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CORROSION OF ALLOYS IN AQUEOUS HYDROFLUORIC - NITRIC ACID SOLUTIONS

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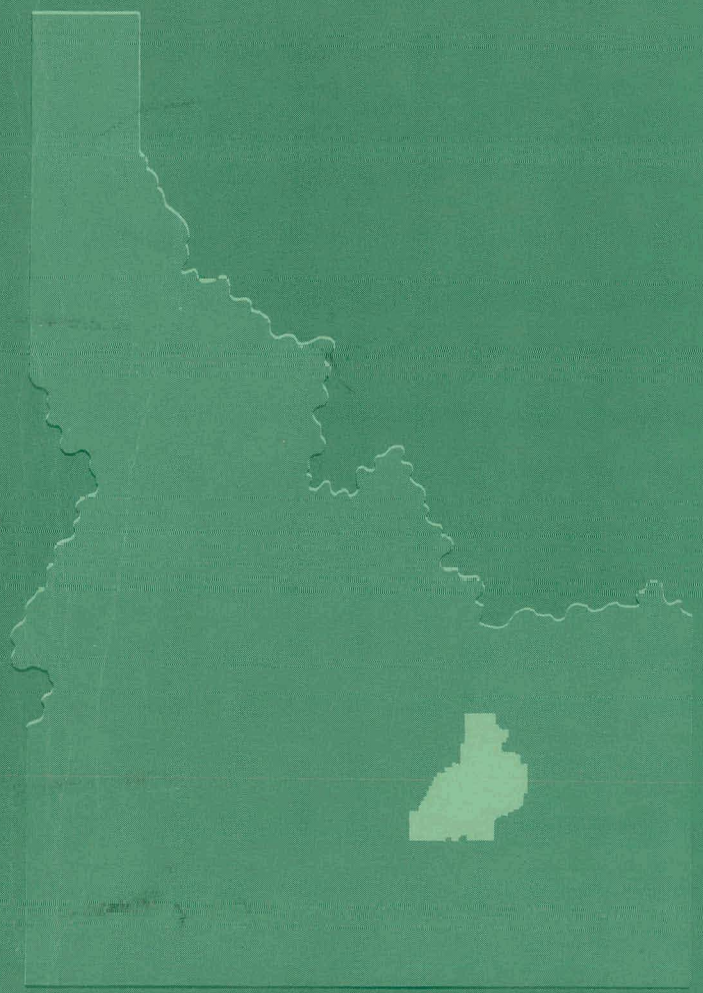

PHILLIPS PETROLEUM COMPANY

ATOMIC ENERGY DIVISION

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IDAHO CHEMICAL PROCESSING PLANT

Chemical Development Branch

CORROSION OF ALLOYS IN AQUEOUS HYDROFLUORIC-NITRIC ACID SOLUTIONS

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SUMMARY

The following materials for construction of dissolvers, columns, evaporators, and piping were evaluated in boiling mixtures of hydrofluoric-nitric acids for three 48-hour periods: Carpenter-20 (columbium stabilized), Hastelloy F, Incoloy 804, Monel, tantalum, types 309 (columbium stabilized), and 316 extra low carbon content stainless steel. The data indicated that none of the materials tested was suitable on a long-term basis for process equipment at the acid concentrations studied.

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HYDROFLUORIC-NITRIC ACID SOLUTIONS

TABLE OF CONTENTS

LIST OF TABLES

(CONTINUED)

(LIST OF TABLES CONTINUED)

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INTRODUCTION

The mixture of nitric and hydrofluoric acids furnishes a versatile dissolvent for fuel alloys of uranium and zirconium or for uranium dioxide clad with zirconium. Additionally, mixtures of these acids appear in solvent extraction flowsheet streams in several advanced zirconium processes. Preliminary corrosion data were thus desirable to permit evaluation of these flowsheets.

The compositions of interest ranged from the one STR process dissolvent, about 4M hydrofluoric acid, and 1.5M nitric acid, to the dissolvent for high uranium alloys, 13M nitric acid and 1M hydrofluoric acid.

The metals evaluated were stainless steel 316 extra low carbon content, 309 Cb stabilized, Carpenter-20 Cb stabilized, Hastelloy F, Incoloy 804, Monel, and tantalum. All samples were unwelded.

EXPERIMENTAL PROCEDURES

Specimens consisting of unwelded stainless steels 316 extra low carbon content, 309 Cb stabilized, Carpenter-20 Cb stabilized, Hastelloy F, Incoloy 804, Monel, and tantalum were evaluated in HF-HNO_3 mixtures at boiling temperatures.

All specimens except tantalum were milled to a number 60 finish on all sides. The tantalum specimens came from the manufacturer with a number 40 finish which was more than adequate for the tests.

Specimens used for tests were milled to a definite size as follows:

316 extra low carbon content - 1-1/2" x 1" x 1/8",
309 Cb stabilized - 1-1/2" x 1" x 1/16",
Carpenter-20 Cb stabilized - 1-1/2" x 1" x 1/8",
Hastelloy F - 1-1/2" x 1" x 1/8",
Incoloy 804 - 1-1/2" x 1" x 1/8",
Monel - 1-1/4" x 1" x 1/8", and
tantalum - 1" x 3/4" x 1/16".

Teflon beakers placed in an oil bath served as containers for the specimens, in groups of three, during the test. Samples were held

at interface level by teflon jigs for both vapor and aqueous study of corrosive effects of acids. Cooling water circulated in round bottom flasks covered with polyethylene film and placed on top of the beakers to serve as condensers, so the system operated under reflux conditions. The solutions in the teflon beakers were kept at the boiling point during each of the three 48-hour periods. After each test period, specimens were bristle brushed, water rinsed, acetone rinsed, and weighed. After weighing, the specimens were placed in a new solution of the same chemical composition as the previous one; one hundred milliliters of solution per square inch of sample were used. Corrosion evaluation was based upon visual observation and corrosion rates, based upon weight losses, calculated as inches per month.

CONCLUSIONS

Specimens of 309, columbium stabilized, 316 extra low carbon content stainless steels, Carpenter-20 columbium stabilized, Hastelloy F, Incoloy 804, Monel, and tantalum were evaluated for three 48-hour test periods in mixtures of $HF-HNO_3$ acids.

Corrosion rates calculated from weight losses of specimens in various concentrations of aqueous $HF-HNO_3$ mixtures ranged from 0.1403 inches per month to 0.9364 inches per month. Corrosion rates of 0.002 inches per month without grain boundary attack are allowable in process equipment at the Idaho Chemical Processing Plant. The exposed specimens suffered severe grain boundary attack, pitting, laminations, and dissolution throughout the test series. The high corrosion rates did not justify the extension of the study to welded samples or to longer exposures.

The results obtained indicate that none of the metals evaluated would be satisfactory for process equipment using an $HF-HNO_3$ dissolver system.

Table 1

CORROSION RATES - INCHES PER MONTH - OF ALLOYS IN BOILING $HF-HNO_3$

Three 48-Hour Exposures

Solution	Metal	309 Cb Stabilized	Carpenter-20 Cb Stabilized	Hastelloy F	Incoloy 804	316 Extra Low Carbon Content	Monel
10.0M	HF	0.5160	0.0698	0.1942	0.0541	0.7956	0.0208
8.0M 1.0M	HF HNO_3	0.1528	0.1785	0.1309	0.1874	0.4524	No Sample
6.0M 0.0M	HF HNO_3	No Sample	0.1706	No Sample	0.1573	No Sample	0.1721
6.0M 0.25M	HF HNO_3	No Sample	0.1056	No Sample	0.0854	No Sample	0.0553
6.0M 6.0M 0.5M	HF HNO_3 Al^{+++}	0.1192	0.1904	0.1919	0.2479	0.2404	No Sample
3.0M 6.0M 1.0M	HF HNO_3 Al^{+++}	0.0230	0.0350	0.0297	0.0599	0.0450	No Sample
2.0M 6.0M	HF HNO_3	0.1290	0.2477	0.1359	0.0760	No Sample	No Sample
1.0M 13.0M	HF HNO_3	0.0364	0.1611	0.1263	0.2639	0.1529	No Sample
1.0M 6.0M	HF HNO_3	No Sample	0.1503	No Sample	No Sample	No Sample	No Sample

Table 2

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
10.0M HF FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.0698	General corrosion, mild pitting, and severe edge lamination.
Hastelloy F	0.1942	Severe granular attack.
Incoloy 804	0.0541	Small amount of pitting, granular attack, and edge lamination.
309 Cb Stabilized	0.1560	Complete dissolution during first exposure period.
316 Extra Low Carbon Content	0.7956	Complete dissolution during first exposure period.
Monel	0.0208	General corrosion.

Table 3

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
8.0M HF - 1.0M HNO_3 FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.1785	Severe pitting and edge lamination.
Hastelloy F	0.1309	Severe pitting and etching.
Incoloy 804	0.1874	General corrosion and slight granular attack.
309 Cb Stabilized	0.5128	Complete dissolution during first exposure period.
316 Extra Low Carbon Content	0.4524	Complete dissolution during second exposure period.
Carpenter-20 Welded, Cb Stabilized	0.4893	Welded specimens put into test for last period. Specimens suffered severe knifeline attack at edge of weld.

Table 4

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
6.0M HF - 1.0M HNO_3 FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.1706	Intermediate pitting and severe edge lamination.
Incoloy 804	0.1573	Received intermediate granular attack and pitting.
Monel	0.1721	Complete dissolution during third test period.

Table 5

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
6.0M HF - 0.25M HNO_3 FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.1056	Mild pitting and lamination at edges.
Incoloy 804	0.0854	Intermediate amount of granular attack.
Monel	0.0553	Small amount of pitting present.

Table 6

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
6.0M HF - 6.0M HNO_3 - 0.5M Al^{+++} FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.1904	Severe pitting and edge lamination.
Hastelloy F	0.1919	Complete dissolution during third test period.
Incoloy 804	0.2479	Complete dissolution during third test period.
309 Cb Stabilized	0.1192	General corrosion and severe edge pitting.
316 Extra Low Carbon Content	0.2404	Complete dissolution during third test period.

Table 7

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
3.0M HF - 6.0M HNO_3 - 1.0M Al^{+++} FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.0350	Minor pitting with edge lamination.
Hastelloy F	0.0297	Intermediate granular attack.
Incoloy 804	0.0599	Severe granular attack.
309 Cb Stabilized	0.0230	Small amount of general attack and pitting on ends and sides.
316 Extra Low Carbon Content	0.0450	Severe pitting.
Carpenter-20 Cb Stabilized, Welded	0.450	Severe knifeline attack along weld edges. Intermediate pitting in weld heat affected area.

Table 8

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
2.0M HF - 6.0M HNO_3 FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.2477	General corrosion and severe edge pitting.
Hastelloy F	0.1395	Severe granular attack.
Incoloy 804	0.0760	Intermediate granular attack and severe edge attack.
309 Cb Stabilized	0.1290	Severe pitting and granular attack.
Tantalum	0.4362	Complete dissolution during first test period.

Table 9

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
1.0M HF - 13.0M HNO_3 FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.1611	Small amount of pitting with severe pitting and lamination of edges.
Hastelloy F	0.1263	Severe granular attack with edge lamination.
Incoloy 804	0.2639	Dissolved beyond identification during third test period.
309 Cb Stabilized	0.9364	Intermediate pitting with severe edge attack.
316 Extra Low Carbon Content	0.1529	Intermediate pitting with severe edge attack.

Table 10

AVERAGE CUMULATIVE CORROSION RATES IN BOILING
1.0M HF - 6.0M HNO_3 FOR THREE 48-HOUR EXPOSURE PERIODS

Alloy	IPM	Appearance After Exposure Periods
Carpenter-20 Cb Stabilized	0.1503	General attack with severe edge pitting and lamination.

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