DECLASSIFIED

ORNL 804
Series B
Declassified

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360810 2

9B

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

# THE CORROSION RESISTANCE OF VARIOUS STAINLESS STEELS IN AQUEOUS SOLUTIONS IN THE PRESENCE OF DOWEX #50 RESIN

ARNOLD S. OLSEN

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS DIVISION
UNION CARBIDE AND CARBON CORPORATION
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

DECLASSIFIED

DECLASSIFIED

ORNL 804
This document consists
of 17 pages.
Copy 9 of 144.

Series B

Contract No. W-7405, eng 26

REACTOR TECHNOLOGY DIVISION

# THE CORROSION RESISTANCE OF VARIOUS STAINLESS STEELS IN AQUEOUS SOLUTIONS IN THE PRESENCE OF DOWEX #50 RESIN

Arnold R. Olsen

Date Issued: NOV 20 1950

OAK RIDGE NATIONAL LABORATORY
operated by
CARBIDE AND CARBON CHEMICALS DIVISION
Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

DECLASSIFIED

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360810 2

Internal Distribution

| | | | | | |
|---|---|---|---|---|---|
| 1 | G. T. Felbeck (C&CCD) | 23 | C. E. Winters | 40 | C. B. Graham |
| 2-3 | 706-A Library | 24 | C. B. Ellis | 41 | W. R. Gall |
| 4 | 706-B Library | 25 | M. M. Mann | 42 | S. E. Beall |
| 5 | Biology Library | 26 | E. H. Taylor | 43 | W. E. Jordan |
| 6 | Health Physics Library | 27 | A. Hollaender | 44 | W. M. Breazealle |
| 7 | Metallurgy Library | 28 | A. H. Snell | 45 | E. D. Shipley |
| 8-9 | Training School Library | 29 | K. Z. Morgan | 46 | E. C. Miller |
| 10-13 | Central Files | 30 | F. L. Steahly | 47 | E. P. Blizard |
| 14 | C. E. Center | 31 | D. W. Cardwell | 48 | W. K. Ergen |
| 15 | C. E. Larson | 32 | M. T. Kelley | 49 | C. E. Clifford |
| 16 | W. B. Hines (K-25) | 33 | W. H. Pennington | 50 | D. S. Billington |
| 17 | W. D. Lavers (Y-12) | 34 | J. A. Lane | 51 | M. J. Skinner |
| 18 | A. M. Weinberg | 35 | A. S. Kitzes | 52 | J. L. English |
| 19 | J. A. Swartout | 36 | H. F. Poppendiek | 53 | I. R. Higgins |
| 20 | E. J. Murphy | 37 | O. Sisman | 54 | A. R. Olsen |
| 21 | F. C. VonderLage | 38 | A. S. Householder | 55 | Central Files (O.P.) |
| 22 | R. N. Lyon | 39 | R. W. Stoughton | 56 | Central Files (O.P.) |

External Distribution

| | |
|---|---|
| 57-64 | Argonne National Laboratory |
| 65 | Armed Forces Special Weapons Project |
| 66-67 | Atomic Energy Commission, Washington |
| 68 | Battelle Memorial Institute |
| 69 | Brush Beryllium Company |
| 70-77 | Brookhaven National Laboratory |
| 78 | Bureau of Ships |
| 79-82 | Carbide & Carbon Chemicals Division (K-25) |
| 83-86 | Carbide & Carbon Chemicals Division (Y-12) |
| 87 | Chicago Operations Office |
| 88 | Columbia University (J. R. Dunning) |
| 89-91 | General Electric, Richland |
| 92 | Idaho Operations Office |
| 93-94 | Iowa State College |
| 95-98 | Knolls Atomic Power Laboratory |
| 99-101 | Los Alamos Scientific Laboratory |
| 102 | Massachusetts Institute of Technology (A. Kaufmann) |
| 103-105 | Mound Laboratory |
| 106-107 | National Advisory Committee for Aeronautics |
| 108-109 | National Bureau of Standards |
| 110-114 | New York Operations Office |
| 115 | North American Aviation, Inc. |
| 116 | Patent Branch (Washington) |
| 117 | Sandia Laboratory |
| 118 | Santa Fe Operations Office |
| 119-133 | Technical Information Division (Oak Ridge) |
| 134-135 | USAF, NEPA |
| 136-140 | University of California Radiation Laboratory |
| 141-144 | Westinghouse Electric Company |

## TABLE OF CONTENTS


| | | Page No. |
|---|---|---|
| 1.0 | INTRODUCTION | 4 |
| 2.0 | ABSTRACT | 4 |
| 3.0 | CORROSION TESTING METHODS AND CONDITIONS | 5 |
| 4.0 | TEST MATERIALS | 5 |
| | 4.1 Types of Materials | 5 |
| | 4.2 History of Test Materials | 6 |
| | 4.3 Preparation and Defilming of Test Specimens | 7 |
| 5.0 | RESULTS OF THIRTY DAY CORROSION TESTS | 7 |
| | 5.1 Dowex #50 Resin and Distilled Water | 7 |
| | 5.2 Dowex #50 Resin and 6 Molar Nitric Acid | 8 |
| | 5.3 Dowex #50 Resin and 5% Oxalic Acid | 8 |
| 6.0 | LONGER TERM TESTS OF VARIOUS STAINLESS STEELS IN AQUEOUS SOLUTION-DOWEX #50 RESIN SLURRIES | 9 |
| | 6.1 Dowex #50 Resin and Distilled Water | 10 |
| | 6.2 Dowex #50 Resin and Six Molar Nitric Acid | 12 |
| | 6.3 Dowex #50 Resin and 5% Oxalic Acid | 14 |
| 7.0 | DISCUSSION OF RESULTS | 14 |
| 8.0 | ACKNOWLEDGEMENTS | 16 |

## 1.0 INTRODUCTION

Since many reactions involving ion exchange resins take place in corrosive media, corrosion of the resin containers becomes a problem. In view of the lack of relevant information, the corrosion group selected Dowex No. 50 resin in three classes of corrosive media with which to conduct a survey of the more common stainless steels. Distilled water, 6 molar nitric acid, and 5% exalic acid were the solutions chosen.

## 2.0 ABSTRACT

Tests were made to determine the comparative corrosion resistance of stainless steel Types 304, 309, 316, 347, 410 and 430, when exposed to Dowex #50 resin saturated with distilled water, 6M $HNO_3$ and 5% oxalic acid for two and four months periods.

The results indicate that Type 304 and Type 347 be used for unwelded and welded containers respectively. The penetration rates for these steels are less than 0.12 mils per year.

## 3.0 CORROSION TESTING METHODS AND CONDITIONS

Materials were tested by suspending the samples on pyrex glass hooks in covered one liter beakers filled with a slurry of Dowex #50 resin saturated with the aqueous media desired. These solutions were: distilled water, 6 molar nitric acid, and 5% oxalic acid. All tests were conducted at room temperature, approximately 85°F. Two tests periods were employed; 30 days and 120 days.

Solution control consisted in maintaining the proper concentrations of the acids by weekly check and additions. It was found that the solution tended to concentrate as a result of normal evaporation losses despite the fact that the beakers were covered.

All samples were totally immersed in the slurry. Corrosion rates on the original group of samples were so low that it was considered inexpedient to run control samples, i.e., without the presence of Dowex #50 resin.

## 4.0 TEST MATERIALS

### 4.1 Types of Materials

Six different grades of stainless steel were tested; four austenitic types and two of the hardenable ferritic types. These steels together with their nominal chemical compositions are listed in Table I.

**TABLE I**[1]

| AISI Type | 304 | 316 | 347 | 309 | 410 | 430 |
|---|---|---|---|---|---|---|
| Classification | Aus. | Aus. | Aus. | Aus. | Ferr. | Ferr. |
| Composition in percent | | | | | | |
| Carbon | .08 Max. | .10 Max. | .10 Max. | .15 Max. | .15 Max. | .12 Max. |
| Manganese | 1.25 " | 2.0 " | 1.50 " | 2.0 " | .25-.50 | .25-.60 |
| Phosphorous | .03 " | .03 " | .03 " | .03 " | .03 max | .03 max |
| Sulphur | .03 " | .03 " | .03 " | .03 " | .03 " | .03 " |
| Silicon | .70 " | .70 " | .75 " | 1.25 " | .70 " | .70 " |
| Chromium | 18.0-20.0 | 16.0-18.0 | 17.0-19.0 | 22.0-25.0 | 11.0-14.0 | 16.0-18.0 |
| Nickel | 8.0-10.0 | 10.0-14.0 | 9.0-12.0 | 12.0-15.0 | .50 max. | .50 max. |
| Molybdenum | | 2.0-3.0 | | | | |
| Columbium | | | 8 x C min | | | |
| Density g/cm$^3$ | 7.92 | 8.00 | 7.98 | 7.88 | 7.75 | 7.70 |

## 4.2 History of Test Materials

All of the austenitic stainless steel samples were welded using standard arc techniques and coated filler rods prior to being machined to size. The ferritic steels were machined directly from full annealed stock. In general the sample size was 1" x 2" x 1/4" with a 1/4" hole drilled near one end for suspension purposes.

## 4.0 TEST MATERIALS (CONT'D)

### 4.3 Preparation and Defilming of Test Specimens

All as machined samples were polished on a belt sander using No. 80 followed by No. 120 grit paper before the dimensions were measured. The samples were then precleaned in an etching solution containing 2% HF and 10% $HNO_3$ by weight at 65°C for 10 minutes. They were scrubbed under cold running water; degreased in acetone; rinsed in alcohol and dried at 120°C for 20 minutes before being cooled in a dessicator and weighed. This preparation removes all grease and protective oxide coatings exposing clean surfaces to the corroding medium.

At the completion of the test period, the samples were removed, washed in running water, rinsed in acetone and alcohol, dried and weighed as before. Normally this is followed by post-test defilming treatment to remove any accumulated scale. In this series of tests, however, this treatment was unnecessary as the weight changes were within the accuracy of the balance (0.1 mg).

## 5.0 RESULTS OF THIRTY DAY CORROSION TESTS

### 5.1 Dowex #50 Resin and Distilled Water

The corrosion rates of stainless steels Type 309 and Type 347, after exposure to the resin and water slurry for 30 days, are tabulated in Table II.

TABLE II

| Material | Time (hours) | Weight Loss (MDM)* | Penetration Rate (mils/month) |
|---|---|---|---|
| 347 | 720 | 977.7** | |
| | 744 | 2.5 | $1.2 \times 10^{-3}$ |
| | 720 | 0.3 | .15 " |
| | 744 | 0.9 | .45 " |
| 309 | 720 | 6.2 | $3.2 \times 10^{-3}$ |
| | 744 | 7.6 | 3.7 |
| | 720 | 6.1 | 3.1 |
| | 744 | 7.4 | 3.6 |

* MDM - Throughout this report represents milligrams per square decimeter per month.

** This sample showed a flaw along the weld line and the large weight loss was probably due to the dissolving of entrapped welding flux.

## 5.0 RESULTS OF THIRTY DAY CORROSION TESTS (CONT'D)

### 5.2 Dowex #50 Resin and 6 Molar Nitric Acid

Table III contains the results of 30 day corrosion tests on Type 309 and Type 347 stainless steel in resin saturated with 6M $HNO_3$.

The results of these tests indicate that the resistance of Type 309 stainless steel is markedly affected by the presence of the resin. A proposed explanation of this phenomenon is that the resin reacts with the protective oxide film removing it from the surface and exposing clean metal to the $HNO_3$ medium.

TABLE III

| Material | Time (hours) | Weight Loss (MDM) | Penetration Rate (mils/month) |
|---|---|---|---|
| 347 | 720 | neg. | neg. |
| | 744 | 0.7 | $0.30 \times 10^{-3}$ |
| | 720 | 3.3 | 1.6 " |
| | 744 | 0.3 | 0.15 " |
| 309 | 720 | 518.6 | $258.7 \times 10^{-3}$ |
| | 744 | 857.6 | 413.5 |
| | 720 | 525.7 | 262.3 |
| | 744 | 927.1 | 447.3 |

### 5.3 Dowex #50 Resin and 5% Oxalic Acid

The differences in corrosion resistance of Types 309 and 347 stainless steel in Dowex #50 resin and 5% oxalic acid slurry is in line with their resistance to 5% oxalic acid solution alone[2]. These data are reported in Table IV.

## 5.0 RESULTS OF THIRTY DAY CORROSION TESTS (CONT'D)

### 5.3 Dowex #50 Resin and 5% Oxalic Acid (Cont'd)

**TABLE IV**

| Material | Time (hours) | Weight Loss (MDM) | Penetration Rate (mils/month) |
|---|---|---|---|
| 347 | 720 | 0.3 | $0.15 \times 10^{-3}$ |
| | 744 | 0.3 | 0.15 |
| | 720 | 2.5 | 1.1 |
| | 744 | 0.9 | 0.45 |
| 309 | 720 | 23.5 | $11.7 \times 10^{-3}$ |
| | 744 | 23.8 | 11.4 |
| | 720 | 22.4 | 11.2 |
| | 744 | 18.2 | 8.8 |

## 6.0 LONGER TERM TESTS OF VARIOUS STAINLESS STEELS IN AQUEOUS SOLUTION-DOWEX #50 RESIN SLURRIES

On completion of the 30 day tests, although the weight loss on Type 347 stainless steel was negligible from the viewpoint of metal loss, the ionic pickup for the process under consideration was too high, consequently it was decided to test other types of stainless steel and at the same time increase the exposure time. Five grades of stainless were then exposed to the same solution-resin combinations for four months (2,878.5 hours). Type 309 was eliminated from this series because of its poorer resistance in the 30 day tests.

The results of this second series are tabulated in Tables V, VI, and VII. For ready comparison the various weight losses have been graphed in Figures I, II and III. Duplicate samples were tested in all cases and both figures are reported and graphed.

## 6.0 LONGER TERM TESTS OF VARIOUS STAINLESS STEELS IN AQUEOUS SOLUTION-DOWEX #50 RESIN SLURRIES (CONT'D)

### 6.1 Dowex #50 Resin and Distilled Water

TABLE V

CORROSION RATES ON VARIOUS STAINLESS STEELS EXPOSED TO DOWEX #50 RESIN SATURATED WITH DISTILLED WATER FOR FOUR MONTHS AT ROOM TEMPERATURE

| Material Type | Weight Loss MDM | Sample Description |
|---|---|---|
| 304 | Negligible | Bright, clean, smooth surfaces |
| | Negligible | Bright, clean, smooth surfaces |
| 316 | 0.3 | Shiny, adherent thin oxide film |
| | 0.3 | Shiny, adherent thin oxide film |
| 347 | 0.4 | Bright, clean, smooth surfaces |
| | 0.2 | Bright, clean, smooth surfaces |
| 410 | 14,902 | Badly etched, approximately 1/2 sample corroded away |
| | 15,229 | Badly etched, approximately 1/2 sample corroded away |
| 430 | 1.5 | Very thin, adherent oxide film |
| | 0.9 | Very thin, adherent oxide film |

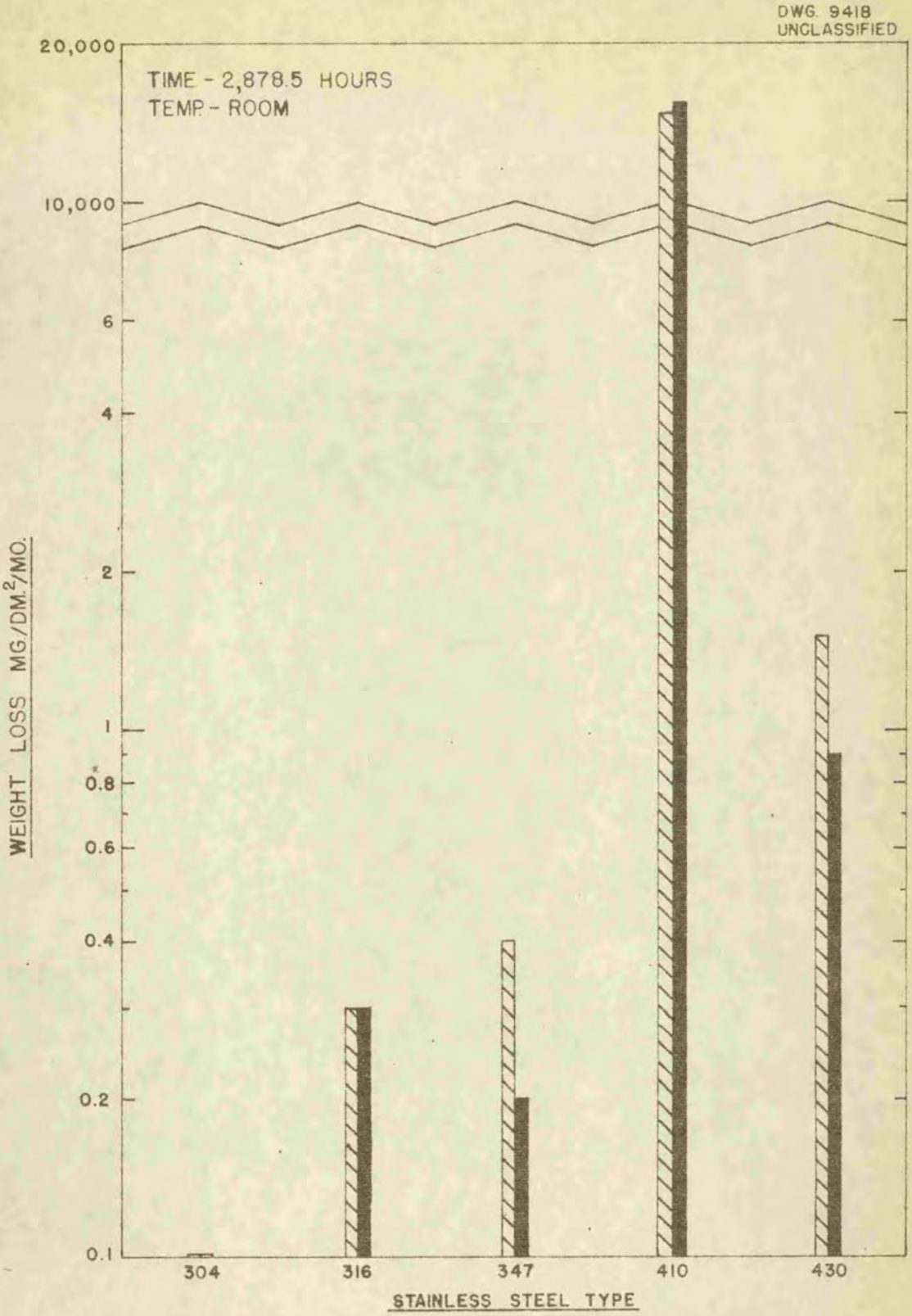


FIG. 1 CORROSION RATES ON VARIOUS STAINLESS STEELS EXPOSED TO DOWEX NO. 50 RESIN SATURATED WITH DISTILLED WATER

## 6.0 LONGER TERM TESTS OF VARIOUS STAINLESS STEELS IN AQUEOUS SOLUTION-DOWEX #50 RESIN SLURRIES (CONT'D)

### 6.2 Dowex #50 Resin and Six Molar Nitric Acid

TABLE VI

CORROSION RATES ON VARIOUS STAINLESS STEELS EXPOSED TO DOWEX #50 RESIN SATURATED WITH 6M $HNO_3$ FOR FOUR MONTHS AT ROOM TEMPERATURE

| Material Type | Weight Loss (MDM) | Sample Description |
|---|---|---|
| 304 | 0.4 | Bright, clean, smooth surfaces |
| | Neg. | Bright, clean, smooth surfaces |
| 316 | 0.3 | Thin, dull, adherent oxide film |
| | 0.5 | Bright, clean, smooth surfaces |
| 347 | 0.6 | Thin, dull, adherent oxide film |
| | 0.6 | Thin, dull, adherent oxide film |
| 410 | 19.0 | Dull, dark film on all surfaces - minor pitting |
| | 18.0 | Dull, dark film on all surfaces - minor pitting |
| 430 | 1.9 | Spots of gray brown stain, minor etching |
| | 2.1 | Spots of gray brown stain, minor etching |

DWG. 9419
UNCLASSIFIED

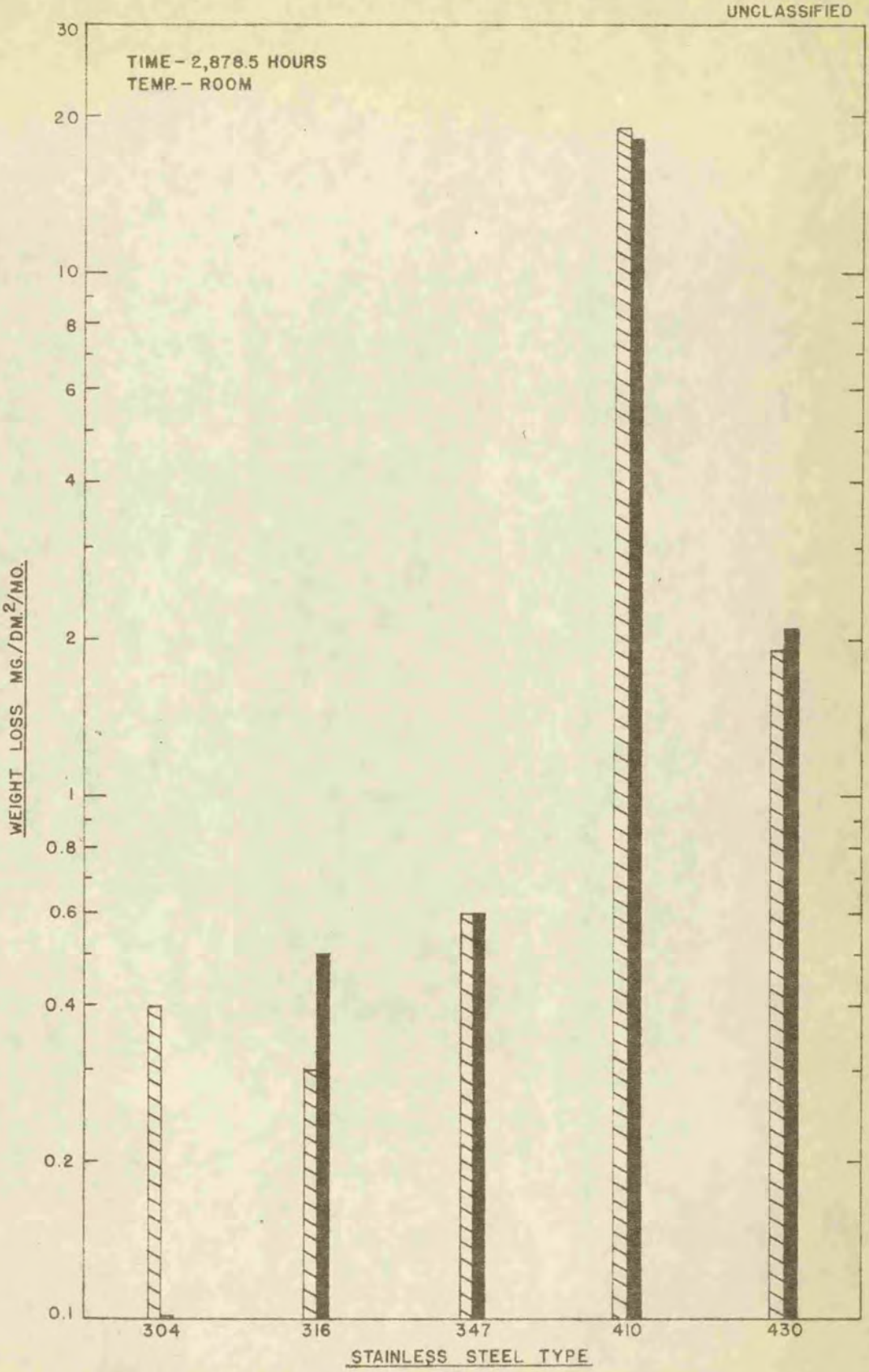


FIG. 2 CORROSION RATES ON VARIOUS STAINLESS STEELS EXPOSED TO DOWEX NO. 50 RESIN SATURATED WITH 6M $HNO_3$

## 6.0 LONGER TERM TESTS OF VARIOUS STAINLESS STEELS IN AQUEOUS SOLUTION-DOWEX #50 RESIN SLURRIES (CONT'D)

### 6.3 Dowex #50 Resin and Five Percent Oxalic Acid

TABLE VII

CORROSION RATES ON VARIOUS STAINLESS STEELS EXPOSED TO DOWEX #50 RESIN SATURATED WITH 5% OXALIC ACID FOR FOUR MONTHS AT ROOM TEMPERATURE

| Material Type | Weight Loss (MDM) | Sample Description |
|---|---|---|
| 304 | 0.3 | Bright, clean, smooth surface |
| | 0.2 | Bright, clean, smooth surface |
| 316 | 0.9 | Thin film, minor etching of weld arm |
| | 0.3 | Thin film, minor etching of weld arm |
| 347 | 0.6 | Bright, clean, smooth surface |
| | 0.6 | Bright, clean, smooth surface |
| 410 | 23,045 | Approximately 85% of the metal dissolved |
| | 24,395 | Approximately 85% of the metal dissolved |
| 430 | 1.2 | Bright, clean, smooth surface |
| | 1.5 | Bright, clean, smooth surface |

## 7.0 DISCUSSION OF RESULTS

From this series of tests, it is evident that stainless steel Type 304 shows the best resistance to corrosion for all three types of media in the presence of Dowex #50 resin. Type 347 closely follows Type 304 and is on a par with the more expensive Type 316. The Ferritic type stainless steels, even in the nonwelded, fully annealed condition, are not satisfactory.

It would seem from these data that where no welding was to be done, Type 304 stainless steel would be the choice while where welding is to be done either Type 304 ELC or Type 347 would be the choice. This would hold costs to a minimum and reduce the probability of intergranular or stress corrosion susceptibility.

DWG. 9420
UNCLASSIFIED

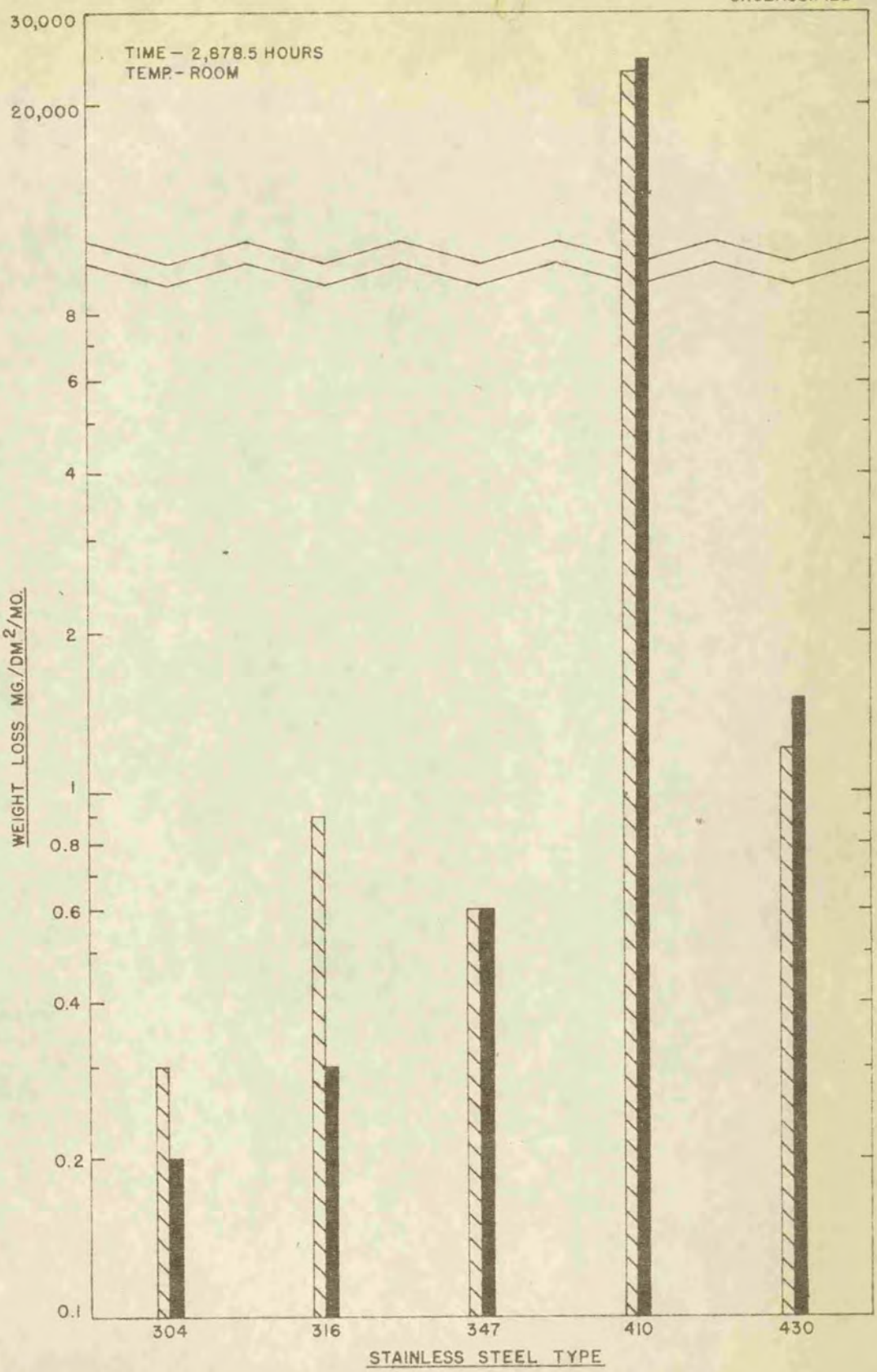


FIG. 3 CORROSION RATES ON VARIOUS STAINLESS STEELS EXPOSED TO DOWEX NO. 50 RESIN SATURATED WITH 5% OXALIC ACID

## 8.0 ACKNOWLEDGEMENTS

The writer wishes to express his thanks to S. H. Wheeler and H. Barker for their assistance in the handling of corrosion samples, and control and maintenance of testing media.

AR Olsen

## REFERENCES

(1) "Eastern Stainless Steel Sheets", 1945, pp 83 and 85

(2) "Chemical and Metallurgical Engineering", September 1944, p 122