X-822

MASTER

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation
UCC
Post Office Box X
Oak Ridge, Tennessee

6016

~~INTERNAL USE ONLY~~

ORNL
CENTRAL FILES NUMBER
59-1-137

COPY NO. 38

DATE: January 15, 1959

SUBJECT: Review of the Maximum Allowable Chloride Concentration in the Proposed Darex Pilot Plant Product

TO: H. E. Goeller

FROM: J. M. Holmes

ABSTRACT

A review of corrosion data on the effect of chlorides in nitric acid solutions upon stainless steel indicates that the proposed maximum chloride specification of 350 ppm chloride in the Darex Pilot Plant product is reasonable.

APPROVED BY
PATENT DEPARTMENT
1-29-59
DATE SIGNATURE

867 001

DISCLAIMER

1.0 INTRODUCTION

The Darex process will be installed to completely dissolve stainless steel-UO_2 fuel assemblies in a solution of 5 N HNO_3 and 2 N HCl. After dissolution the chloride concentration will be reduced to a level where the stainless steel extraction and storage equipment downstream of the head-end step will not be corroded. The worst possible situation, where solution is boiled in stainless steel equipment, will be considered since there is a possibility that the Darex IAW stream may be stored in a non-cooled stainless steel vessel, and the fission product activity might be sufficiently high to initiate boiling.

A maximum allowable chloride concentration of 350 ppm was proposed recently for the design of the Darex Pilot Plant. This report contains a review of the proposed specification.

2.0 SUMMARY

1) Corrosion data obtained by Battelle Memorial Institute and Hanford indicate that cold nitric acid solutions containing up to 8000 ppm chloride were not corrosive to types 347, 309 SCb, 316 and Carpenter-20 stainless steels.

2) Corrosion data presented in reports by the Catalytic Construction Company and Battelle Memorial Institute indicate that boiling nitric acid solutions containing up to 1000 ppm would not cause serious attack on type 304 ELC, 309 CB, and 347 stainless steels.

3) Specifications in common use for the maximum allowable chloride in nitric acid solutions vary between 500 and 1000 ppm. However, the 1000 ppm specification at Y-12 covers solutions that are diluted to about 100 ppm before processing in stainless steel equipment.

4) A review of the available data on the corrosion of stainless steels by nitric acid solutions containing chloride indicates that the proposed specification of 350 ppm maximum chloride concentration in the Darex Pilot Plant product solution appears reasonable.

3.0 CHLORIDE CORROSION IN COLD NITRIC ACID SOLUTIONS

Battelle Memorial Institute (BMI-1242) performed corrosion tests on stressed and unstressed type 347 stainless steel in solutions comparable to those in a 1A column only with chloride concentrations between 2 and 10,000 ppm. Tests were run for six months at room temperature. The report summarized the results as follows: "There has been no sign of stress corrosion cracking nor has any pitting or other noticeable corrosive attack occurred even in the presence of 1.0 w/o chloride.

Hanford (HW-33602) tested the corrosion of austenitic stainless steels (types 309 SCb, 347, 316 and Carpenter-20) in chloride bearing Purex process streams. Very low rates were measured throughout the tests, even at chloride concentrations as high as 8000 ppm.

867802

4.0 CHLORIDE CORROSION IN BOILING NITRIC ACID SOLUTIONS

4.1 CATALYTIC CONSTRUCTION COMPANY STUDY

The Catalytic Construction Company of Philadelphia, Pennsylvania, prepared a report (NYO-1182) in October, 1953, on the effect of chloride on the design and operation of nitric acid recovery facilities. The report covered Hanford Laboratory corrosion data on type 304 ELC, 309 Cb and 347 stainless steels by chlorides in 42 weight per cent boiling nitric acid solutions. The Hanford work (HW-24641, May, 1952) postulated that the "threshold" value for chloride concentration, or concentration above which excessive corrosion results in nitric acid solutions of approximately 42 weight per cent, is between 3,000 and 5,200 ppm chloride.

Laboratory corrosion tests were run by the W. B. Coleman Company for the Catalytic Construction Company (see Table 1). These tests indicated very low corrosion rates (average = .00024 ipy) at chloride concentrations between 100 and 500 ppm in boiling 15 weight per cent nitric acid on type 309 Cb. Corrosion rates above 0.001 ipy were not attained until a chloride concentration of 20,000 ppm was tested. However, a maximum design chloride concentration of 500 ppm in boiling 15 per cent nitric acid was considered safe for design purposes by the NYO-1182 report.

4.2 BATTELLE MEMORIAL INSTITUTE STUDY AT REDUCED PRESSURES

Battelle Memorial Institute (BMI-1220) conducted a series of tests at reduced pressures to determine the effect of boiling nitric acid chloride solutions on type 304 ELC stainless steels. Table II shows the maximum corrosion rates encountered for nitric acid concentrations between 5 and 45 w/o and chloride concentrations between 0 and 10,000 ppm. The data show that no serious attack occurred in solutions containing 1000 ppm chloride or less. Serious attack occurred with 3000 ppm only in the case where the nitric acid concentration was 45 w/o. A series of short-term tests were run using 38 w/o HNO_3 containing aluminum, chloride and fluoride additions, with and without additions of iron. Preliminary results for three 48-hour periods indicated that the iron afforded a significant amount of protection to the specimens in both liquid and vapor phases.

4.3 HANFORD STUDY FOR DAREX PILOT PLANT

In an address before the Aqua Regia-Zirflex Processes Meeting at Arco, Idaho, on July 29, 1958, R. E. Burns stated that corrosion tests run at Hanford indicated that chloride concentrations up to 350 ppm would be acceptable for the product solution from their Darex Pilot Plant.

5.0 CHLORIDE SPECIFICATIONS IN COMMON USE

5.1 Y-12 DAFFODIL RECYCLE OPERATIONS

This operation in the B-1 Wing of Building 9212 is concerned with the recovery of fissionable materials from chloride-containing nitric acid solutions by solvent extraction. The solvent extraction columns and feed preparation tanks

are stainless steel. Their present maximum chloride specification for solutions entering the system is 1000 ppm, which was recently increased from 500 ppm. However, these solutions are diluted during processing such that the average chloride concentration is probably in the vicinity of 100 ppm. No stainless steel corrosion has been observed except in an evaporator vapor line where chloride-containing solutions are concentrated. However, there is no conclusive evidence that this corrosion was caused by chlorides, since the feed solutions also contain traces of fluoride.

5.2 NITRIC ACID ABSORBERS

Report NYO-1182 states that it is general industrial practice to purge stainless steel nitric acid absorbers whenever the chloride concentration reaches about 500 ppm in the 23 w/o acid zone. The chlorides enter the absorber towers with the NO_2 feed gas and tend to concentrate in the 22 to 23 w/o acid zone. The report states that failure to properly purge the absorbers could result in excessive corrosion of the absorber in the zone of high chloride concentration.

5.3 FERNALD FEED MATERIALS PRODUCTION CENTER

Fred Myers of the Fernald Feed Materials Production Center stated that extensive testing over a period of several years has shown that chloride concentrations up to 1000 ppm did not cause excessive corrosion in their nitric acid fractionator. They maintain the chlorides below this concentration by reacting a side stream from one plate with ozone to volatilize the chloride. The side stream is then returned to the column. Mr. Myers also indicated that their normal fractionator chloride level is about 500 ppm plus about 30-40 ppm of fluoride. However, they have found that when the chloride concentrations gets above 1000 ppm, corrosion occurs in the 15-20% nitric acid zone and when the fluoride concentration gets above 100 ppm, corrosion occurs in the 35-40 per cent nitric acid zone.

6.0 PROPOSED SPECIFICATION FOR ORNL DAREX PILOT PLANT

Batch Darex experiments by the UNOP and Chemical Development Sections have shown that the chloride can be removed from the dissolver product stream down to a 100 - 350 ppm range under reasonable operating conditions. Therefore, the feed stream to the solvent extraction might contain up to 350 ppm of chloride. Data from ORNL-CF-58-9-77 indicate that dilution in the 1A column would reduce this concentration to about 260 ppm in the 1AW stream. Further dilution by neutralization solution and the 2AW stream would reduce the chloride concentration down to the 100-200 ppm range before waste storage.

All of the corrosion data surveyed indicate that these concentrations would not cause significant corrosion of stainless steel vessels at room temperature or even if the solutions were boiled. Therefore, a 350 ppm chloride specification appears reasonable in the Darex Pilot Plant for flow through the stainless steel extraction columns or even where the solution is stored in a stainless steel vessel and allowed to heat up during fission product decay.

If acid recovery is required, standard nitric acid fractionator purge methods will have to be used to reduce the chloride buildup in the column.

This procedure would have to be used regardless of the chloride concentration in the tower feed. This was demonstrated by a Hanford Pilot Plant acid recovery column where the acid feed to the column contained 800 ppm chloride and the maximum chloride concentration in the column was about 1.4% in the 12% nitric acid zone (NYO-1182).

J. M. Holmes

J. M. Holmes
Process Design Section
Chemical Technology Division

JMH/nr

Table 1. Summary of Corrosion Rates of Stainless Steel Type 309 Cb in 15 Weight Per Cent Nitric Acid and Chloride Ion

Solution Cl - Conc. Wt. %	Specimen Position, Phase	Corrosion Penetration Rate, Inches/Month Accumulated Testing Time 36 hrs.	84 hrs.	132 hrs.	180 hrs.
.01	Vapor	.00008	.00010	.00003	
	Interface	.00012	.00003	.00002	
	Liquid	.00005	.00003	.00000	
.05	Vapor	.00007	.00005	.00001	
	Interface	.00007	.00000	.00002	
	Liquid	.00010	.00006	.00000	
.20	Vapor	.00016	.00007	.00001	
	Interface	.00006	.00005	.00002	
	Liquid	.00005	.00004	.00001	
.50	Vapor	.00009	.00001	.00003	.00004
	Interface	.00003	.00000	.00000	.00004
	Liquid	.00004	.00000	.00002	.00004
1.00	Vapor	.00001	.00005	.00000	.00003
	Interface	.00002	.00001	.00003	.00000
	Liquid	.00005	.00001	.00006	.00005
2.00	Vapor	.00006	.00005	.00009	.00011
	Interface	.00003	.00003	.09016	.00003
	Liquid	.00011	.00003	.17898	.00003

Table 2. Status of the Reduced-Pressure Exposure Tests of Type 304 ELC Stainless Steel In Chloride-Contaminated Nitric Acid

HNO_3 w/o	Cl^- w/o	Pressure mm Hg	~Boiling Point °C	Hr on Test	Maximum Corrosion Rate Mils/Mo.	Specimen Position[a]	Remarks
5.0	0.00	200	-	5000	0.001	IL	
	0.05	200		5000	0.001	VIL	
	0.10	200		5000	0.022	I	
	0.15	200		1000	0.200	L	
	0.30	200		3000	0.256	L	
	0.50	200		4000	0.980	I	Discontinued
	1.00	200		2000	4.14	I	Discontinued
18.0	0.00	200	69	6500	0.002	IL	
	0.00	200		3500	0.002	IL	Discontinued
	0.05	200		6500	0.004	I	
	0.05	200		6500	0.002	I	
	0.10	200		6500	0.002	VIL	
	0.10	200		6500	0.002	VIL	
	0.30	200		6500	0.003	IL	
	0.50	200		5000	0.004	IL	
30.0	0.00	250	78	6500	0.013	I	Discontinued
	0.025	250		6500	0.013	I	Discontinued
	0.05	250		6500	0.013	I	Discontinued
	0.10	250		6500	0.011	VIL	Discontinued
	0.15	250		1000	0.016	I	
	0.20	250		1000	0.015	L	
	0.30	250		5000	0.020	I	Discontinued
	0.50	250		5500	1.51	I	Discontinued
38.0	0.00	250	82	500	0.028	L	
	0.05	250		500	0.049	L	
	0.10	250		500	0.057	I	
	0.10	250		500	0.058	I	
	0.15	250		500	0.048	L	
	0.20	250		500	0.060	I	
	0.20	250		500	0.057	I	
	0.25	250		500	0.070	I	
45.0	0.00	250	85	336	0.040	I	
	0.00	250		336	0.038	I	
	0.05	250		336	0.055	V	
	0.05	250		336	0.056	L	
	0.10	250		336	0.068	V	
	0.10	250		336	0.081	I	
	0.30	250		336	24.0	V	
	0.50	250		336	28.9	I	

a) The position of the specimen or specimen exhibiting the max. cor. rate is designated by V = vapor, I = interface, and L = liquid.

867 007

DISTRIBUTION

1. A. R. Irvine
2. R. E. Blanco
3. B. F. Bottenfield
4. J. C. Bresee
5. R. E. Brooksbank
6. K. B. Brown
7. F. R. Bruce
8. W. E. Clark
9. F. L. Culler
10. W. K. Eister
11. D. E. Ferguson
12. L. M. Ferris
13. B. C. Finney
14. J. R. Flanary
15. H. E. Goeller
16. J. H. Goode
17. J. M. Holmes
18. F. G. Kitts
19. C. E. Lamb
20. W. H. Lewis
21. R. B. Lindauer
22. J. L. Matherne
23. W. T. McDuffee
24. J. P. Nichols
25. J. R. Parrott
26. A. C. Schafer, Jr.
27. J. W. Ullmann
28-30. E. M. Shank
31. C. D. Watson
32. W. R. Winsbro
33. ORNL-RC
34-35. Central Research Library
36-37. Document Reference Library
38-40. Laboratory Records
41. M. J. Skinner