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THE CORROSION OF VARIOUS STAINLESS STEELS IN
SYNTHETIC WASTE SOLUTIONS

James L. English

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1.0 ABSTRACT

Types 309, 316, and 347 stainless steel were tested for a total of 779 to 828 hours in three different synthetic waste solutions. The sodium chloride content of these solutions ranged from 0.007 to 0.028M. The test specimens were checked under conditions of total immersion, liquid-vapor exposure, and exposure to the vapor phase. Tests were run at boiling temperatures.

The best all-around corrosion resistance to the test conditions was exhibited by 316 stainless steel although in one solution 347 stainless steel was slightly more resistant. Maximum corrosion rates obtained in the most corrosive of the three solutions were:

Type 309	1.4 mils/year
Type 316	0.3 mil/year
Type 347	95.5 mils/year

2.0 INTRODUCTION

At the request of Mr. T. A. Crehart of the Chemical Technology Division, a study was undertaken to investigate the corrosion resistance of various stainless steels in synthetic waste solutions at boiling temperatures.

Along with the development of the tributyl phosphate process for recovery of uranium from Hanford metal waste solutions, the feasibility of recovering the free nitric acid content from the tributyl phosphate waste was also studied. This latter process involves a continuous evaporation of the waste to near the "freezing point" and concentrating the dilute acid vapors in a fractionating column.

The process was proved sound economically because of the acid and storage volume savings, but a question of doubt was raised as to whether stainless steels could be utilized to handle the corrosive liquids. Some reports have indicated that the stainless steels were corroded excessively by the presence of chlorides in the waste solutions. However, an inspection of equipment used for a short time in the nitric acid recovery process from wastes containing chlorides did not verify this report.

Therefore, in order to more clearly clarify the situation, an investigation was made to determine the corrosion resistance of various stainless steels in synthetic waste solutions containing different chloride concentrations.

3.0 TEST MATERIALS

Three types of stainless steels, 309, 316, and 347, were investigated to determine their respective corrosion resistance to synthetic waste solutions under various conditions of exposure. Samples approximately 3.15 cm in diameter and 0.45 cm in thickness were machined from cold rolled bar stock. The average total surface area of the specimens exposed to the test media was 11.4 cm². Prior to test, all samples were polished, degreased, dried, and weighed.

The nominal chemical compositions of the three stainless steels used appear below. Values are in percent.

<u>Element</u>	<u>Type 309</u>	<u>Type 316</u>	<u>Type 347</u>
Carbon	0.20 max.	0.10 max.	0.10 max.
Manganese	2.00 max.	2.00 max.	2.00 max.
Silicon	0.75 max.	0.75 max.	0.75 max.
Chromium	22.0-24.0	16.0-18.0	17.0-19.0
Nickel	12.0-15.0	10.0-14.0	9.0-12.0
Molybdenum	--	2.0-3.0	--
Niobium	--	--	8 x C

Three synthetic waste solutions were prepared with increasing sodium chloride concentration. The solutions were made by dissolving C.P. reagents in distilled water. The chemical compositions of the media were:

<u>Material</u>	<u>Solution 1</u>	<u>Solution 2</u>	<u>Solution 3</u>
Na ₂ SO ₄	0.18M	0.36M	0.18M
Na ₃ PO ₄	0.18M	0.36M	0.18M
NaNO ₃	2.00M	4.00M	2.00M
HNO ₃	3.90M	3.90M	3.90M
NaCl	0.007M	0.014M	0.028M

4.0 TEST CONDITIONS

A volume of 4000 ml of solution was used for each set of test specimens and was contained in a five liter cylindrical Pyrex flask. Solutions were maintained at boiling temperatures during the course of the test under a condition of total reflux. Specimens were suspended, by means of glass hooks, at three different points in the corrosion environment: total immersion, liquid-vapor interface, and the vapor phase. The position in the vapor phase was selected so that the specimen would also be contacted by the reflux liquid. Boiling temperature for Solution 1 and 3 was 105°C; the boiling temperature for Solution 2 was 108°C. Specimens were removed at periodic intervals for weight change measurements in order to establish weight change vs. time relationships. The total time of the tests ranged from 779 to 828 hours.

5.0 CORROSION DATA

The corrosion data obtained from this series of tests appear in the following tables. Results are cumulative.

5.0 CORROSION DATA (CONT'D)

TABLE I
THE CORROSION OF 309 STAINLESS STEEL IN
SYNTHETIC WASTE SOLUTIONS AT
105-108°C

Solution	Exposure hr.	Total Immersion		Liquid-Vapor		Vapor	
		mdd*	mpy**	mdd	mpy	mdd	mpy
1	45	-7.2	1.3	-6.6	1.2	+0.3	-
1	115	-3.1	0.6	-3.1	0.6	-0.3	0.06
1	282	-1.5	0.3	-1.4	0.3	-0.1	0.02
1	445	-1.1	0.2	-1.1	0.2	-0.3	0.06
1	611	-1.0	0.2	-1.1	0.2	-0.5	0.08
1	779	-0.9	0.16	-0.7	0.1	-0.1	0.02
2	45	-25.6	4.6	-15.7	2.8	+0.8	-
2	115	-9.8	1.8	-5.9	1.1	-0.1	0.02
2	282	-4.3	0.8	-2.9	0.5	-0.1	0.02
2	445	-2.9	0.5	-1.9	0.4	-0.1	0.02
2	611	-2.4	0.4	-1.7	0.3	-0.4	0.08
2	779	-1.8	0.3	-1.2	0.2	-0.2	0.03
3	45	-126.3	22.8	-96.9	17.5	0.0	0.0
3	115	-49.3	8.9	-37.5	6.8	+0.1	-
3	282	-20.5	3.7	-15.8	2.9	-0.4	0.07
3	445	-13.2	2.4	-10.2	1.8	-0.3	0.06
3	611	-10.0	1.8	-7.7	1.4	-0.5	0.08
3	779	-7.7	1.4	-5.8	1.0	-0.2	0.03

*mdd - mg/dm²/day

**mpy - mils/year

5.0 CORROSION DATA (CONT'D)

TABLE II

THE CORROSION OF 316 STAINLESS STEEL IN SYNTHETIC
WASTE SOLUTIONS AT 105-108°C

Solution	Exposure hr	Total Immersion		Liquid-Vapor		Vapor	
		mdd	mpy	mdd	mpy	mdd	mpy
1	45	-1.4	0.3	-0.8	0.14	0.0	0.0
1	115	-0.4	0.08	-0.2	0.04	+0.4	-
1	282	-1.3	0.2	-1.0	0.17	-0.5	0.09
1	445	-1.3	0.2	-1.1	0.20	-0.3	0.06
1	611	-1.4	0.3	-1.0	0.19	-0.5	0.08
1	779	-1.2	0.2	-0.8	0.15	-0.3	0.05
2	45	-1.4	0.30	-0.5	0.09	+1.40	-
2	115	-0.1	0.02	+0.4	-	+0.80	-
2	282	-0.8	0.14	-0.4	0.08	-0.04	0.007
2	445	-0.6	0.10	-0.3	0.06	-0.08	0.014
2	611	-0.8	0.14	-0.6	0.11	-0.28	0.051
2	779	-0.6	0.10	-0.4	0.08	-0.13	0.023
3	45	-1.1	0.20	-0.5	0.01	0.0	0.00
3	115	-0.8	0.14	0.0	0.00	+0.2	-
3	282	-1.6	0.28	-1.2	0.21	-0.4	0.08
3	445	-1.5	0.27	-1.0	0.19	-0.4	0.08
3	611	-1.8	0.32	-1.3	0.23	-0.5	0.09
3	779	-1.6	0.21	-0.9	0.17	-0.2	0.04

5.0 CORROSION DATA (CONT'D)

TABLE III

THE CORROSION OF 347 STAINLESS STEEL IN SYNTHETIC
WASTE SOLUTIONS AT 105-108°C

Solution	Exposure hr	Total Immersion		Liquid-Vapor		Vapor	
		mdd	mpy	mdd	mpy	mdd	mpy
1	21	-24.0	4.30	-309.0	55.8	-11.6	2.10
1	91	-1.9	0.30	-71.3	12.1	-3.1	0.60
1	162	-0.9	0.20	-39.4	7.1	-0.9	0.20
1	328	-0.3	0.06	-19.5	3.5	-0.3	0.05
1	494	-0.3	0.06	-13.0	2.4	-0.4	0.07
1	660	-0.4	0.07	-11.0	2.0	-0.5	0.09
1	828	-0.3	0.06	- 7.9	1.4	-0.3	0.06
2	21	-15.3	2.80	-8.8	1.60	-7.7	1.40
2	91	-4.1	0.74	-2.3	0.40	-2.5	0.44
2	162	-1.2	0.22	-0.4	0.07	-0.7	0.12
2	328	-0.7	0.13	+0.03	-	-0.2	0.04
2	494	-0.8	0.15	-0.3	0.05	-0.3	0.05
2	660	-1.0	0.18	-0.5	0.09	-0.5	0.09
2	828	-0.7	0.13	-0.3	0.05	-0.2	0.04
3	21	-20925.2	3779.1	-6714.6	1212.6	-17.0	3.10
3	91	-4828.6	872.1	-1549.8	279.9	-4.5	0.80
3	162	-2642.2	477.2	- 829.7	149.8	-1.8	0.30
3	328	-1334.6	241.0	- 419.7	75.8	-0.8	0.14
3	494	-886.6	160.1	- 282.7	51.1	-0.6	0.11
3	660	-664.0	119.9	- 212.3	38.3	-0.7	0.13
3	828	-528.9	95.5	- 169.3	30.6	-0.4	0.08

6.0 DISCUSSION OF DATA

The Effect of Chloride Concentration. The effect of increasing the chloride concentration from 0.007M to 0.028M in the test solutions was to increase the corrosion attack on all three types of stainless steel by varying degrees of intensity. This phenomenon is clearly shown by an inspection of the data in the preceding tables. A mild increase in the corrosion rate for 309 stainless steel was observed on the specimens exposed under conditions of total immersion, liquid-vapor exposure, and vapor exposures. The most pronounced increase occurred on the total-immersed specimen with 0.028M sodium chloride concentration; the rate increased from 0.16 mil/year to 1.4 mils/year. The least effect of increased chloride concentration was noted on the vapor-exposed specimen; here, the rate increased from 0.02 to 0.03 mil/year. Corrosion attack on the liquid-vapor specimen increased by a factor of 10, from 0.1 to 1.0 mil/year, as the sodium chloride was increased from 0.007M to 0.028M. Type 316 stainless steel showed excellent resistance to the effect of increased chloride concentration. For conditions of total immersion, the rate increased from 0.2 to 0.28 mil/year; for conditions of liquid-vapor exposure, the rate increased from 0.15 to 0.17 mil/year, and for conditions of vapor exposure, corrosion decreased from 0.05 to 0.04 mil/year. By far, the most severe corrosion attack as a result of the increased chloride concentration occurred on the 347 stainless steel specimens. Under conditions of total immersion, the corrosion rate increased from 0.06 mil/year to 95.5 mils/year as the sodium chloride concentration was increased from 0.007M to 0.028M. These rates are based on a total exposure of 828 hours. The liquid-vapor specimens exhibited an increase from 1.4 to 30.6 mils/year under similar conditions. The specimens exposed to the vapors showed a very slight increase, 0.06 to 0.08 mil/year, as the chloride increased.

These data show that corrosion attack is directly influenced by chloride concentration. The most severe effect of increasing chloride concentration occurred under conditions of total exposure; the least severe effect occurred under conditions of exposure to the vapor phase. Type 316 stainless steel exhibited the most superior corrosion resistance to all three types of exposure; total immersion, liquid-vapor, and vapor.

Figures 1, 2, and 3 show graphically the effect of increasing the sodium chloride concentration on the corrosion of the three stainless steels.

A question of doubt was raised as to whether or not there was any escape of the chloride ion from the test solution during its operation. Since the same solutions were used throughout the tests, the escape of chloride during the early stages of the test would lead to erroneous conclusions on the determination of corrosion resistance. It was believed that escape of chloride could not occur under the conditions of total reflux by which the tests were run but an additional test was conducted to check specifically for this effect. Type 316 stainless steel was selected for the test since it had shown the most favorable corrosion resistance; Solution 3 was selected because it contained the

FIG. 1 THE EFFECT OF SODIUM CHLORIDE CONCENTRATION ON THE CORROSION OF TOTALLY IMMERSED STAINLESS STEEL SPECIMENS IN SYNTHETIC WASTE SOLUTIONS AT 105-108°C FOR 779-826 HOURS

FIG. 2 THE EFFECT OF SODIUM CHLORIDE CONCENTRATION ON THE CORROSION OF STAINLESS STEEL SPECIMENS EXPOSED TO LIQUID-VAPOR PHASE OF SYNTHETIC WASTE SOLUTIONS AT 105-108°C FOR 779-828 HOURS

FIG. 3 THE EFFECT OF SODIUM CHLORIDE CONCENTRATION ON THE CORROSION OF STAINLESS STEEL SPECIMENS EXPOSED TO THE VAPOR PHASE OF SYNTHETIC WASTE SOLUTIONS AT 105-108°C FOR 779-828 HOURS

6.0 DISCUSSION OF DATA (CONT'D)

highest sodium chloride concentration, 1.64 gm/liter, and was the most corrosive test solution, and condition of total immersion was selected because it represented the most severe corrosion exposure.

This test was run in exactly the same manner as the tests already described except for one condition; the test solution was removed at the end of 48 hour periods and replaced with completely new solution. This procedure was repeated eight times. Samples were weighed at the end of each 48 hour period and sodium chloride analyses were made on the final test solution for each period of exposure.

Duplicate specimens of 316 stainless steel were used and the figures included in the following table represent average values.

Total hr	Sodium Chloride, gm/l		Cumulative Wt. Loss		Corrosion Rate mil/year
	Initial*	Final	mg	mdd	
48	1.64	1.75	2.9	7.1	1.3
96	1.64	1.72	1.3	1.6	0.3
144	1.64	1.72	3.7	3.0	0.5
192	1.64	1.43	3.3	2.0	0.4
240	1.64	1.72	2.6	1.3	0.2
288	1.64	1.66	3.1	1.3	0.2
336	1.64	1.70	4.1	1.4	0.3
400	1.64	1.71	5.0	1.5	0.3

*This is not a result of a chemical analysis, but represents weighed amounts of sodium chloride which were added in the preparation of the test solution.

These data show conclusively that the test method was satisfactory and that there was no escape of chloride from the system. The slight discrepancy between initial and final chloride concentrations may be attributed to a combination of small error in initial weighing of the sodium chloride and the plus or minus variations in the accuracy of the analytical determinations. The important fact remains that the final sodium chloride concentrations were sufficiently constant to eliminate any possibility that chloride had escaped during the operation of the test.

The corrosion rate of 0.3 mil/year for the 316 stainless steel after 400 hours is in excellent agreement with the corrosion rate of 0.27 mil/year for 445 hours as shown in Table II.

The Effect of Total Immersion. Under conditions of total immersion, Type 316 stainless steel exhibited the best all-around corrosion resistance to the three test solutions. Based on individual solutions, the following table presents a listing of the stainless steels in order of their preferred selection in the three test solutions:

6.0 DISCUSSION OF DATA (CONT'D)

<u>Solution</u>	<u>1st Choice</u>	<u>2nd Choice</u>	<u>3rd Choice</u>
1	347	309	316
2	316	347	309
3	316	309	(N.R.)*

*Not recommended

The corrosion rates for 309 and 316 stainless steels in Solution 1 were nearly identical, thus making the use of either material satisfactory as a second choice.

Figure 4, 5, and 6 are graphic presentations which show comparatively the corrosion attack on the three stainless steels exposed to conditions of total immersion in the three test solutions.

The Effect of Liquid-Vapor Exposure. In general, corrosion attack on specimens which were exposed to the liquid-vapor interface was not as pronounced as for conditions of total exposure. In the former tests, specimens were located in the test flasks so that approximately 50% of the surface area was in the solution and the other 50% was exposed to the vapor. The most severe corrosion was exhibited by 347 stainless steel in Solution 3. Here, the corrosion rate was 30.6 mils/year after 828 hours of test. A table showing the selection preference of the stainless steels in the three test solutions for liquid-vapor exposure is listed as follows:

<u>Solution</u>	<u>1st Choice</u>	<u>2nd Choice</u>	<u>3rd Choice</u>
1	309	316	347
2	316	347	309
3	316	309	347 (N.R.)*

*Not recommended

Figures 7, 8, and 9 present a graphic comparison of the corrosion resistance of the three stainless steels exposed to the liquid-vapor phase in the three synthetic waste solutions.

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FIG. 4 CUMULATIVE WEIGHT LOSSES ON STAINLESS
STEELS TOTALLY IMMERSSED IN WASTE
SOLUTION NO.1 AT 105-106°C

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FIG. 5 CUMULATIVE WEIGHT LOSSES ON STAINLESS
STEELS TOTALLY IMMERSSED IN WASTE SOLUTION
NO. 2 AT 105-106°C

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DWG. 10352

FIG. 6 CUMULATIVE WEIGHT LOSSES ON STAINLESS
STEELS TOTALLY IMMERSSED IN WASTE SOLUTION
NO. 3 AT 105-108°C

FIG.7 CUMULATIVE WEIGHT LOSSES ON STAINLESS STEELS
EXPOSED TO THE LIQUID-VAPOR PHASE
IN WASTE SOLUTION NO.1 AT 105-108°C

FIG 6 CUMULATIVE WEIGHT CHANGES ON STAINLESS STEELS
EXPOSED TO THE LIQUID-VAPOR PHASE
IN WASTE SOLUTION, NO2 AT 105-108°C

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FIG. 9 CUMULATIVE WEIGHT LOSSES ON STAINLESS STEELS
EXPOSED TO THE LIQUID-VAPOR PHASE
IN WASTE SOLUTION NO.3 AT 105-108° C

6.0 DISCUSSION OF DATA (CONT'D)

The Effect of Vapor Exposure. Corrosion attack on all of the stainless steels exposed in the vapor phase above the three test solutions was very mild. Overall corrosion rates averaged from 0.02-0.08 mil/year and there were no significant differences in the rates obtained in the three test media. Inasmuch as there was no great variation in the corrosion resistance of the materials, data are not plotted as in the previous cases for total immersion and liquid-vapor exposures.

Based upon these results, the use of 309, 316 or 347 stainless steel for vapor exposures in any or all of the test media is satisfactory.

Sample Condition. In general, the appearance of the samples as removed from the test solutions was very good. For total immersion exposures, the 347 stainless steel specimens appeared deeply etched in Solution 3. Other samples in the three solutions exhibited a slightly etched appearance. Samples exposed to the liquid-vapor interface showed no sign of water-line corrosion attack. In cases where the solution was particularly corrosive to a stainless steel specimen, the totally immersed portion of the specimen was etched and the portion of the surface exposed to the vapor remained bright and metallic.

Samples exposed to the vapor phase retained their original metallic luster in most cases. None of the specimens tested showed any signs of localized or pitting corrosion attack.

7.0 CONCLUSIONS

The selection of a stainless steel for maximum corrosion resistance is dependent entirely on the composition of the synthetic waste solution that will be used. For maximum corrosion resistance in the three different solutions under conditions of total immersion, liquid-vapor exposure, and vapor exposure, Type 316 stainless steel is preferred over Type 309 and 347.

The first choice of the stainless steels tested for exposure to the three synthetic waste solutions at 105-108°C is summarized in the following table:

	<u>Solution 1</u>	<u>Solution 2</u>	<u>Solution 3</u>
Total immersion	347	316	316
Liquid-vapor	309	316	316
Vapor	347	316	347-316

7.0 CONCLUSIONS

The use of 316 stainless steel for the construction of distillation and evaporation equipment should be made with certain considerations, especially where welding operations are involved. The material can be welded without difficulty, but is somewhat susceptible to carbide precipitation. The maximum carbon content of 0.10 percent tends to minimize the extent of this carbide precipitation. In cases where the corrosiveness of the solution being used is not too severe and where service temperatures do not fall in the range of 900-1600°F, the steel may be used satisfactorily in the as-welded condition. On the other hand, when the solution is corrosive, as the case of Solution 3 in this investigation, it is recommended that an annealing process follow the welding operation in order to obtain maximum corrosion resistance. The annealing operation consists of heating the fabricated parts to 1950-2000°F for an established time and then cooling quickly through the range of 900-1600°F. This process redissolves any precipitated carbides which otherwise could cause intergranular corrosion attack under severe operating conditions.

8.0 ACKNOWLEDGEMENTS

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END