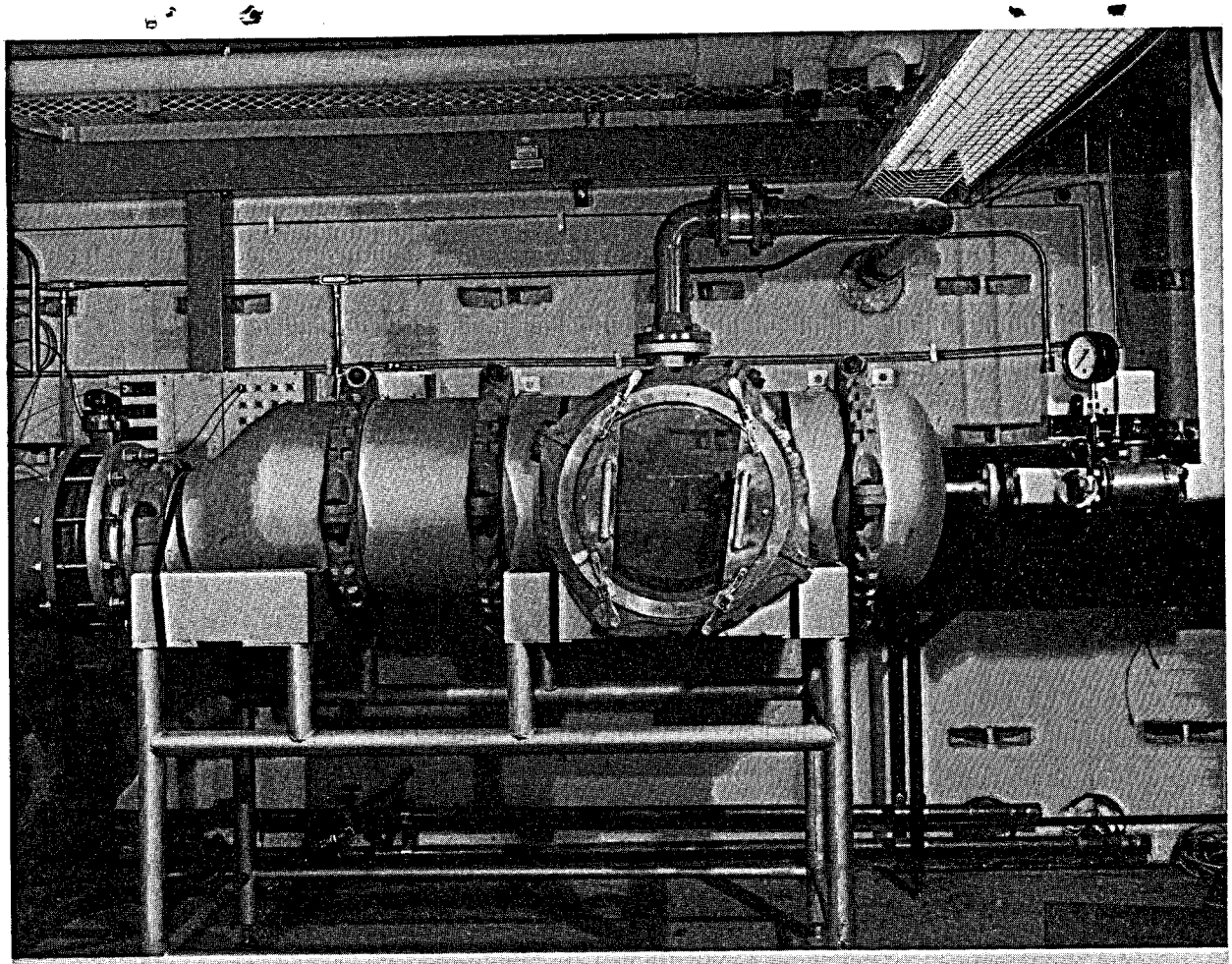

Fig. 9. Geothermal Test Facility Chamber for erosion testing.

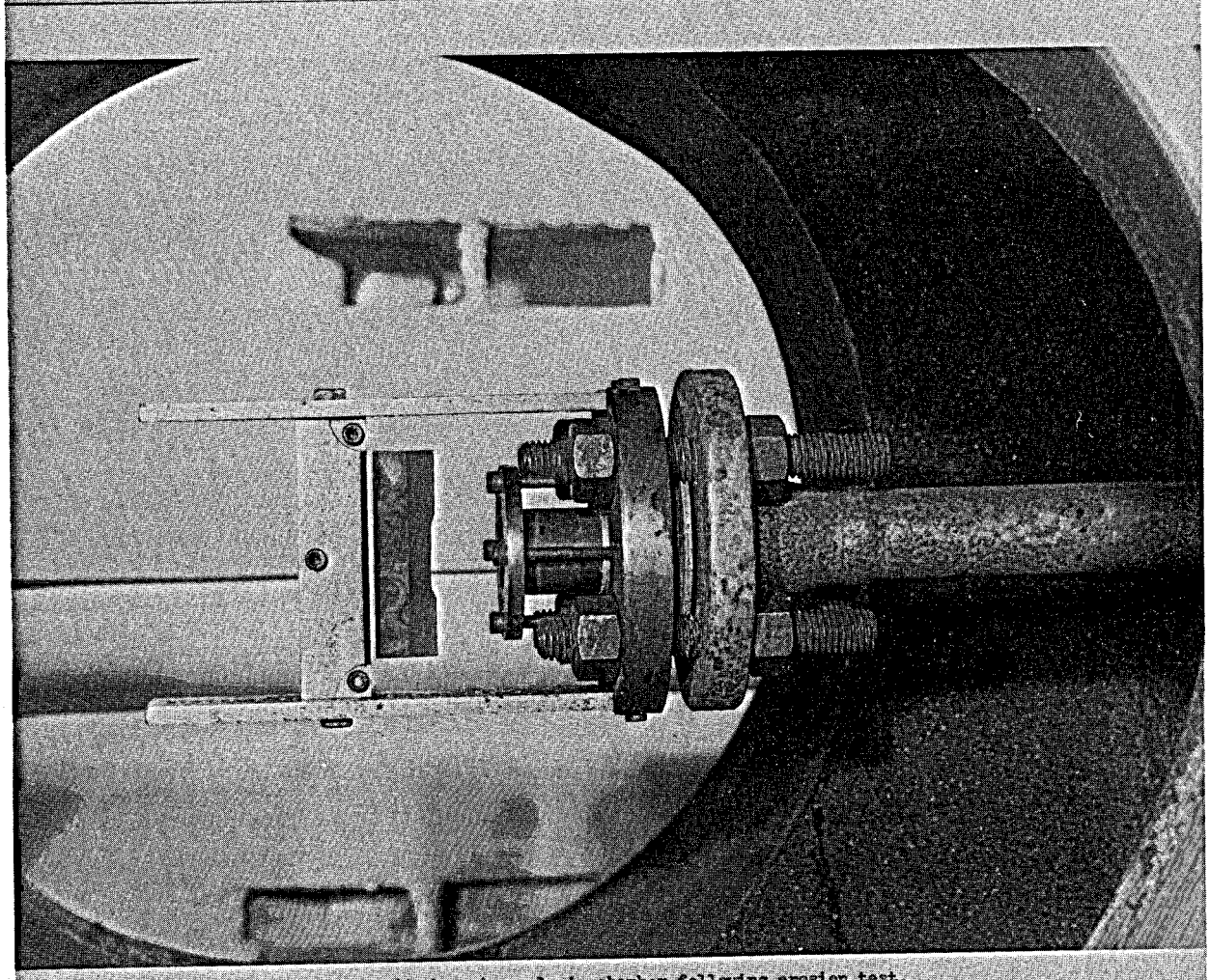

Fig. 10. Wear blade and nozzle in chamber following erosion test.

Table 1. Analysis of scale and deposits on Teflon TFE fibers.

Element	Relative Intensities* (energy dispersive spectroscopy) Scale	Rods and Hair
Na	0.08	0.06
Si	0.25	0.08
Cl	0.14	0.09
Ca	0.04	0.22
Cu	0.08	0.02
Fe	0.36	0.64
(1)	0.05	
Total	1.00	1.00

*Oxygen not analyzed
(1) Contains small amounts of S, K, Mn & Ni

Table 2. Comparison of scaling data for Teflons PFA and TFE from second and third field tests.

	Second test PFA	Second test TFE	Third test PFA	Third test TFE
Maximum scale thickness, mm	0.25	0.76	1-2	2.5
Exposure time, h	130	110	82	67
Scaling rate mm/24 h	0.05	0.17	0.59	0.88
Nozzle expansion ratio	3.7	3.7	2.2	2.2

Table 3. Erosion resistance versus material hardness.

Materials (in order of decreasing erosion resistance)	Shore D	Barcol Hardness
Tefzel HT-200 (glass filled)	67	0
PPQ/HTS fiber	78	63
Ekonol/TFE	62	0
Ryton R4 (glass filled)	76	45
PPQ 401	74	36
Teflon PFA	59	0
Haveg HRX composite	72	17
Teflon TFE	59	0
Ekonol 900 (filler present)	74	28
Tefzel 280	60	0