AN EVALUATION OF MATERIALS OF CONSTRUCTION FOR THE SULFLEX AND ZIRFLEX PROCESSES

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Abstract

The corrosion resistance of a number of potential materials of construction for both the Sulfex and Zirflex processes has been studied. The results indicate that Ni-o-nel is a satisfactory material for the Sulfex process provided the sulfuric acid concentration is not greater than four molar, and the nitric acid concentration is not greater than five molar. In addition, core dissolutions should be done below the boiling point, and heat transfer surface temperatures during core dissolution should be maintained below 240°F. Carpenter 20 Cb is probably less satisfactory for Sulfex service because of selective weld attack. Neither Ni-o-nel, 309 SCb or 304L is a satisfactory construction material for uninhibited Zirflex solutions. Cupric ion lowers the corrosion rate of 309 SCb to 30-40 mils per year, but is not a satisfactory inhibitor for 304L or Ni-o-nel.

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AN EVALUATION OF MATERIALS OF CONSTRUCTION
FOR THE SULFEX AND ZIRFLEX PROCESSES

Many of the civilian power reactors in operation or under construction utilize fuel elements consisting of UO_2 clad in alloys of high corrosion resistance, such as stainless steel or Zircalloy. The preparation of these fuels for chemical reprocessing by solvent extraction techniques, therefore, requires the use of highly corrosive solutions to dissolve the cladding, and thus presents some problems in finding a suitable material of construction for the dissolver vessel.

One of the processes which has been developed for dissolution of stainless steel clad oxide fuels is the Sulfex process (1)(2). This process consists of chemical decladding in 4-6M H_2SO_4 , removal of the decladding solution, followed by dissolution of the oxide core in nitric acid. The Zirflex process (3)(4), developed for the dissolution of Zircalloy clad fuels, consists of decladding in 6M NH_4F - 0.5 M NH_4NO_3 , also followed by removal of the decladding solution and dissolution of the oxide core in nitric acid.

Although some corrosion data is available for potential materials of construction for both these processes, there are some important gaps and areas of disagreement in the existing data, and it is sometimes difficult to compare the work of different investigators because of differences in test procedures or lack of information on the procedures used. This report describes the results of a series of

corrosion tests on Ni-o-nel and Carpenter 20 Cb in Sulfex solutions, and Ni-o-nel. 304-L and 309 SCb stainless steel in Zirflex solutions. Tests in Sulfex solutions, particularly with Ni-o-nel, were extensive, and it is felt that all the information which can be obtained from laboratory data is now available for evaluating this system. Tests in Zirflex solutions were of a scouting nature to see whether suitable corrosion inhibitors could be found to allow the use of a stainless steel dissolver for this process.

I. Description of Materials and Test Procedures

The composition of the alloys studied are shown in Table I. Three different heats of Ni-o-nel were used in these studies, but the variations in composition were minor, and there was no difference in corrosion resistance among the three.

All specimens, except the heavy Ni-o-nel weld specimens were cut from 1/4" plate, and were prepared for testing according the the following procedure.

1. Polish with 120 grit emery paper
2. Trichloroethylene vapor degrease
3. Hot dip in trisodium phosphate solution containing 13 g/l phosphate and 5 g/l Aerosol OT, followed by distilled water rinse.
4. Dip in 5 weight per cent H_2SO_4 , at room temperature, followed by distilled water rinse.
5. Pickle 10-15 minutes at 50-65 degrees C. in 10 vol. % HNO_3 - 1 to 2 vol. % HF, followed by distilled water

TABLE I
Composition of Materials of Construction

	Ni-o-nel	Carpenter 20	309 sCb	304L
Ni	41.63	34.74	12-15	8-12
Cr	20.90	20.13	22-24	18-20
Mo	2.95	2.25	-	-
Cu	1.69	3.25	-	-
Cb	-	0.83	-	-
Ti	0.85	-	-	-
Mn	0.76	-	2.00	2.00
S	0.007	-	-	.030
Si	0.32	-	1.00	1.00
Al	0.09	-	-	-
C	0.03	0.06	0.1	.03
P			-	.045
Cb & Ta			10 x C min.	

5. rinse.
6. Passivation for 2 minutes in 10 weight % HNO_3 at 65 degrees C., followed by distilled water rinse and drying
7. Weighing and measuring, followed by another degreasing and passivation just prior to use.

The only exceptions to this procedure were that welded specimens were not polished prior to cleaning, and step (5) was omitted in the case of stainless steel specimens.

All isothermal tests, except with Zirflex solutions, were run in three neck, 1 liter, round bottom glass flasks, heated with mantles to maintain the solution at the atmospheric boiling point. Zirflex tests were run in all Teflon equipment. Unless otherwise stated straight updraft condensers were used, and the solutions were not sparged. Liquid phase specimens were supported in glass baskets and were fully immersed in the liquid phase. Vapor phase specimens were suspended above the solution and were at least partially wetted by condensate. Volumes of solution were varied so as to maintain a ratio of solution volume to metal surface area of about 200 ml per square inch. Unless otherwise noted, technical grade reagents were

used.

Tests were run for multiples of forty-eight hour periods, except for those tests run in the presence of dissolving metal, where the period was determined by the dissolution time. Test specimens were rinsed, dried, and weighed after each test period, and immersed in fresh solution for the next period. In the case of tests with heat transfer surfaces, the solutions were changed every forty-eight hours without removing the test specimen, which were weighed only at the termination of the test.

II. Ni-o-nel - Sulfuric Acid

A. Corrosion in 3 and 4M H_2SO_4

1. Wrought Ni-o-nel

The first set of runs in 4M H_2SO_4 were made to determine whether there were significant variations in the behavior of Ni-o-nel from heat to heat, and to determine whether there was any difference in corrosion rates in technical grade and C.P. acid. These results are shown in Table II, along with the results of two tests in 3M H_2SO_4 . It is apparent that the corrosion rate in 4M H_2SO_4 is independent of either the heat of Ni-o-nel or the grade of acid used. For this reason, technical grade acid was used in all subsequent tests in this system. Although the corrosion rate in 3M H_2SO_4 is less than in 4M, no further work was done in 3M H_2SO_4 because of probable difficulty in initiating the dissolution of stainless steel cladding in this low an acid concentration. A typical photomicrograph of

TABLE II

CORROSION OF WROUGHT NI-O-NEL IN 3-4M H₂SO₄
Corrosion Rate, mils per year

Solution	Exposure Time Hours	Heat 8865F.	Heat 9597F.	Heat 128F.
Boiling 4M H ₂ SO ₄ Tech Grade	48	19.9	11.8	30.4
	96	17.1	26.1	45.3
	144	26.6	12.3	15.4
	192	8.8	39.6	20.4
	240	42.0	LOST	15.9
	AVG.	22.9	22.5	25.5
Boiling 4M H ₂ SO ₄ C. P. Grade	48	24.3	41.4	17.8
	96	26.2	19.4	15.6
	144	35.6	20.2	15.0
	192	15.3	41.7	17.7
	240	16.2	19.5	15.0
	AVG.	23.5	28.5	16.2
Boiling 3M H ₂ SO ₄ Tech Grade	48		18.7	15.9
	96		14.8	13.0
	144		13.2	13.8
	192		11.2	11.7
	240		13.0	11.9
	AVG.		14.2	13.2

wrought Ni-o-nel exposed to $4M$ H_2SO_4 for 240 hours is shown in Fig. I.

Two additional series of tests of wrought Ni-o-nel in $4M$ H_2SO_4 were run in order to determine the effect of dissolved air on the corrosion rate. In one of these tests, a cold finger condenser with a pop safety vent was used, and in the other a conventional updraft condenser was used and the solution was sparged with air. These results are shown in Table III. The air sparge had essentially no effect on the corrosion, and the use of a cold finger condenser approximately doubled the corrosion rate.

The effect of dissolved stainless steel on the corrosion rate is shown in Table IV. Dissolved 348 or 304 L stainless steel lowered the corrosion rate by a factor of about ten. This effect was independent of the concentration of dissolved stainless steel. in the range of 5 to 50 grams per liter of dissolved steel. The effect of actively dissolving stainless steel was measured in a series of five dissolutions, with times varying from 4.9 to 9.5 hours. The average corrosion rate in these tests was 13.2 mils per year, which is higher than expected in view of the data in Table IV. However, the short time period of the tests with dissolving stainless steel probably makes those data less reliable. Two additional series of tests were run with $4M$ H_2SO_4 containing 25 grams per liter of dissolved stainless steel, one using a cold finger condenser, and the other with an air sparge. These results checked very closely with those shown in Table IV, showing that the effect of the dissolved stainless steel was

TABLE III
CORROSION OF WROUGHT NI-O-NEL IN 4M H₂SO₄
 Corrosion Rate, mils per year

<u>Solution</u>	<u>Exposure Time Hours</u>		
Boiling 4M H ₂ SO ₄	48	37.4	35.8
Cold Finger Cond.	96	48.0	65.0
	144	25.2	50.9
	192	45.6	48.5
	240	16.3	53.3
	AVG.	34.5	50.7
<hr/>			
Boiling 4M H ₂ SO ₄	48	1.1	25.3
LIEBIG Cond.	96	32.1	23.8
Constant air	144	32.6	23.4
Sparge .9-1.5 l/min.	192	23.4	22.2
	240	22.9	23.8
	AVG.	22.4	23.7

TABLE IV
CORROSION OF WROUGHT NI-O-NEL IN 4M H₂SO₄
PLUS DISSOLVED STAINLESS STEEL
 Corrosion Rate, mils per year

<u>Solution</u>	<u>Exposure Time Hours</u>		
Boiling 4M H ₂ SO ₄ + 5 g/l dissolved 348 S.S.	48	1.8	2.5
	96	3.6	2.2
	144	1.1	1.4
	192	1.3	LOST
	240	2.4	LOST
	AVG.	2.0	2.0
Boiling 4M H ₂ SO ₄ + 25 g/l dissolved 348 S.S.	48	2.7	20.1
	96	2.1	25.7
	144	0.8	1.0
	192	1.2	1.2
	240	LOST	1.0
	AVG.	1.7	9.8
Boiling 4M H ₂ SO ₄ + 50 g/l dissolved 348 S.S.	48	1.7	2.1
	96	0.8	2.5
	144	1.4	1.5
	192	1.2	1.2
	240	1.2	13.8
	AVG.	1.3	4.2
Boiling 4M H ₂ SO ₄ + 25 g/l dissolved 304 S.S.	48	1.1	0.5
	96	0.8	0.4
	144	0.7	0.9
	192	1.2	0.7
	240	0.7	0.7
	AVG.	0.9	0.7

much greater than that due to the use of a cold finger condenser.

2. Welded Ni-o-nel

For testing of welded Ni-o-nel, both metal arc and inert gas welds were used, and three different sets of specimens were tested with each type of weld. The first set of specimens were one quarter inch plate, which was inert gas welded with 5 to 6 passes of #65 wire or metal arc welded with 9 passes of #135 wire. The next set of specimens were one half inch plate, which simulated more closely the welding practices on typical plant dissolver vessels. These specimens were metal arc welded with 9 passes of #135 wire, or inert gas welded with 3 passes of #65 wire and filled in with metal arc welding. Thus in the latter case both metal arc and inert gas welds were exposed to the solution. The third set of specimens were one half inch plate with cross welds, to determine the effect of resensitizing the heat affected zone. For these, a small groove was milled at right angles to the original weld, and filled in with 2 to 3 passes of either metal arc or inert gas welding.

Results of tests with one quarter inch welded plate are shown in Table V and VI. The data in Table V indicate that there is no difference in corrosion rate between metal arc and inert gas welds, and that both show rates about one half those observed with wrought specimens. These data also confirm the unvarying behavior of different heats of Ni-o-nel. In Table VI are shown the results of longer term tests with TIG welded specimens in both the liquid and vapor phases. These results generally confirm the results of shorter term tests, and

TABLE V

CORROSION OF WELDED NI-O-NEL IN 4M H₂SO₄
Corrosion Rate, mils per year

Solution	Exposure Time	Heat 8865F.		Heat 9597F.		Heat 128F.	
	Hours						
Boiling 4M H ₂ SO ₄	48	20.2	12.4	14.0	14.2	9.6	17.9
	96	13.0	13.0	12.5	13.4	11.3	15.0
Metal Arc Weld	144	12.6	12.7	13.3	12.9	4.0	6.2
	192	25.8	12.4	13.2	19.1	6.0	7.2
135 Wire	240	15.6	11.9	14.9	14.2	17.6	16.5
	AVG.	17.4	12.5	13.5	14.8	9.7	12.5
<hr/>							
Boiling 4M H ₂ SO ₄	48	15.0	20.8	21.5	22.6	27.5	17.8
	96	11.2	16.5	16.4	17.0	16.0	14.2
TIG Weld	144	9.7	12.6	6.7	12.9	13.2	8.5
	192	14.7	17.3	8.2	16.2	13.8	9.6
65 Wire	240	14.0	11.8	19.6	15.7	13.5	19.5
	AVG.	12.9	15.8	14.4	16.9	16.8	13.9

TABLE VI
CORROSION OF WELDED NI-O-NEL IN 4M H₂SO₄
Corrosion Rate, mils per year

Solution	Exposure Time Hours	Heat 128F		Heat 9597	
		Liquid	Vapor	Liquid	Vapor
Boiling 4M H ₂ SO ₄	48	21.6	16.1	33.1	8.4
	96	21.6	6.9	29.7	8.3
TIG Weld	144	7.5	11.7	20.8	10.5
	192	7.5	11.9	20.2	9.4
	240	6.1	10.0	16.4	10.1
	288	0.6	0.9	7.0	9.5
	336	2.4	13.2	12.2	13.3
	384	0.8	0.7	7.1	10.9
	432	0.7	10.2	15.4	12.5
	480	13.9	7.6	7.9	8.7
	528	10.2	10.5	15.8	1.2
	576	14.7	11.6	0.8	2.1
	624	1.2	1.4	15.6	1.5
	672	15.8	12.1	11.8	15.3
	720			12.5	13.0
	768			11.8	10.8
	816			12.2	10.5
	AVG.	8.9	8.9	14.8	9.2
<hr/>					
Boiling 4M H ₂ SO ₄	48	46.6	21.2		
TIG Weld	96	11.8	18.2		
	144	13.9	17.3		
	192	16.0	37.6		
	240	16.6	22.2		
	AVG.	21.0	23.3		

indicate that vapor phase corrosion rates are about the same as those in the liquid phase.

Results of tests with one half inch welded plate are shown in Tables VII and VIII. The heavier welded plate, with either single or cross welds, inert gas or metal arc, shows essentially the same corrosion rate as the thinner plate.

The effect of dissolved stainless steel on corrosion welded specimens is shown in Table IX. The effect of dissolved stainless steel is smaller with welded than with wrought specimens, lowering the corrosion rate by only a factor of two to three. Similar results were obtained on duplicate runs with cross welded specimens, with both metal arc and inert gas welds.

Photomicrographs of welded Ni-o-nel exposed to $4M$ H_2SO_4 and $4M$ H_2SO_4 plus dissolved stainless steel for 240 hour periods are shown in Figs. 2, 3, & 4.

B. Corrosion in $6M$ Sulfuric Acid

Initial tests with $6M$ sulfuric acid were run for 240 hour periods and showed liquid phase corrosion rates of 30-40 mils per year for both wrought and welded specimens. However, later tests run for longer periods, indicated sharply increasing corrosion rates due to intergranular attack. Therefore, only these longer tests are being reported. These results are shown in Tables X. A sharp rise in the corrosion rate can be seen after periods ranging between 240 and 430 hours for welded specimens, and somewhat longer for the wrought specimens. Visual examination of these specimens showed severe inter-

TABLE VII
CORROSION OF WELDED HEAVY NI-O-NEL IN 4M H₂SO₄
 Corrosion Rate, mils per year

Solution	Exposure Time Hours		
Boiling 4M H ₂ SO ₄	48	29.5	19.5
	96	26.7	19.6
TIG Weld	144	24.1	15.4
	192	16.4	11.3
	240	17.1	15.4
	AVG.	22.8	16.2
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Boiling 4M H ₂ SO ₄	48	19.5	26.8
Metal Arc Weld	96	7.1	12.5
	144	10.5	18.4
	192	10.8	12.6
	240	12.3	10.7
	AVG.	12.0	16.2

TABLE VIII
CORROSION OF CROSS WELDED HEAVY NI-O-NEL IN 4M H₂SO₄
 Corrosion Rate, mils per year

Solution	Exposure Time Hours		
Boiling 4M H ₂ SO ₄	48	17.4	34.9
	96	13.3	16.4
TIG Cross Welds	144	12.6	11.0
	192	29.0	12.3
	240	7.4	9.3
	AVG.	16.0	16.8
<hr/>			
Boiling 4M H ₂ SO ₄	48	27.6	28.8
Metal Arc Cross Welds	96	25.2	33.4
	144	9.6	8.1
	192	11.9	11.8
	240	23.9	14.4
	AVG.	19.6	19.3

TABLE IX
CORROSION OF WELDED NI-O-NEL IN 4M H₂SO₄
PLUS DISSOLVED STAINLESS STEEL
 Corrosion Rate, mils per year

Solution	Exposure Time Hours		
Boiling 4M H ₂ SO ₄ +	48	4.6	6.4
25 g/l dissolved	96	26.3	31.2
	144	4.9	5.7
348 S.S.	192	34.0	39.0
Metal Arc Weld	240	33.6	39.2
	AVG.	20.7	24.3
Boiling 4M H ₂ SO ₄ +	48	9.8	10.2
25 g/l dissolved	96	11.7	10.6
	144	16.2	14.8
348 S.S.	192	2.8	20.4
TIG Weld	240	1.5	2.2
	AVG.	8.4	11.6
Boiling 4M H ₂ SO ₄ +	48	2.2	2.4
25 g/l dissolved	96	6.9	1.8
	144	11.6	1.5
348 S.S.	192	1.6	1.3
Heavy TIG Weld	240	1.2	1.3
	AVG.	4.7	1.7
Boiling 4M H ₂ SO ₄ +	48	7.5	6.7
25 g/l dissolved	96	7.2	6.9
	144	10.9	6.9
348 S.S.	192	10.2	10.1
Heavy Metal Arc Weld	240	8.8	8.8
	AVG.	8.9	7.9

TABLE X
CORROSION OF NI-O-NEL IN 6M H₂SO₄
Corrosion Rate, mils per year⁴

Solution	Exposure Time	Liquid	Vapor	Liquid	Vapor
	Hours				
Boiling 6M H ₂ SO ₄	48	22.1	14.7	8.3	5.9
	96	22.6	11.6	10.7	2.0
TIG Weld	144	3.2	1.7	14.4	4.3
	192	5.0	1.6	34.6	2.5
	240	7.2	5.4	64.0	4.2
	288	11.3	6.2	50.5	4.5
	336	28.0	13.3	110.2	3.5
	384	62.6	26.6		
	432	45.0	16.8		
	480	90.6	50.1		
<hr/>					
Boiling 6M H ₂ SO ₄	48	25.6	Boiling 6M H ₂ SO ₄	26.9	
	96	23.7		33.2	
Wrought	144	24.0	Metal Arc Weld	24.2	
	192	32.6		38.3	
	240	29.8		16.3	
	288	11.1		16.2	
	336	11.5		25.0	
	384	21.6		12.0	
	432	25.3		28.3	
	480	28.4		12.7	
	528	24.7		32.6	
	576	32.4		59.8	
	624	13.9			
	672	38.5			
	720	18.8			
	768	57.5			
	816	134			

granular attack of the base metal, with no visible attack of the weld. In two 240 hour tests, 25 grams per liter of dissolved stainless steel had no effect on the corrosion rate in 6M sulfuric acid.

On the basis of these results it is apparent that Ni-o-nel is unsuitable for long term service in 6M sulfuric acid.

C. Corrosion of Heat Transfer Surfaces

Since the surfaces of heating coils in a dissolver vessel will be at some temperature above the boiling point of the solution it is necessary to determine the effect of metal surface temperature on the corrosion rate. For this purpose, an apparatus similar to that developed by Groves(5) was used, and is shown in Fig. 5. The sample was a one quarter inch disk heated from below by the soldering iron. The head of the soldering iron was removed and replaced with an aluminum adapter to hold the sample. Teflon gaskets were used to assemble the apparatus. Thermocouples were inserted in the mid-point of the specimen and in the solution. Auxiliary heating was provided to control the solution temperature independently of the metal surface temperature. Rough calculations indicated that the temperature gradient from the mid-point to the surface of the specimen was not more than 5 degrees F, and probably about 2 degrees F. Because of the problem of crevice corrosion which resulted from improper seating of the gasket, the apparatus was not disassembled during the course of a run. In earlier runs when it was attempted to weigh the specimen after each forty eight period, crevice corrosion resulted unless the gasket was positioned in precisely the same location each time.

The results of heat transfer tests with sulfuric acid are shown in Table XI. The corrosion rate in 4M sulfuric acid is independent of the metal surface temperature from the solution boiling point up to 300 degrees F, and is slightly lowered by the presence of dissolved stainless steel.

III. Ni-o-nel - Nitric Acid

A. Isothermal Tests

Initial tests in this system were run with liquid phase specimens only for 240 hour periods and showed corrosion rates of less than one mil per year in 4M nitric acid and two to four mils per year in 10M nitric acid for both wrought and welded specimens. However, later results showed that vapor phase corrosion was a serious problem in this system, and a series of long term tests with both liquid and vapor phase specimens were run.

The results of tests in 8 and 10M nitric acid are shown in Table XII. In both these solutions there was a rapidly increasing corrosion rate of the vapor phase specimen due to severe intergranular attack. In the case of welded specimens there was preferential attack of the base metal. In all cases, the buildup of corrosion products in solution resulting from vapor phase attack caused an accelerated corrosion rate in the liquid phase.

A similar run, using a wrought specimen, was made using C.P. nitric acid in order to determine whether the vapor phase attack might be due to the presence of a volatile impurity in technical grade acid. The results proved to be independent of the grade of acid used.

TABLE XI

CORROSION OF NI-O-NEL HEAT TRANSFER SURFACES IN 4M H₂SO₄

Period of Test	Solution	Specimen Center		Corrosion
		Line	Temp of °F	Rate mils per year
240	4M H ₂ SO ₄		260	29.0
240	4M H ₂ SO ₄		260	31.0
240	4M H ₂ SO ₄		280	36.8
240	4M H ₂ SO ₄		300	34.0
240	4M H ₂ SO ₄ + 25 g/l dissolved stainless steel		300	19.6

TABLE XII
CORROSION OF NI-O-NEL IN 8-10M HNO₃
Corrosion Rate, mils per year

Solution	Exposure Time	Liquid	Vapor
	Hours		
Boiling 8M HNO ₃	48	2.3	1.4
	96	1.4	0.7
	144	1.3	0.6
	192	2.7	1.4
	240	2.8	1.6
	288	5.3	2.7
	336	8.0	6.1
	384	12.6	9.0
	432	22.3	23.6
	480	35.3	64.6
<hr/>			
Solution		Liquid Phase	Vapor Phase
Boiling 10M HNO ₃	48	3.4	1.9
	96	4.6	2.3
	144	16.0	93.0
	192	87.0	294
	240	317	655
<hr/>			
Boiling 10M HNO ₃	48	6.9	4.3
Metal Arc Weld	96	8.8	5.3
	144	9.7	8.1
	192	10.0	20.6
	240	12.9	133
<hr/>			
Boiling 10M HNO ₃	48	5.9	10.3
TIG Weld	96	14.5	20.8
	144	46.1	211
	192	111	202
	240	348	688

In order to check the apparatus and technique, a 240 hour test was run with 304 L stainless steel in 10M nitric acid. This test showed average corrosion rates of 3.2 mils per year in the liquid phase and 4.3 mils per year in the vapor phase, and the rates were constant throughout the tests. Thus the apparatus and techniques appeared to be satisfactory.

Results in 5M nitric acid are shown in Table XIII. Vapor phase attack is much less severe in this case but there was definite evidence of intergranular attack, with corrosion rates reaching 40 to 50 mils per year after about 1800 hours. A similar test was run with wrought specimens, and showed a vapor phase corrosion rate of 4 mils per year after 1344 hours, when the test was terminated. One test in 6M nitric acid was run for 1008 hours, with the vapor phase specimen showing a corrosion rate of 4 mils per year at that time. Vapor phase specimens were also inserted in four heat transfer tests in 5M nitric acid, with the solution maintained at 90 degrees C. Under these conditions, there was no measurable vapor phase corrosion for periods up to 624 hours. On the basis of these results, it would appear to be desirable to conduct core dissolutions in a Ni-o-nel vessel below the boiling point.

Several tests were also run to determine the effects of a heel from the decladding solution on nitric acid corrosion rates in the liquid phase. In these runs the solutions were made 0.025M in sulfuric acid and 0.0077M in stainless steel. Runs were made in both 4 and 10M nitric acid and were run for 240 hours. Both wrought and

TABLE XIII

CORROSION OF NI-O-NEL IN 5M HNO₃
Corrosion Rate, mils per year³

Solution	Exposure Time	Liquid	Vapor	Solution	Exposure Time	Liquid	Vapor
	Hours				Hours		
Boiling 5M HNO ₃	48	0.4	0.1	Boiling 5M HNO ₃	48	0.7	
	96	0.9	0.6		96	1.6	0.9
TIG Weld	144	0.7	0.4	Metal Arc Weld	144	1.5	0.4
	192	0.9	1.3		192	1.4	0.9
	240	0.8	0.7		240	1.3	0.7
	288	1.0	0.6		288	1.8	0.5
	336	1.3	1.0		336	1.6	1.2
	384	1.4	1.0		384	3.7	2.0
	432	2.6	2.6		432	5.1	3.2
	480	1.8	2.0		480	3.6	2.9
	528	1.9	1.3		528	3.7	2.1
	576	1.6	1.4		576	2.9	1.6
	624	2.2	1.4		624	3.0	2.2
	672	1.9	0.8		672	3.3	2.5
	720	1.9	1.5		720	3.2	3.4
	768	1.9	2.3		768	3.6	2.5
	816	2.5	1.5		816	2.7	2.5
	864	1.8	1.9		864	3.6	2.9
	912	2.0	2.4		912	2.7	2.7
	960	1.9	2.4		960	3.1	2.8
	1008	2.5	2.5		1008	3.2	5.3
	1056	2.5	3.4		1056	3.4	5.9
	1104	2.9	3.0		1104	3.4	4.0
	1152	2.2	3.6		1152	3.2	8.6
	1200	4.2	4.6		1200	3.4	5.6
	1248	2.3	3.7		1248	4.2	9.1

TABLE XIII (cont.)

CORROSION OF NI-O-NEL IN 5M HNO₃
Corrosion Rate, mils per year

Solution	Exposure Time	Liquid	Vapor	Solution	Exposure Time	Liquid	Vapor
	Hours				Hours		
Boiling 5M HNO ₃ TIG Weld	1296	2.7	2.7	Boiling 5M HNO ₃ Metal Arc Weld	1296	3.7	8.0
	1344	2.1	1.5		1344	3.6	6.6
	1392	2.1	3.4		1392	3.9	12.2
	1440	2.5	4.9		1440	4.2	14.3
	1488	3.3	6.2		1488	3.9	13.6
	1536	4.4	8.0		1536	4.6	22.5
	1584	4.9	12.3		1584	4.4	19.7
	1632	4.4	12.7		1632	5.0	25.6
	1680	3.5	13.3		1680	4.8	23.8
	1728	4.7	14.4				
	1776	5.2	51.1				
	1824	5.3	39.6				
	1872	4.8	48.6				
	1920	4.6	47.2				
	1968	4.4	43.2				

all types of welded specimens were tested. The presence of a heel had no effect on corrosion rates in any case. Several tests were run to determine the effect of boric acid in solution on nitric acid corrosion rates. Boric acid may be useful as a soluble poison in dissolving enriched fuels, and in these runs 3 grams per liter of boron was added to 10M nitric acid. Tests were run with liquid phase specimens only for 240 hours. and the presence of boron had no effect on the corrosion rate.

Photomicrographs of welded Ni-o-nel specimens exposed to 4M HNO_3 plus a heel, and to the vapor phase over 10M HNO_3 , both for 240 hours, are shown in Figs. 6 & 7.

B. Heat Transfer Tests

The results of corrosion tests of Ni-o-nel heat transfer surfaces in nitric acid are shown in Table XIV. It is apparent that 10M nitric acid could not be used for core dissolution in a Ni-o-nel vessel. Even the isothermal tests, during which the specimen centerline temperature was controlled to ± 5 degrees F of the boiling point, showed severe corrosion. The attack in all cases was intergranular.

With 5M HNO_3 , intergranular attack was noted in all tests except the isothermal one, and was severe with specimen centerline temperatures over 240°F. There is a very sharp increase in the corrosion rate at temperatures between 240 and 250°F, and even at 240°F, the corrosion rate reached 21.9 mils per year after 768 hours of exposure. The corrosion rate appeared to be independent of the solution temperature, depending only on the metal surface temperature. Thus there may

TABLE XIV

CORROSION OF NI-O-NEL HEAT TRANSFER SURFACES BY 5-10M HNO₃

Period of Test Hours	Solution	Specimen Center Line Temp of	Corrosion Rate mils per year
240	10M HNO ₃	242	185
240	10M HNO ₃	260	1430
240	10M HNO ₃	280	1030
240	10M HNO ₃	300	185
624	5M HNO ₃	226	3.2
624	5M HNO ₃ (90 °C)	226	7.7
768	5M HNO ₃	240	21.9
480	5M HNO ₃	242	8.4
480	5M HNO ₃	247	145
432	5M HNO ₃	250	230
240	5M HNO ₃	260	23.7
336	5M HNO ₃	260	378
672	5M HNO ₃ (90 °C)	260	370
240	5M HNO ₃	300	56.7

be serious corrosion of Ni-o-nel heat transfer surfaces during core dissolutions even using 5M HNO_3 below the boiling point. In order to minimize this problem, heat transfer surfaces should be maintained at a temperature below 240°F.

IV. Carpenter 20 - Sulfex

Carpenter 20 has been considered as an alternate material of construction for the Sulfex process, and therefore it was also tested in Sulfex solutions. These tests were less extensive than those with Ni-o-nel, because Carpenter 20 seemed to show no advantage over Ni-o-nel, and may have certain disadvantages.

A. Sulfuric Acid Tests

The results of tests in 4M sulfuric acid are shown in Table XV. In general, these rates are very similar to those observed in Ni-o-nel sulfuric acid system, except that in the case of Carpenter 20, welded specimens corroded at almost double the rate of wrought specimens. Dissolved stainless steel lowered the corrosion rate by about the same order of magnitude as with Ni-o-nel. No tests were done in this system at higher sulfuric acid concentrations, or with vapor phase or heat transfer surfaces.

B. Nitric Acid Tests

The results of liquid phase tests in nitric acid are shown in Table XVI. The results with wrought specimens are about the same as those observed with Ni-o-nel, but the corrosion rates increased by a factor of five to ten with inert gas welded specimens, and were completely unsatisfactory with fusion welded specimens. One additional

TABLE XV

CORROSION OF CARPENTER 20Cb IN 4M H₂SO₄
Corrosion Rate, mils per year

Solution	Exposure Time Hours			Solution	Exposure Time Hours		
Boiling 4M H ₂ SO ₄	48	4.7	29.5	Boiling 4M H ₂ SO ₄ + 25 g/l dissolved 348 S.S	48	5.0	4.9
	96	5.7	17.3		96	3.0	4.1
	144	5.4	13.1		144	2.8	2.4
	192	29.7	10.5		192	2.8	2.4
	240	18.8	20.3		240	2.4	2.4
	AVG.	12.9	18.1		AVG.	3.2	3.2
Boiling 4M H ₂ SO ₄ Fusion Weld	48	48.7	25.9	Boiling 4M H ₂ SO ₄ + 25 g/l dissolved 343 S.S. TIG Weld Carp. Sq. Wire	48	12.7	11.7
	96	27.0	14.9		96	15.3	15.6
	144	24.6	17.7		144	19.0	19.3
	192	25.0	20.7		192	20.1	22.8
	240	35.8	26.4		240	24.1	26.6
	AVG.	32.2	21.2		AVG.	18.2	19.2
Boiling 4M H ₂ SO ₄ TIG Weld	48	25.8	31.0				
	96	23.5	90.7				
	144	16.0	11.2				
	192	3.5	2.9				
	240	46.5	4.0				
	AVG.	23.0	28.0				

TABLE XVI

CORROSION OF CARPENTER 20Cb IN 4-10M HNO₃
Corrosion Rate, mils per year

Solution	Exposure Time Hours			Solution	Exposure Time Hours		
Boiling 4M HNO ₃	48	2.4	2.6	Boiling 10M HNO ₃	48	26.2	22.4
	96	2.3	1.7		96	35.6	31.6
	144	0.4	0.4		144	51.0	39.6
	192	0.4	0.8		192	46.5	38.8
	240	1.8	1.3		240	49.7	49.5
	AVG.	1.5	1.4		AVG.	41.8	36.4
Boiling 4M HNO ₃	48	3.6	2.5	Boiling 10M HNO ₃	48	12.6	
	96	4.1	3.4		96	39.0	
	144	16.8	99.5		144	108	
	192	7.0	5.1		192	216	
	240	2.4	2.4		240	246	
	AVG.	37.0	22.5				
TIG Weld		AVG. without 3rd period	4.3	Fusion Weld			
			3.3				
Boiling 10M HNO ₃	48	10.0	10.0	Boiling 10M HNO ₃	48	3.8	2.8
	96	5.7	5.2		96	4.5	3.2
	144	4.4	3.2		144	4.3	4.4
	192	4.2	2.8		192	4.0	4.8
	240	5.0	0.5		240	4.3	7.2
	AVG.	5.8	4.3		288	3.8	8.9
					336	3.8	18.7

Liquid Vapor

test was done in 10M nitric acid, which included a vapor phase specimen. This result is shown in Table XVII. The vapor phase specimen showed a continually increasing corrosion rate, and by the termination of the test, there was visual evidence of accelerating intergranular attack.

Because of the generally poor performance of Carpenter 20 welds, particularly in nitric acid, and since the nitric acid vapor phase corrosion problem appeared to be no less serious with Carpenter 20 than with Ni-o-nel, no further work was done with Carpenter 20 in Sulfex solutions.

V. Zirflex Corrosion Studies

A. 309 SCb

Tests with 309 SCb in uninhibited Zirflex solutions showed obviously unsatisfactory corrosion rates of about 150 mils per year in forty eight hour tests. The presence of dissolved Zircalloy at concentrations of 0.3 and 0.5M had no effect on the corrosion rate, but a concentration of 0.75M lowered the corrosion rate to about 2 mils per year. It was not possible to determine the effect of dissolving Zircalloy, since short term tests even in the absence of dissolving Zircalloy showed low but erratic corrosion rates.

The effect of hydrogen peroxide on corrosion rates was studied very briefly and preliminary results indicate that it may be an effective inhibitor, but that it may be necessary to make continuous or periodic additions in order to maintain a sufficient concentration in solution. For instance, with 1M H_2O_2 , the corrosion rate in a 24 hour test was 43.8 mils per year, but in a 48 hour test it was 122

mils per year. Further studies of the stability of peroxide in these solutions are needed.

The effect of cupric nitrate on corrosion rates was studied somewhat more extensively, and these results are shown in Table XVII. The addition of 0.01M cupric ion lowers the corrosion rate by a factor of four to five, and the addition of 0.1M cupric ion is somewhat less effective. Copper is slowly lost from these solutions by plating out on stainless steel surfaces, particularly welds, but the loss is slow enough so that additions during a dissolution should not be necessary. There was never evidence of loss of copper before 48 hours. Thus in the presence of 0.01M cupric ion a corrosion rate of 30-40 mils per year would be expected, in the starting solution and this may be lower in the presence of dissolving Zircalloy, and would certainly be lower in the final solution. Several tests at 90 degrees C showed corrosion rates in this solution of only two to four mils per year, but Zircalloy dissolution rates at this temperature were unsatisfactory. Vapor phase corrosion rates in this system are negligible. Further work is necessary to determine the effect of both peroxide and cupric ion on core losses.

B. 304L

The corrosion rate of 304L in uninhibited Zirflex solutions is also unsatisfactory, averaging about 300 mils per year. The effect of cupric ion on corrosion of 304L stainless steel by Zirflex solutions is shown in Table XVIII. The loss of copper from solution is much more rapid and less predictable than with 309 SCb. Therefore the corrosion

TABLE XVII
CORROSION OF 309 SCb BY ZIRFLEX SOLUTIONS
Corrosion Rate, mils per year

Solution	Exposure Time Hours		Solution	Exposure Time Hours	
6M NH ₄ F -	27	19.8	6M NH ₄ F -	24	40.1
	49	31.1		48	50.9
.5M NH ₄ NO ₃ -	72.5	36.6	.5M NH ₄ NO ₃ -	72	61.3
	96.5	39.1		96	60.4
.01M Cu(NO ₃) ₂	120.5	40.4	.1M Cu(NO ₃) ₂	120	79.0
	144.5	47.1		144	73.0
				168	57.3
			<u>Liquid Phase</u>		<u>Vapor Phase</u>
6M NH ₄ F -	24		37.0		1.5
	48		31.8		0
.5M NH ₄ NO ₃ -	72		31.1		0
	96		29.9		0
.01M Cu(NO ₃) ₂	120		30.6		0
TIG Weld					

TABLE XVIII
CORROSION OF 304L BY ZIRFLEX SOLUTIONS
Corrosion Rate, mils per year

Solution	Exposure Time Hours		Remarks
6M NH ₄ F - .5M NH ₄ NO ₃ - .01M Cu(NO ₃) ₂	24	112	Slight Cu plate
	48	226	Heavy Cu plate
6M NH ₄ F - .5M NH ₄ NO ₃ - .01M Cu(NO ₃) ₂	24	62.5	No Cu plate
	48	118	Cu plate
	72	158	Cu plate
6M NH ₄ F - .5M NH ₄ NO ₃ - .01M Cu(NO ₃) ₂	24	36.0	No Cu plate
	48	38.0	No Cu plate
	72	58.4	Slight Cu plate
	96	64.1	Cu plate
	120	58.4	Cu plate
6M NH ₄ F - .5M NH ₄ NO ₃ - .01M Cu(NO ₃) ₂	24	165	Heavy Cu plate
	48	249	Heavy Cu plate
	72	292	Heavy Cu plate
	96	234	Heavy Cu plate
6M NH ₄ F - .5M NH ₄ NO ₃ - .1M Cu(NO ₃) ₂	24	62.0	No Cu plate
	48	123	No Cu plate
	72	192	Slight Cu plate
	96	222	Slight Cu plate
	120	178	Heavy Cu plate
6M NH ₄ F - .5M NH ₄ NO ₃ - .1M Cu(NO ₃) ₂	24	47.1	No Cu plate
	48	46.9	No Cu plate
	72	55.7	No Cu plate
	96	Heater Failed	No Cu plate
	120	148	No Cu plate
6M NH ₄ F - .5M NH ₄ NO ₃ - .1M Cu(NO ₃) ₂	24	110	No Cu plate
	48	147	No Cu plate
6M NH ₄ F - .5M NH ₄ NO ₃ - .1M Cu(NO ₃) ₂	24	46.6	No Cu plate
	48	43.3	No Cu plate
	72	49.9	No Cu plate
	96	47.1	No Cu plate
	120	45.0	No Cu plate

data show wide scatter but are generally much too high. Cupric ion was the only inhibitor studies in this system, and does not appear to be effective.

C. Ni-o-nel

Ni-o-nel showed a corrosion rate of about 250 mils per year in uninhibited Zirflex solutions. Dissolved Zircalloy at concentrations of 0.3 and 0.5M had no effect on the corrosion rate, but at a concentration of 0.75M lowered the corrosion rate to about 10 mils per year. In the presence of dissolving Zircalloy, the corrosion rate was lowered to about 30 mils per year, but because of the short period of these tests, the data scattered widely.

Data on the effect of cupric ion as an inhibitor are shown on Table XIX. Cupric ion is not as effective in this system as with 309 SCb, mainly due to a more rapid loss of inhibitor, and even the inhibited rates do not appear to be satisfactory. Vapor phase corrosion rates are very low in this system.

A photomicrograph of a welded Ni-o-nel specimen exposed Zirflex solution containing 0.1M Cu for 120 hours is shown in Fig. 8.

TABLE XIX
CORROSION OF NI-O-NEL BY ZIRFLEX SOLUTIONS
Corrosion Rate, mils per year

Solution	Exposure Time Hours		Solution	Exposure Time Hours	
6M NH_4F -	27	62.0	6M NH_4F -	24	85.0
	49	66.5		48	108
.5M NH_4NO_3 -	72.5	52.4	.5M NH_4NO_3 -	72	121
.01M $\text{Cu}(\text{NO}_3)_2$	96.5	115	.1M $\text{Cu}(\text{NO}_3)_2$	96	135
	120.5	99.8		120	106
TIG Weld	144.5	236	TIG Weld	144	61.3
				168	65.4
				192	86.0
			<u>Liquid Phase</u>	<u>Vapor Phase</u>	
			Metal Arc Weld	Tig Weld	
6M NH_4F -	24		92.2		
	48		77.8	6.6	
.5M NH_4NO_3 -	72		77.1	3.0	
	96		93.5	2.4	
.01 $\text{Cu}(\text{NO}_3)_2$	120		110	0.4	

Summary and Conclusions

1. Ni-o-nel is a satisfactory material of construction for the Sulfex process. subject to the following limitations:
 - a) Sulfuric acid concentration should be limited to 4M. Ni-o-nel is subject to severe intergranular attack in 6M sulfuric acid.
 - b) Nitric acid concentrations should be less than 6M, and maintained below the boiling point, in order to avoid intergranular attack in the vapor phase.
 - c) Heat transfer surfaces should be maintained at a temperature less than 240°F during core dissolutions.
2. Carpenter 20 is less satisfactory than Ni-o-nel for application to the Sulfex process, because of selective attack of welds, particularly in nitric acid solutions.
3. Neither Ni-o-nel or 309 SCb or 304L stainless steel are satisfactory for use with uninhibited Zirflex solutions.
4. Cupric ion. and possibly peroxide, significantly lower corrosion rates of 309 SCb by Zirflex solutions. With 0.01M cupric ion the corrosion rate is lowered to 30-40 mils per year. Corrosion rates of Ni-o-nel and 304L by Zirflex solutions are considerably higher than this using either of these inhibitors.

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Figure 1. Wrought Ni-o-nel exposed to boiling 4M H₂SO₄. Transverse section - 250 $\times$. Corrosion rate - 22 mils per year - 240 hour exposure.

Figure 2. TIG welded Ni-o-nel exposed to $4M$ H_2SO_4 .
Transverse section - $250\times$. Corrosion rate - 14 mils per
year - 240 hour exposure.

BASE METAL

WELD METAL

Figure 3. TIG welded Ni-o-nel exposed to $4M H_2SO_4 + 25 \text{ g/l}$ dissolved stainless steel. Transverse sections - $250\times$. Corrosion rate - 8.4 mils per year - 240 hour exposure.

BASE METAL

WELD METAL

Figure 4. Metal arc welded Ni-o-nel exposed to 4M H_2SO_4 + 25 g/l dissolved stainless steel. Transverse sections - 250 $\times$. Corrosion rate - 20.7 mils per year - 240 hour exposure.

Figure 5. Heat transfer corrosion test apparatus.

BASE METAL

WELD METAL

Figure 6. TIG welded Ni-o-nel exposed to $4M$ HNO_3 + heel. Transverse section - $250\times$. Corrosion rate - 0.9 mils per year - 240 hour exposure.

WELD METAL

HEAT AFFECTED ZONE

BASE METAL

Figure 7. Metal arc welded Ni-o-nel exposed to 10M HNO_3 vapor phase. Transverse sections - 250 $\times$. 240 hour exposure.

WELD METAL

HEAT AFFECTED ZONE

BASE METAL

Figure 8. TIG welded Ni-o-nel exposed Zirflex solution + $0.1M \text{Cu}(\text{NO}_3)_2$. Transverse sections $250\times$. 120 hour exposure.