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MATERIALS SELECTION AND CORROSION PROBLEMS

I. Cornet	Professor and Project Investigator
R. Greif	Professor and Project Investigator
R. S. Treseder	Senior Development Engineer

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REA

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PART I

INTRODUCTION AND DISCUSSION

The group working on Materials Selection and Corrosion Problems of the LBL Hydrothermal project has various objectives. It will of course answer specific questions on materials selection for components for the specific site at which the LBL Hydrothermal Project will build its power plant. In addition, this group will furnish information which will be useful in the successful development of geothermal power plants in the United States, plants required to meet our national needs for energy.

To date there has been no specification of the site or the composition of the geothermal fluid to be expected at that site. From an open file report of the USDI Geological Survey (Mariner, et. al., 1974), data have been tabulated for chemical compositions of geothermal waters in four areas of interest in Nevada: Beowawe "steam" well and Beowawe Hot Spring (Eureka County), Buffalo Valley Hot Springs (Lander County), Kyle Hot Springs and Leach Hot Spring (Pershing County). These data are presented in Table I. No information is given on sulfide or bisulfide content, but these constituents are present in each of these wells and springs, as indicated by reaction with silver (personal communication--from A. J. Hebert). With this limited information, material recommendations have been prepared for the Nevada geothermal well (cf. Part II).

Due to current shortages, recommended materials may not be available from time to time. It may therefore be necessary to use casing, for example, which is susceptible to stress cracking in the presence of hydrogen sulfide. If such a calculated risk must be taken, one should note that if a well is not completely shut down and if sufficient fluid is produced to maintain metal temperatures above 70°C, corrosion problems may be partially controlled.

A field corrosion test program is planned for the Nevada test well. A detailed program is submitted in Part III of this report. Objectives of this program are to obtain information on the performance of materials; obtain information on the effect of production variables such as temperature, pressure, and flow rate on the performance of materials; obtain data for improved and more economic selection of materials for plant design and construction; and furnish guidelines and procedures for geothermal plants in general (cf. Part III).

A laboratory research program is continuing on Velocity Effects in Corrosion. The purpose of this program is to establish a basis for quantitative scale-up of corrosion effects in design of components such as pump impellers or mixing propellers. A progress report is presented in Part IV.

In addition, a tubeflow system has been constructed, and preliminary tests are being carried out.

References

I. 1. Mariner, R. H., Rapp, J. B., Willey, L. M., and Presser, T. S.; "The Chemical Composition and Estimated Minimum Thermal Reservoir Temperatures of the Principle Hot Springs of Northern and Central Nevada"; Open-File Report, United States Department of the Interior Geological Survey; Menlo Park, California, May, 1974.

TABLE 1

Chemical Analyses of Selected Hot Springs and Wells

(Concentrations in milligrams per liter)

	Beowawe "steam" well	Beowawe Hot Spring	Buffalo Valley Hot Springs	Kyle Hot Springs	Leach Hot Spring
Temperature ($^\circ$C)	---	98	49	77	92
pH	9.38	8.98	6.53	6.50	7.40
Specific conductance	1,490	1,020	1,530	3,220	811
Silica (SiO_2)	500	320	80	150	135
Calcium (Ca)	1.3	1.0	45	95	8.8
Magnesium (Mg)	.2	$<.1$	4.9	25.5	.5
Sodium (Na)	250	230	250	540	160
Potassium (K)	38	16	34	80	13
Lithium (Li)	2.1	1.3	.80	3.1	1.7
Bicarbonate (HCO_3)	505	321	813	544	366
Carbonate (CO_3)	81	32	<1	<1	1
Sulfate (SO_4)	64	130	110	51	53
Chloride (Cl)	70	69	29	770	29
Fluoride (F)	$<.05$	17	4.8	5.7	7.8
Boron (B)	2.5	2.1	2.3	3.8	1.2

PART II

MATERIALS RECOMMENDATIONS FOR NEVADA GEOTHERMAL WELL

This section summarizes recommendations for materials for the geothermal well planned for a Nevada test site. It covers down-the-hole tubular goods, wellhead equipment, and flowlines. A subsequent report will cover subsurface equipment involved in fluid handling and power generation. These recommendations are subject to modification as more information becomes available on well operating conditions and nature of the produced steam and brine.

The corrosivity of the produced steam and brine is not known and cannot be defined with accuracy until the well is producing. For the present, it is assumed that the corrosion rate of carbon steel will be low enough that steel can be used for major equipment items. The basis for this assumption is that the composition and temperature reported for brines from several Nevada wells previously drilled are similar to those for relatively non-corrosive wells reported in the literature; this subject will be dealt with in detail in a subsequent report.

Since hydrogen sulfide is expected to be present in the produced steam, it is recommended that all pressure-containing items be constructed of materials which are considered to be resistant to hydrogen embrittlement (known also as sulfide corrosion cracking and sulfide stress cracking). In general this involves avoidance of high strength steels (i.e., above about 80,000 psi minimum yield strength). The specific guidelines used in this report follow those used in the oil industry which are given in NACE Publication 1F166 (1973 Revision), a copy of which is attached.

A major argument for using steel in the test well is the desirability of establishing early in the project the feasibility of using steel, since the higher cost of alloys for major equipment, e.g., casing, could have a marked adverse effect on the economics of the project. The use of steel requires that equipment items be inspected at frequent intervals to provide protection from failure in service.

Drilling Equipment

It is assumed that conventional oil well drilling equipment will be used and that a water-base mud will be the drilling fluid, with the option that air drilling may be used when drilling in the producing formation. It is also assumed that hydrogen sulfide will be present in the produced steam.

To avoid sulfide corrosion cracking, use of API Grade D drill pipe is recommended. Grade E drill pipe can be used if it is made by the quench-and-temper process. To minimize stresses, and thus minimize corrosion fatigue problems, the drill pipe should be as large as is convenient. Also, the drill pipe should be coated on the inside with a plastic coating of a type commonly used in oil field drilling. It is preferred that the drilling mud be alkaline (to neutralize any hydrogen sulfide) and contain components which have oxygen scavenging properties (to minimize corrosion fatigue).

Because the produced fluid will be at a temperature higher than commonly encountered in oil well drilling, the elastomers used in the blowout preventer should have good high temperature properties.

Casing

Surface casing, since it is not in contact with the produced brine and steam, can be whatever pipe is available that meets the mechanical design requirements.

To avoid sulfide corrosion cracking, the production casing should be either API Grade H-40, J-55, K-55, or C-75. Some pipe manufacturers make a modified N-80 Grade by the quench-and-temper process which would be acceptable; however, the acceptability of a specific brand should be confirmed by us before ordering. Couplings should be of the same grade as the pipe. Assuming that the well will be produced with the steam and brine in contact with the casing, it would be desirable to use a heavier weight casing than necessary for mechanical design in order to provide a corrosion allowance. The selection of the size, weight, and grade of casing to provide the necessary mechanical strength for a specific well will be specified once the design parameters are established.

If a liner is used, the material could be any of those listed above that meet the mechanical requirements. In addition, API Grade N-80, C-95, or P-110 could be used if it can be established that the temperature of the liner would be above 70°C at all times. This exception to the general rule against using high strength steels in hydrogen sulfide systems results from recently published data showing sulfide corrosion cracking severity of a hydrogen sulfide environment to decrease markedly with increasing temperature. This approach does not apply generally to the production of casing, since during shut-in periods the upper part of the casing string will drop in temperature to values below that considered acceptable for higher strength steels.

Tubing

It is assumed that there will be a string of tubing in the well to provide a means of controlling the well even though the well would be produced through the casing. Although a full-length string of tubing may not be required from an operating viewpoint, there is justification for such a tubing string to obtain corrosion data as a function of depth. In addition, the tubing string would provide a means of testing alternative materials in the most corrosive locations.

Steels acceptable for tubing from the hydrogen embrittlement aspect include API Grades J-55 and C-75.

Wellhead Equipment

Materials used for wellhead equipment should follow API Specification 6A, particularly items 1.4.3 and 1.4.6 (see attachment) which describe materials acceptable for resistance to hydrogen embrittlement. The external bolting of wellhead equipment should meet the above requirements because of the possibility of exposure of the bolts to hydrogen sulfide.

For equipment items requiring a high degree of resistance to general corrosion, pitting corrosion, hydrogen embrittlement, and stress corrosion cracking, the following alloys should be used: Hastelloy C, Hastelloy C-4, ASTM A453 Grade 660 (A-286), or titanium. Satisfactory trim materials include ASTM A-399 RCoCr and A-399 RNiCr.

Use of austenitic stainless steels (e.g., Types 304 and 316) for pressure-containing components should be avoided because of the possibility of chloride stress corrosion cracking. Martensitic stainless steels (e.g., Type 410) should be avoided because of their poor resistance to pitting corrosion in chloride systems and their poor resistance to hydrogen embrittlement.

Flowlines

Flowlines should be made of API Grade 5L pipe with the added specification that hardness of the welds should not exceed 200 Brinell to avoid hydrogen embrittlement. If feasible, a heavier wall thickness than required for mechanical strength should be used so as to provide a corrosion and erosion allowance. Valves should follow API Apecification 6D. Use of bellows type expansion joints should be avoided since the thin and highly stressed metal in such joints is highly susceptible to failure from corrosion pitting or stress corrosion cracking.

Attachments:

Excerpt from API Specification 6A

NACE Publication 1F166 (1973 Revision)

1.4.3 API Flange, Bonnet, Cover Bolting, and Nut Materials to Resist Sulfide Stress Cracking. Chemical composition, heat treatment, and hardness are significant factors influencing the suitability of a material for this service. Therefore, flange, bonnet, cover bolting, and nut material for this service shall conform to requirements defined in National Association of Corrosion Engineers (NACE) publication 1F166 (1973 revision).

Bolting Material — ASTM A193, Grade B7M is acceptable. When 80,000 psi minimum yield strength bolting is used, the working pressure deratings listed in Table 1.5 will apply, except as specified in footnotes 2 and 3 to the table.

Monel K-500 in the hot rolled and aged hardened condition is acceptable at a hardness of Rc 35 and below. ASTM A453, Grade 660, solution treated and aged hardened is acceptable at hardness of Rc 35 maximum and lower. To be used without derating as required in Table 1.5, either of these materials must be heat treated to 105,000 psi minimum yield strength without exceeding the maximum hardness specified.

Bolt marking shall be in accordance with ASTM A193 for B7M material.

Bolt marking for Grade 660 material shall be in accordance with ASTM A453.

Nut Material — ASTM A194, Grade 2M.

Monel K-500 in the hot rolled and aged hardened condition is acceptable at hardness of Rc 35 and below. ASTM A453, Grade 660, solution treated and aged hardened is acceptable at hardness of Rc 35 and below.

Nut marking shall be in accordance with ASTM A194 for 2M material. Nut marking for Grade 660 material shall be in accordance with ASTM A453.

> NOTE: *See Par. 1.4.8, Note 1, for bolting materials suitable for use in low temperature hydrogen-sulfide-environment service.*

TABLE 1.5
WORKING PRESSURE DERATING[1] FOR REDUCED HARDNESS BOLTS

1	2
API Working Pressure psi	Working Pressure with Reduced Hardness Bolts in End Flanges psi
2,000	No Derating
3,000	No Derating
5,000 (type 6B Flange)	No Derating
5,000 (type 6BX Flange)	3,800
10,000 (type 6BX Flange)	7,600[2]
15,000 (type 6BX Flange)	11,400[3]
20,000 (type 6BX Flange)	No Derating
API 2900 (10,000)[4]	9,000

[1] When materials acceptable under National Association of Corrosion Engineers Publication 1F166 (1973 revision): *Sulfide Cracking Resistant Metallic Materials for Valves for Production and Pipeline Service* are used at the strength levels which meet the minimum requirements of ASTM A193, Grade B7 (105,000 psi minimum yield), the pressure rating of the valve and flanges need not be reduced.

[2] 10,000 psi 6BX working pressure flanges in the $1\frac{13}{16}$", $2\frac{1}{16}$", $2\frac{9}{16}$", and $3\frac{1}{16}$" sizes can be fully rated with 80,000 psi minimum yield strength material.

[3] 15,000 psi 6BX working pressure flange in the $1\frac{13}{16}$" size can be fully rated with 80,000 psi minimum yield strength material.

CAUTION: *The magnitude of the resistance to external bending moments is reduced when flanges are equipped with reduced strength bolting material.*

[4] Obsolete series, see Appendix G.

1.4.4 Sealing Materials. The non-metallic, resilient, rubber-like materials used in the construction of the annular static pressure sealing mechanisms of wellheads, preventers, and valves shall be capable of sustaining the designated operating pressure and temperature of the particular unit as specified on the purchase order.

1.4.5 Ring-Joint Gasket Materials. Ring-joint gaskets shall be of material and hardness as specified in Table 1.6.

TABLE 1.6
API RING-JOINT GASKET MATERIAL AND IDENTIFICATION

1	2	3	4
Material	Brinell Hardness Number,* Max.	Rockwell "B" Scale,† Max.	Identification Mark
Soft iron‡	90	50	D
Low-carbon steel‡	120	68	S
Type 304 stainless steel	160	83	S304
Type 316 stainless steel	160	83	S316

*Brinell hardness measured with 3,000-kg load except soft iron, which is measured with 500-kg load.

†Rockwell "B" measured with 100-kg load and 1/16-in. diameter ball.

‡Unless otherwise specified on the purchase order, soft iron and steel gaskets to be cadmium plated 0.0002-0.0005 inches.

1.4.6 Materials to Resist Sulfide Stress Cracking. Chemical composition, heat treatment, and hardness are significant factors influencing the suitability of a material for this service. Therefore, for the intended service, materials should be chosen such that the combination of chemical composition, heat treatment, and hardness is within the limits indicated for the hydrogen sulfide-containing corrosive environment. Where the hardness limit results in tensile properties lower than customarily employed, the design or service rating should be reviewed and modified as necessary. This is an engineering problem to be resolved between the manufacturer and user. Reference is made to National Association of Corrosion Engineers Publication 1F166 (1973 Revision). *Sulfide Cracking Resistant Metallic Materials for Valves for Production and Pipeline Service.*

> NOTE: *See paragraph 1.4.3 for bolting and nut materials suitable for this service.*

1.4.7 Materials for Low Temperature Service. All materials for the shell or pressure containing structure, such as bodies, bonnets, covers, end flanges, and welding ends as well as all bolting materials for metal temperatures below —20F shall be tested in accordance with the latest revision of ASTM E-23: *Notch Bar Impact Testing of Metallic Materials,* using the Charpy V notch technique.

A minimum of one impact test shall be conducted on a test block from each melt furnace heat. The mechanical properties of the test block shall be representative of those of the material used in the product. The test block shall accompany a product charge through the entire heat treating process.

The standard impact test temperature shall be in 25 degree F increments and shall be —25F, —50F, and —75F. The user shall clearly indicate on the purchase order the test metal temperature required for his particular need. Impact test coupons shall be cut from materials as noted in the asterisk-designated footnote to Par. 1.4.1.

NACE Publication 1F166 (1973 Revision)

Report of NACE Unit Committee T-1F* on Metallurgy of Oil Field Equipment, prepared by Task Group T-1F-1** on Sulfide Cracking Resistant Metallic Materials for Valves for Production.

Technical
Practices
Committee

Sulfide Cracking Resistant Metallic Materials for Valves for Production and Pipeline Service

Foreword

Many metallic materials are subject to spontaneous brittle failure when exposed under stress to environments containing hydrogen sulfide. The failure has various names, but in this report it will be referred to as sulfide stress cracking (SSC). The materials described in this report have been found by experience and laboratory testing to be highly resistant to SSC.

Scope

This report covers metallic materials requirement for resistance to sulfide stress cracking (SSC) for valves. These recommendations are applicable to the materials used for equipment covered by API Standards 6A and 6D, and are not intended to include design requirements.

Note: Although this report concerns valve materials intended for sulfide service, it is not to be construed as a guarantee that products conforming to these requirements will resist attack by sulfide containing media under all conditions.

Nothing contained in this report is to be construed as granting any right by implication or otherwise for manufacture, sale, or use in connection with any method, apparatus or product covered by letters patent nor as insuring anyone against liability for infringement of letters patent. This report is for the convenience of purchasers and manufacturers in ordering and producing materials for products and is not intended to inhibit purchasers and producers from purchasing and producing materials for products meeting requirements other than those contained herein.

Materials

Most ferrous materials hardenable by heat treatment can be made susceptible to SSC. Conversely, most ferrous materials can be heat treated to be highly resistant to SSC. The following recommendations are intended to assure heat treatments which will provide materials which are highly resistant to SSC.

The recommendations shown under the various material categories are applicable to that material when the material is used in an equipment component.

Carbon Steel

Carbon steels such as ASTM A-216, API Types 1 and 4, and AISI 1010 to 1045, inclusive, are satisfactory at hardness levels of Rc22 or lower. If cold worked or cold rolled materials are employed, the item should be tempered at 1150 F (621 C) minimum to a hardness level of Rc22 or below after cold working.

Low and Medium Alloy Steels

Low and medium alloy steels, wrought and cast, such as API Types 2 and 3, ASTM Types A-148, A-487, A-193, A-194, A-352, AISI Types 4130, 4140, 4145, 8630, 8640 should be annealed or quenched or normalized followed by tempering at 1150 F (621 C) minimum, to a hardness level of Rc22 or below. Low alloy steels containing over approximately 1% nickel are subject to SSC at hardnesses lower than Rc22. Subsequently to any cold working or welding, the whole part should be reheat treated by tempering at 1150 F (621 C) minimum to a hardness level of Rc22 or below.

Note: Flange, bonnet and cover bolting: Carbon and low alloy steel bolting manufactured to the above requirements will not meet the 105,000 minimum yield strength requirements of API Standards 6A and 6D which specify hardnesses at higher levels than those required by SSC service. Carbon and low alloy steel bolting for SSC service should be heat treated to obtain 80,000 psi minimum yield strength and a maximum hardness of Rc22.

Designers are cautioned that it may be necessary to derate pressures or to use bolting not susceptible to SSC at the strength levels required by the API standards.

Bolting is defined as studs, bolts, cap screws, slotted machine screws, etc. Nuts holding critical components, and nuts exposed directly to the sour environment, shall meet the requirements for bolting.

Free-Machining Steels

Rephosphorized and/or resulfurized free-machining steels should be used only for noncritical parts.

Carbon and low and medium alloy steels to which lead has been added to promote machinability (not rephosphorized nor resulfurized) are satisfactory at hardnesses of Rc22 and below provided the requirements of the paragraphs on "Carbon Steels" and/or "Low and Medium Alloy Steels" listed above are complied with.

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*J. B. Greer, Esso Production Research, P. O. Box 2189, Houston, Texas 77001, chairman.

**M. R. Chance, Thornhill-Craver Co., P. O. Box 1184, Houston, Texas 77001, chairman.

Stainless Steels

Austenitic chromium-nickel steels (such as 304 and 316) and ferritic chromium steels (such as 405 and 430), wrought or cast, should be in the annealed condition free of cold work. The hardness level should be Rc22 maximum.

Martensitic chromium stainless steels (such as 410), wrought or cast, should be heat treated by quenching and double tempering at 1150 F (621 C) minimum to a hardness level of Rc22 maximum. However, some straight chromium (martensitic) stainless steels with proper chemistry when properly heat treated are satisfactory at hardnesses over Rc22 but should not generally be used without the permission of the purchaser.

Some precipitation hardening stainless steels are satisfactory for use when properly heat treated at hardness levels which may be over Rc22 but should not be used in parts without permission of the purchaser.

ASTM A453 Grade 660 (A 286), solution treated and age hardened, is acceptable at hardnesses below Rc36.

Nickel-Copper-Aluminum Alloys

Nickel-copper-aluminum alloys (such as Monel alloy K-500) are satisfactory in the hot rolled and age hardened condition at hardnesses of Rc35 and below.

Nickel-Coper Alloys

Nickel-copper alloys such as ASTM B-127 and B-164 (Monel) are considered satisfactory.

Nickel-Chromium-Iron Alloys

Nickel-chromium-iron alloys, such as ASTM B-166 (Inconel 600 or 604) are satisfactory annealed or cold worked.

Nickel-Chromium-Iron Alloys

Nickel-chromium-iron alloys (such as Inconel X-750) at hardness levels below Rc35 are satisfactory.

Nickel-Molybdenum and Nickel-Molybdenum-Chromium Alloys

Nickel-molybdenum and nickel-molybdenum-chromium alloys such as ASTM A-494 (Hastelloy B and Hastelloy C) are considered satisfactory.

Cobalt-Chromium-Tungsten Alloys and Nickel-Boron Alloys

Cobalt-chromium-tungsten alloys and nickel-boron alloys such as ASTM A-399 RCoCr and A-399 RNiCr (Stellite and Colmonoy) are considered satisfactory as trim materials. After the trim application, the part should be reheat treated by tempering at 1150 F (621 C) minimum to maintain the hardness level of the part being trimmed at Rc22 maximum.

Cemented Carbides

Cemented carbides are considered satisfactory. When used as trim materials and applied by the fusion or welding process, the part trimmed should be subsequently tempered at 1150 F (621 C) minimum. The hardness of the base material should be limited to Rc22 maximum.

Copper Base Alloys

Bronze and other copper base alloys are not generally satisfactory for highly stressed parts in sour service and should not be used in parts without permission of the purchaser.

Cast Iron

Cast iron is not permitted for use as pressure containing members in equipment covered by API Standards 6A and 6D. Cast iron in nonpressure containing internal parts should not generally be used without permission of the purchaser.

Plating

The use of plating (i.e., nickel, chromium, cadmium, electroless nickel, etc.) to prevent SSC is not satisfactory. For other purposes, the use of plating over materials satisfactory for use in sour environments is a matter for agreement between the producer and user.

Fabrication

Welding

Repair welding to cast components should be in accordance with ASTM A-488 and the appropriate ASTM material specification.

All fabrication welds should be made in accordance with the procedure and by welders or welding operators qualified under Section IX of the ASME Boiler and Pressure Vessel Code.

Subsequent to any welding, repair or otherwise, the whole part should be heat treated at 1150 F (621 C) minimum to produce uniform structures, to relieve internal stresses, and to limit the hardness to Rc22 maximum.

Overlaying

When overlays are applied by a process involving heat, the parts should be subsequently heat treated at a temperature of 1150 F (621 C) minimum to a base metal hardness of Rc22 maximum.

Cold Working

Subsequent to any cold deformation by rolling, straightening, cold forging, or other process which results in uncontrolled residual stresses incident to such operations, the part should be heat treated at a temperature of 1150 F (621 C) minimum to a hardness of Rc22 maximum.

PART III

FIELD CORROSION TEST PROGRAM FOR NEVADA GEOTHERMAL WELL

The following field corrosion test program is proposed for the geothermal test well being planned for a Nevada site. The program is divided into sections based on location: down-the-hole, wellhead, flowline, power plant, and brine disposal. Within each section are tests designed to obtain: (1) short term data to reflect the influence of operating variables, and (2) long term data to establish suitability of specific materials.

I. Down-the-hole

A. Short range

1. The material of interest is carbon steel, which presumably will be the material used for the down-the-hole tubulars. It is proposed that the progress of corrosion be determined by daily analyses of the produced brine for iron. There is the problem of not knowing the bottom-hole iron values, but changes may be indicative of changes in the corrosion rate, and thus indicate the most corrosive and the least corrosive operating condition.

2. Another approach would be to use a radioactive specimen down-the-hole, and monitor corrosion by counting the produced fluid. A technique that has been used successfully in oil wells is described by Gordon, Raifsnider, and Lilly (1966). This technique would require (1) presence of tubing in the hole to support the specimen, and (2) knowledge of the most corrosive zone so as to place the

specimen where it would be most useful. Therefore, it is suggested that implementation of this approach be deferred until the initial long range data (see below) become available.

B. Long range

1. If there is a possibility that the casing or liner will be removed at a later date, the pipe should be measured before it is run in the hole to establish base data. Measurements could include, for example, wall thickness by caliper at three locations near each end of each joint, and the joints identified by a stamped number.

2. The tubing should be measured in the same way as suggested above for the casing.

3. Special tubular specimens of alloys of interest should be prepared which could be attached to the tubing string. These could be in the form of sleeve type specimens which could be clamped to the outside of the tubing with an insulating sheet of Teflon between the specimen and the tubing to prevent galvanic effects. If the well is produced through the tubing, the specimens would be located on the inside of the tubing. Initially three locations would be used: bottom of the hole, mid-way, and top. If initial results indicate the necessity of obtaining more reliable performance data for a specific alloy than obtainable with specimens, this could be done by means of pup joints made from that alloy.

4. If the casing is not to be recovered, arrangements should be made for inspection of the casing before the well is produced and at a reasonable interval after. This could be done by commercially available survey equipment using either caliper or eddy current

techniques; selection of the best approach could be made by discussion with potential suppliers of the service after size and type of casing to be used are known.

5. To obtain data on the corrosiveness of the drilling operation, several ring type corrosion specimens should be incorporated in the drill string. These can be weighed to determine corrosion rate and inspected for pits. In addition the drill string can be inspected for corrosion damage.

II. Wellhead

A. Short range

1. Provision should be made for insertion of an *electrical resistance corrosion measurement* probe at the wellhead. This will provide a means of obtaining fairly short term measurements of the corrosion rate at this location and serve as a guide for timing the long range tests.

2. An additional location should be provided for a *polarization resistance corrosion rate measurement* probe at the wellhead. This will provide instantaneous corrosion rate measurements which will be of value in evaluating the effect of changes in operating variables.

3. Conventional *corrosion specimens* of a variety of alloys of interest should be placed in the outlet from the wellhead. This is conveniently done by attaching the specimens to a rod which is attached to a plug fitting which screws into a tee connection at the wellhead. These would be removed for examination on a weekly basis and new specimens exposed. In addition to weight loss specimens,

U-bend stress corrosion specimens and welded specimens would be included in each specimen assembly.

4. An assembly for evaluating velocity effects would be attached to the wellhead. This would consist of a bypass line of 1-inch pipe designed with machined test sections that could be removed for weight loss measurements, plus the necessary equipment to measure and control flow rate.

B. Long range

1. All equipment items in the wellhead assembly should be inspected prior to assembly of the wellhead and the wall thickness (or I.D. if thickness not applicable) measured at several points on each item, and the points identified for later reference. If there are internal components that are easily disassembled, this should be done and the components measured and weighed (if small enough to be meaningful). After exposure for a period to be determined by the short range tests, the items are to be inspected and re-measured.

2. If significant corrosion is found on any of the equipment items, they should be replaced with items fabricated from an alloy expected to be resistant to corrosion and the above procedure repeated.

3. In the event that short range tests indicate significant corrosion, but it is not practical to shut down and disassemble the wellhead, a tentative measure of the severity of the attack can be obtained by x-ray inspection of the wellhead.

III. Flowlines

A. Short range

1. The corrosion data obtained at the wellhead and at the plant should allow adequate measure of the effect of operating variables on flowline corrosion, and also provide advance warning of any serious corrosion problem. Therefore, no short range test program is indicated.

B. Long range

1. Ultrasonic thickness measurements should be made at a number of locations along the flowline, the exact number being determined by the length of the line. At each location sufficient measurements should be made to obtain a picture of any circumferential effect of corrosion. These measurements should be made prior to putting the line in service and at periodic intervals, the frequency being determined by the nature of the short range data obtained at the wellhead and at the plant.

2. Based on the above data, sections of the line should be cut out for detailed inspection and measurement.

3. If the above data indicate a significant corrosion problem, a program should be initiated to test alternate pipe materials; the test would consist of test spools of materials of interest placed in the flowline and inspected at intervals to provide an early evaluation of their suitability.

IV. Power Plant and Brine Disposal

Since a detailed design of the plant is not available, the corrosion test program can be treated only in general terms.

A. Short range

1. Provisions would be made for insertion of both electrical resistance and polarization resistance corrosion measurement probes. These would be used to monitor the corrosivity of major process streams.

2. Locations should be provided for corrosion specimens (both weight loss and stress corrosion). These would be more numerous than the above, since it would be desirable to define the corrosion characteristics of all process streams.

B. Long range

1. All major equipment items should be measured at several critical points prior to being put in service to provide base points for subsequent inspections. This includes in particular such items as pump impellers, heat exchange tubing, turbine components, vessel walls, and major piping. In addition, ultrasonic measurements should be made on all pressure vessels and major pressure piping so that corrosion damage can be detected conveniently to avoid any hazard.

2. Any heat exchanger should contain test tubes of alternate alloys, arranged in cluster patterns to minimize galvanic effects. Major piping runs, e.g., effluent brine piping, should contain test sections of alternate materials.

3. The effect of inhibitors and non-Newtonian additives on

corrosion should be investigated. This would be carried out in laboratory or pilot plant operations. Beneficial effects have been reported, and this may prove to be useful in reducing corrosion.

Summary

Attached is a table summarizing the above program and defining the modifications of normal design required to accomodate each aspect of the program plus a description of the auxiliary equipment required to conduct the tests.

Detailed designs of the individual test units and cost estimates can be prepared after agreement is reached on the corrosion test program; these designs would be coordinated with the design of the test well and the power plant and brine disposal system.

References

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Table 1. EQUIPMENT REQUIREMENTS FOR CORROSION TESTS

Location	Test No.	Description	Additions to Regular Equip.	Special Equipment
Down-the-hole	I A 1	Analyses	Sample valve at wellhead	a)
	I A 2	Radioactive specimens	Special tubing joint	Radioactive specimen; counting app.
	I B 1	Casing measure	None	Calipers
	I B 2	Tubing measure	None	Calipers
	I B 3	Tubular specimens	Special tubing joints (3)	Specimens (3 per alloy)
	I B 4	Caliper survey	None	Survey tool b)
Wellhead	II A 1	Resistance probe	½"NPT connection with 6" free space c)	Meter, probes
	II A 2	Polarization probe	3/4"NPT connection with 6" free space	Meter, probes
	II A 3	Corrosion specimens	1½"NPT connection with 24" free space	Support rod, specimens
	II A 4	Velocity test	1"NPT connections (2) with valves	Test section to be designed
	II B 1	Measurements	None	Calipers,balance
	II B 2	Alloy test	Replacement item	None
	II B 3	X-ray inspection	None	X-ray equip. b)
Flowlines	III B 1	Ultrasonic insp.	None	Ultrasonic equip. b)
	III B 2	Measurement	Replacement pipe	None
	III B 3	Alloy test	Replacement pipe	None
Plant	IV A 1	Resistance, polarization probes	½"&3/4" NPT connections with 6" free space (x)	Meters(from II A), probes
	IV A 2	Corrosion specimens	1½"NPT connections (y) with 24" free space	Support rods, specimens
	IV B 1	Measurements	None	Calipers, Ultrasonic equip. b)
	IV B 2	Alloy test	Replacement items	None

a) Analytical laboratory facilities, not necessarily on site.
b) Provided by service company on contract, with operator.
c) Distance that must be left free beyond opening in axial direction of opening; this is to accommodate the probe or specimens.

PART IV

VELOCITY EFFECTS IN CORROSION

Preliminary Investigation of Mass Transfer Controlled Corrosion of Prototype Impellers/Propellers

Abstract

Mass transfer data was obtained for the cathodic polarization of three different vertically mounted brass propeller/impeller shapes: a 3.81 cm diameter cylinder 36.83 cm long, a flat blade 0.635 cm by 5.08 cm by 36.83 cm, and a pitched blade with the same dimensions as the flat blade but with a 10° pitch. The potential for the mass transfer limiting current was determined to be .950 millivolts negative to a silver/silver chloride electrode for the 3.5% NaCl solution at 21°C.

The average Sherwood numbers determined for Reynolds numbers from 9,900 to 43,000 were of the form:

$$\overline{Sh}_{\text{cylinder}} = 1.35 \quad Re^{0.614}$$

$$\overline{Sh}_{\text{flat blade}} = 0.358 \quad Re^{0.731}$$

$$\overline{Sh}_{\text{pitched blade}} = 1.24 \quad Re^{0.631}$$

These correlations permit conservative estimates of maximum corrosion rates under the conditions of test, and furnish quantitative information on current requirements for cathodic protection. The systematic and predictable correlations obtained indicate that it is practical to test more complicated systems, and even actual propellers and impellers, to obtain correlations which will be useful for design and scale up purposes.

Introduction

High velocities, even attaining sonic flow, are reached in processing geothermal fluids, due to high pressure drops or to flashing of hot brine. In nozzles, orifices, valves, in heat exchangers and flow lines, such high velocity flows can cause accelerated corrosion. It is desirable therefore to understand the relation between flow velocity and corrosion in order to evaluate effects and design accordingly.

Research conducted over a period of years has shown that in many systems the corrosion of metal in a moving fluid is controlled by mass transfer processes in the fluid (Cornet, et al., 1961, 1969a; Mahato, et al., 1968). Much of this early work has involved aerated systems, where access of oxygen to the metal surface results in cathodic reduction of oxygen to form hydroxyl ions. This cathodic reaction determines the rate of the anodic or corrosion reaction.

Recent work has shown that in non-aerated systems also convective mass transfer in the fluid may control corrosion (Ellison, et al., 1974).

Typically where a metal has little scale or oxide cover to act as a diffusion barrier, mass transport through the fluid phase is more likely to affect the corrosion rate. Quantitative relationships have been obtained for simple geometric shapes, such as discs (Ellison, et al., 1971), cylinders (Cornet, et al., 1969b), and cones (Kappesser, 1973) rotating in quiescent fluids. Investigation in many cases is based on electrochemical techniques, because such techniques are precise, duplicable and convenient.

A metal is polarized to a protective potential, and a mass transfer limiting current is determined. The potential is a function of the metal; thus at 25°C, steel may be protected at a potential of -0.77 and a bronze at -0.93 volts relative to a calomel reference electrode in aerated salt solution (Cornet, et al., 1965). The mass transfer limiting current depends on the access of oxygen to the metal; this current is also the corrosion current in an unpolarized system. The corrosion rate therefore can be calculated quantitatively if the concentration and diffusivity of oxygen in the saline solution are known. Furthermore, Reynolds analogy may permit quantitative correlations of corrosion rates with momentum, heat, and mass transport equations.

To apply the laboratory and theoretical corrosion equations to large scale engineering design, an investigation was undertaken on prototype impeller-propeller systems.

Experimental System

The apparatus used in this investigation consisted of three different vertically mounted brass propellers: a 3.81 cm diameter cylinder 36.83 cm long, a flat blade 0.635 cm by 5.08 cm by 36.83 cm, and a pitched blade with the same dimensions as the flat blade but with 10° pitch. Each was mounted separately on a 6.35 cm diameter acrylic plastic cylinder with a brass female mounting shaft which mated to the male main drive shaft. The propellers were immersed in 113 liters of 3.5% NaCl aqueous solution with a 25.4 cm head. The anode of the system was a thin circular sheet of titanium located at the bottom of the 113 liter container and 50 cm from the propeller. A compressed Micarta material 1cm thick was used to fabricate baffles to reduce the core velocity of the solution.

The reference electrode for the system was a silver/silver chloride cell. The control potential and current source were provided by a Brinkmann Wenking potentiostat.

Drive for the propellers was produced by a 1/2 horsepower A.C. motor. The speed of rotation of the propeller was measured from a 60 tooth gear on the main drive shaft by a magnetic pickup and an electronic digital counter.

Details of the experimental system are shown in Figures 1-5.

Procedure

The 3.5% NaCl solution was mixed the day before the experiment and stored overnight in a plastic covered tank to allow the solution to reach a steady state with respect to the dissolved oxygen concentration. Fifty gallons of city tap water were mixed with 15.1 pounds of reagent grade NaCl to give a 3.5% solution.

The electronic counter and Wenking potentiostat were turned on and left in standby to warm up.

In order to maintain a reproducible surface, each day the surface of the propeller used was polished with 500 grit aluminum oxide paper and washed with city tap water and rinsed in distilled water.

The propeller was then inserted through the center hole in the plexiglas lid and threaded hand tight on the main drive shaft.

The entire drive apparatus mounted on a heavy table was raised three feet by a hoist and the working tank/baffle/counter electrode assembly was positioned under the raised propeller. The drive apparatus was then slowly lowered down back to the deck with the propeller inside the working tank. See Figures 2, 5.

The 3.5% NaCl solution was drained from the mixing tank with a rubber hose and into the working tank with care taken not to cause splashing or other vigorous aeration.

Two samples, one for dissolved oxygen (D.O.), the other for chlorinity (Cl), were then drawn from the working tank and the solution temperature was recorded.

After the wiring and the baffle clearance were visually checked, the potentiostat was used to measure E_R, the rest potential between the working and reference electrode while no current is flowing.

The first part of the experimental work was to obtain a plot of the potential vs current curve so that the mass transfer limiting current and its associated potential could be determined. This was accomplished by setting potentials of from 700 millivolts to 1400 millivolts on the vernier of the potentiostat and switching to I, the actual working position of the potentiostat, to record the current. The first run was made at a constant 43 rpm so that a uniform polarization would take place. The system was then stopped and second run of from 500 millivolts to 1250 millivolts was recorded. The initial polarization of the propeller was then read as current vs time.

After the current reached a slowly declining value .2 ma per

30 second period, the apparatus was started at the lowest rpm and the current read. For 10 rpm increments, there was no change in the value of the current vs time, so that the reading of current could be taken directly after the reading of rpm.

This iterative process continued until the drive motor of the apparatus stalled, at which time the system was shut down.

Two additional samples for dissolved oxygen and chlorinity were taken within minutes after shutdown, but still the froth from the high rpms had settled to a point that the entrained air in the solution could not be obtained for analysis. The final solution temperature was recorded.

The propeller and drive assembly were then hoisted clear of the solution and washed down. The solution was either drained or covered for the following day's use.

The dissolved oxygen and chlorinity samples were then immediately analyzed.

Results and Discussion

Representative current-voltage data are shown in Figure 6, for potential sweeps at 0 and 43 rpm. There are two scales for the abscissa. There is arbitrariness in selection of 0.950 volts (negative to Ag-AgCl electrode) as the potential at which limiting current is obtained, but even so, the limiting current is determinable within ± 3%. The irregularities in the curve at the inflection may actually imply stepwise reduction of oxygen to hydroxyl ion, but there was no attempt to examine such mechanisms.

Data obtained was next converted to a mass transfer coefficient, ma/(cm^2 ppm$_{O_2}$), plotted against RPM in Figure 7.

The data was then converted to Sherwood Number vs Reynolds Numbers, Figures 8, 9, 10, and attempts were made to correlate with various equations in the literature.

Empirical equations obtained are shown in Figure 8. Correlations for the cylinder propeller are shown in Figure 9, and for the horizontal flat blade propeller in Figure 10. No attempt has been made to take into account the effect of the baffles on the mass transfer, although baffles are known to affect the hydrodynamic performance and therefore would affect heat and mass transport (Daily and Nece, 1960).

Correlations with various two dimensional model equations for the rotating cylinder and flat blade gave agreement generally within ± 30%, which may be considered reasonable inasmuch as the effect of baffles was neglected. The effect of the 10° pitch has not been fully rationalized as yet.

Mass transfer information of the type obtained here has been shown to correlate directly with maximum corrosion rates, and also with the current required for cathodic protection to prevent corrosion. The systematic and predictable changes measured in this investigation are encouraging in that they warrant further research, with flat blades at different angles of attack and subsequently with impeller and propeller systems. The assurance that corrosion effects can be rationalized and predicted will permit rational design and scale up of components.

Conclusions

Prototype impeller/propeller shapes were rotated in aerated 3.5% salt solutions at 21°C and polarization curves obtained. For a range of Reynolds numbers from 9,900 to 43,000 the average Sherwood numbers were:

$$\overline{Sh}_{\text{cylinder}} = 1.35 \quad Re^{0.614}$$

$$\overline{Sh}_{\text{flat blade}} = 0.358 \quad Re^{0.731}$$

$$\overline{Sh}_{\text{pitched blade}} = 1.24 \quad Re^{0.631}$$

These correlations agreed within ± 30% with predictions of two dimensional models, even though the effect of baffles in the vicinity of the rotating shapes was not taken into account.

Mass transfer increased as a power of Reynolds Number. The systematic relationship warrants further investigation, to permit interpolation rather than unproven extrapolation for design purposes.

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* "Preliminary Investigation of Mass Transfer Controlled Corrosion of Prototype Impellers/Propellers", by I. Cornet, R. Greif, and Fred Roehler; presented in the Symposium on Advances in Corrosion Control and Prevention, at the 77th National Meeting of the American Institute of Chemical Engineers, Pittsburgh, Pennsylvania, June 5, 1974.

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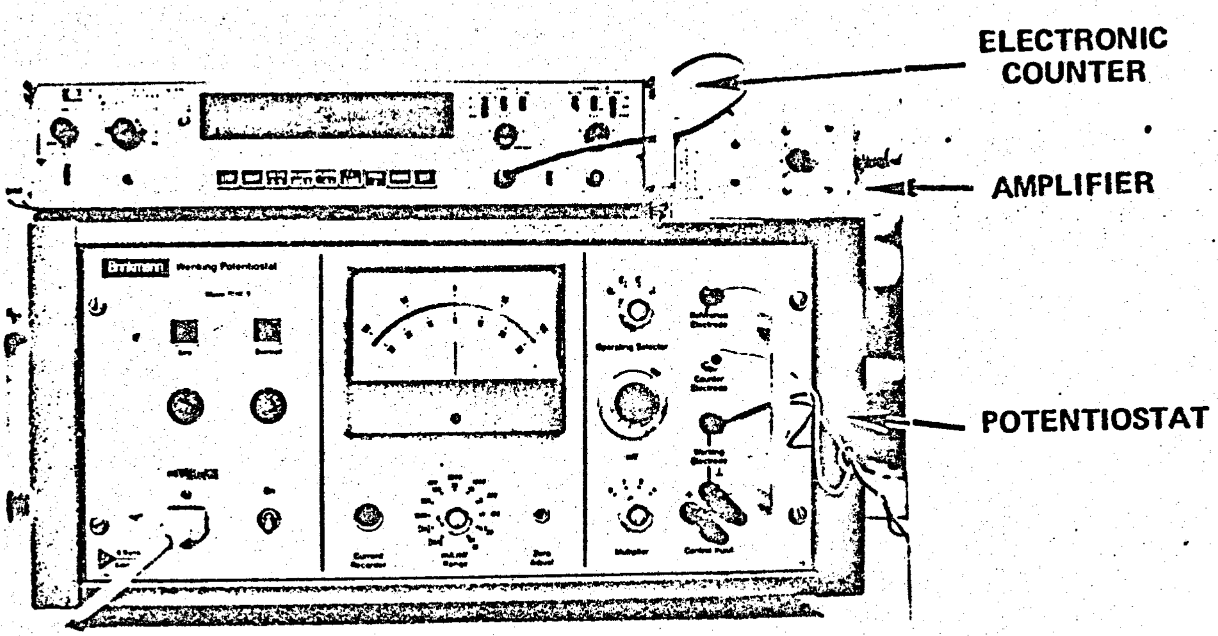

FIGURE 1 POTENTIOSTAT, COUNTER AND AMPLIFIER

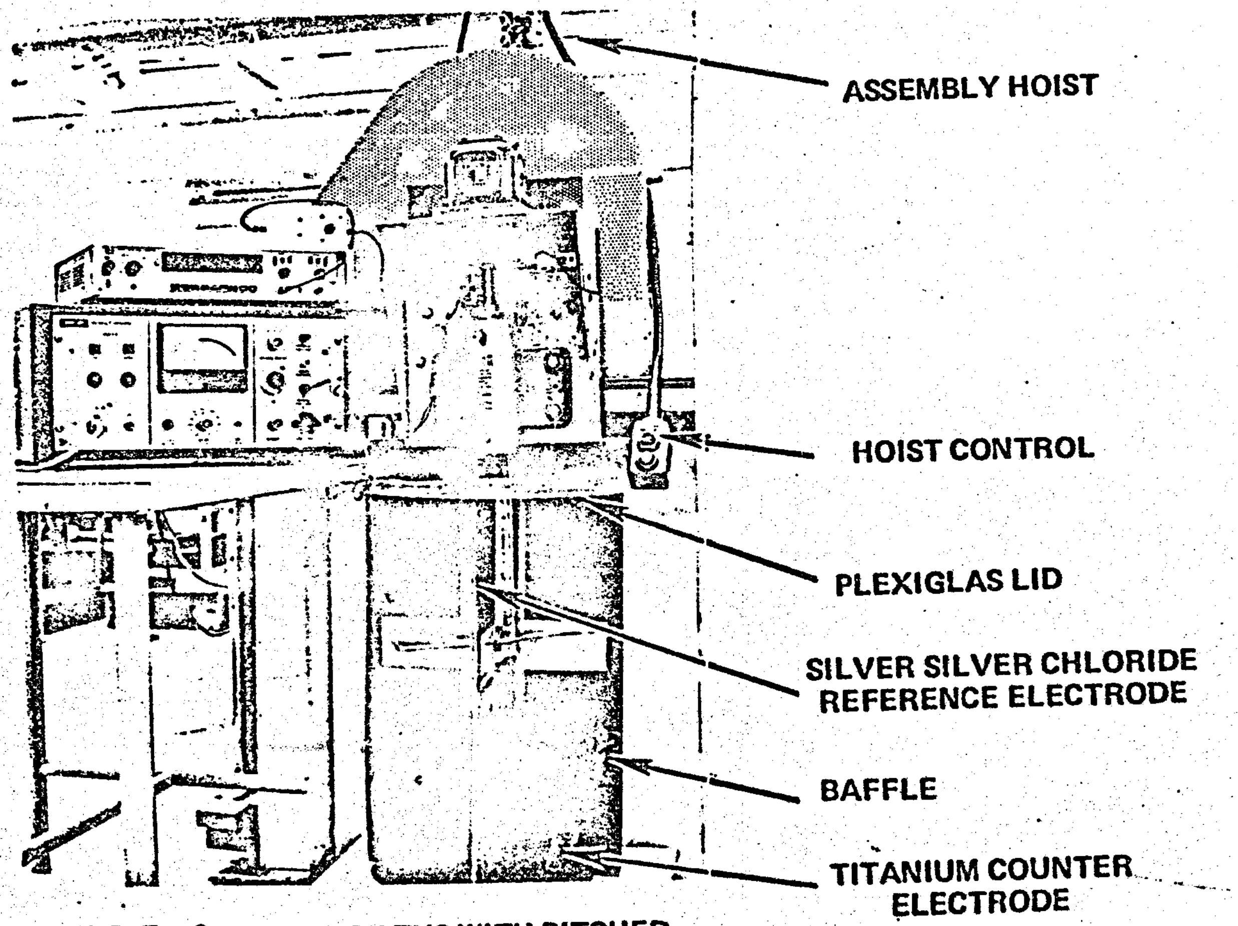

FIGURE 2 APPARATUS WITH PITCHED BLADE PROPELLER LESS PLASTIC TANK

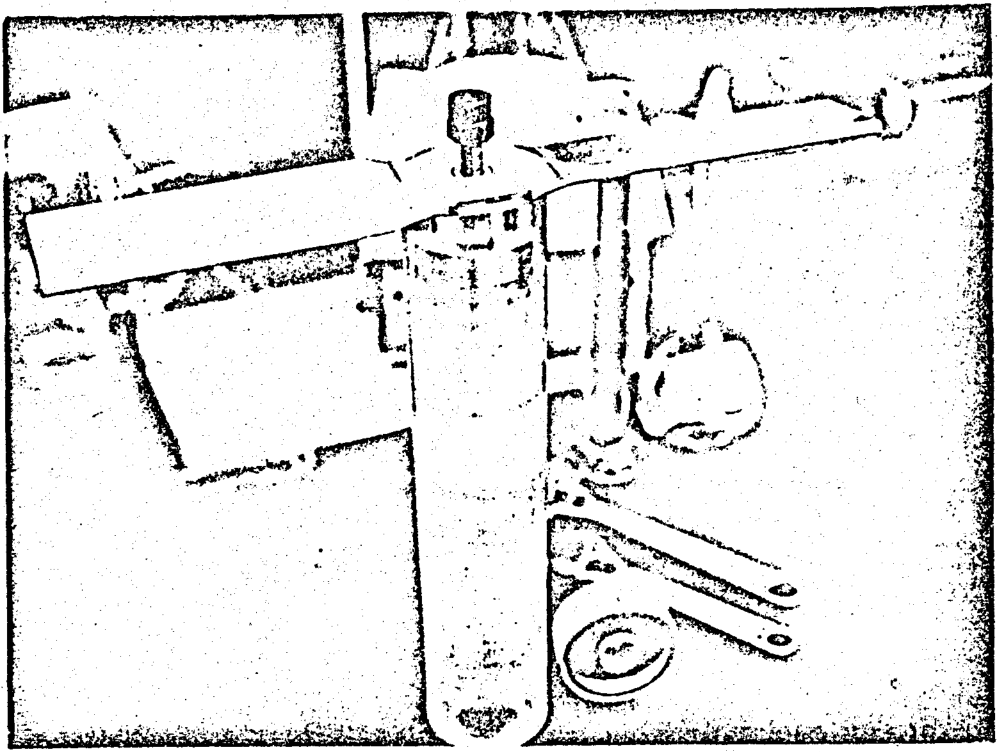

FIGURE 3 **PARTIAL DISASSEMBLY OF PITCHED BLADE PROPELLER**

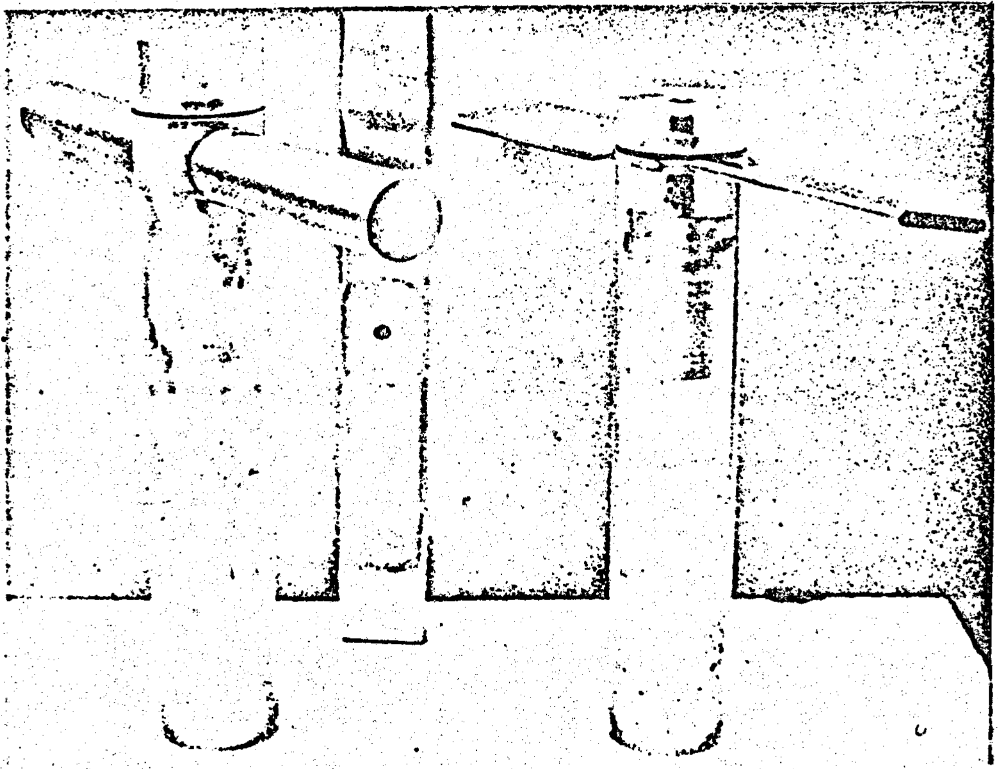

FIGURE 4 **CYLINDRICAL, FLAT BLADE AND PITCHED BLADE PROPELLERS**

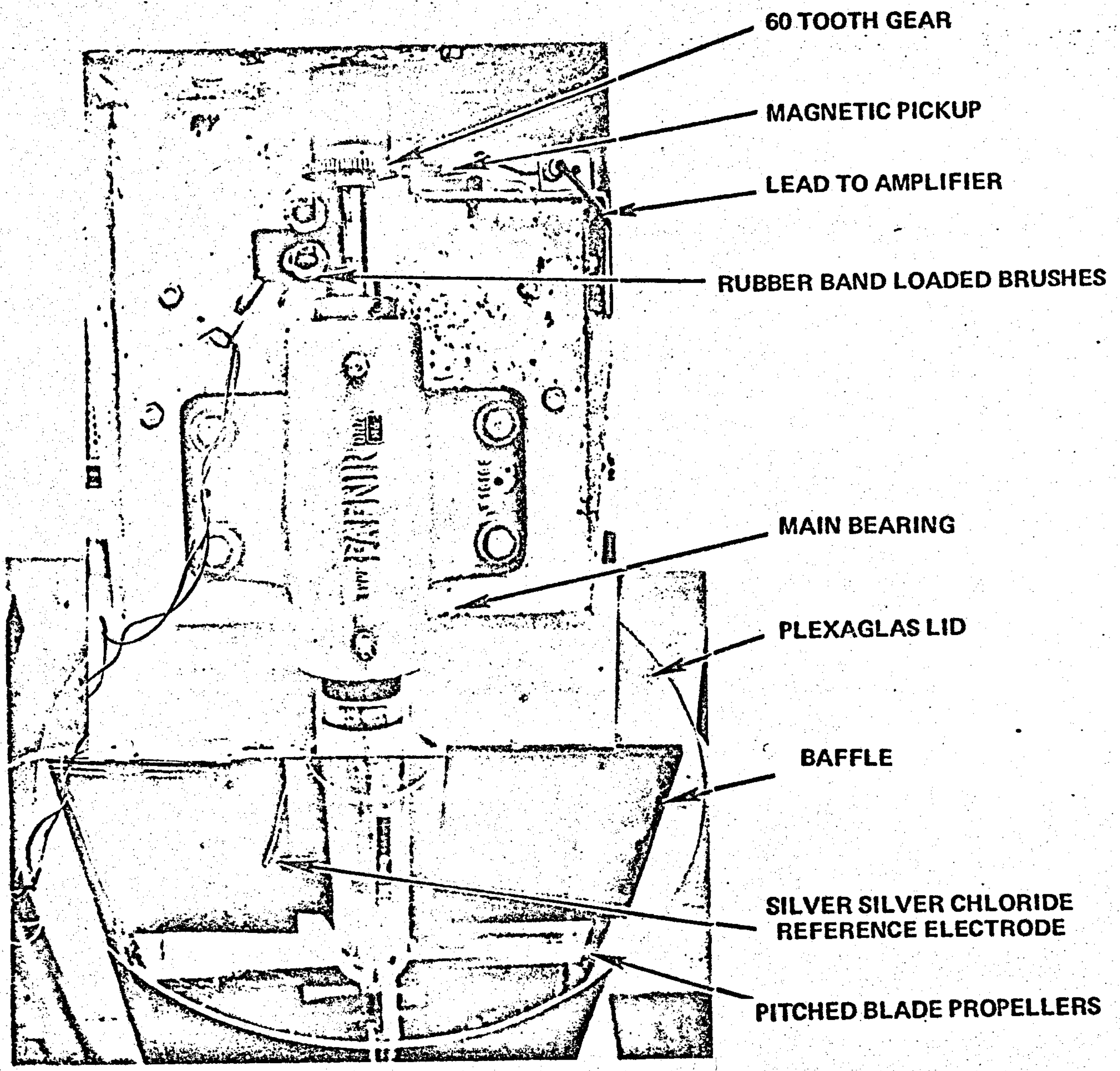

FIGURE 5 COMPOSITE OF MAIN SHAFT BAFFLE ASSEMBLY

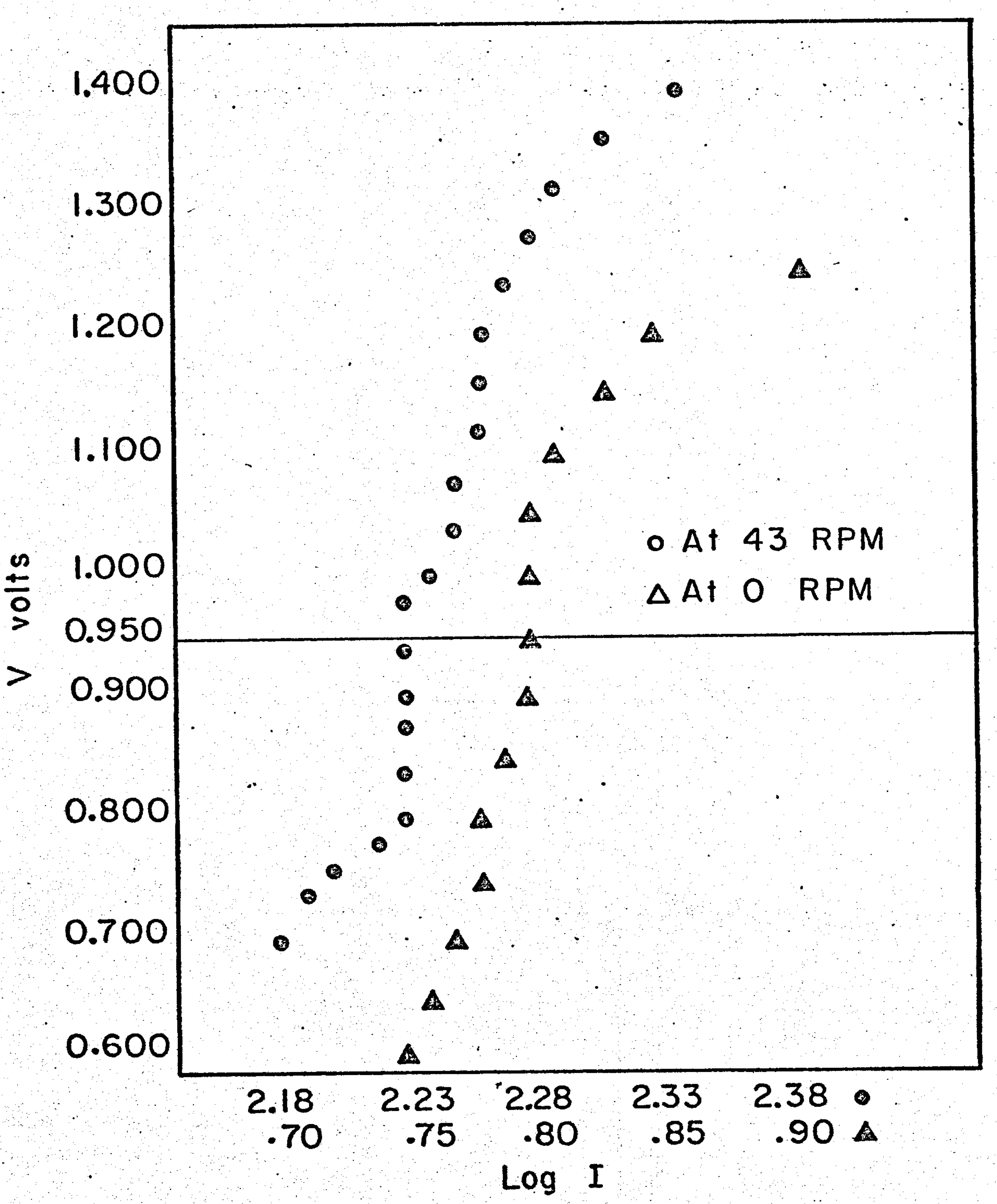

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FIGURE 6 CURRENT VS. VOLTAGE

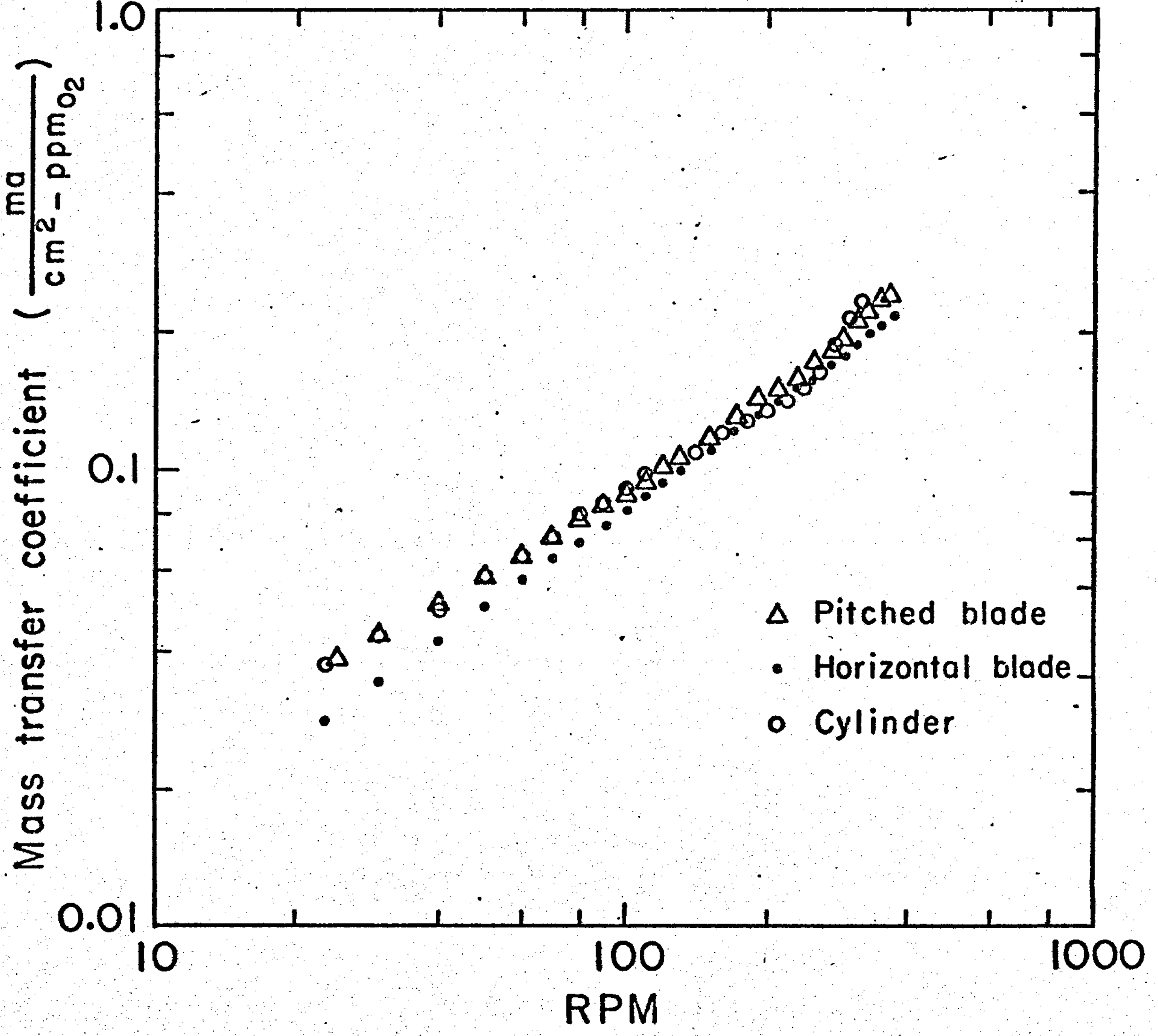

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FIGURE 7 MASS TRANSFER VS. RPM

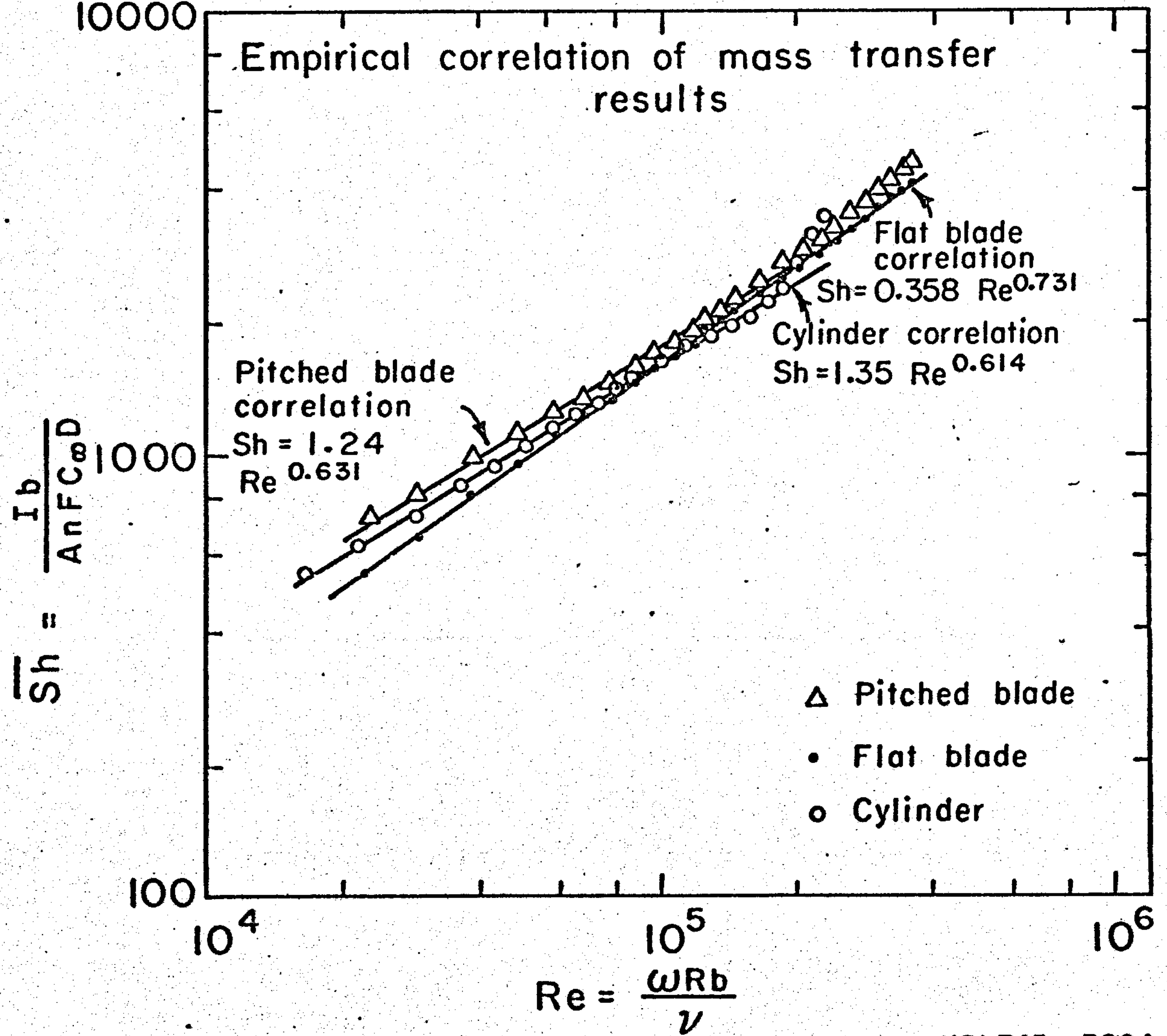

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FIGURE 8 EMPIRICAL CORRELATIONS

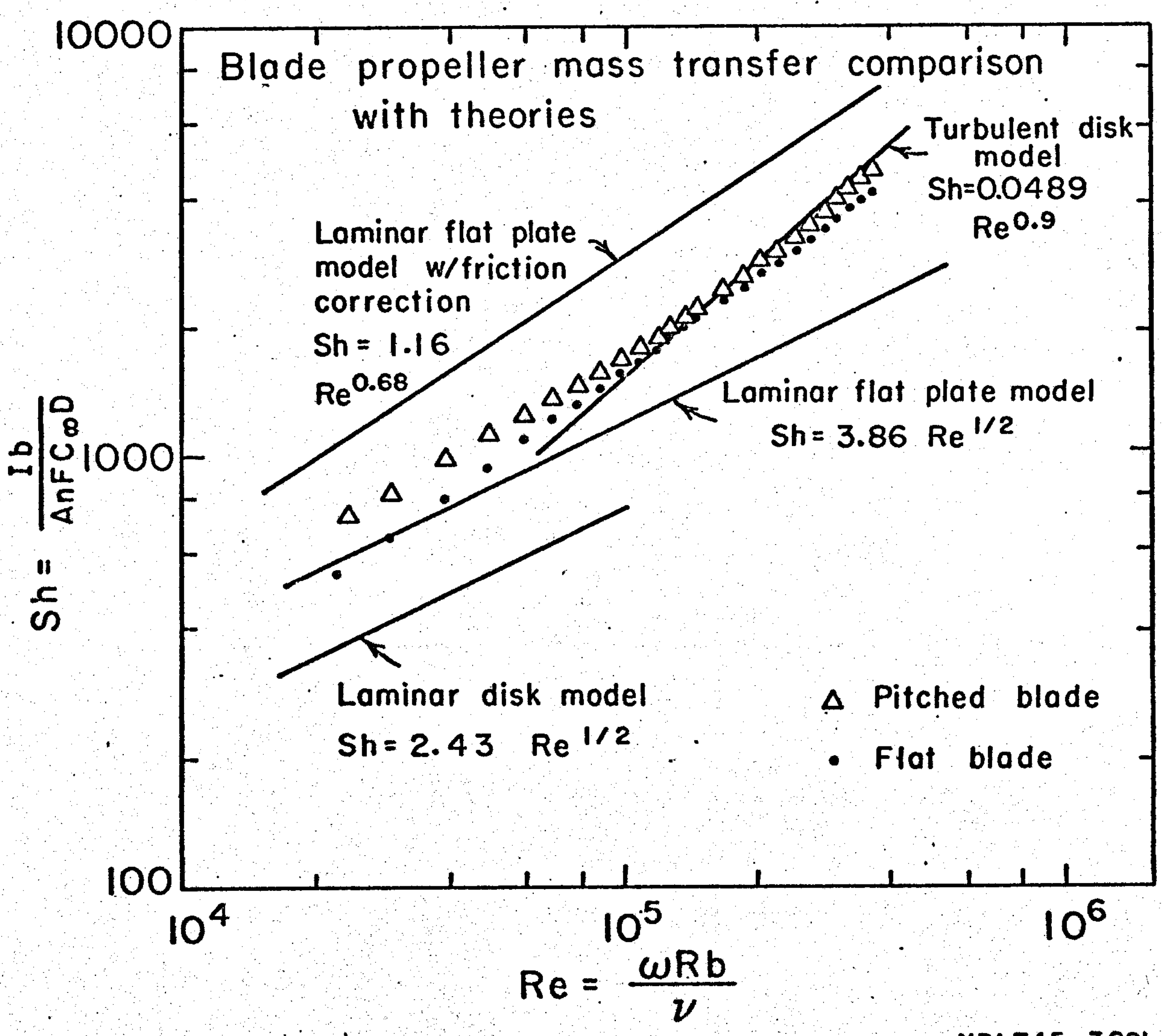

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FIGURE 9 BLADE PROPELLER MASS TRANSFER COMPARISON WITH THEORIES