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CORROSION OF STAINLESS STEEL IN ACIDIC
NITRATE WASTE SOLUTIONS FROM PROCESSING
STAINLESS STEEL REACTOR FUELS

D. N. Hess
L. Rice
B. Willis
E. S. Snively
W. E. Clark

OAK RIDGE NATIONAL LABORATORY

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U.S. ATOMIC ENERGY COMMISSION

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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B
and
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CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	1
2. EXPERIMENTAL	2
3. RESULTS	3
4. CONCLUSIONS	26
5. ACKNOWLEDGMENT	27
6. REFERENCES	28

CORROSION OF STAINLESS STEEL IN ACIDIC NITRATE WASTE SOLUTIONS FROM PROCESSING STAINLESS STEEL REACTOR FUELS

D. N. Hess, L. Rice, B. Willis, E. S. Snavely, and W. E. Clark
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ABSTRACT

Stainless steel tanks appear to be useful for long-term containment of acid wastes from the reprocessing of stainless steel fuel elements provided that the temperature of the container is kept $\leq 50^{\circ}\text{C}$ and that tanks are constructed so as not to expose grain ends to the solution.

Chloride ions up to about 0.02 M and fluoride up to about 0.04 M produced no accelerating effect on the corrosion. Certain organic compounds, for example, glycerol, acted as corrosion inhibitors, as did nitrite. Ferric iron in high concentrations was responsible for a grain-boundary attack that increased in rate with increase in temperature and with increase in free acid concentration. Catastrophic end-grain attack was observed under the most aggressive conditions. In the usual case, true intergranular attack did not develop even after exposure times of 7000 hr. The presence of Cr(III) appeared to accelerate the attack, but only when Fe(III) was also present. Polarization studies indicated that neither anodic nor cathodic protection would be markedly helpful. Appreciable concentrations of Cr(VI) were shown to be absent from the solution at temperatures as high as 80°C . Radiolysis of these solutions is expected to produce corrosion inhibitors (e.g. NO, NO₂, H₂O₂) rather than accelerators.

1. INTRODUCTION

The development of nuclear power plants will, of necessity, be accompanied by the production of large quantities of high-level radioactive wastes. The impossibility of achieving complete burnup of the fissionable material in one pass through the reactor necessitates procedures for recovering and recycling the fissionable materials and for safe disposal of wastes to prevent contamination of the biosphere.

The great majority of research and production reactors employ fuel consisting of uranium, uranium alloys, or UO₂ clad with aluminum. The common reprocessing schemes have all involved dissolution of the fuel in nitric acid and solvent extraction of the uranium from the nitrate solution. Consequently, the technology of solvent extraction from these solutions is well developed. Their application to the reprocessing of stainless steel fuels to be used in civilian power reactors requires relatively minor changes in operating procedures and in existing equipment once a nitrate solution of the fuel has been prepared. Dissolution can be accomplished either by anodization of the fuel elements in nitric

acid¹⁻⁴ or by chemical dissolution in mixed nitric and hydrochloric acid followed by removal of the chloride from the solution (Darex Process).⁵ In either case the waste solution after feed adjustment and solvent extraction consists of stainless steel dissolved in nitric acid containing at most 200 to 300 ppm of chloride ion. The concentration of free acid in the waste solution may vary from about 1 to 5 M. Dissolution of fuels containing appreciable amounts of thorium requires the addition of small amounts of fluoride to the nitric acid dissolvent.⁶ This fluoride remains in the raffinate from the solvent extraction step.

Regardless of whether permanent tank storage, calcination to solids, or some other method is adopted for ultimate disposal of high-level radioactive wastes, there will be a need for some interim storage of these solutions. If they are to remain indefinitely in the storage tank they may be neutralized with alkali, but if they are ever to be completely removed it is advantageous to keep them acid in order to minimize sludge formation and waste volume. Some method of removing the radiolytic heat will be necessary. Stainless steel is the obvious candidate of construction for these tanks but its long-term resistance to corrosion by the solutions of interest must be established.

In general, the austenitic stainless steels are classed as having good resistance to nitric acid and to nitrate solutions of most metal ions. The presence of very small amounts of chromate causes intergranular attack, particularly in heat-affected areas surrounding weldments.⁷⁻⁹ Reports of intergranular attack due to high concentrations of $\text{Fe}^{(+3)}$ in nitric acid have been somewhat conflicting.^{7,8} The addition of as much as 800 ppm Cl^- to such solutions had no effect on the rate of attack.⁹

2. EXPERIMENTAL

Specimens of types 304L and 347 stainless steels were exposed in the solution and vapor phases of simulated wastes from the solvent extraction (Purex Process) of residual uranium from the Darex (stainless steel -- UO_2 fuel) and Darex-Thorex (stainless steel clad, UO_2 - ThO_2 fuel) dissolution processes (Table 1). No simulation of fission products was attempted. Corrosion specimens of type 304L stainless steel were welded with type 308L weld rod; those of type 347 were welded with type 347 weld rod. No heat treatment was given the specimens after welding. In some, but not all cases, weld beads were ground smooth before exposure. The effect of this grinding on the corrosion rate appeared to be primarily a decrease in the surface area of the specimen. In some experiments, stress specimens in the form of bolted U-bends were exposed in the solution phase. Exposures were made at temperatures of 50, 65, and 80°C in both waste solutions and at 43°C and 35°C in Darex solutions containing 2 M free acid. Test containers were glass for the Darex exposures; polyethylene or Kel-F was employed for containment of the Darex-Thorex waste solutions in order to prevent complications due to reaction of the fluoride with the container material.

Table 1. Compositions of Darex-Purex and Darex-Thorex Waste Solutions

Component	Concentration (g-moles/liter)	
	Darex-Purex	Darex-Thorex
H ⁺	2 to 5	1.13
Stainless Steel (304L)	1.82	1.82
Al(III)	--	0.28
Cl ⁻	0.003 (100 ppm)	0.003 (100 ppm)
F ⁻	--	0.036-0.04
NO ₃ ⁻	To balance	To balance

Specimens were removed weekly or bi-weekly for weighing and visual inspection. After exposures of several thousand hours, or upon the appearance of some peculiar phenomenon, specimens were examined metallographically to determine the nature of the attack and its extent in cases of localized attack. The simulated waste solutions were not renewed during testing since there would be no renewal during storage. After the corrosion behavior of the waste had been firmly established, additions were sometimes made to the solutions during confirmatory exposures to determine the effect of these additions on incremental corrosion rates. Exceptions to this procedure were made in the case of inhibitors such as polyethylene, which were found to destroy the free acid. Periodic additions of acid were necessary in such cases in order to eliminate any effect of the decrease in acid concentration.

Electrode potentials were measured with a potentiometer in the conventional way by the use of a saturated calomel electrode. Brief polarization measurements were made by conventional methods.¹⁰ The results were confirmed by an independent source.^{11,12}

3. RESULTS

Overall corrosion rates in Darex-Purex solutions (Table 1), based on weight losses, varied from less than 0.01 mil/month in the 2 M acid solution at 35°C to 0.9 mil/month in the 5 M acid solution at 80°C. Corrosion rates on type 347 were invariably higher than on type 304L, and with both steels rates increased rapidly with increasing temperature (Tables 2-5, Figs. 1-5). Preliminary tests on Ni-0-nel were discontinued after 431 hr of exposure because of intergranular attack.

In all tests at or above 50°C in the absence of inhibitors, grain boundary attack eventually became visible on all solution-phase specimens. Lowering the temperature of exposure or the concentration of free acid in the solution lowered the overall corrosion rate and extended the time before inception of the grain boundary attack (Figs. 2-6; Tables 2-5).

Table 2. Corrosion Rates of Welded Specimens^a of Types 304L and 347 Stainless Steels in Simulated High-Acid Waste Solutions^b at 80°C

Test Period (hr)	Type of Stainless Steel	Corrosion Rate (mil/month)		
		Vapor	Interface	Solution
168	347 304L	0.01	0.17	0.29
		0.02	0.18	0.29
336	347 304L	0.01	0.18	0.32
		0.01	0.17	0.27
570	347 304L	0.01	0.22	0.43
		0.01	0.17	0.29
738	347 304L	0.01	0.25	0.52
		0.01	0.17	0.31
906	347 304L	0.01	0.28	0.58
		0.01	0.18	0.34
1074	347 304L	0.01	0.30	0.63
		0.01	0.19	0.36
1574	347 304L	0.01	0.35	0.70
		0.01	0.21	0.43
2074	347 304L	0.01	0.41	0.78
		0.01	0.25	0.51
3082	347 304L	0.01	0.45	0.81
		0.01	0.29	0.61
4082	347 304L	0.01	0.51	0.90
		0.01	0.36	0.75
5082	347 304L	0.01	0.52	0.88
		0.01	0.39	0.77
6082	347 304L	0.01	0.53	0.89
		0.01	0.43	0.80

^aAll specimen surfaces polished with 120-grit paper.

^bSolution composition: 5.0 M HNO₃, 1.82 M stainless steel, 100 ppm Cl⁻.

Table 3. Corrosion Rates of Welded Specimens of Types 304L and 347 Stainless Steels in Simulated High-Acid Darex-Purex Waste Solutions^a at 65°C
(Average of results for two specimens)

Test Period (hr)	Type of Stainless Steel	Cumulative Corrosion Rate (mil/month)		
		Vapor	Interface	Solution
168	347	0.04	0.08	0.10
	304L	wt gain.	0.02	0.02
336	347	0.02	0.08	0.11
	304L	0	0.02	0.04
504	347	0.02	0.08	0.11
	304L	0.01	0.03	0.05
672	347	0.02	0.08	0.11
	304L	0.01	0.04	0.07
840	347	0.01	0.08	0.11
859	304L	0.01	0.04	0.07
1008	347	0.01	0.08	0.12
1176	347	0.01	0.09	0.12
	304L	0.01	0.05	0.09
1273	304L	0.01	0.05	0.09

^aSolution Composition: 5.0 M HNO₃, 1.82 M stainless steel, 0.003 M Cl .

Table 4. Corrosion Rates of Welded Specimens of Type 304L Stainless Steel in Simulated High-Acid Darex-Thorex Waste Solution^a at 50°C
(Average of results for two specimens)

Test Period (hr)	Cumulative Corrosion Rate (mil/month)		
	Vapor	Interface	Solution
336	0.01	0.01	0.01
504	0.01	0.01	0.01
691	0.01	0.05	0.06
859	0.01	0.06	0.07
1027	0.01	0.05	0.06
1195	0.01	0.04	0.01
1363	0.01	0.04	0.04
1521	0.01	0.05	0.05

^aSolution composition: 5.0 M HNO₃, 1.82 M stainless steel, 0.003 M Cl .

Table 5. Corrosion Rates of Welded Types 347 and 304L Stainless Steel in Simulated Low-Acid Darex-Purex Waste Solutions^a

Location of Specimen	Alloy	Corrosion Rate (mil/month)																	
		168 hr			336 hr				504 hr				672 hr				840 hr		
		50°C	65°C	80°C	43°C	50°C	65°C	80°C	35°C	50°C	65°C	80°C	43°C	50°C	65°C	80°C	50°C	65°C	80°C
Vapor	347	0.02	0.02	0.04	0.003	0.01	0.02	0.03	0.01	0.01	0.01	0.02	0.01			0.02	0.01	0.01	0.02
	347	0.02	0.03	0.04		0.01	0.02	0.03	0.01	0.01	0.01	0.02				0.02	0.01	0.01	0.02
	304L	0.01	0.01	0.03	0.004	0.01	0.02	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.02
	304L	Neg.	0.02	0.02		0.01	0.01	0.02	0.01	0.01	0.01	0.02		0.01	0.01	0.01	0.01	0.01	0.01
Interface	347	0.02	0.05	0.14	0.002	0.02	0.05	0.16	0.01	0.01	0.05	0.15	0.008			0.15	0.01	0.04	0.16
	347	0.02	0.05	0.17		0.01	0.05	0.16	0.01	0.01	0.05	0.15				0.16	0.01	0.04	0.16
	304L	0.01	0.03	0.12	0.006	0.01	0.03	0.12	0.01	0.01	0.03	0.12	0.002	0.01	0.03	0.11	0.01	0.03	0.12
	304L	0.01	0.04	0.11		0.01	0.03	0.12	0.01	0.01	0.03	0.11		0.01	0.03	0.12	0.01	0.03	0.12
Solution	347	0.02	0.07	0.26	0.002	0.02	0.06	0.25	0.01	0.02	0.07	0.26	0.003			0.26	0.01	0.07	0.30
	347	0.03	0.07	0.24		0.02	0.06	0.24	0.01	0.02	0.06	0.25				0.25	0.01	0.06	0.29
	304L	0.02	0.04	0.17	0.004	0.02	0.04	0.19	0.01	0.01	0.05	0.19	0.002	0.01	0.05	0.20	0.01	0.05	0.21
	304L	0.02	0.05	0.17		0.01	0.04	0.19	0.01	0.01	0.05	0.19		0.02	0.05	0.20	0.01	0.05	0.21

^aComposition of waste: 2.0 M HNO₃, 1.82 M stainless steel, 0.003 M Cl⁻.

Fig. 1. Temperature Dependence of the Corrosion of Types 304L and 347 Stainless Steel in Simulated Darex-Purex Waste Solutions (a) 2 M in Free Acid, (b) 5 M in Free Acid.

Fig. 2. Average Weight Loss at Three Temperatures of Two Welded, Type 304L Stainless Steel Specimens in Simulated Darex-Purex, Waste Solution. (Solution 5.0 M HNO_3 , 1.82 M stainless steel, 100 ppm Cl^- .) Vertical arrows indicate times at which grain boundary attack was first noted.

Fig. 3. Average Weight Loss at Two Temperatures for Two Welded, Type 347 Stainless Steel Specimens in Simulated Darex-Purex, Waste Solution. (Solution 5.0 M HNO_3 , 1.82 M stainless steel, 100 ppm Cl^- .) Vertical arrows indicate times at which grain boundary attack was first noted.

Fig. 4. Average Weight Loss at Three Temperatures of Two Welded, Type 304L Stainless Steel Specimens in Simulated Darex-Purex Waste Solution. (Solution 2.0 M HNO_3 , 1.82 M stainless steel, 100 ppm Cl^- .) Vertical arrows represent times at which grain boundary attack was first noted.

Fig. 5. Average Weight Loss at Three Temperatures of Two Welded, Type 347 Stainless Steel Specimens in Simulated Durex-Purex Waste Solution. Composition of solution: 2.0 M HNO_3 , 1.82 M stainless steel, 100 ppm Cl^- . Vertical arrows indicate times at which grain boundary attack was first noted.

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Fig. 6. Effect of Acid Concentration, Edge Area, and Inhibitor on the Corrosion of Type 304L Stainless Steel During Long-Term Exposure at 80°C.

Even at 80°C and 7000 hr of exposure, however, this corrosion failed to develop into true intergranular attack.

In all cases the highest corrosion rates were experienced by specimens exposed in the solution phase. Specimens that presented no edge surface to the solution corroded at slightly lower rates than ordinary specimens (Fig. 6). Stressed specimens showed no increase in corrosion compared with unstressed specimens (Fig. 7).

The initial exposures in Darex-Thorex solutions (Table 1) resulted in lower rates than those observed in the Darex-Purex solutions that contained no fluoride. Further investigation revealed that this inhibition was due to some unidentified material leached from the polyethylene containers (Table 6). When the Darex-Thorex exposures were repeated with fluorocarbon plastic containers the results were consistent with the acid effect observed in Darex-Purex waste solutions (Fig. 6). The presence of the small amount of fluoride did not, therefore, appear to have any significant effect on the corrosion process.

The most aggressive attack observed below reflux temperatures consisted of end-grain attack, which at 80°C was sometimes catastrophic (Fig. 8).

The addition of polyethylene chips to the waste solution reduced the corrosion rate in the low acid (2 M) solution from 0.36 to 0.02 mil/month for exposures of 6036 hr (Table 6, Fig. 6). During this exposure it was noted that the polyethylene reduced the concentration of the free nitric acid considerably; enough extra nitric acid was added periodically to have made the starting solution 6.3 M in free acid, whereas, in the absence of polyethylene, the additional acid required to replace evaporation and other losses would have increased the initial acid concentration to only 2.3 M had it all been present initially. The inhibitor appeared to be eventually consumed. The same inhibiting effect was obtained by exposing the specimens in a solution in which polyethylene chips had been refluxed for 50 hr. This phenomenon has not been adequately explained nor has the inhibitor been identified. The grain-boundary attack characteristic of these waste solutions appeared on the specimens long before the inhibitor was consumed.

The occurrence of the grain-boundary attack with the corresponding increase in overall corrosion rate, plus the fact that some leachant from polyethylene acted as an inhibitor, made it desirable to determine the agent responsible for the attack and to investigate the possibility of effectively inhibiting it. A number of diagnostic exposures were therefore made in which the solution constituents were varied. All these exposures were made at 80°C in order to accelerate the corrosion rate as much as possible without the complications which would be introduced by exposure in a boiling solution. Type 304L specimens were used in these tests. The results of some of the more conclusive tests are presented graphically in Figs. 9-12, in which the average incremental weight losses of duplicate specimens are plotted vs the number of exposure periods.

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Fig. 7. Corrosion Rates of Stressed Type 304L vs Unstressed Type 304L.
Composition of solution: 5.0 M HNO_3 , 1.82 M stainless steel, 100 ppm Cl^- ;
80°C.

Table 6. Corrosion Rates of Types 304L Stainless Steel in Simulated Low-Acid Darex-Purex Solution^a at 80°C with and without added Polyethylene Chips

(Average of two specimens)

Test Period (hr)	Additive	Cumulative Corrosion Rate (mil/month)		
		Vapor	Interface	Solution
168	No ^a	0.03	0.07	0.10
	Yes ^b	0.02	0.01	0.01
336	No ^a	--	--	--
	Yes ^b	0.01	0.01	0.01
504	No ^a	0.02	0.08	0.11
	Yes ^b	0.01	0.01	0.01
1008	No ^a	0.01	0.08	0.12
	Yes ^b	0.01	0.01	0.01
1536	No ^a	0.01	0.08	0.14
	Yes ^b	0.01	0.01	0.01
2040	No ^a	0.01	0.10	0.16
	Yes ^b	0.01	0.01	0.01
3040	No ^a	0.02	0.11	0.20
	Yes ^b	0.01	0.01	0.01
4052	No ^a	0.01	0.14	0.27
	Yes ^b	0.01	0.01	0.01
5052	No ^a	0.01	0.17	0.32
	Yes ^b	0.01	0.01	0.01
6036	No ^a	0.01	0.18	0.36
	Yes ^b	0.01	0.02	0.02

^aSolution composition: 1.13 M HNO₃, 1.82 M stainless steel, 0.003 M Cl⁻.

^bSolution composition: 2.0 M HNO₃, 1.82 M stainless steel, 0.003 M Cl⁻.

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Fig. 8. Severe End-Grain Attack on Type 304L Stainless Steel in Simulated Darex-Purex Waste Solution at 80°C. 100X

Comparison of the corrosion in a solution prepared by dissolving stainless steel with that in one prepared directly from reagents indicated that the initial corrosion was higher in the first case but that the two reached approximately equivalent rates after about 4000 hr (24 weeks) of exposure (Fig. 9). Decreasing the concentration of Fe(III) in the solution from 1.27 to 0.13 M reduced the weight loss from about 5 to about 0.65 mg for the first 10 weeks (about 1680 hr) of exposure; corresponding cumulative corrosion rates over this exposure time were 0.4 and 0.07 mil/month, respectively. Lowering the concentration of Fe(III) to 4.2×10^{-4} M lowered the initial weight loss to 0.33 mg and the corresponding cumulative rates to about 0.07 mil/month. These are almost identical with the results obtained in solutions containing no added Fe(III); at these low concentrations the iron present as contaminant was probably as great as that added. Since 0.1 to 0.2 mg may be considered the limit of precision in weighing specimens of the gross weight used (9 to 12 g), variations in weight below about 0.5 mg are significant only if enough measurements are made to ensure statistical validity.

Increasing the concentration of Fe(III) from 0.13 to 1.0 M after 10 weeks exposure resulted in a sharp increase in the rate of corrosion until it approximated that of the simulated synthetic waste solution. Omission of the Fe(III) from the simulated waste solution lowered the average weight loss of the corrosion specimens to 0.25 mg/cm²·2 weeks or less for exposures of 10 weeks or longer (Figs. 9, 10). The substitution of 3 M free acid, 1.27 M Cr(III) nitrate or 1.27 M Al(III) nitrate for the 1.27 M Fe(III) did not noticeably increase the corrosion above that in the solution with no Fe(III). Omission of Cr(III) from the simulated waste usually resulted in decreased corrosion (Fig. 11). Addition of Cr(IV) in concentrations equal to or greater than 1×10^{-3} M invariably increased the corrosion rate. In the absence of Fe(III) this increase was usually temporary (Fig. 10). In some instances Cr(III) appeared to stabilize the increased rate in a manner similar to Fe(III) while in others it appeared to exert no such effect. Test solutions containing Cr(VI) which were heated to 80°C for 24 hours prior to insertion of the specimens failed to produce the accelerated attack characteristic of Cr(VI). The latter is, therefore, concluded to be unstable in these solutions. Analytical tests for Cr(VI) were inconclusive.

A number of organic and inorganic compounds were tested for possible effectiveness as inhibitors in the simulated waste solution. Of the inorganic materials tested, NaH₂PO₄ and Zn(II) either had no effect or accelerated the corrosion slightly, while Fe(II) sulfate was a mild inhibitor (Table 7). All the organic materials inhibited to some degree, but all were eventually consumed in the process, and NO₂ was slowly evolved during exposures in solutions containing inhibitors. Intermittent bubbling of NO₂ through a waste solution produced some inhibition. The corrosion rate increased sharply when the NO₂ was stopped, and increased even more when O₂ or N₂ was substituted for NO₂ (Fig. 12). Of the

Fig. 9. The Effect of Fe(NO₃)₃ Concentration on the Corrosion of Type 304L Stainless Steel in Synthetic Darex-Purex Waste Solution at 80°C.

Fig. 10. The Effect of Substituting Other Cations for Fe(III) or the Corrosion of Type 304L Stainless Steel in Synthetic Darex-Purex Waste Solution at 80°C.

Fig. 11. The Effect of $\text{Cr}(\text{NO}_3)_3$ on the Corrosion of Type 304L Stainless Steel in Synthetic Darex-Purex Waste Solution at 80°C. Points represent average of two determinations.

Fig. 12. The Effect of Glycerol and NO₂ on the Corrosion of Type 304L Stainless Steel in Darex-Purex Waste at 80°C.

Table 7. The Effect of Compounds Added to Darex-Purex Solution
at 80°C on the Corrosion of Stainless Steel

Compound	Incremental Weight Loss (mg/cm ² per 2 weeks (336 hr))				Cumulative Corrosion Rate (mil/month)			
	Type 304L		Type 347		Type 304L		Type 347	
	1 wk	2 wks	1 wk	2 wks	1 wk	2 wks	1 wk	2 wks
None	2.12	2.29	3.95	5.56	0.23	0.24	0.43	0.51
Na ₂ H(PO ₄) ₃ , 0.1 M	2.72	2.69	--	--	0.30	0.29	--	--
Tributyl phosphate, 0.02 M	1.20	1.45	3.45	4.52	0.13	0.16	0.37	0.42
Dextrose, 0.02 M	2.56	2.52	--	--	0.28	0.28	--	--
Ethanolamine, 0.7 M	0.60	0.49	--	--	0.06	0.06	--	--
Zn(NO ₃) ₂ , 0.05 M	2.66	2.87	--	--	0.29	0.30	--	--
o-Cresol, 0.02 M	0.70	2.08	--	--	0.08	0.15	--	--
FeSO ₄ , 0.05 M	1.84	--	--	--	0.20	--	--	--
Glycerol, 0.02 M	0.36	0.31	0.30	0.22	0.04	0.04	0.03	0.03

inhibitors studied, glycerol appeared to be generally the most effective. The periodic addition of glycerol so as to keep NO_2 visible above the solution resulted in weight losses of 0.3 to 0.6 mg per cm^2 per 2 weeks, even on specimens that had previously suffered weight losses 10 to 20 times this size just prior to the addition of the inhibitor (Fig. 12).

A series of rather approximate emf measurements was made on platinum and on stainless steel electrodes in 5 M HNO_3 at 80°C , and in simulated waste solution at 80°C both before and after the addition of various concentrations of Cr(VI) and hydrogen peroxide. The results indicated the corrosion potential of stainless steel in the waste solution at 80°C to be about 930 mv positive to the saturated calomel electrode. Addition of 5×10^{-2} M Cr(VI) raised this potential to about +960 mv vs the SCE. After the addition of Cr(VI) , considerable time, cooling, or the addition of a reducing agent, was necessary to cause the stainless steel potential to revert to its normal corrosion value. The addition of glycerol lowered the potential to about +885 mv vs the SCE. A plot of potential vs the molarity of Cr(VI) for the platinum electrode in 5 M HNO_3 at 80°C had a slope approximating that for a three electron valence change (i.e., 0.027 vs 0.023 theoretical) for $\text{Cr(VI)} + 3e \rightleftharpoons \text{Cr(III)}$, but the presence of a stainless steel electrode in the same solution caused the potentials of the platinum to shift to much lower values, a plot of which did not closely correspond to any single, simple valence change (Fig. 13). This mixed potential behavior is doubtless due to the presence of a mixture of Fe(II) , Fe(III) , and oxides of nitrogen in the solution. The potential of platinum in the simulated waste solution containing Cr(VI) was much lower than in 5 M HNO_3 in the presence of Cr(VI) and a stainless steel electrode, but increased slowly with time. In the absence of added chromate and of undissolved stainless steel, a platinum electrode at 80°C assumed a potential of about +990 mv vs the SCE in 5 M acid and in the simulated waste solution. By comparison, a platinum electrode in a waste solution containing about 0.05 M Cr(VI) at 80°C and in the presence of a stainless steel electrode assumed a potential of between +1040 and +1085 mv vs the SCE; boiling the solution followed by addition of excess H_2O_2 , cooling to 30°C and reheating to 80°C resulted in return of the platinum potential to +990 to +1000 mv vs the SCE. It does not, therefore, appear likely that any appreciable equilibrium concentration of Cr(VI) can exist in an actual waste solution.

Brief polarization studies of stainless steel in the waste solution at 30°C indicated an open-circuit potential of about +900 mv vs the SCE. Aggressive corrosion was shown to begin at potentials more positive than 1000 mv, but between this potential and about +400 mv there was relatively little change in the corrosion current (Fig. 14). Assuming the polarization curve to have the same general shape at 80°C as at 25°C , it may be possible to prevent the onset of very aggressive corrosion by polarizing the tank to about 700 to 800 mv positive to the SCE. There appears to be no real danger of such attack occurring when dealing with actual radioactive waste solutions because of the expected slow generation of oxides of nitrogen by radiolysis of dissolved nitrate. Results confirming the nature and shape of the polarization curve were obtained from two independent sources.^{11,12}

Fig. 13. The Potential of Smooth Platinum Electrodes as a Function of Cr(VI) Concentration in 5 M HNO₃ Solutions at 80°C.

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Fig. 14. Polarization of Type 304L Stainless Steel at 30°C in Simulated Darex-Purex Waste Solution. (5.0 M HNO₃, 1.82 M S.S., 100 ppm Cl⁻) (1 mil/month $\approx$ 1002 -a/cm²).

4. CONCLUSIONS

Purex raffinates from the reprocessing of stainless steel reactor fuels can be contained in stainless steel tanks without danger of catastrophic corrosion. Low storage temperatures, low acid concentration, and proper fabrication techniques (e.g., the avoiding of end grain exposure) will improve the margin of safety. Use of organic inhibitors may also help, but the production of oxides of nitrogen by radiolysis of the nitrate solution present will probably serve the same purpose. The effect of fission products (e.g., ruthenium) on corrosion has not been determined. Anodic protection of the tank is not feasible; cathodic protection, if practicable, appears unnecessary because of the generation of oxides of nitrogen by radiolysis. Tanks should be open to the atmosphere to ensure that the air in them does not become depleted in oxygen.

The mechanism of the grain boundary attack has not been adequately investigated, but it has been shown to be caused by the presence of high concentrations of Fe(III) in the solution. This attack is accelerated in some manner by Cr(III). Attack due to Fe(III) has been noted by others.^{1,3} The presence of even minute concentrations of Cr(VI) causes accelerated corrosion, which would doubtless develop into true intergranular attack if these concentrations were maintained. The apparent linearity of the plot of the logarithm of the rate vs the reciprocal of the temperature indicates the probability (though it does not prove) that the primary mechanism of attack is the same over the entire temperature range studied.

From a combination of electrode potential and polarization measurements it appears likely that the grain boundary attack on the steel involves dissolution of chromium as Cr(VI), which decomposes rapidly in the solution at and below 80°C. At appreciably higher temperatures any oxides of nitrogen formed will be driven from the solution, Cr(VI) will be stable, and the corrosion will become much more aggressive. The roles played by Fe(III) as instigator and by Cr(III) as accelerator of the corrosion process are not clear. The reason why the corrosion does not develop into true intergranular attack is likewise undetermined.

5. ACKNOWLEDGMENT

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